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"Nec araneorum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." JUST. *Lips. Polit.* lib. i. cap. 1. Not.

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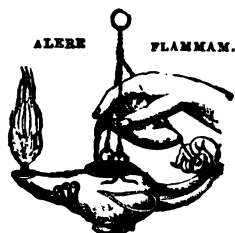
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"Meditationis est perscrutari occulta; contemplationis est admirari perspicua . . . Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

—“Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condât,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina cœlo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu.”

J. B. Pinelli ad Mazonium.



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[FIFTH SERIES.]

JULY 1893.

- I. *The Foundations of Dynamics.* By OLIVER LODGE, F.R.S.,
Professor of Physics in University College, Liverpool.*

PART I.—*The Nature of Axioms.*

IT is a matter of congratulation with me that a critic who has devoted so much thought to Newton's laws of motion and similar fundamental doctrines should have begun a discussion of my papers on the subject of Energy; and I shall willingly consider his objections in order to see what modifications, if any, should be made in my original statements. But Dr. MacGregor's temporary attitude towards Physical problems is exhibited rather strikingly in a treatise on "The Fundamental Hypotheses of Abstract Dynamics," which he published as a Presidential Address to a section of the Royal Society of Canada (Transactions 1892). Hence, before replying to his criticisms on my writings, as made in your February issue, page 134, I should like to make a few general observations suggested by this other deliverance of his, so as to indicate what seem to me the rather different points of view from which we, or if not we some other writers, approach these fundamental doctrines of Mechanics and Physics. The difference in attitude may be briefly summarised thus:—Some philosophers seek to advance truth by detecting or inventing complications in what was apparently simple; whereas others aim at making simple statements concerning things which are apparently or really complicated. A generalization like this is

* Communicated by the Physical Society: read May 12, 1893.
Phil. Mag. S. 5. Vol. 36. No. 218. July 1893. B

not one which will bear pressing into individual cases, but if it contains an element of truth it has reference to no personal detail, as it seems to me, but to a difference in type; and I sometimes think that most minds, except those few of the very highest order who are above classification, may be said to fall into, or at least to lean toward, one or other of these categories*. Each type of mind performs its service, and each type has its appropriate danger.

The detection of a real complication is a service to truth; the invention of a needless complexity is a disservice and temporary obstruction. The reduction of apparently complex facts to a simple statement in commonplace language is, I believe, a service; the over-simple and incomplete summary of what is really complex is not an equal service, but I do not perceive that it is likely to be any serious obstruction: it seems to me rather of the nature of a first approximation, which is often temporarily helpful.

When Ohm stated his law that current is proportional to E.M.F., he did not know that it was really true. It has turned out to be precisely true for copper and for sulphate of copper—the only substances for which it has been seriously tested; but even if it had not been so accurate, its statement was a service, since it enabled half a century to walk in the light instead of in the dark. There is no evidence that it is accurately true for every variety of solid and liquid conductor, but by this time it is the fashion to assume its truth in ordinary simple cases. And rightly so, as it seems to me; the burden of proof rests now with the enterprising experimenter who can detect a flaw in it. His evidence will be listened to, but till it is forthcoming vague doubts can be legitimately ignored.

Take another example:—The characteristic equation of gases in the simple form $p v = R T$ has done good service, though it turns out to be untrue for every actual substance. Without it, however, we should have been unnecessarily floundering in the dark. Even now it is more used in dealing with gases

* I see no reason in Dr. MacGregor's book on Dynamics for including him in the first category: it is his Presidential Address on the Laws of Motion that alone suggested it. I do not intend the classification as in any way offensive: I should think that Prof. Karl Pearson, for instance, would willingly enrol himself under the first head rather than under the second, judging by his 'Grammar of Science.' But very likely MacGregor has stated the laws of motion in their simplest conceivable form if attraction and repulsion across a distance are to be contemplated. That is the essential difference between us: he is willing to base Physics on action at a distance; I am not. From the action-at-a-distance point of view his statements are in many respects admirable, especially those near the conclusion of his essay. The remarks in the text are intended to have only a general and impersonal application.

than any other equation. The improved statement of Van der Waals, adding a term to p and subtracting one from v , was another distinct service, and enabled a mass of experimental evidence concerning the structure of liquids to be conveniently and simply summarised. In its turn, however, it has had to give place to more complex empirical statements, and the complete law has not yet appeared.

The examples I have chosen, one of a precise, the other of an approximate, simple statement, are not indeed of the nature of axioms; and it may be held that it would be unsatisfactory to base our axioms on such a tentative sort of footing.

And yet what other course is open? Truly axiomatic statements can only be effectively made concerning things of which the race has had a long course of experience,—things to which they have grown familiarly accustomed. If they can be actually proved, they are theorems, not axioms.

The setting forth of an axiom I regard as a kind of challenge, equivalent to the statement:—"Here is what seems to me to be a short summary of a universal truth; disprove it if you can. I cannot prove it, it is too simple and fundamental for proof, I can only adduce hundreds of instances where it holds. I have indeed critically examined a few special cases and never found it fail, but a single contrary instance will suffice to overthrow it; hence, though it be hard to prove, yet if not true its disproof should be easy: find that contrary instance if you can." If no disproof is forthcoming for a few generations, the axiom is likely to get accepted. Meanwhile its undeniable simplicity is a practical advantage, even though in the course of centuries a flaw or needful modification in its statement may be discovered.

This is the kind of basis on which such a law as that of the Conservation of Energy or the Conservation of Matter rests. That the perpetual motion is impossible, that matter is indestructible, that energy never diminishes in the act of transfer, all these must be regarded as generalizations based on a great series of experiments, some consciously directed to the upsetting of one or other of the laws if possible, some aimed at establishing them, but most of a non-contentious and collateral character. If we are challenged to produce direct evidence that in any given chemical reaction the mass of the reagents is unchanged, not only in the initial and final stages but at every stage of the process, the proof may be exceedingly difficult. Heat is liable to be developed which would interfere with delicate weighings, and the reaction challenged may be an explosive or otherwise inconvenient one. But we do not attempt the proof, we shift the burden on to the shoulders

of the doubter and say to him, Disprove it if you can ; and so we practically say for all our axioms, and for all laws which are so simple and fundamental as to be hardly distinguishable from axioms.

Experiments are often made or adduced in support of a law as if they were part of its foundation : thus Newton tried experiments on impact before stating his third law, but the experiments did not really prove it with accuracy even for the particular case examined. All they could show was that there was nothing obviously wrong with it. He saw no reason for supposing it wrong, and so after consideration stated it as an axiom, to be hereafter challenged and found inaccurate if so the progress of experience turned out.

I should say that an axiom or fundamental physical law is a simple statement, suggested by familiar or easily ascertained facts, probable in itself, readily grasped, and not disproved or apparently liable to disproof throughout a long course of experience.

If a statement is capable of exact examination and verification, either by reasoning or by experiment, it is called a law, but not a fundamental law ; i. e. it is no longer part of the foundation, it is supported on something else. If it has no support, except the absence of evidence against it, it is an axiom. Far be it from me to decry the use of experiments of verification. The necessity for them whenever feasible is conspicuous and universally admitted, and much ingenuity may be usefully spent upon them ; but I do say that in time a theory can become established by processes other than direct experimental verification ; and in fact that really valid and flawless experimental verification is frequently an impossibility.

An instructive example of the legitimate strength of a theory, even when opposed by apparent facts, is contained in an article by Lord Rayleigh in the *Philosophical Magazine* for March 1889, "On the History of the Doctrine of Radiant Energy."

It appears that W. Herschel conceived the idea that the radiation which excites the sensation of light and the radiation which produces heat in black bodies are essentially different ; and this view, which was contrary to his original intuition, was based upon a crucial prismatic experiment, made for the purpose of ascertaining "whether the heat of the red rays is occasioned by the light of those rays" or not. A definite question, *answered by experiment in the negative*. On this Lord Rayleigh remarks:—

"I am disposed to think that it was this erroneous conclu-

sion from experiment, more perhaps than preconceived views about caloric, that retarded progress in radiant heat for so many years. We are reminded of Darwin's saying that a bad observation is more mischievous than unsound theory. It would be interesting to inquire upon what grounds we now reject the plain answer which Herschel thought himself to have received from experiment. I do not recall a modern investigation in which the heat and light absorptions are proved to be equal for the various parts of the visible spectrum. Can it be that after all we have nothing but theory to oppose to Herschel's facts?"

Yes, that is all, and, as Lord Rayleigh well knows, it is amply enough. Whoever examines the facts again will do so not to substantiate our present theory but in the hope of upsetting it. Success is of course just conceivable, but, when it comes, there will be time enough to reopen the question. Lord Rayleigh's words may be distorted, and may even suggest false meanings to minds with a crooked turn in them; so may many of the apparent admissions about unprovableness in this paper of mine, but, whether it gives occasion to the enemy to blaspheme or not, it is true that a host of doctrines are believed because they form part of a consistent scheme rather than because of any seriously attempted, still less any really achieved, experimental proof. And to pull one of these neatly fitting blocks from its niche will demand the strength of more than one, of more than several, so-called crucial experiments. There comes a time indeed when the weight of experimental evidence suffices to uproot a portion of tightly fitting theory; but seldom, as I think, without some looseness or uneasiness being first detected, and never without a betrayal of rottenness at the root.

Why do Physicists deny that matter can be moved by mental power from a distance without physical mechanism? Why does modern science reject the whole of a certain class of miracles, in the teeth of an immense record of direct experimental evidence? Solely because these things do not fit in with such coherent views of the universe as they have at present been able to frame.

Why, again, do we accept a multitude of unverified statements, such as, that every portion of radiation, whether it be of light or of sound, is intrinsically energy, and must, if absorbed, result in heat; that every muscular contraction of an animal corresponds to the combustion of a portion of his food; that a given gas consists of particles of approximately specified size and weight travelling at a certain average speed; that a medium connects every pair of bodies which are

perceived to exert force on each other ; and so on ? Solely because these things do fit into a coherent and self-consistent scheme of the universe.

Any scheme or doctrine *sufficiently* harmonious and consistent goes far thereby towards establishing itself as truth. So conspicuously is this the case, when one comes to reflect, that there are not wanting some who conjecture that by our thought we are, so to speak, *constructing*, or at least helping to construct, the cosmic scheme.

Some axioms the human race has now given up challenging, and by so abstaining has silently accepted as corresponding to the truth of things. Others it occasionally exercises its ingenuity in degrading or depreciating, not into untruths, but into special cases of a higher and super-sensuous generalization. Varieties of space are imagined, and mathematically treated, where more than one line can be drawn through a point parallel to a given line, where the shortest distance between two points is not straight, where the three angles of a triangle are not equal to half a revolution, where a closed surface is an incomplete boundary, and where more than three lines can be perpendicular to each other. These things are imagined, and for all I know they may in some occult fashion exist. To set bounds to the possibilities of the universe on the limited evidence of our few sense-organs would be absurd. But I say that any proof of their actual existence within our more developed ken rests with the experimentalist. As soon as facts are forthcoming which clearly and definitely are inexplicable on the basis of our present notions concerning space, I for one am willing to enlarge those notions and to contemplate provisionally whatever hypothesis suggests itself as most simple and plausible. Till then there is plenty of work for a physicist in interpreting, systematizing, and clarifying the facts of the universe, as it appeals to him through the agency of his ordinary three-dimensional senses, aided by his undimensional common-sense.

But I hold that with all these vague possibilities of ultimate development in front of him (not so vague but that they are in some sort conceivable, or at least tractable by reason), a natural philosopher need not confuse himself by endeavouring to complicate what is already transparently simple ; nor will he be wise to attempt an over-laborious scrutiny of his fundamental axioms ; for the more neatly and quietly he can lay his foundations the more time will he have for building the super-structure, and the more gorgeous he may hope to make it. By all means let him avoid a rotten or insecure element in his foundation. It must be as sound and strong as possible ;

but his underground work need not be decorated with fanciful and laborious conceits, it may be as plain as it is substantial, and he may leave its edges rough in order to connection with structures as yet unbuilt and unimagined.

Of this plain and substantial character would I seek to keep the laws of motion. If a statement like the first law of motion cannot be made in simple and readily intelligible language, I should despair of Physics. In that case the Physics of the future could be little better than a barbarous jargon of technicalities. There are plenty of really difficult places where technical language and unfamiliar modes of thought are for the present essential. The developments of the superstructure erected during the present century are indeed now so stupendous that for myself I should be satisfied if, without appreciably adding to them, I could by consolidation and restatement remove the necessity for some of this artificiality, and so make their harmony and beauty more readily appreciated. But in order to do this a simple and unlaborious foundation is a necessity. I hope to try before long to display the bold outlines of the foundation already laid by men of surpassing genius, every unnecessary accretion being cleared away, and the whole simplified to the uttermost; and then, if the attempt be not too ambitious, I should wish to extend the process to some portion of the superstructure.

PART II.

The First and Third Laws of Motion.

So much for general preamble; now turning to Dr. MacGregor's address, we find that he objects to the Newtonian statement of the first law of motion on the same ground that Prof. Karl Pearson, Prof. Mach, Mr. Macaulay of King's College, Cambridge, and several others* have objected to it, on the ground, namely, that uniform motion is unintelligible or meaningless unless you specify its direction and velocity with reference to a set of axes. And directly you try to specify axes you get into difficulties, for, although a uniform translation is permissible to them, any rotation or any acceleration of the axes is fatal to a simple statement of the behaviour of a body acted on by no force. It is useless to say that the axes must be stationary, because one cannot define what that means; so the attempt is made to say that the axes must not rotate and must not be acted on by force; but this last condition is of no use unless they possess

* See for instance a correspondent in 'Nature,' vol. xxxvi. p. 366.

inertia; so the axes are sometimes supposed to be generated by particles of matter projected in different directions and subsequently free from force *; or else the axes are made of infinite mass so that no finite force may be able to affect them.

Now I hold that all such notions as axes of reference are artificial scaffolding, necessary for the numerical specification of a velocity, but not at all necessary for the apprehension of what is meant by a uniform velocity. It is in the specification of any absolute velocity that the difficulties cited about an origin and axes of reference legitimately occur. It is in fact impossible to specify the absolute velocity of anything, because we have literally no criterion of rest. We shall, I believe, hereafter find it convenient to postulate the Ether as a body absolutely at rest; but none of these physical or geometrical complications should enter into an axiomatic statement.

All that the first law asserts is that the motion of a body not acted on by force is uniform in magnitude and direction. There is no need to attempt the impossible and say what that magnitude and direction absolutely are. Whatever they are they remain constant. If asked to prove this statement, we should at once decline, and throw the burden of disproof on the doubter. This is what Maxwell does† when he says (virtually):—If the speed and direction of a freely moving body vary they must vary in some definite manner; very well, tell me in what manner they are varying. You cannot, unless you can show me absolutely fixed lines of reference.

The fact is that the conception of uniform motion is based upon a simple primary muscular sensation, or at any rate upon a succession of such sensations; everybody understands what it means, so far as it is possible to understand anything in this material universe, and the sense in which it is understood is amply sufficient as a basis for a physical superstructure. The first law is a true axiom, and its boldest and simplest form is not only the best, but is the only one that can with any justice be called axiomatic. How can one appeal to the experience of the human race with reference to coordinate axes of infinite or any other mass? How can we utilize as axes the trajectory of particles free from force, without tacitly assuming the first law continually? The whole attempt to complicate the statement of the first law of motion seems to me absurd.

* Thomson and Tait, vol. i. Part I. (1879), § 249. But although these writers do propose to use such axes to fix direction, or, better, the invariable plane of a rotating system, §§ 267, 245, they quite logically deduce these things from Newton's laws, and do not use them in the statement of those laws.

† Matter and Motion, art. xli. p. 36.

The well-known other objection, that a statement of the first law is unnecessary because it is only a special case of the second, rests on a different footing. Thomson and Tait have pointed out that it acts as a definition of equal intervals of time. Prof. MacGregor denies that the first law gives us any more useful definition of time than the second does; but seeing that every clock is an attempt at a uniform mover, and that the second law is concerned with the more complex notion of acceleration rather than with the simple idea of velocity, I do not imagine that he will seriously adhere to this view; and therefore, fully admitting the obvious fact that the first law is a special case of the second, I still hold that its separate statement is desirable, because it is so simple, and because it does afford a clear practical definition of the mode of measuring time. But were this its intended meaning it could have been expressed more straightforwardly. Newton probably considered it as a qualitative statement introductory to his second law: and as such it is entirely suitable.

None of the objectors to the first law have the slightest doubt of its truth,—that is what makes their contentions so practically futile; it would appear that it is too simple to please them; they seem to wish to complicate its statement so as to make it look more like the difficult things with which they are accustomed to deal. I feel convinced that many mathematicians mistrust a simple statement in English, and hardly conceive that such a language can really express an important law; their trained ability to deal with difficult conceptions leads them, as I think, astray.

I am not quite clear what the word *logomachy* means, but much of the discussion which has been bandied about concerning the statement of the first law seems to me to be rightly designated by some such opprobrious or perhaps complimentary epithet.

When Dr. MacGregor goes on to consider the third law, and to deny that it can properly be regarded as a deduction from the first, he is urging a very minor matter, if what I have said concerning axioms has any truth in it. Still the question has some interest. Whether it is deducible from the first law or not may be held to depend on how general the terms are in which that law has been stated. If it can be axiomatically asserted that the *centre of mass of a rigid system* moves uniformly until an external force acts on the system, and also that the system does not begin to spin, then the third law is established. For since zero acceleration means zero force, it follows that all the internal forces add up to zero, and have no moment; and since the system

can be dissected bit by bit without ceasing to be a system within the scope of the first law, it follows that no stress can contain an unbalanced force or couple.

If the law be doubted for the case of a pair of bodies attracting each other from a distance, Newton says* (virtually):— Jam the bodies apart with a rigid obstacle, then you have reduced their action to contact action; and since you have a balanced stress at each point of contact, and likewise between the ends of the introduced obstacle, it follows that the attracting forces of the distant bodies are also balanced.

Now Dr. MacGregor's objections are (1) that Newton's proof only aims at extending the law from contact action to actions across a distance, while for contact action he is content to assume it as an axiom or to verify it by experiment; and (2) that the proof breaks down for a particle or single body which cannot be analysed into parts.

It is quite possible that Newton thought it best to state his third law as an axiom; because the fact that the centre of mass of a complex system of bodies obeys the first law is hardly an experience that can be confidently appealed to, even though all the bodies are in contact. That fact and the third law are intimately *connected*, but whichever is the simpler had better be stated as the axiom, and the other be made a deduction from it. Thus the centre of mass statement follows from the third law, and so very likely Newton preferred to arrange it. It is frequently difficult to know which of two very simple statements is the more axiomatic; and methods of proof are notoriously susceptible of considerable variation. The important thing is to notice the link or tie between two facts, to show that they mutually strengthen each other, not to pretend that one is beneath the other and supports it.

Attempts to build even so simple a structure as geometry in the form of a single column, stone upon stone, have been found artificial and in the long run impracticable. An enlarged basis of direct appeal to experience is not only necessary but desirable, and all fundamental matters should be kept low down, as nearly in contact with first principles as possible.

The so-called deduction of the third law from the first or second is important as a clear and strong cross-connexion between the two things, and need not be considered as a rigorous proof. It is rigorous enough if the premisses are granted, but if not, then there is a certain outstanding axiomatic or unprovable character to be shared between them; but this outstanding portion is, by reason of the cross-connexion,

* *Principia*, Scholium to *Axiomata*.

so slight as to remove all difficulty from what otherwise would seem, and indeed, strange to say, to many still does seem, an exceedingly tough morsel to swallow.

[I mean that one constantly finds examination candidates, and even Engineers, when catechized about a horse pulling a cart, though they may, some of them, politely admit that approximately the pull of the horse and the pull of the cart are equal (constituting the stress in the trace whose inertia we may agree to neglect), yet nevertheless assert that in reality the pull of the horse must be *the least little bit* bigger than the pull back of the trace, else the thing could not start. The fact is that the universal truth of the third law is *not* axiomatic, or at least is not obvious*, and hence its deduction from the other two laws is really a useful deduction.]

I do not see any point in Dr. MacGregor's second objection that the proof is inapplicable to a body without parts. For if such a body anywhere exists, plainly its parts cannot act on each other, and so there are no actions or reactions in such a body worth troubling about.

The concluding portion of Prof. MacGregor's address has to do with the Conservation of Energy and the question of how far it can be deduced from the third law. But all these questions respecting energy we must fight out at greater length. Dr. MacGregor well knows that from the third law and the denial of action at distance together I claim to have deduced a law of conservation simpler and more precise than the ordinary law; but his objection to this† is that though such a law may come to be accepted as sufficient in the future, when the universality of contact-action is fully recognized, it is inadequate for the present, when action at a distance still holds a portion of the field; by which I suppose he really only means that many mathematical methods of treatment are based at present on action-at-a-distance modes of expression. I have no fault to find with any convenient mode of attacking specific problems; it is permissible to everyone to use the language of distance-action for practical purposes; but when it comes to formulating fundamental laws I have no ambition to legislate for such cases until they can be shown actually to occur. I am open to experimental proof of their existence, but to none other. It is premature to legislate for them. If any action other than contact-action exists, we had better know more about it before formulating its laws. If the will-power of a "medium" for instance can really move a chair without

* See for instance 'Nature,' vol. xxxvii. p. 558; and see all recent volumes of 'The Engineer' *passim*, especially about 1885 and 1891.

† Expressed elsewhere, viz. Phil. Mag. February 1893.

any kind of contact or physical connexion, it will be wise to look carefully for the seat of the other component of the stress, if there is one, and for the source of the energy concerned, but I myself should feel extremely hazy as to their probable locality.

When action at a distance does present itself in Nature (and if it ever does it is clearly going to be in connexion with the operations of Life), it will be very well to overhaul our axioms to see if they require modification. Till then I propose to state them in terms of the facts we know. This I will attempt in another Part.

PART III.

The Conservation of Energy and Universal Contact-action.

The ground is now clear, I think, for a reply to Professor MacGregor's criticism, as made in the *Phil. Mag.* (vol. xxxv. p. 134) for February 1893; and incidentally I may hope to answer or at least discuss the matter with some other critics, notably Mr. Heaviside in his paper in the *Phil. Trans.* 1892.

The first objection is that in my definition of energy I assume the ordinary law of conservation, because I say, in an early paper (*Phil. Mag.* Oct. 1879, viii. p. 278), "Whenever work is done upon a body, an effect is produced in it which is found to increase the working-power of that body (by an amount not greater than the work done); hence this effect is called energy, and it is measured by the quantity of work done in producing it." "The words 'is found,'" says Dr. MacGregor, "indicate an appeal to experience." Most true, so they do. My position is this:—Before making any definition it is desirable and only civil to show the reasonableness of it. To thrust a statement out without preamble or explanation, under cover of the contention that being only a definition or an enunciation one is at liberty to define or enunciate as one pleases, is I fear a thing frequently done, but it is barely polite, and it is apt to excite either resentment or else undue and slavish submission.

It is from no lack of love for Cambridge and the great men she has nurtured that I venture to hold that the typically Cambridge plan of text-book is liable to err in this direction. An attitude of blind faith and mere assimilation is required of a student for many of the earlier chapters, sometimes for the whole of a book. The life, the interest, of the subject to be treated, an exhibition of the reasonableness of the adopted mode of treating it, are all neglected, and a ghastly skeleton is presented to you bone by bone; which truly is an admirable structure when subsequently clothed in flesh by men of sufficient genius, but which is liable to excite repulsion in a

thinking student who possesses some physical instincts but is devoid of the artificial galvanic stimulus called Examination*.

It may be that I myself err in an opposite direction, being so interested in the muscles and the clothing that I forget here and there a bone or two. If it be so it is a grievous fault, and grievously shall I have to answer for it. It is not a fault that I ever attempt to justify. Flabby and boneless science is no science at all.

In defining Energy, then, I first appeal to experience that something in the popular sense *energetic* is often plainly produced in a body when work is done upon it; *e. g.* when a bow is stretched or a stone flung; and I proceed to say that that something is always produced, even when not obvious, and that it has been called Energy because it frequently confers upon the body possessing it the power of itself doing work. I know well enough that the common definition runs, Energy = power of doing work, but there is a difficulty about this definition: plenty of energy has no power of doing work, or at least no power that we can get hold of. Therefore I prefer to give a name to the result of work done, whether it be obviously energetic or not, and to justify the name energy by appealing to the many cases where its possession does confer a power of doing at any rate some work; but in the definition I make no statement that energy must necessarily be able to do work, or must necessarily continue constant in quantity, because such statements, so far as they are true, are part of the law which is being led up to, not part of the definition.

My definition of "energy" stands on all fours with the customary definition of the potential function. It is a name for the line-integral of a force, considered as a quantity that can be stored. The line-integral of a force in action is *work*, the result of it is *energy*. Or, otherwise:—The scalar product of force and velocity is *activity* (sometimes called power); the result of activity lasting a finite time is energy.

Some conception of what energy is like can be gained by appeals to familiar experience; and the fact that it can be stored more or less completely, and can ultimately reproduce an activity similar to that which generated it, can also be illustrated in a selection of cases. The law of energy asserts, what cannot be so readily demonstrated, that in *all* cases it can be stored without loss, except in so far as it leaks away, or until it is discharged, in some kind of equivalent activity; and that even when thus dispersed or transferred or lost to

* Valuable enough, however, in its proper place. I am not joining in the outcry against examinations. They are a most useful and much needed stimulus to right intellectual conduct, and partially replace the old belief in purgatory.

the body in which it was generated, it still exists in other bodies in undiminished quantity, and so is capable of transference and retransference, by means of activity, and activity alone, for ever.

But how is such a wide-sweeping statement to be justified? Not by any hasty appeals to experience, not even by the laborious researches of a Joule. Such experiments can indeed examine the obviously weak places and can show that there is no manifest flaw there, that all the apparent flaws disappear on closer inspection, and, so far as can be seen, do not exist. The law itself as a universal generalization must be itself axiomatic, or else must be deduced from some other and simpler axioms.

I hold that it can be deduced from Newton's third law and from the denial of action at a distance, thus:—Bodies can only act on one another while in contact, hence if they move they must move over the same distance*; but their action consists of a pair of equal opposite forces; therefore the works they do, or their activities, are equal and opposite; therefore, by definition (p. 13), whatever energy the one loses the other gains. In other words: in all cases of activity, energy is simply transferred from one body to another, without alteration in quantity.

I claim also that the law of conservation thus established is more precise than the ordinary law (which I confess always seems to me rather vague, especially when such absurdities as "possible" and "actual" energy are put into its statement,—a denier of the law could use no more deadly word than "possible"); more precise and definite, I say, because it is the law not only of *conservation* but of *identity*. I believe that questions arising from this law of the identity of energy—a study of the paths by which any given now-existing bit of energy has reached its present locality, and of all that has happened to it in the past—may prove in the future to be as fruitful a region of enquiry as are studies in the history of any given piece of matter, say the earth or the sun, or, to step forward a little, the history of an individual mind, when we realise some day that this, too, has a continuous, and perhaps traceable, existence.

However, Prof. MacGregor objects (p. 135) that my deduction of the conservation of energy proves it during *transfer*

* Motion in the line of stress is here directly contemplated. As has been already several times noticed, the possible *slipping* of bodies in contact is not apparently allowed for, but in so far as they are smooth their slip is ineffective, and if they are rough there is a tangential stress to be taken into account as well as a normal pressure; the friction-stress is intermittent instead of steady, and molecular instead of molar, but otherwise the above statement applies without complication, so far as it ever applies to the immediate action of ordinary material bodies.

merely, and leaves untouched the question of what happens during simple storage.

That is true, and I do not think that I had noticed the objection before. My deduction proves that in all cases of activity energy passes on without loss ; it does not prove that without any activity energy may not leak away in some silent unobtrusive fashion, leaving no trace, but simply vanishing.

To meet this objection, an appeal may be made to the definition ; it may be called on to assert that anything that can thus disappear without force or motion is not energy, according to its terms ; but I doubt whether such an appeal is perfectly cogent, though it has some, perhaps much, plausibility. I think that the non-disappearance of energy in this occult manner had perhaps better be regarded as an axiom, a statement which may be believed until some clear experimental disproof is forthcoming : no such disproof being meanwhile in the least expected.

Briefly summarised, the matter stands thus :—

(1) If energy can only be got rid of by activity, and (2) if that activity never affects its quantity, the law of conservation is completely stated. My proof covers (2), but not (1). I may therefore agree with what I suppose Prof. MacGregor to mean, that the portion (1) must be left as an axiom based on experience.

Prof. MacGregor goes on to say (p. 137) that my law of conservation during mutual action has no deeper meaning than the conservation of their joint momentum, and is quite consistent with the non-conservation of their working-power.

To this I reply, first, that I mistrust the vague term "working-power," it is apt to mean whatever may be convenient ; from one point of view a given amount of energy may have an infinite "working-power," since it can do work at every transfer without itself diminishing ; while from another point of view it is rather bold to maintain the conservation of working-power in face of the doctrine of the dissipation of energy. And secondly I reply, that the conservation of *momentum* rests on the equality of the forces exerted by two mutually operative bodies, combined with the obvious equality of the *durations* or times of action of these forces. Whereas the conservation of *energy* rests on the equality of the forces, combined with the altogether less obvious fact of the equality of *velocities*, or *distances traversed*, by each of two operative bodies. Anyone in his senses who believes in action at a distance would deny that the velocities of two directly acting bodies are necessarily equal (no other bodies being assumed present, so as to simplify the problem) ; and in so doing he practically denies the conservation of energy.

Energy is only really conserved under conditions of universal contact-action.

Of course the believer in action at a distance is not at a loss: in order to retain his fiction he has invented another unreality, which he calls possible energy. He says (truly enough for many purposes) that when a stone is raised from the earth a great deal more work is done on the stone than on the earth; and hence that, although at every instant the stone and earth have equal opposite momenta, the energy is nearly all possessed by the raised stone. But since the energy of an inert mass is by no means apparent, since it only has the power of gaining actual energy when let drop, its energy when inert and merely elevated is called possible or potential. Or sometimes, rather more accurately but much more vaguely, energy is said to belong to the *configuration* of earth and stone*.

Now this idea of potential energy is convenient as a mathematical expression, and used in its proper signification it is an essential reality; but used in the sense above quoted, a very common mode of using it, it is a mere receptacle for stowing away any portion of energy which it is not convenient for the moment to attend to; and I defy anyone to realize it as a thing.

Yet I myself constantly employ the term potential or static energy, and assert that every activity not only transfers energy from one body to another, but also transforms it from kinetic to potential, or *vice versâ*.

Yes, but I also assert that the transformation can only accompany transference, and that transference cannot occur without transformation. Whereas, on the ordinary view, the energy of the raised stone is supposed to gradually transform itself into kinetic as the stone drops, but to remain in the stone all the time.

I say that the energy was no more in the stone when merely elevated than it is in a strung arrow or the bullet of a cartridge. The energy is in the bow, or in the powder, and is rightly said to be in a static, or strain, or potential form. It can transfer itself to the projectile, and simultaneously transform itself into kinetic, at the pull of a trigger †.

* Cf. Phil Mag. June 1881, p. 532, and June 1885, xix. p. 484.

† On page 141, Prof. MacGregor makes a statement in which I entirely fail to catch his meaning. It runs as follows:—"When Prof. Lodge states that 'a bullet fired upwards gradually transfers its undissipated energy to the gravitation medium, transforming it at the same time into potential,' he seems to me to assume that the bullet is rigid and that the medium is without inertia." Surely my critic does not consider that either plasticity in a projectile or inertia in a gravitating medium is essentially involved in determining the height attained by a body thrown up.

It is easy to express oneself so as to be understood to object to the whole idea of potential energy. It is not to the use of the term that I object, nor even to its misuse, so long as it be done in the temporary interest of some specific problem. It is by no means necessary always to attend to everything: acting mechanism is frequently, with convenience and brevity, ignored, especially when one is really ignorant of its dynamical nature; but in laying foundations we should not make these omissions and slurrings. It is the erroneous localization of energy in a fundamental or theoretical treatment of the subject that I deprecate, and I believe that everyone will agree that in all such treatment convenient fictions are better avoided.

There certainly exists potential energy in the case of a raised stone, but it does not belong to the stone; it belongs to the medium, whatever it is, which is exerting force on the stone and on the earth, and pressing the two lumps of matter together. It is properly called static, as distinguished from kinetic, because it is the energy of force, not the energy of motion*. As I have frequently pointed out, the two forms of energy correspond to the two factors of the product work or activity. Both factors are necessary for the actual performance of work. Until both factors are present, the energy is merely stored. As soon as the missing factor is supplied, it is *transferred* from the body acting to the body acted upon, *e. g.*, from the gravitation medium to the stone.

But it will be said, suppose the stone is not allowed to drop freely, but is used as a clock-weight; it is doing work all the time it slowly falls, hence when raised it must have had energy. But in this case I should deny that the stone is doing anything active; it is a necessary concomitant, it is a link of communication, it is not really itself doing work. Its presence indeed and that of the earth are necessary to the existence of the stress in the ether [permitting that or some other equivalent hypothesis for the moment]; but it is the ether stress which is doing the work and driving the wheels of the clock. A

* I do not mean to assert or deny anything concerning the nature of gravity. It may be that all energy is *ultimately* of the nature of motion, as we know Lord Kelvin has taught us may be the case with elastic stress for instance; but *force* is the proximate mode of action of a coiled spring, and so it may properly be described as *static energy*, whatever its ultimate nature. The reasons for affixing to static energy the epithet potential are mainly mathematical and historical. There is much convenience in thus linking it on to the potential function, and there is no particular inconvenience unless the adjective be misunderstood in the sense of "possible." It is indeed possible *work* or possible *activity*, but so is every kind of available energy; it is not possible *energy*, for that term is equivalent to the assertion that not yet is it energy at all.

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clock-weight has somewhat the same function as the string of a bow ; it was the convenient means of generating the potential energy, and it is the means of communicating it to the thing to be driven, but it is not itself energetic, any more than the chain and ratchet-wheel which helped to wind it up were energetic. Or, to take another example, it is like the piston of an air-gun : without it the gas would not have been compressed, and it might be (though it is not usually) employed to let the pressure reversibly down again, but it is not itself an active agent either in the charge or the discharge. It is like a Holtz machine or a dynamo : needful to the charging of Leyden jars or storage-cells, but not in itself doing the work, either when used for charging or, when running as a motor, for discharging.

I fear I am explaining elementary matters at some length ; but, although elementary in one sense, they are not quite easy to seize by the right end ; and the fact that they are so elementary tends actually to retard their apprehension, for unless people have patience to think them out they will not grasp what is meant. The difficulty in all these matters is that everybody thinks he understands them already, and is quite satisfied with his own prehistoric way of regarding them. Now I want to say that I have thought these things out with some care and labour ; and I believe that although no doubt everybody does understand them sufficiently for practical purposes, yet, if anyone has faith and patience enough to consent to reconsider them from my point of view (assuming, of course, as in most cases I safely may, that it is not his already), he will sooner or later realize the advantage of it. This belief may be presumptuous, but if so I am willing to presume to that extent.

With the substance of the following quotation from Professor MacGregor, on p. 138, February Phil. Mag., I entirely agree.

"If there be actions in nature which are not actions at constant distance" [*i. e.* practically contact-actions] "Prof. Lodge's law is not applicable to them, while the ordinary law is. Even if it be admitted that all actions in nature are contact-actions, there are many groups of phenomena which, in the present state of our knowledge of them, cannot be investigated on the hypothesis of contact-action. The early stages of their investigation must be conducted by the aid of the fiction of action at a distance ; and in such stages Prof. Lodge's law is not applicable, while the ordinary law is. Hence Prof. Lodge's law is not so general in its applicability as the ordinary law."

I might prefer to express it differently : I would say that it

is no discredit to the true law not to lend itself to fictions ; but I would also say, and freely admit, that it is often permissible for practical purposes to work in a fictitious or incomplete manner (as, for instance, when dealing with the diurnal motion of the sun or the libration of the moon), ignoring communicating mechanism in cases where one is ignorant of or need not attend to its nature, and in fact proceeding as the great physicists have constantly proceeded when engaged on a practical quest.

Never have I imagined that the practice of men of genius is other than the practice most suited to their immediate end. But when it comes to the philosophy and essence of the matter, I do think that there is some fear lest a constant habit of ignoring unknown essentials for practical and temporary convenience should lead these great mathematicians into forgetting that they have ignored anything, should in the long run delude them into treating their fictions as if they corresponded to the reality of things ; and it is permissible for me or others, as lookers-on seeing the structure from another point of view, unobtrusively to point out to the master builders, in their moments of leisure, the fact that while they have been engaged in the upper stories the foundations have almost automatically expanded, that the available basis of axiomatic reality has become broader and simpler than could be perceived when they started on their work, and that now some portion of their temporary scaffolding and underpinning may without danger, and with advantage to the general appreciation of the fabric, be discreetly and quietly removed.

PART IV.

The Dissipation of Energy, the Nature of Potential Energy, and the Second Law of Thermodynamics.

Passing on to Prof. MacGregor's fourth objection (p. 140) that I have not proved that transformation and transference necessarily go together, I hope to be able to meet him more nearly than has been possible to me on most of the other counts of his indictment.

My proposition was that the change of form is always from kinetic to potential or *vice versa*. But it is not necessary to attach the same importance to this law as an ultimate fact, because it is so extremely probable that most or all cases of potential energy will ultimately be resolved into essential motion. Nevertheless it is for the present a convenient statement of truth, having the same sort of validity that the second law of Thermodynamics possesses.

The following is my demonstration of the law of transference and transformation : being indeed the detailed statement of the essential phenomena accompanying transfer of energy, on the hypothesis of contact-action.

A body or other medium exerting force at any point, and there moving in the sense of the force it is exerting, is in a state of activity: it is passing energy on ahead. If its speed continues constant, the force just spoken of cannot be the sole force, the resultant force on it must be zero; in that case it is a mere transmitter, not itself active, only passing on what it receives. But if it is itself active, i. e. parting with its own energy, then its speed at the acting point (the place of application of the force) must either decrease or increase.*

If its speed decreases, it must be parting with kinetic energy; if its speed increases, it is parting with potential energy.

Contrariwise :—

A body or other medium exerting force and being moved in the sense opposed to that force is receiving energy.

If it is not merely passing it on, in which case the resultant force acting on it is zero, its velocity must vary.

If the velocity increases it is gaining kinetic energy; if its velocity decreases it is gaining potential.

Now the two bodies or things here spoken of are necessarily existent in every case of activity; one is the agent the other the patient, one the emitter the other the receiver, one the actor the other the reactor, one the driver the other the driven; and they are in contact while the activity lasts.

Being in contact, their velocities along the line of stress must increase or decrease together.

If their common velocity is decreasing, then the driver loses kinetic and the driven gains potential.

If their common velocity is increasing, the driver loses potential, the driven gains kinetic.

This is my proof of the necessary concomitance of transfer and transformation, and of the alternation of transformations. But it will be well to illustrate the matter further.

Let me first explain how I define potential or static energy as used in the proposition criticised. I mean by it simply the energy of a body under stress; an elastic body which is exerting force may always be said to have potential energy, notwithstanding that when the force comes to be analysed it

* Meaning by "a body" a thing of constant mass, an identical lump of matter. A thing of variable mass, like a rain-drop or a railway-train or a layer of moving gas, is gaining or losing matter as well as energy; and cannot be regarded as one simple body.

may be perceived to result from some kind of motion. Thus a reservoir of compressed air is a store of potential energy, though it is well known that all the pressure is due to the motion of unstressed particles, and is really just as much kinetic as any of the energy of planets and comets. A powder-magazine is a store of potential energy, though quite possibly the forces awaiting a trigger to liberate them into activity are due to atomic or etherial motions; and the same may be said of a charged Leyden jar and of a bent bow.

Briefly the idea of potential energy corresponds to the idea of elastic force when the cause of that force is not sought. The idea of kinetic energy corresponds to the idea of sustained motion. Each corresponds to one of the factors in the product "activity," or Fv .

In order that a body may possess energy it must be capable of exerting force and also of moving; but it need be doing only one of these things, and so long as it merely stores energy it *must* be doing only one of them. Both factors must concur before it can be active, both factors must be possible before it can be said to possess energy. The only question is, which factor does it possess meanwhile? If it is exerting force, but stationary, then its energy is potential or static; if it is moving quite freely, then its energy is kinetic.

So long as the other factor is absent no activity manifests itself, no work is done, and the energy is merely stored. Directly the other factor is supplied transference begins, energy leaves the body storing it, and passes to the body supplying the other factor.

Now to make a *moving* body do work, a resisting obstacle must be supplied, and this second body thus exerting force receives a due proportion of the energy; and it receives it by reason of the force it exerts, that is, it receives static or potential energy from a body which possessed kinetic.

To make a *strained* body do work, motion must be permitted; the thing which is moved gains energy, and it gains it in the kinetic form from a body possessing potential.

Of course in both cases the body immediately receiving the energy need not retain it, but may rapidly or instantaneously pass it on to something else—in which case it resumes its first form; by simple alternation of transformations.

Also it is not essential that the potential energy of the particles of a spring shall be communicated to any *foreign* body: if it is transferred to the spring as a whole, considered as a mass possessing inertia, that is sufficient; in other words, it may be transferred from one set of particles to another set

of particles, all forming part of what we usually speak of as a single body*.

To take one of the examples of Prof. MacGregor, viz. a loaded air-gun with its muzzle plugged, so that its bullet or wad is not allowed to be shot. The compressed air has potential energy; on its release its energy is transferred to the moving wad, which instantaneously hands it on to the air near the muzzle, compressing it, and thus retransforming itself into the potential form.

If it be objected that the energy never at any instant all existed in the kinetic form, the answer is no, but it necessarily passed through that form; it could only be by the intervention of motion that the energy of the air at one end was transferred to the air at the other end. The wad itself is unnecessary and may be dematerialized; the only thing moving may be the gas atoms themselves, but the atoms which are rushing are not the same as those under strain; the moving atoms are precisely those which have escaped from strain. As everybody knows, where the rush of gas is greatest in a constricted pipe there the pressure is least. Air rushing from one reservoir into another illustrates the law precisely, though I choose it as a case at first sight favourable to Prof. MacGregor's contention; in the narrow part of the pipe air is flowing against a higher pressure in front of it, it is compressing the air ahead of it by reason of its own momentum; the energy of each molecule is available kinetic to precisely the extent to which it ceases to be potential, and any residual potential energy which does not become momentarily kinetic, and kinetic in the available sense of a windy rush, has not been transferred at all, but remains simply stored, as it would have been had nothing been released and no activity been manifested.

If the two reservoirs (or two Leyden jars) are for instance equal in capacity, and if one had been originally empty, then one quarter the original energy remains still potential in the originally full vessel, another quarter has been transferred by the rush of gas into the originally empty vessel, and two quarters have been dissipated, so to speak, converted into heat by friction. If there is no friction, then this half of the original energy remains alternating for ever from the kinetic to the potential form, like the bob of a pendulum, and transferring itself at every half swing from the one vessel to the other.

Lest this last statement should permit misconception, it may be necessary to state explicitly that the energy is only hazily attributed to the vessel—the energy belongs of course

* This sentence is true in one sense, but it is not a final or complete statement, and in a later paper a modification will be introduced.

to the gas molecules—and, further, that the molecules which are in motion are not the same as those which are under strain. The energy, that is the portion of energy concerned with the particular amount of activity contemplated, is continuously leaving the molecules recovering from strain and transferring itself to those in accelerated motion, and as continuously leaving those in retarded motion and transferring itself to those acquiring strain*.

Further to avoid misconception it is necessary to admit distinctly that in speaking of the pressure-energy of a mass of gas we are subjecting ourselves to an unnecessary though convenient limitation. It is chosen as an example just *because* so much is known about it; it would have been easy to choose elastic solid examples, where the elastic stress is not so readily analysable, and where the idea of potential energy and the statistical grouping of a mass of molecules was not optional but necessary, in our present state of ignorance. I know well enough that the pressure of gas in a reservoir is really due to the motion of the particles, and I am willing freely to contemplate the case of Davy's "repulsive motion," no real contact or elastic impact between particles ever occurring, but only a rapid swing or asymptotic orbit round their common centre of gravity; but this rapid centripetal swing of particles getting within each other's molecular range is at present essentially an unknown process, and has to be relegated to the sphere of potential energy quite as much as in the not perhaps really dissimilar cases of elastic impact and gravitation.

Whenever an atom after collision retains its energy intact, there is no need to say that there has been either transference or transformation; mere retention or storage is sufficient for practical purposes (though if we attend to the details of a collision we find there really is always a double transference and a double transformation †); and if this is typical of what

* See, however, the footnote on preceding page.

† *E.g.*, suppose a quick molecule A strikes or otherwise collides with a slow but similar molecule B. The mechanism of the collision, being unknown, is unimportant, and is most conveniently thought of in terms of elasticity. A and B undergo distortion as they approach, and a certain portion of A's energy is communicated to whatever medium it is which keeps them asunder. This medium by its recoil then drives them apart, sending off B with the energy which A originally had, and transferring to A the small portion received from B. [This matter is discussed at greater length in Appendix 2.] Any part of the energy which was not transformed is also not transferred. Everything transferred from A to B necessarily underwent rapidly a double transformation. When other occurrences are analysed it will be found that the above is typical of what constantly happens. Yet it is not always necessary to attend to all details, and in the text above I speak as if A and B passed through each other, each retaining its original energy.

happens in every atomic encounter, whether it be with the walls of the vessel or with another free molecule, then, so long as the air remains compressed, there is merely a storage of energy, each molecule possessing and retaining its own share. But directly an opening is made, or a communication established with an empty vessel, it is equivalent to the removal of a portion of wall, and some of the atoms, with their energy, pass along without obstruction into a new region of space.

In one sense each may still be said to retain its original energy; but in order to regard it thus we must be capable of dealing with the atoms individually. If the atoms escaping from confinement are lost in the vastness of space, their energy is unavailable, and their pressure, on which entirely depends the potential energy of a compressed mass of gas, is *nil*. If they escape into another equal vessel, then only the first individuals can enter freely without obstruction, all the others experience encounters on the way, as if the hole in the wall were gradually being restored; and though at the end of the operation, when everything has finally settled down, each atom may be said to possess its original energy, yet the pressure, on which depends the potential energy of the compressed gas, has been halved, and the other half is unavailable or has been dissipated.

Plainly the idea of potential energy belongs to the temporary order of ideas, to which the dissipation of energy and the second law of thermodynamics belong, and is appropriate to the present period when we have not yet learnt how to deal with molecules individually.

The kinetic energy of a set of gas molecules is only really available when it is combined with momentum or angular momentum, *i. e.* when the motion of a majority of molecules has the same sign, when there are more plus terms than minus in either their translational or their angular velocity; in other words, when there is a wind or cyclone*. A stream of particles can be utilised, as by a windmill or a Pelton water-wheel, and that is an example of available kinetic energy. But usually the energy of fluids can only be

* It may be worth while to point out that the reason why momentum is necessarily preserved in cases of impact, while translatory energy is usually not conserved, is because momentum depends on the first power of velocity, and therefore is unconcerned with vibrations; while every kind of vibration, whether it be of sound or of heat, enters into the sum total of a thing depending on an even power of velocity, like energy, whose translational value is therefore to that extent diminished by the production of vibratory disturbances.

utilised in the potential form ; as in a hydraulic-press or steam-boiler.

To say that all potential energy will turn out to be really kinetic may be true enough, but it is not at present a specially helpful truth, for even in cases (such as compressed air) when we actually *know* it to be kinetic, we are bound for all practical purposes to treat it as potential, since the available working-power of a spring, or of compressed air, of gunpowder, of Leyden jars, and of many other things, depends on their potential energy alone ; and such other energy as they may possess is conveniently ignored, as not concerned in any practical transformations or activities which we can bring about : it remains as an untransferable, and therefore inactive or useless residuum.

This is the real meaning of available energy, it is the portion concerned in transferences, the portion which can be transformed, *the portion which is able to transfer itself*. Potential energy, as commonly spoken of, is always of this character. An unwound watch-spring has lost its potential energy, it retains a quantity of untransferable heat-energy. A hot body cooling is in the same case ; so long as it is hot, some of its heat-energy is transferable ; and the transferable portion may well be regarded as and styled potential.

Available or potential heat-energy readily transfers itself to space or to other bodies, just as compressed air readily leaks out of its reservoir ; and in so doing becomes less potential*. Even if it is all received by other bodies in the room, the potential energy of the contents of the room is to the extent of the leakage diminished.

To say that heat-energy is constant in quantity is the same as saying that the molecules of an escaping gas need not part with their energy but may individually retain it. In the abstract either proposition is true, but just as it was only the compression part of gas energy that was potential or available for us, so also it is only the high-temperature part of heat-energy that is similarly available.

It is customary and correct to say that the available part of heat-energy is converted into other forms when allowed to be active and do work. A distinction is thus apparently drawn between heat-engines, on the one hand, and water-engines, compressed-air engines, or electric engines, on the other ; because in them the water, the air, and the electricity flow away undiminished in quantity and only at a lower level, pressure, or potential.

* It is tempting thus to use the adjective "potential" in the sense of available. I do not at present wish to justify this secondary usage of the word, but I let it stand as a suggestive and harmless eccentricity.

This distinction is the cause of some confusion or bewilderment, and I verily believe of some incredulity. Prof. Osborne Reynolds has shown, in his interesting biography of Joule, how great were the difficulties felt by the most eminent men in realising that heat actually disappeared in a heat-engine: that less heat was given to condenser than was received from boiler; that not only temperature fell but *also* heat was lost; and we all know how Carnot's theory was based on the contrary hypothesis.

But one mode of avoiding what is reasonably felt to be an artificial and puzzling distinction, is to say that in *all* the engines mentioned transformation of available energy occurs as soon as activity begins, and that that engine is perfect which enables all the energy available to transform itself in the desired way.

The potential energy of the raised water (so to speak for the moment), of the compressed air, of the separated chemicals, disappears, and transforms itself into the motion of a turbine, a bullet, or a motor-dynamo; the potential energy of the hot "working-substance" disappears in like manner, and results in the motion of fly-wheel belts and shafting*.

It is inconvenient to speak of the energy of heat as kinetic. It is much of it kinetic, just as the energy of compressed air and everything else may be kinetic; but to us here and now its available portion is not kinetic, but potential. When we can deal with molecules it can be regarded how we please—alternately kinetic and potential, probably, like the energy of a vibrating fork, or on the average half-and-half, like waves;—but till then the kinetic energy of individual atoms is useless, it is the average energy of a group which alone is useful, and this is all that we attempt to utilise in every one of the cases cited. Practically useful kinetic molecular energy exists only when all the molecules are rushing one way, and that is never the case with heat.

By the energy of a spring we mean its energy over and above its useless energy of average temperature; by the energy of a storage-battery we mean the portion corresponding to the reduced lead and the peroxide; by the energy of a waterfall we do not mean to include the warmth of the water above absolute zero; we always mean that portion of its total energy which we aim at utilising, and so speaking we say that a watch, or a dynamo, or a turbine, are efficient machines. By

* Prof. Fitzgerald has pointed out to me that this analogy will work well if I use *entropy* as the analogue of the water in a waterfall, because entropy does really fall in temperature and remain constant in quantity while a perfect heat-engine is working. This suggestion I hope to develop along with other thermodynamic matters in a future paper.

the energy of a hot body we ought to mean that portion of its energy which it has over and above its useless energy of average temperature, the portion which it is willing and able to part with, the only portion we hope to use or aim at using; and so speaking we might call a heat-engine an efficient machine.

We get a notion of low efficiency in the one case, of high efficiency in the others—we confuse ourselves sometimes with statements about the dissipation of energy—all because we perversely *attend* to the energy of average temperature in the one case but not in any of the others. We have done it naturally enough, because in that one case our attention was specially directed to the subject of heat; but it may be a help to realise that all the cases are essentially similar and on the same footing.

True a steam-engine and boiler is *not* an efficient arrangement, only about 8 or 9 per cent. at the best, but that is because of the great unnecessary drop of temperature between furnace and boiler; starting with the temperature of the *boiler*, and ignoring all energy below the temperature of the condenser, it may be efficient enough, 80 or 90 per cent. I suppose. It is better not to pretend to be able to use average molecular energy until we have learnt how to do it.

The portion of heat which can at a single operation be converted into work is very nearly the same as that which leaks away when the body is allowed to cool; just as it is the potential portion which disappears from a standing Leyden jar, or a running-down weight, or a rusting spring, or a leaky reservoir. The difference between the cases is that whereas the capacity of Leyden jars and tanks is constant, capacity for heat is apt to vary with the other conditions of a body; hence intrinsic energy is not solely a function of temperature, but subordinately of volume also. This fact necessitates caution before the above statement can be regarded as complete.

What a body will freely yield throughout a cycle of operations, that can be utilised. We cannot advantageously gain energy by pumping it. Whatever must be pumped is unavailable. We require an artesian well or automatic supply of energy if we are to get work out of it.

A further statement also is necessary if we are to concern ourselves with practical modes of utilising the theoretically available energy; some such statement as the following:—Available energy can only be continually utilised by means of reversible operations. Unless the working-substance is restored to its original condition the process cannot continually go on; and any operation which is not reversible involves dissipation of energy or needless waste of availability.

That the available portion of heat should bear to the whole heat the same ratio which the available drop of temperature bears to the absolute temperature, is essentially but a definition of temperature ; it is an assertion that temperature is best measured as proportional to heat, or that the zero of temperature may conveniently be taken to correspond with the zero of heat.

An essential part of the second law of Thermodynamics therefore proceeds to state itself in a very general and purely commonsense form, thus :--

The portion of energy which a body can automatically part with is alone available for doing work ; and only that portion which is parted with reversibly is actually utilised.

There is no need to mention "heat;" it is equally true of every form of energy. When a cell has run down, or a reservoir leaked itself empty, as empty as it wants to, any further energy it may have is useless ; and any portion which flowed out in an uncontrolled or irreversible manner will have been wasted.

There is something specific to be said about each form of energy in order to apply the above statement definitely to that form ; and in the case of heat the supplementary statement needed is that heat will not automatically leave a body for others at higher temperature : if it goes to a hotter body it must be carried by matter, or electricity, or something else, so that it is not a pure and simple flow of heat. In other words, heat will not flow "uphill" by pure conduction ; and conduction is the only mode of automatic conveyance of heat as heat*. Water, air, or electricity can flow "uphill" for a time and can do work at the same time, by reason of their property of inertia. Heat cannot : it has no inertia. None of the uphill processes can go on continually or cyclically†.

The law of dissipation of energy states itself thus :—

If a body has any portion of energy in such condition that it is able irreversibly to leave the body, that portion usually does leave, sooner or later. This is only a rewording of the customary statement that the potential energy of a system tends towards a minimum ; or, really, except that circumstances often delay the consummation unpractically long, towards zero. The universe will be stagnant, though by no means stationary, when its potential energy is nothing. There

* Radiation is not heat, but another quite distinct form of energy. The phrase "radiant heat" is responsible for immense confusion.

† Work and heat may be coaxed out of a body below the temperature of surrounding objects, as, for instance, by letting air escape from a high-pressure reservoir ; but such a process is not cyclical until the air is put back again, and by that operation the heat has to be put back too. Heat by itself cannot flow uphill at all.

will then be abundance of motion but no force, and therefore no "activity."

To make use of the readily detachable portion of energy may not be a very simple thing, and commonly requires a machine, sometimes an ingenious machine. Give a savage a charged Leyden jar, and he will probably detach from it its available energy pretty soon. But give him a charged storage-battery and he will not know what to do. A bit of thin wire, however, is all the mechanism absolutely needed in order to afford him some light and heat; if mechanical motion is required then some form of dynamo or electromagnetic motor must be supplied. Often and often we do not know how fairly to utilise even the portion of energy automatically streaming off from a body—from a gas-flame for instance when we need light. To utilise more of a body's energy than it will part with is impossible; but the progress of science may conceivably teach us, not only how to utilise the whole of what bodies already freely give off, but also perhaps even how to make bodies (say molecules for instance) part with much energy which at present, if left to themselves, they permanently retain.

The first and most general portion of the second law of Thermodynamics, stated above in italics, will always remain true, even when the second part, about the non-uphill flow of heat, has by future discovery been upset; because the application of a machine for the purpose of extracting otherwise retained energy, not by a process analogous to pumping but by enabling it automatically to flow whereas without the machine it could not, can hardly be regarded as other than automatic; else would the present machines for directing the flow of already available heat be liable to a similar objection. Even if the contrivance necessary for extracting molecular energy turn out to be a live thing,—and this Dr. Johnstone Stoney* most suggestively conceives it possible may be the function of some bacteria [a remarkably appropriate demoniacal function for the producers of disease], yet life, too, so far as it falls into the scheme of physics, must be considered as an automatic process, and only the energy which by any device a body can be made automatically to yield without pumping can ever be utilised. But statements about heat not flowing up hill, or about not cooling bodies below

surrounding objects, or about $\int \frac{dQ}{T} = 0$, or $dQ = Td\phi$, &c.;

these are liable to ultimate modification with the progress of science, since the very terms Heat and Temperature are

* Phil. Mag. April 1893.

undynamical blinkers appropriate to the consideration of particles in the lump.

APPENDIX 1.—*The Objectivity of Energy and the Question of Gravitation.*

Mr. Heaviside* freely contemplates the flux of energy, but declines to admit its identity, or as he calls it objectivity. And he further doubts my proposition about transformation accompanying transference, because, he says, "convection of energy," i. e. simple locomotion of stored energy, "is a true flux." So it is, but it is not what I meant by *transfer*. Locomotion is so absolutely essential to translational kinetic energy that I hardly think it can be desirable ever to speak of mere locomotion as transfer, even although the moving thing be a bent bow or stretched spring. It is, however, a question of convenience, and undeniably convection must enter into a flux equation, for a bullet entering a partitioned-off region of space brings into it energy which was not there before, and, when it leaves, conveys it out again.

My proposition amounts to just this, that whatever energy appears in a bounded region must necessarily have passed through the boundary. This, if true, seems to me to confer upon energy the same kind of identity or continuous existence (or if you please objectivity) as matter possesses.

The ordinary law of conservation does not assert or contemplate continuous existence: it has no objection to seeing energy disappear from existence in one place provided an equal quantity reappears somewhere else—say inside a bounded region. Either it does not attend to or believe in the fact of transfer, or else it is satisfied with a kind of fourth-dimensional out-of-space path.

As to "objectivity" or "reality," there are always metaphysical difficulties about predicating that; and Mr. Heaviside's objection that since motion is relative, energy can hardly be absolute, must be allowed due weight. This is a point on which Professor Newcomb has written in *Phil. Mag.* February 1889; arguing that it actually limits the generality of the law of conservation. I hope some day to discuss this at more length; meanwhile my belief is that it will be ascertained that motion with respect to the ether is the energetic thing and that other absolute motion is meaningless.

The fact (if fact it be) that energy has a continuous existence, or that if it appears in a closed region it must

* *Phil. Trans.* 1892, p. 427, "On the Forces, Stresses, and Fluxes of Energy in the Electromagnetic Field," by Oliver Heaviside, F.R.S.

have penetrated the walls, is expressed quite clearly by Mr. Heaviside's equation

$$\text{conv } eu = \dot{e},$$

where e is the energy per unit volume, u is its velocity of locomotion, and where *conv.* stands for $S\nabla$, or $d/dx + d/dy + d/dz$.

But Mr. Heaviside is not satisfied with this simple equation of continuity, and proceeds to complicate it by introducing:—

(1) Intrinsic sources ; *i. e.* creation or fourth-dimensional apparition of energy ; of which the chief example is the gravitation bogey, whose path and nature no man yet knows.

(2) Flux of energy travelling not with matter at a definite speed, but in some other way so that its speed is uncertain. For example of this he instances radiation, but surely that has a definite enough velocity. He might have instanced conduction of heat ; but there again, treated merely as a flux of energy, the amount crossing unit area per second is definite enough. Mr. Heaviside would probably agree, but would prefer not to analyse it into two factors e and u ; and to this I cannot object.

(3) But to his third category Q, the rate of waste of energy, I am bound to object. The insertion of dissipation of energy as if it were a mysterious disappearance term, is open to the objection suggested above against (1), and also to the objection that it unduly elevates the available portion of energy into being the whole of it.

So long as these various terms are only introduced for practical purposes, *i. e.* to direct attention to what might otherwise get overlooked, they are well enough ; but they must not be supposed to represent the reality of things. It is true that the case of gravitation, if it be transmitted instantaneously, as seems not unlikely, is a curious simulacrum of action at a distance ; whereby of course energy could be generated *de novo* inside closed boundaries readily enough ; but infinite speed of transmission only requires infinite incompressibility in a medium, it does not dispense with a medium ; and if a medium of transmission exists, as all analogy and coherence urges if not insists, then gravitation is no exception, and its energy must pass through the walls in order to get inside a boundary, although it may pass through at an infinite pace. It may be better, however, not to assume the pace infinite till proved, but to have a term in the most general energy-equations expressive of the possible propagation of gravitation in time, notwithstanding that its speed is unknown and certainly excessively great.

I may refer to another reply I have made to Mr. Heaviside in 'Nature,' vol. xlvii. p. 293 (January 26, 1893).

APPENDIX 2.—*More detailed Discussion of the Transmission of Energy in difficult cases.*

When I say (as I do on pp. 14, 15, and 20) that acting bodies have the same velocity, I of course mean their action to be immediate. If indirect action is contemplated, it is too obvious that a clock-weight has not the same speed as the tip of the second-hand or the hammer of its bell; but at the contact of every cog, two wheels, driver and driven, are moving at the same pace. But now, it may be asked, if all action is contact-action, if all action is direct, how is it possible ever to get a variation in speed? This is a question worth answering.

It is done and only done by means of rotation. The type of all such actions is a rotating wheel propelled by an uncentral force. In such a wheel, regarded as a single rigid body, we have every gradation of speed from a maximum to nothing, and we can make use of or transmit elsewhere what speed we like. This is the essence of levers, and mechanism in general: without rotation the speed of all parts is the same, and therefore the same as the point to which the driving force is applied.

But now, treating the wheel as what it is—an assemblage of particles—how comes it that they can act on each other so as to generate differences of speed? How can a force applied tangentially to the face of a sphere cause part of the opposite hemisphere to move backwards?

If we accept the sphere as a rigid body, nothing is easier than to equate the momentum generated to the impulse of the applied force, and its moment of momentum to the moment of the impulse; but if we treat it as an assemblage of connected particles it is not so easy to tackle the problem. As is well known it did historically give trouble, until it was realised, on the ground of Newton's third law (or D'Alembert's Principle as it was called), that all internal stresses balanced each other, and might therefore be ignored for the purpose of deducing the final result.

There is now no controversy as to final result; the only question is how universal contact-action, with equal velocity between agent and patient, or driver and driven, can account for the ultimate result of all grades of velocity through zero even to minus.

There is no need to take refuge behind any such blinkers as D'Alembert's Principle: an assemblage of connected particles can be directly contemplated. Let one of them receive a blow, it is passed on to the others and the momentum spreads laterally by oblique impacts, the amount of obliquity

being limited only by the arrangement of the molecules; and the component of the blow or thrust transmitted in any direction is diminished in accordance with the suitable cosine law. The process is notoriously not an easy one to follow into detail, even in a simple case, partly for lack of data; and there is some uncertainty as to the disposal of the energy for the case of a blow, though even in that case there is no uncertainty about the momentum; while for a steady force the body, however essentially elastic, gets rapidly into a practically rigid state, and the molecules then merely act as transmitters of the energy. They are, as it were, connected by massless struts and ties, and along these the energy is transmitted, partitioning itself off into several directions, much as it did in the case of impact, and producing local velocities determined by the arrangement of the particles, that is, by the shape and other circumstances of the body*.

The conception of a rigid body, to which a couple can be applied, and which moves as a whole without dislocation of parts, every portion instantaneously feeling whatever force there is to reach it, simplifies problems enormously; and it may be said that just as a moving body retains its kinetic energy and carries it through space without transfer or transformation, so a rigid body conveys thrust or potential energy through space, receiving it at one point, delivering it up at other points, and transmitting it instantaneously without transfer or transformation. The thrust of a connecting-rod, the torque of a shaft, the tension of a belt, and the tangential stress of a cog-wheel, are typical instances of this practically instantaneous communication, or locomotion of potential energy, caused by a rigid body.

The simplest way to think of the ordinary case of gearing and shafting is thus to ignore its molecular structure and treat it as a linkage of entirely rigid bodies, where the potential energy communicated to one point is conveyed elsewhere as a simple flux without transfer or transformation, as kinetic is conveyed when a bullet is shot across an empty space.

But that this blindfold treatment does not exhaust the matter can be seen at once by thinking of a moving fly-wheel suddenly geared on to a stationary cog-wheel, so as to transmit a portion of its kinetic energy to machinery. The stress necessary to effect the transfer is too gigantic, and results in damage unless some elasticity is provided in shaft or spokes wherewith to store it temporarily and subsequently give it

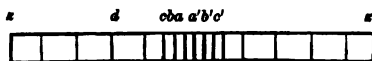
* In Thomson and Tait, vol. i. part 1, §§ 311-318, the effect of an impact on a number of elastically connected particles is treated. So it is partly in a review in 'Nature,' vol. xlvii. p. 601 (April 27, 1893).

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out again in the kinetic form, or unless by means of slip a good deal of energy is dissipated. But some dissipation is essential anyhow: a certain fraction, equal to the ratio of the moving mass to the whole mass, must assume a vibrational form of some kind.

It is instructive to recollect certain elementary facts, such as that in the impact of two perfectly elastic bodies, one moving, one stationary, all the energy and all the momentum *may* be transmitted complete, but that in this case the resulting motion of the two bodies cannot be the same. Whereas, if by reason of elastic vibrations, or by reason of heat dissipation, it is arranged that two equal bodies shall after impact move together, then only one half the momentum and only one quarter of the energy is transmitted, the remaining half of the energy having been diverted or wasted in heat or vibration.

So it is with any system of shafting or mill-gearing to which motion has to be communicated from a revolving fly-wheel. The conservation of moment of momentum gives part of the circumstances; the refusal of ultimate mutual recoil gives the other part. And the amount of ultimate vibrational dissipation of energy is precisely the same, under these circumstances, for perfectly elastic as for perfectly inelastic bodies. The case is not unlike the opening of a stopcock between a full and empty pair of reservoirs. A certain fraction of the energy is necessarily either dissipated in heat or left as permanent vibration.



Consider the circumstance of the impact of a couple of equal elastic rods moving end-on. Conceive them in transverse strata labelled $a, b, c, \dots z$ for each rod. Let one rod be stationary, and the other strike it longitudinally with velocity v . At the beginning of the impact a strikes a' , and the two move on in contact with the speed $\frac{1}{2}v$. b now strikes the mass a' , and would accelerate it, but at the same instant a' strikes b' , communicating the motion to it and neutralizing the acceleration on itself; so that now the four strata are all moving with speed $\frac{1}{2}v$, while all the rest of one rod is still stationary, and all the rest of the other rod is still moving with original velocity v . The length of the half-speed piece about the point of contact continually increases, and behaves as a body under gradually increasing compression as it receives blow after blow on either end. At length z and z' strike, and the recoil is ready to begin. This is the middle of the impact,

half the momentum has been transmitted and half the energy ; but of the transmitted half energy, one-half again, or a quarter of the original only is in the kinetic form, the other quarter is in the potential or elastic-stress form.

If the rods are inelastic everything so far has happened similarly, but nothing further happens ; what I have called the middle of the elastic impact is the end of the inelastic one. Kinetic energy from w and y has been transmitted to w' and y' through the intervention of the quasi-rigid compressed portion of each rod, and energy from z has reached z' . A quarter of the whole energy has been transmitted direct as kinetic, and there is no potential because there is no recoil. One half the original energy has been lost.

If the rods are elastic the recoil brings z to rest and flings z' on with the original velocity v ; then y stops and y' flies on after z' , and so on, till at the end of the impact the rods part asunder, the first one completely stationary, the second one completely moving with all the energy simply kinetic.

If the rods are partially elastic some of the potential energy is dissipated and some utilised, while if they are of unequal length or material the pulses are not timed similarly in both ; the shorter one (supposed the striker) is struck dead as before, the longer one is left with a pulse in it after they have separated, and its residual potential energy then assumes the sound-vibrational form : the strata progressing jerkily for some time.

If the rod to be moved is incompressible, its pulse travels instantaneously and it all gets moved at once. A blow to such a rod transmits energy instantaneously, and all in the kinetic form, but there is nothing in mere speed to affect the amount transmitted.

By the consideration of instances we have thus been led to the induction that energy can be transmitted without obvious change of form by substances with infinite properties, *e. g.* by an incompressible solid ; all molecular processes being either non-existent or being ignored ; but that with ordinary matter there is always some percentage of obvious transformation, though we may apparently have all grades of it from complete to very small.

Thinking of these impact cases alone, it might appear as if I had been overhasty in saying that the whole of energy must be transformed when it is transferred. Yet observe that it has to pass *through* the intermediate condition. A row of ivory balls in contact has another thrown against one end, and from the other end one leaps off. The energy has been transmitted through the row somewhat as it is transmitted through the

compressed strata of two impinging rods. Yet if the elastic connexions of every stratum are attended to, and if these be regarded as massless, I think it will be found that all the transmitted kinetic has really passed through a momentary existence as potential. The fact of necessary transformation is not so obvious when you come to look into some of these special cases ; but I would refer once more to the proof given at the beginning of Part IV., which seems to me conclusive as to essential fact.

The difficulty arises because when an elastic body is struck (say a massive molecule with a massless spiral spring connexion) it begins to move a little directly the spring is the least compressed, and is moving half speed when the spring is fully compressed ; but I venture to say that on any view of the identity of energy the bit of kinetic which it first attains is a bit of energy that has been transmitted through the elastic stress of the spring, and that just as the second half of the energy must admittedly exist in the spring before it can reach the mass, so the first half has already passed through the spring and has reached the mass only after transmutation, although the transformation is disguised while the transference is obvious.

I have now written enough to emphasize what I want to bring forward as the simple doctrine of energy. Some years ago* I attempted it with brevity, but failed to make it clear or to call proper attention to it. Now I have set it forth at length, with illustrative cases, as matter for discussion. It remains to try and formulate briefly and strictly the extended laws of motion appropriate to our present knowledge.

* Especially in *Phil. Mag.* for October 1879, page 278 *et seq.*, for January 1881, p. 37, and June 1881, p. 530, and for June 1885, p. 482. Also in 'Elementary Mechanics' (Chambers), which was written in 1876 and revised about 1884, without change in the energy chapter so far as I remember ; I am not responsible for dates on title-pages.

My attention has just been called to a "Smith's Prize" essay by Mr. R. F. Muirhead, communicated by Professor James Thomson to the *Philosophical Magazine* for June 1887. This essay, both in itself and in its numerous quotations and criticisms, is an instructive and useful summary or exposition of nearly everything that is foggy, confusing, and utterly unsatisfactory in the fundamental treatment of Dynamics. It is hardly too much to say broadly that the entire order of ideas in that essay is antipodal to the conceptions I am endeavouring to urge on the acceptance of Physicists.

II. *On the Methods of Theoretical Physics.*

By LUDWIG BOLTZMANN*.

[This Article was written for and published in the 'Catalogue of the Mathematical Exhibition,' which the Association of German Mathematicians had arranged to be held last year at Nuremberg, but which was at the last moment postponed to September in this year at Munich.

It contains such a clear exposition of the views held at different times about the methods in Mathematical Physics, and more especially of Maxwell's views, and of his use of models and apparatus constructed to imitate dynamically natural phenomena, that the Council of the Physical Society have thought it desirable to make it more easily accessible to English Physicists by publishing this translation.]

CALLED upon by the Editors of the Catalogue to deal with this subject, I soon became aware that little which is new could be said, so much and such sterling matter having in recent times been written about it. An almost exaggerated criticism of the methods of scientific investigation is indeed a characteristic of the present day ; an intensified Critique of Pure Reason we might say, if this expression were not perhaps somewhat too presumptuous. It cannot be my object again to criticise this criticism. I will only offer a few guiding remarks for those who, without being specially occupied with these questions, nevertheless take an interest in them.

In mathematics and in geometry it was at first undoubtedly the necessity for economizing labour which led from purely analytical to synthetical methods, as well as to their illustration by models. Even if this necessity appears to be a purely practical and obvious one, we here find ourselves on ground on which a whole species of modern methodological speculations have grown up, which have been expressed by Mach in the most definite and ingenious manner. He, indeed, directly maintains that the sole object of Science is economy of labour.

Seeing that in business affairs the greatest economy is desirable, it might, with equal justice, be maintained that this is simply the object of the sale-room, and of money in general, which in a certain sense would be true. Yet when we search into the distances, the motions, the magnitudes, the physical and chemical structure of the fixed stars, when microscopes are invented and we thereby discover the origins of disease, we shall not be very apt to describe this as mere economy.

But it is after all a matter of definition what we denote as an object, and what are the means for obtaining that object. It in fact depends on our own definition of existence what

* Communicated by the Physical Society.

we recognize as existing ; whether substances, or their energy, or, in general, their properties, so that we may perhaps at last define away even our own existence.

But let this pass ; the necessity exists for the most complete utilization of our different powers of conception ; and since it is by aid of the eye that the greatest mass of facts can be grasped simultaneously, it becomes desirable to make the results of our calculation perceptible, and that not merely by the imagination, but visible to the eye and at the same time palpable to the touch by means of gypsum and of cardboard.

How little was done in this direction in my student days ! Mathematical instruments were almost wholly unknown, and physical experiments were often made in such a manner that they could only be seen by the Lecturer himself. And as, further, owing to shortness of sight I was unable to see writing on the blackboard, my imagination was constantly kept on the stretch. I had almost said to my good fortune. Yet this latter statement would be in opposition to the object of the present Catalogue, which can only be to praise the infinite equipment of models in the mathematics of the present day ; and it would, moreover, be quite incorrect. For even if my growing organically powers of conception had gained, it could only have been at the expense of the range of my acquired knowledge. At that time the theory of surfaces of the second order was still the summit of geometrical knowledge, and an egg, a napkin ring, or a saddle was sufficient. What a host of shapes, singularities, and of forms growing organically out of each other, must not the geometrician of the present day impress on his memory ! and how greatly is he not helped by plaster casts, models with fixed and movable strings, links, and all kinds of joints !

Not only so, but those machines make more and more way which serve not for mere illustration, but save the trouble of making actual calculations, from the ordinary four rules of arithmetic to the most complicated integrations.

As a matter of course both kinds of apparatus are most extensively used by physicists, who, in any case, are continually accustomed to the manipulation of all kinds of apparatus. Optical wave-surfaces, thermodynamical surfaces in gypsum, wave-machines of all kinds, apparatus for illustrating the laws of the refraction of light and other laws of nature, are examples of models of the first kind.

In the construction of instruments of the second kind some have even gone so far as to attempt the evaluation of the integrals of differential equations which hold equally for a phenomenon difficult to observe (like the friction of gases)

and another which allows of easy measurements (like the distribution of an electric current in a conductor of suitable shape) by observations of the latter, and then to utilize these values for the determination of the constant of friction. We may also remember the graphical utilization of the series and integrals occurring in the theory of tides, in electrodynamics by Lord Kelvin, who, in his 'Lectures on Molecular Dynamics,' suggests even the establishment of a mathematical institution for such calculations.

In theoretical physics other models are more and more coming into use which I am inclined to class as a third species, for they owe their origin to a peculiar method which is more and more being applied in this science. I believe this is due rather to practical physical needs than to speculations as to the theory of cognition. The method has, nevertheless, an eminently philosophical stamp, and we must accordingly enter afresh the field of the theory of cognition.

At the time of the French Revolution and afterwards the great mathematicians of Paris had built up a sharply defined method of theoretical physics on the basis laid by Galilei and Newton. Mechanical assumptions were made, from which a group of natural phenomena could be explained by means of mechanical principles which had attained a kind of geometrical evidence. Men were conscious that the assumptions could not with complete certainty be described as correct, yet up to a certain point it was held to be probable that they were in exact conformity with fact, and accordingly they were called hypotheses. Matter, the luminiferous æther for explaining the phenomena of light, and the two electrical fluids as sums of mathematical points were thus conceived. Between each pair of such points a force was supposed to act having its direction in the line joining the two points, and whose strength was a function of their distance, still to be determined. (*Boscovich.*)

An intellect knowing all the initial positions, and initial velocities of all these material particles, as well as all the forces, and which could integrate all the differential equations arising out of them, would be able to calculate beforehand the whole course of the universe just as the astronomer can predict a solar eclipse. (*Laplace.*)

There was no hesitation in declaring those forces, which were accepted as axiomatically given and not further explainable, to be the causes of the phenomena, and the determination of their values by aid of their differential equations to be their explanation.

To this was afterwards added the hypothesis that even in

bodies at rest their particles are themselves in a state of motion, which give rise to thermal phenomena, and whose nature is especially sharply defined in the case of gases. (*Clausius*.)

The theory of gases led to surprising prognoses ; thus, for instance, that the coefficient of friction was independent of the pressure, and certain relations between friction, diffusion, and conductivity for heat, &c., &c. (*Maxwell*.)

The aggregate of these methods was so successful that to explain natural phenomena was defined as the aim of natural science ; and what were formerly called the descriptive natural sciences triumphed, when Darwin's hypothesis made it possible not only to describe the various living forms and phenomena, but also to explain them. Strangely enough Physics made almost exactly at the same time a turn in the opposite direction.

To Kirchhoff, more especially, it seemed doubtful whether it was justifiable to assign to Forces that prominent position to which they were raised by characterizing them as the causes of the phenomena.

Whether, with Kepler, the form of the orbit of a planet and the velocity at each point is defined, or, with Newton, the force at each point, both are really only different methods of describing the facts ; and Newton's merit is only the discovery that the description of the motion of the celestial bodies is especially simple if the second differential of their coordinates in respect of time is given (Acceleration, Force). In half a page forces were defined away, and physics made a really descriptive natural science. The framework of mechanics was too firmly fixed for this change in the external aspect to have any effect on the interior. The theories of elasticity which did not involve the conception of molecules were of older date (*Stokes, Lamé, Clebsch*). Yet in the development of other branches of physics, Electrodynamics, theories of pyro- and of piezoelectricity, the view gained ground that it could not be the object of theory to penetrate the mechanism of Nature, but that, merely starting from the simplest assumptions (that certain magnitudes are linear or other elementary functions), to establish equations as elementary as possible which enable the natural phenomena to be calculated with the closest approximation ; as Hertz characteristically says, only to express by bare equations the phenomena directly observed without the variegated garments with which our fantasy clothes them.

Meanwhile several investigators had, from another side,

assailed the old system of centres of force and forces at a distance; it might be said to have been from the exactly opposite side, because they were particularly fond of the variegated garment of mechanical representation; it might also be said to be from an adjacent side, as they also dispensed with the recognition of a mechanism lying at the basis of the phenomena, and in the mechanism which they themselves invented they did not see those of Nature, but mere images and analogies*. Several men of science, following the lead of Faraday, had established a totally different conception of Nature. While the older system had held the centres of force to be the real, and the forces themselves to be mathematical conceptions, Faraday saw distinctly the continuous working of the forces from point to point in the intermediate space. The Potential, which had hitherto been only a formula for lightening the work of calculation, was for him the really existing bond in space, the cause of the action of force itself. Faraday's ideas were far less lucid than the earlier hypotheses, defined as they were with mathematical precision, and many a mathematician of the old school had but a low opinion of Faraday's theories, without, however, by the clearness of his own conceptions making such great discoveries.

But soon, and especially in England, it was attempted to get as plain and tangible a representation of the ideas and

* The relation of the directions of the old system of centres of force, and of forces at a distance to the purely mathematical one represented by Kirchhoff, to Maxwell's own point of view is expressed by him in the following words:—"The results of this simplification may take the form of a purely mathematical formula (*Kirchhoff*), or of a physical hypothesis (*Poisson*). In the first case we entirely lose sight of the phenomena to be explained and though we may trace out the consequences of given laws, we can never obtain more extended views of the connexions of the subject. If, on the other hand, we adopt a physical hypothesis, we see the phenomena only through a medium, and are liable to that blindness to facts and rashness in assumption which a partial explanation encourages. We must therefore discover some method of investigation which allows the mind at every step to lay hold of a clear physical conception without being committed to any theory in physical science from which that conception is borrowed, so that it is neither drawn aside by analytical subtleties, nor carried beyond the truth by a favourite hypothesis."

Compare the theory of elasticity worked out by Kirchhoff in his Lectures, of almost ethereal delicacy, clear as crystal but colourless, with that given by Thomson in the third volume of his *Mathematical and Physical Papers*, a sturdy realistic one, not of an ideal elastic body but of steel, india-rubber or glue; or with Maxwell's language, often almost childlike in its naivety, who, right in the middle of his formulæ, casually gives a really good method of removing grease spots.

conceptions which before had played a part in Analysis only. From this endeavour towards clearness arose the graphical representations of the fundamental conceptions of mechanics in Maxwell's 'Matter and Motion,' the geometrical representation of the superposition of two sine motions, all the illustrations due to the theory of quaternions: thus, the geometrical interpretation of the symbol

$$\Delta = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}.*$$

There was another matter. The most surprising and far-reaching analogies were seen to exist between natural phenomena which were apparently quite unlike. Nature seemed in a certain sense to have built up the most diversified things after exactly the same pattern; as the analyst dryly observes, the same differential equations hold for the most diversified phenomena.

Thus the conductivity of heat, diffusion, and the propagation of electricity in conductors takes place according to the same laws. The same equation may be considered as the solution of a problem in hydrodynamics or in the theory of potential. The theory of vortices in fluids as well as those of the friction of gases exhibits the most surprising analogy with that of electromagnetism, &c., &c. Compare on this point Maxwell, 'Scientific Papers,' vol. i. p. 156.

Maxwell also, when he undertook the mathematical treatment of Faraday's conceptions, was from the very outset impelled by their influences into a new path. Thomson † had already pointed out a series of analogies between problems in the theory of elasticity and those of electromagnetism. In his first paper on Electricity Maxwell ‡ explained that it was not his intention to propound a theory of electricity; that is, that he himself did not believe in the reality of the incompressible fluids and of the resistances which he there assumes, but that he simply intends to give a

* Maxwell, 'Treatise on Electricity and Magnetism,' 1873, vol. i. art. 29, nature of the operator ∇ and ∇^2 ; this was also afterwards observed by others. Mach on M. Guebhard's representation of Equipotential Curves, *Wien. Sitzungsbericht*, vol. lxxxvi. p. 8, 1882. Compare also Riemann, "Electricität und Magnetism," *Wied. Beiblätter*, vol. vii. p. 10; *Comptes Rendus*, vol. xcv. p. 479.

† Cambridge and Dublin Math. Journal, 1847; Math. and Phys. Papers, vol. i.

‡ Maxwell, on Faraday's Lines of Force. Cambridge Phil. Trans. vol. x; Scient. Papers, vol. i. p. 157.

méchanical example which shows great analogy with electrical phenomena, and he wishes to bring the latter into a form in which the understanding can readily grasp them*.

In his second paper he goes still further, and from liquid vortices, and friction wheels working within cells with elastic sides, he constructs a wonderful mechanism which serves as a mechanical model for electromagnetism. This mechanism was of course mocked at by those who, like Zöllner, regarded it as a hypothesis in the older sense of the word, and who thought that Maxwell ascribed to it a real existence: this he decidedly repudiates, and only modestly hopes "that by such mechanical fictions any one who understands the provisional and temporary character of this hypothesis will find himself rather helped than hindered by it in his search after the true interpretation of the phenomena." And they were so helped; for by his model Maxwell arrived at those equations whose peculiar, almost magical power Hertz, the person most of all competent to judge, thus vigorously depicts in his lecture on the relations between Light and Electricity:—"We cannot study this wonderful theory without at times feeling as if an independent life and a reason of its own dwelt in these mathematical formulæ; as if they were wiser than we were, wiser even than their discoverer; as if they gave out more than had been put into them." I should like to add to these words of Hertz only this, that Maxwell's formulæ are simple consequences from his mechanical models; and Hertz's enthusiastic praise is due in the first place, not to Maxwell's analysis, but to his acute penetration in the discovery of mechanical analogies.

It is in Maxwell's third important paper† and in his Text-book that the formulæ more and more detach themselves from the model, which process was completed by Heaviside, Poynting, Rowland, Hertz, and Cohn. Maxwell still uses the mechanical analogy, or, as he says, the dynamical illustration. But he no longer pursues it into detail, but rather searches for the most general mechanical assumptions calculated to lead to phenomena which are analogous to those of Electromagnetism. Thomson was led, by an extension of the ideas which have already been cited, to the quasi elastic and the quasi labile æther, as well as to its representation by the gyrostatic-dynamic model.

Maxwell of course applied the same treatment to other

* Maxwell, *Scientific Papers*, vol. i. p. 157.

† Maxwell. "A Dynamical Theory of the Electro-magnetic Field." *Scientific Papers*, i. pp. 526; *Roy. Soc. Trans.* vol. 155. p. 459, 1865.

branches of theoretical physics. As mechanical analogies may be cited Maxwell's gas molecules which repel each other with a force inversely proportional to the fifth power of their distance, and at first investigators were not wanting who, not understanding Maxwell's tendency, considered his hypothesis to be improbable and absurd.

The new ideas, however, gradually found entrance into all regions. In the theory of heat I need only mention Helmholtz's celebrated memoirs on the mechanical analogies of the second law of thermodynamics. It was seen indeed that they corresponded better to the spirit of science than the old hypotheses, and were also more convenient for the investigator himself. For the old hypotheses could only be kept up as long as everything just fitted; but now a few failures of agreement did no harm, for it can be no reproach against a mere analogy if it fits rather loosely in some places. Hence the old theories, such as the elastic theory of light, the theory of gases, the schemes of chemists for the benzole rings were now only regarded as mechanical analogies, and philosophy at last generalized Maxwell's ideas in the doctrine that cognition is on the whole nothing else than the discovery of analogies. With this the older scientific method was defined out of the way, and Science now only spoke in parables.

All these mechanical models at first existed indeed only in idea; they were dynamical illustrations in the fancy, and they could not be carried out in practice, even in this general form, yet their great importance was an incitement to realize at any rate their fundamental types.

In the second part of this Catalogue is a description of such an attempt made by Maxwell himself, and of one by the author of these lines. Fitzgerald's model is also at present in the Exhibition, as well as Bjerknes' model, which owe their origin to similar tendencies. Other models which have to be classed with these have been constructed by Oliver Lodge, Lord Rayleigh, and others.

They all show how the new tendency to relinquish perfect congruence with Nature is compensated by the more striking prominence of points of similarity. To this belongs the immediate future; yet, mistaken as it was to consider the old method as the only correct one, it would be just as one-sided to consider it, after all it has accomplished, as quite played out, and not to cultivate it along with the new one.

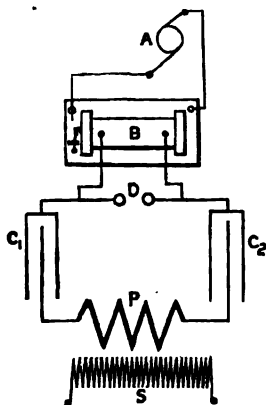
III. *Some Notes on Brush Discharges in Gases.*

By W. H. HARVEY and F. HIRD, B.A.*

WHILE experimenting on high-frequency discharges we came across a remarkable difference in the behaviour of positive and negative electricity, which forms the subject of these notes.

The apparatus was arranged in the now well-known manner for obtaining oscillatory discharges of high potential and high frequency, from the discharge of a condenser. The accompanying diagram and description will make clear the exact arrangement.

Fig. 1.



A is a small magneto-machine giving a continuous current at about 8 volts.

B is an ordinary induction-coil capable of giving about an inch spark.

C_1 and C_2 are equal condensers, consisting of shellacked glass plates coated with tin-foil. The capacity of each was approximately $\cdot 0038$ microfarad.

D is an adjustable spark-gap.

P and S are the primary and secondary of a transformer without iron core, the elements of which are as follows:—

P: mean diameter 5.65 centim.; axial length 20.3 centim.; wound with 9 turns of copper-strip 20 millim. \times $\cdot 064$ millim.; approximately $L=1123$ centim.

S: mean diameter 9.4 centim.; axial length 11 centim.; wound with 78 turns of $\cdot 38$ millim. wire silk-covered,

* Communicated by the Authors.

and each convolution separated from the next by a strand of silk equal in diameter to the wire.

The secondary was suspended by silk cords, so as not to be in contact with any part of the primary, and the whole was immersed in oil, in order to prevent the passage of brush-discharges.

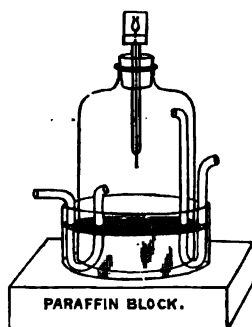
With this apparatus vivid brush-discharges are obtained.

It was observed that the brushes were most brilliant when allowed to take place between a point and a plate, especially if the latter had a fair capacity; also that the plate was always charged positively, although the discharge was of course oscillatory.

In order to put this fully to the test the experiment was varied in many ways. The current in the primary of the induction-coil was reversed, both mechanical and automatic breaks were used, and the two ends of the secondary of the transformer were in turn connected to the point (the unused end remaining immersed in oil), but the result was always the same, the plate being strongly charged positively. We may add that the charge was steady and, as near as we could tell, equal in amount with any of the above combinations.

We now added to our apparatus in order to test these brush-discharges in various gases. For this purpose a bell-jar (fig. 2) was fitted with a rubber bung, through which passed a

Fig. 2.



glass tube with a platinum point sealed in the lower end; from this point a wire leads into an upper tube and terminates in a small clip for making contact with either end of S.

Both tubes were entirely filled with oil, this being the only means we found of preventing brushes onto the glass of the bell-jar, which produced local charges and obscured the result.

The jar stood in a deep glass dish containing mercury, the level of which could be adjusted by means of a syphon (not

shown); two bent glass tubes afford an inlet and outlet for the gas to be experimented on.

During the experiments a continuous steady flow of gas was maintained through the bell-jar, the clip was connected alternately to the two ends of the secondary, and the current in the primary of the induction-coil was reversed in each case. The unused end of the secondary was insulated and entirely immersed in oil. The mercury in the glass dish was electrically connected to the plate of a gold-leaf electroscope, the sign of the charge on which was determined in the usual manner.

In the first case the jar was filled with dry air, of which a steady stream was kept up. The results confirmed those previously mentioned, the charge of the gold leaves being always strong and steady positive.

Next we passed into the jar a stream of dry hydrogen, and kept this steadily flowing during the experiments, which were of course commenced only after the air was all expelled.

In this case the leaves were always strong and steady negative.

This result was confirmed in a remarkable manner by using the ordinary induction-coil only, connected onto the bell-jar. Although there was no visible discharge, yet the electroscope was charged as follows:—

1. A. Strong steady negative.
2. A. Leaves go in and out but are always negative.
2. B. Strong steady negative.
1. B. Leaves go in and out but are always negative.

In the above table A and B represent the secondary terminals of the induction-coil, whilst 1 and 2 represent the direction of the current in the primary. When this was 1 the end A was made negative by the break and positive by the make.

Thus it appears that in the case of our induction-coil the weak E.M.F. due to the make could produce a greater silent discharge than could the strong E.M.F. due to the break, apparently because a negative discharge passes more easily in hydrogen than does a positive.

Reverting to the previous arrangement of condensers, &c., the jar was next filled with oxygen and the experiments repeated. In this case the electroscope was always charged strongly positive.

When the induction-coil alone was used, the charge on the leaves changed with the sign of the E.M.F. due to break, as would naturally be expected, but the positive charges were stronger than the negative.

We have also experimented with other gases, but owing to difficulties in obtaining them in a state of purity, on account of limited space and want of general conveniences, we have not obtained reliable results.

The results given above, however, may be depended upon, as they were all repeated some hundreds of times under varying conditions, and have always been satisfactory and consistent.

We may therefore sum up the results which we have established as follows:—

In a brush-discharge in air positive electricity passes more readily than negative from a point onto any neighbouring conductor.

In oxygen the same is the case.

In hydrogen the reverse holds, negative electricity passing more readily.

To a certain extent these results are anticipated by previous experiments. It has long been known that positive brushes were somewhat stronger than negative. Again, Guthrie has shown that a red-hot conductor in air will retain a negative but not a positive charge (*Phil. Mag.* vol. xlv. p. 257, 1873). This experiment, as having a bearing on our subject, we have repeated and confirmed.

In conclusion we may mention a few precautions which must be taken in conducting these experiments.

(1) The arrangement of two condensers in series was suggested by Prof. J. J. Thomson in his paper on "Discharges in Gases without Electrodes." We have found it a very necessary precaution: if the discharge of only one condenser is used the unsymmetrical arrangement of the apparatus leads to very confusing results.

(2) The greatest care must be taken with the insulation of the transformer, both in insulating the primary from the secondary and also in insulating the turns of the secondary itself.

(3) It is advisable to prevent all brush-discharges except at the point where they are to be observed. This, as far as we know, can only be done by immersion of every part of the conductor in oil.

(4) It is necessary to use the gases in large bulk or to keep up a continuous flow, as otherwise they acquire a charge which confuses the results.

(5) The distance between the point and the conductor which is to be charged must be so adjusted that no spark passes. If a spark does pass, the conductor is entirely discharged.

IV. *A New Table of Standard Wave-lengths.*

By Prof. HENRY A. ROWLAND*.

DURING the last ten years I have made many observations of wave-lengths, and have published a preliminary and a final table of the wave-lengths of several hundred lines in the solar spectrum.

For the purpose of a new table I have worked over all my old observations, besides many thousand new ones, principally made on photographs, and have added measurements of metallic lines so as to make the number of standards nearly one thousand.

Nearly all the new measurements have been made on a new measuring-machine whose screw was specially made by my process† to correspond with the plates and to measure wave-lengths direct with only a small correction.

The new measures were made by Mr. L. E. Jewell, who has now become so expert as to have the probable error of one setting about $\frac{1}{1000}$ division of Ångström, or 1 part in 5,000,000 of the wave-length. Many of these observations, however, being made with different measuring-instruments, and before such experience had been obtained, have a greater probable error. This is especially true of those measurements made with eye-observations on the spectrum direct. The reductions of the readings were made by myself.

Many gratings of 6 in. diameter and $21\frac{1}{2}$ ft. radius were used; and the observations were extended over about ten years.

The *standard* wave-length was obtained as follows:—Dr. Bell's value of D_1 was first slightly corrected and became 5896·20. C. S. Peirce's value of the same line was corrected as the result of some measurements made on his grating and became 5896·20. The values of the wave-length then become:—

| Weight. | Observer. | D. |
|-----------|------------------------------------|----------|
| 1. | Ångström, corrected by Thalén..... | 5895·81 |
| 2. | Müller & Kempf..... | 5896·25 |
| 2. | Kurlbaum | 5895·90 |
| 5. | Peirce | 5896·20 |
| 10. | Bell | 5896·20 |
| Mean..... | | 5896·156 |

* Reprinted from a separate copy from the 'Astronom. and Astero-Physics,' communicated by the Author.

† See *Encyc. Brit.*, art. Screw.

As the relative values are more important for spectroscopic work than the absolute, I take this value without further remark. It was utilized as follows :—

1st. By the method of coincidences with the concave grating, the wave-lengths of 14 more lines throughout the visible spectrum were determined from this with great accuracy for primary standards.

2nd. The solar standards were measured from one end of the spectrum to the other many times ; and a curve of error drawn to correct to these primary standards.

3rd. Flat gratings were also used.

4th. Measurements of photographic plates from 10 to 19 inches long were made. These plates had upon them two portions of the solar spectrum of different orders. Thus the blue, violet, and ultra-violet spectra were compared with the visible spectrum, giving many checks on the first series of standards.

5th. Measurements were made of photographic plates having the solar spectrum in coincidence with metallic spectra, often of three orders, thus giving the relative wave-lengths of three points in the spectrum.

Often the same line in the ultra-violet had its wave-length determined by two different routes back to two different lines of the visible spectrum. The agreement of these to $\frac{1}{100}$ division of Ångström in nearly every case showed the accuracy of the work.

6th. Finally, the important lines had from 10 to 20 measurements on them, connecting them with their neighbours and many points in the spectrum, both visible and invisible ; and the mean values bound the whole system together so intimately that no changes could be made in any part without changing the whole.

This unique way of working has resulted in a table of wave-lengths from 2100 to 7700 whose accuracy might be estimated as follows :—

Distribute less than $\frac{1}{100}$ division of Ångström properly throughout the table as a correction, and it will become perfect within the limits 2400 and 7000.

The above is only a sketch of the methods used. The complete details of the work are ready for publication, but I have not yet found any journal or society willing to undertake it.

Description of the Table.

The first column gives the name of the element whose wave-length has been measured. If a letter stands at the left, it is the "name" of the line in the solar spectrum. A(o)

and A(wv) denote lines due to absorption by the oxygen and the water-vapour, respectively, in the earth's atmosphere. An ? mark after an element means that it is doubtful if the line is really due to the element named. If two elements are given *on the same line* (e. g. Mn-Di w.l. 3295.957), it is to be understood that they have apparently coinciding lines at that particular wave-length. If two or more elements are bracketed

$$\text{e. g., } \left. \begin{array}{c} \text{Mn} \\ \text{Ti} \\ \text{Fe} \end{array} \right\} \text{w.l. 5260.384,}$$

it means that the first one has a line coinciding with one side of the corresponding line in the solar spectrum, the second one has a line coinciding with the middle, &c., and the appearance of the solar line itself is given in a later column. An ? standing alone denotes that the element which corresponds to the given wave-length is unknown.

The second column gives the intensity of the line in the arc spectrum; the third its appearance, and the fourth and fifth do the same for the line in the solar spectrum. R stands for "reversed;" N, nebulous; d, double; t, triple; ?, doubtful or difficult. The size of the number indicates to some extent the intensity of the line. For instance the intensity 10 means that the line is apparently 10 times as intense as the intensity 1. Measurements of intensity by eye-observations, direct or on photographic plates, are of course most uncertain. And so the figures given are estimates which do not apply to comparisons of different portions of the spectrum, but are intended to give some idea of the relative effects. The intensity of some lines in the arc spectrum of a given substance, e. g. Ca, is often so much greater than that of the others, that the absence of some lines in the solar spectrum is easily understood. The sixth column gives the character of the standard. M means that the line is a standard in the arc spectrum; ☉ means that the line is an ordinary solar standard; ☉', a better solar standard; ☉'', a remarkably good solar standard; and ☉₁ a rather poor solar standard.

The next two columns give the "weights" to be attached to the values of the wave-lengths as standards in the arc and solar spectra, respectively.

The last two columns give the final values of the wave-lengths measured in Ångström units, i. e., in ten millionths of a millimetre in ordinary air at about 20° C. and 760 millim. pressure.

Notes marked J. are by Mr. Jewell.

| Elements | IN ARC. | | IN SUN. | | Kind of Stand-ard. | WEIGHT. | | Wave-length in Arc. | Wave-length in Sun. |
|-----------|-------------|--------------|-------------|--------------|--------------------|---------|---------|---------------------|---------------------|
| | Inten-sity. | Appear-ance. | Inten-sity. | Appear-ance. | | In Arc. | In Sun. | | |
| Sr | 2 | ... | ... | ... | M | 1 | ... | 2152-912 | |
| Sr | 3 | ... | ... | ... | M | 1 | ... | 2165-990 | |
| Si | 2 | ... | ... | ... | M | 2 | ... | 2208-060 | |
| Si | 3 | ... | ... | ... | M | 2 | ... | 2210-939 | |
| Si | 2 | ... | ... | ... | M | 2 | ... | 2211-759 | |
| Si | 4 | ... | ... | ... | M | 2 | ... | 2216-760 | |
| Si | 2 | ... | ... | ... | M | 2 | ... | 2218-146 | |
| Al | 3 | ... | ... | ... | M | 2 | ... | 2263-507 | |
| Al | 4 | ... | ... | ... | M | 2 | ... | 2269-161 | |
| Sr | 10 | R | ... | ... | M | 1 | ... | 2275-876 | |
| Ca | 20 | R | ... | ... | M | 3 | ... | 2275-602 | |
| Fe? | ... | ... | ... | ... | M | 2 | ... | 2298-246 | |
| Ba | 20 | R | ... | ... | M | 1 | ... | 2304-364 | |
| Ba | 20 | R | ... | ... | M | 1 | ... | 2335-267 | |
| Fe | ... | ... | ... | ... | M | 2 | ... | 2343-571 | |
| Fe | ... | ... | ... | ... | M | 2 | ... | 2348-385 | |
| Fe | ... | ... | ... | ... | M | 2 | ... | 2364-897 | |
| Al | 6 | ... | ... | ... | M | 3 | ... | 2367-144 | |
| Al | 7 | ... | ... | ... | M | 3 | ... | 2373-213 | |
| Fe | ... | ... | ... | ... | M | 2 | ... | 2373-771 | |
| Fe? | ... | ... | ... | ... | M | 3 | ... | 2382-122 | |
| Fe | ... | ... | ... | ... | M | 2 | ... | 2388-710 | |
| Fe? | ... | ... | ... | ... | M | 3 | ... | 2395-715 | |
| Ca | 25 | R | ... | ... | M | 5 | ... | 2398-667 | |
| Fe | ... | ... | ... | ... | M | 2 | ... | 2399-328 | |
| Fe | ... | ... | ... | ... | M | 2 | ... | 2404-971 | |
| Fe | ... | ... | ... | ... | M | 2 | ... | 2406-743 | |
| Fe | ... | ... | ... | ... | M | 2 | ... | 2410-604 | |
| Si | 8 | ... | ... | ... | M | 15 | ... | 2435-247 | |
| Si | 3 | ... | ... | ... | M | 10 | ... | 2438-864 | |
| Si | 3 | ... | ... | ... | M | 10 | ... | 2443-460 | |
| Fe? | ... | ... | ... | ... | M | 3 | ... | 2447-785 | |
| Si | 3 | ... | ... | ... | M | 10 | ... | 2452-219 | |
| Fe? | ... | ... | ... | ... | M | 3 | ... | 2457-680 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2462-743 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2472-974 | |
| C* | 10 | ... | ... | ... | M | 15 | ... | 2478-661 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2479-871 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2483-359 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2484-283 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2488-238 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2489-838 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2490-723 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2491-244 | |
| Bo | 15 | ... | ... | ... | M | 20 | ... | 2496-867 | |
| Bo | 20 | ... | ... | ... | M | 20 | ... | 2497-821 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2501-223 | |
| Si | 10 | ... | ... | ... | M | 15 | ... | 2506-994 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2510-934 | |
| Si | 7 | ... | ... | ... | M | 10 | ... | 2514-417 | |
| Si | 15 | ... | ... | ... | M | 7 | ... | 2516-210 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2518-188 | |

* This line seems to be the only single line of carbon, not belonging to a band in the arc spectrum. It was determined to belong to carbon by the spark spectrum. (R.)

| Elements | In Arc. | | In Sun. | | Kind of Stand-ard. | Weight. | | Wave-length in Arc. | Wave-length in Sun. |
|-----------|-------------|--------------|-------------|--------------|--------------------|---------|---------|---------------------|---------------------|
| | Inten-sity. | Appear-ance. | Inten-sity. | Appear-ance. | | In Arc. | In Sun. | | |
| Si | 8 | ... | ... | ... | M | 10 | ... | 2519-297 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2522-948 | |
| Si | 9 | ... | ... | ... | M | 10 | ... | 2524-206 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2527-530 | |
| Si | 10 | ... | ... | ... | M | 5 | ... | 2528-599 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2535-699 | |
| Hg* | 50 | R | ... | ... | M | 2 | ... | 2536-648 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2541-068 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2546-068 | |
| Fe | ... | ... | ... | ... | M | 2 | ... | 2549-704 | |
| Al | 10 | ... | ... | ... | M | 5 | ... | 2568-085 | |
| Al | 10 | ... | ... | ... | M | 5 | ... | 2575-198 | |
| Mn..... | ... | ... | ... | ... | M | 2 | ... | 2576-195 | |
| Fe? | ... | ... | ... | ... | M | 2 | ... | 2584-629 | |
| Fe | ... | ... | ... | ... | M | 2 | ... | 2585-963 | |
| Mn..... | ... | ... | ... | ... | M | 2 | ... | 2593-810 | |
| Fe | ... | ... | ... | ... | M | 2 | ... | 2598-480 | |
| Fe | ... | R | ... | ... | M | 3 | ... | 2599-494 | |
| Fe | ... | ... | ... | ... | M | 2 | ... | 2611-965 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2631-125 | |
| i | 5 | ... | ... | ... | M | 7 | ... | 2631-392 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2679-148 | |
| Fe | ... | ... | ... | ... | M | 2 | ... | 2706-684 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2719-119 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2720-989 | |
| Ca | 5 | ... | ... | ... | M | 1 | ... | 2721-762 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2723-668 | |
| Fe? | ... | ... | ... | ... | M | 3 | ... | 2733-673 | |
| Fe? | ... | ... | ... | ... | M | 3 | ... | 2737-406 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2742-485 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2750-237 | |
| Fe | ... | ... | ... | ... | M | 2 | ... | 2755-837 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2756-427 | |
| Fe | ... | ... | ... | ... | M | 2 | ... | 2761-876 | |
| Fe | ... | ... | ... | ... | M | 2 | ... | 2762-110 | |
| Fe | ... | ... | ... | ... | M | 2 | ... | 2767-630 | |
| Fe | ... | ... | ... | ... | M | 2 | ... | 2772-206 | |
| Mgt | 5 | R | ... | ... | M | 5 | ... | 2776-798 | |
| Fe | ... | ... | ... | ... | M | 2 | ... | 2778-340 | |
| Mgt | 5 | R | ... | ... | M | 3 | ... | 2778-381 | |
| Mgt | 8 | R | ... | ... | M | 5 | ... | 2779-935 | |
| Mgt | 5 | R | ... | ... | M | 5 | ... | 2781-521 | |
| Fe | ... | ... | ... | ... | M | 1 | ... | 2781-945 | |
| Mgt | 5 | R | ... | ... | M | 5 | ... | 2783-077 | |
| Fe | ... | ... | ... | ... | M | 3 | ... | 2788-201 | |
| Mn..... | ... | ... | ... | ... | M | 3 | ... | 2794-911 | |
| Mg..... | 20 | R | ... | ... | M | 12 | ... | 2795-632 | |
| Mn..... | ... | ... | ... | ... | M | 3 | ... | 2798-369 | |
| Mn..... | ... | ... | ... | ... | M | 3 | ... | 2801-183 | |
| Mg..... | 20 | R | ... | ... | M | 10 | ... | 2802-806 | |
| Fe | 5 | ... | ... | ... | M | 3 | ... | 2813-388 | |
| Fe | 3 | ... | ... | ... | M | 1 | ... | 2823-389 | |

* This line appears as a sharp reversal, with no shading, in the spectra of all substances tried that contained any trace of continuous spectrum in this region. (J.)

† A remarkable symmetrical group of five lines in the spectrum of magnesium.

| Elements | IN ARC. | | IN SUN. | | Kind of Stand-ard. | WRIGHT. | | Wave-length in Arc. | Wave-length in Sun. |
|----------|-------------|--------------|-------------|--------------|--------------------|---------|---------|---------------------|---------------------|
| | Inten-sity. | Appear-ance. | Inten-sity. | Appear-ance. | | In Arc. | In Sun. | | |
| Fe | 5 | ... | ... | ... | M | 1 | ... | 2825.667 | |
| Fe | 4 | ... | ... | ... | M | 7 | ... | 2832.545 | |
| Fe | 3 | ... | ... | ... | M | 1 | ... | 2838.226 | |
| Fe | 3 | ... | ... | ... | M | 1 | ... | 2843.744 | |
| Fe | 5 | ... | ... | ... | M | 7 | ... | 2844.085 | |
| Fe | 6 | ... | ... | ... | M | 5 | ... | 2851.904 | |
| Mg | 100 | R | ... | ... | M | 15 | ... | 2852.239 | |
| Si | 15 | ... | ... | ... | M | 12 | ... | 2881.695 | |
| Fe | 7 | R | ... | ... | M | 3 | ... | 2912.275 | |
| Fe | 8 | R | ... | ... | M | 3 | ... | 2929.127 | |
| Fe | 10 | R | ... | ... | M | 4 | ... | 2937.020 | |
| Fe | 8 | R | ... | ... | M | 4 | ... | 2947.993 | |
| Fe | 7 | R | ... | ... | M | 4 | ... | 2954.058 | |
| Fe | 5 | ... | ... | ... | M | 3 | ... | 2957.485 | |
| Fe | 5 | ... | ... | ... | M | 3 | ... | 2965.381 | |
| Fe | ... | ... | ... | ... | M | 1 | ... | 2966.985 | |
| Fe | 8 | R | ... | ... | M | 12 | ... | 2967.016 | |
| Fe | 4 | R | ... | ... | M | 7 | ... | 2970.223 | |
| Fe | 6 | R | ... | ... | M | 7 | ... | 2973.254 | |
| Fe | 12 | R | ... | ... | M | 15 | ... | 2973.358 | |
| Fe | 2 | ... | ... | ... | M | 6 | ... | 2981.570 | |
| Fe | 10 | R | ... | ... | M | 15 | ... | 2983.689 | |
| Fe | ... | ... | ... | ... | M | 1 | ... | 2987.410 | |
| Si | 4 | ... | ... | ... | M | 5 | ... | 2987.766 | |
| Fe | 8 | R | ... | ... | M | 18 | ... | 2994.547 | |
| Ca | 7 | R | ... | ... | M | 3 | ... | 2995.074 | |
| Ca | 10 | R | ... | ... | M | 3 | ... | 2997.430 | |
| Fe | 4 | R | ... | ... | M | 5 | ... | 2999.632 | |
| Ca | 6 | R | ... | ... | M | 3 | ... | 2999.767 | |
| Ca | 8 | R | ... | ... | M | 3 | ... | 3000.976 | |
| Fe | 8 | R | ... | ... | M | 15 | ... | 3001.070 | |
| ? | ... | ... | 3 | ... | ⊙ | 1 | ... | | 3005.160 |
| ? | ... | ... | 4 | ... | ⊙ | 1 | ... | | 3005.404 |
| Ca | 15 | R | ... | ... | M | 3 | ... | 3006.978 | |
| Fe | 2 | ... | ... | ... | M | 1 | ... | 3007.260 | |
| Fe | 1 | ... | ... | ... | M | 3 | ... | 3007.408 | |
| Fe | 6 | R | ... | ... | M | 15 | ... | 3008.255 | |
| Ca | 7 | R | ... | ... | M | 3 | ... | 3009.327 | |
| Fe | 4 | R | ... | ... | M | 3 | ... | 3009.696 | |
| ? | ... | ... | 4 | ... | ⊙ | 5 | ... | | 3012.557 |
| ? | ... | ... | 6 | d? | ⊙ | 4 | ... | | 3014.274 |
| Fe | ... | ... | 3 | ... | M | 1 | ... | 3016.296 | |
| Fe | 5 | ... | ... | ... | M | 1 | ... | 3017.747 | |
| Fe | 5 | ... | ... | ... | M | 1 | ... | 3019.109 | |
| Fe | ... | ... | ... | ... | M | 1 | ... | 3019.752 | |
| Fe | 10 | R | ... | ... | M | 15 | ... | 3020.611 | |
| Fe | 25 | R | ... | ... | M | 18 | ... | 3020.759 | |
| Fe | 15 | R | ... | ... | M | 18 | ... | 3021.191 | |
| Fe | 7 | R | 7 | ... | M | 7 | ... | 3024.154 | |
| ? | ... | ... | 5 | ... | ⊙ | ... | 7 | | 3024.475 |
| ? | ... | ... | 4 | ... | ⊙ | ... | 7 | | 3025.394 |
| Fe | 10 | R | 10 | ... | M | 7 | ... | 3025.958 | |
| Fe | ... | ... | ... | ... | M | 1 | ... | 3027.245 | |
| ? | ... | ... | 5 | ... | ⊙ | 7 | ... | | 3035.850 |
| Fe | 15 | R | 15 | ... | M | 10 | 2 | 3037.506 | 3037.492 |

| Elements | IN ARC. | | IN SUN. | | Kind of Stand-ard. | WRIGHT. | | Wave-length in Arc. | Wave-length in Sun. |
|--------------|-------------|--------------|-------------|--------------|--------------------|---------|---------|---------------------|---------------------|
| | Inten-sity. | Appear-ance. | Inten-sity. | Appear-ance. | | In Arc. | In Sun. | | |
| Ca | 15 | R | 4 | ... | M \odot_1 | 3 | 2 | 3044-114 | 3044-119 |
| Mn | 10 | R | 3 | ... | \odot' | 5 | ... | | 3044-683 |
| ? | ... | ... | ... | ... | \odot' | 1 | ... | | 3046-778 |
| Fe | 20 | R | 20 | ... | M | 13 | ... | 3047-720 | |
| ? | ... | ... | 3 | d | \odot'' | ... | 5 | | 3050-212 |
| Fe | ... | ... | 3 | ... | \odot' | ... | 5 | | 3053-173 |
| ? | ... | ... | 3 | d | \odot' | ... | 1 | | 3053-527 |
| ? | ... | ... | 5 | d? | \odot'' | ... | 5 | | 3055-821 |
| Fe | 10 | R | 10 | ... | M | 8 | ... | 3057-557 | |
| Fe | 10 | R | 10 | ... | M | 15 | ... | 3059-200 | |
| ? | ... | ... | 3 | ... | \odot' | ... | 1 | | 3061-098 |
| Co | 8 | R | 3 | ... | M \odot'' | 1 | 5 | 3061-932 | 3061-930 |
| Fe | 10 | R | 10 | ... | M | 10 | ... | 3067-363 | |
| Ti | 6 | ... | 8 | ... | M | 3 | ... | 3075-339 | |
| Fe | 10 | R | 10 | ... | M | 4 | ... | 3075-849 | |
| Fe | ... | ... | 2 | ... | M | 1 | ... | 3077-216 | |
| ? | ... | ... | 4 | ... | \odot | ... | 6 | | 3077-303 |
| Fe? | ... | ... | 4 | ... | \odot'' | ... | 6 | | 3078-148 |
| Ti | 4 | ... | 6 | ... | M | 3 | ... | 3078-759 | |
| Mn | 7 | ... | 2 | ... | \odot'' | ... | 1 | | 3079-724 |
| ? | ... | ... | 5 | ... | \odot'' | ... | 1 | | 3080-863 |
| Al | 20 | R | 7 | ... | M | 17 | ... | 3082-272 | |
| Fe | 6 | R | 7 | ... | M | 5 | ... | 3083-849 | |
| ? | ... | ... | 4 | ... | \odot'' | ... | 1 | | 3086-891 |
| Ti | 8 | R | 8 | ... | M | 1 | ... | 3088-137 | |
| Al | 20 | R | 10 | ... | M | 15 | ... | 3092-824 | |
| Al | 4 | ... | 2 | ... | M | 8 | ... | 3092-962 | |
| ? | ... | ... | 2 | ... | \odot' | ... | 9 | | 3094-739 |
| Fe | 1 | ... | 3 | ... | \odot' | ... | 9 | | 3095-003 |
| Fe | 4 | ... | 7 | ... | M | 3 | ... | 3100-064 | |
| Fe(Mn) | 4-? | ... | 4 | ... | M | 3 | ... | 3100-415 | |
| Fe | 6 | ... | 6 | ... | M | 3 | ... | 3100-779 | |
| Ni | 20 | R | 8 | ... | M | 3 | ... | 3101-673 | |
| Ni | 10 | R | 6 | ... | M | 3 | ... | 3101-994 | |
| ? | ... | ... | 2 | ... | \odot | ... | 1 | | 3106-677 |
| Cr? | ... | ... | 3 | ... | \odot' | ... | 1 | | 3109-434 |
| Fe | ... | ... | 2 | ... | \odot'' | ... | 3 | | 3115-160 |
| Va* | 7 | ... | 5 | ... | \odot'' | ... | 9 | | 3121-275 |
| Zr | 3 | ... | 1 | ... | \odot' | ... | 5 | | 3129-882 |
| Ni | 10 | R | 8 | ... | M | 1 | ... | 3134-223 | |
| Co | 4 | ... | 2 | ... | \odot' | ... | 3 | | 3137-441 |
| Fe | ... | ... | 3 | ... | \odot' | ... | 5 | | 3140-869 |
| Fe | ... | ... | 2 | ... | \odot' | ... | 3 | | 3153-870 |
| Ca | ... | ... | 8 | ... | M | 1 | 1 | 3158-994 | 3158-988 |
| Mn | ... | ... | 1 | ... | \odot' | ... | 5 | | 3167-290 |
| Fe? | ... | ... | 5 | ... | \odot'' | ... | 1 | | 3172-175 |
| La? | 1 | ... | 1 | ... | \odot' | ... | 5 | | 3176-104 |
| Cr? | 4 | N | 4 | ... | \odot' | ... | 5 | | 3188-164 |
| Ni† | 3 | ... | 3 | ... | M | 1 | 1 | 3195-729 | 3195-702 |
| Ti | 10 | R | 4 | ... | M \odot | 1 | 5 | 3200-040 | 3200-032 |

* There is a very faint line on the violet side in the solar spectrum.

† There is a line towards the red, also.

| Elements | In Arc. | | In Sun. | | Kind of Stand-ard. | Weight. | | Wave-length in Arc. | Wave-length in Sun. |
|--------------------|-------------|--------------|-------------|--------------|--------------------|---------|---------|---------------------|---------------------|
| | Inten-sity. | Appear-ance. | Inten-sity. | Appear-ance. | | In Arc. | In Sun. | | |
| Fe | 5 | ... | 5 | ... | M | 1 | ... | 3214.152 | |
| Ti | 4 | ... | 3 | ... | ⊙'' | ... | 6 | | 3218.390 |
| Fe | ... | ... | 6 | ... | ⊙' | ... | 1 | | 3219.697 |
| Fe | ... | ... | 6 | ... | ⊙' | ... | 1 | | 3219.909 |
| Fe? } ? } | 6 ? | ... | 5 7 | d | M⊙ | 3 | 1 | 3222.197 | 3222.203 |
| Ti | 6 | ... | 4 | ... | ⊙'' | ... | 3 | | 3224.368 |
| Fe | 8 | ... | 8 | ... | M | 3 | 1 | 3225.907 | 3225.923 |
| Ti } ? } | 5 ... | ... | 5 | ... | ⊙'' | ... | 1 | | 3231.421 |
| Ti | 6 | ... | 4 | ... | ⊙ | ... | 12 | | 3232.404 |
| Ti | 10 | R | 8 | ... | M | 1 | 1 | 3236.696 | 3236.697 |
| ? } Fe } | ... | ... | 6 | ... | ⊙'' | ... | 12 | | 3246.124 |
| Cu | 40 | R | 9 | ... | M⊙ ₁ | 15 | 5 | 3247.671 | 3247.680 |
| Mn } Ti } | 4 3 | ... | 4 | ... | ⊙' | ... | 10 | | 3260.384 |
| Fe } Va } | 1 10 | ... | 4 | ... | ⊙'' | ... | 10 | | 3267.839 |
| Cu | 30 | R | 6 | ... | M⊙'' | 15 | 5 | 3274.090 | 3274.092 |
| Ti | 6 | ... | 5 | ... | ⊙'' | ... | 9 | | 3287.791 |
| Fe } Co-T } | 5 4 7 | ... | 5 | d? | ⊙'' | ... | 10 | | 3292.174 |
| Mn-Di } | 3 2 | ... | 4 | ... | ⊙'' | ... | 9 | | 3295.957 |
| Na | 15 | R | 6 | ... | M⊙'' | 1 | 6 | 3302.504 | 3302.501 |
| Na* | 10 | R | 5 | ... | M⊙ ₁ | 1 | 6 | 3303.119 | 3303.107 |
| ? } Fe } | ... | ... | 3 3 | d | ⊙' | ... | 10 | | 3303.648 |
| Fe† | 10 | ... | 7 | ... | M⊙ ₁ | 1 | 5 | 3306.119 | 3306.117 |
| Fe† | 10 | ... | 7 | ... | M⊙ ₁ | 1 | 5 | 3306.481 | 3306.471 |
| Mn... } Co-Ti } | 2 3 6 | ... | 1 4 | d | ⊙'' | ... | 10 | | 3308.928 |
| Ti | 5 | ... | 5 | ... | ⊙'' | ... | 10 | | 3318.163 |
| Fe | 2 | ... | 2 | ... | ⊙' | ... | 8 | | 3331.741 |
| Cr } Fe } | 3 3 | ... | 3 3 | d | ⊙' | ... | 9 | | 3348.011 |
| Fe | 2 | ... | 2 | ... | ⊙' | ... | 9 | | 3351.877 |
| Zr | 4 | ... | 1 | ... | ⊙'' | ... | 8 | | 3356.222 |
| Ti } Ti } | 5 5 | ... | 3 3 | d | ⊙'' | ... | 9 | | 3377.667 |
| Fe | 2 | ... | 2 | ... | ⊙'' | 1 | 12 | 3389.913 | 3389.887 |
| Co } Ti } | 10 1 | R | 3 3 | d | ⊙' | 1 | 12 | 3405.255 | 3405.272 |
| Fe | 2 | ... | 1 | ... | ⊙' | 1 | 18 | 3406.602 | 3406.581 |
| Fe | 5 | ... | 4 | ... | ⊙' | 1 | 18 | 3406.965 | 3406.955 |
| ? } Fe } | ... | ... | 2 5 | ... | ⊙'' M | ... | 15 2 | ... | 3425.721 |
| Fe | 6 | ... | 5 | ... | M | 2 | 1 | 3427.279 | 3427.282 |
| Fe | 15 | R | 15 | ... | M⊙ ₁ | 7 | 4 | 3440.756 | 3440.759 |

* Red component of a double which has a Zn line between. There is another Zn line at about 3302.7 in the solar spectrum.

† Second line from red side of a group of five lines.

‡ Second line from violet side of a group of four lines.

§ A very wide nebulous line of Ba comes here.

|| Red component of a double (the other line being also Fe) having another fainter line at the red edge.

| Elements | In Arc. | | In SUN. | | Kind of Stand-ard. | WEIGHT. | | Wave-length in Arc. | Wave-length in Sun. |
|--------------|-------------|--------------|-------------|--------------|--------------------|---------|---------|---------------------|---------------------|
| | Inten-sity. | Appear-ance. | Inten-sity. | ApPear-ance. | | In Arc. | In Sun. | | |
| Fe | 10 | ... | 10 | ... | M \odot_1 | 6 | 4 | 3441-135 | 3441-135 |
| Fe | 8 | R | 8 | ... | M \odot_1 | 6 | 4 | 3444-024 | 3444-032 |
| Co | 6 | R | 4 | ... | \odot'' | ... | 10 | | 3455-384 |
| Sr? | 8 | ... | 3 | ... | \odot'' | ... | 8 | | 3464-609 |
| Co } * | 10 | R | 4 | d | M | 7 | 3 | 3466-010 | 3465-991 |
| Fe } | 10 | R | 6 | | | | | | |
| Fe† | 10 | R | 10 | ... | M | 7 | 3 | 3475-602 | 3475-594 |
| Fe† | 7 | R | 8 | ... | M | 5 | 2 | 3476-848 | 3476-831 |
| Co } | 2 | ... | 4 | ... | \odot'' | ... | 10 | | 3478-001 |
| Fe } | 3 | | | | | | | | |
| Ni } | 2 | | | | | | | | |
| Ni | 4 | R | 5 | ... | \odot' | ... | 9 | | 3486-036 |
| Fe§ | 10 | R | 10 | ... | M | 7 | 3 | 3490-724 | 3490-721 |
| Co } | 4 | R | 4 | ... | \odot'' | ... | 8 | | 3491-464 |
| ? } | ? | | | | | | | | |
| Fe | 5 | ... | 5 | ... | M | 1 | 1 | 3497-266 | 3497-264 |
| Fe } ¶ | 6 | R | 7 | d | M | 5 | 4 | 3497-991 | 3497-991 |
| ? } | ? | ... | 3 | | | | | | |
| Fe | 2 | ... | 3 | ... | \odot'' | ... | 4 | | 3500-721 |
| Ni | 7 | R | 7 | ... | \odot'' | ... | 4 | | 3500-993 |
| Ti** | 5 | ... | 4 | ... | \odot' | ... | 8 | | 3510-987 |
| Fe†† | 7 | R | 6 | ... | M | 2 | 3 | 3513-981 | 3513-947 |
| Co | 6 | R | 5 | ... | \odot'' | ... | 10 | | 3518-487 |
| Th | 40 | R | ... | ... | M | 1 | ... | 3519-342 | 3521-404 |
| Fe | 5 | R | 7 | ... | M | 6 | 5 | 3521-409 | |
| Th | 20 | R | ... | ... | M | 1 | ... | 3529-547 | 3540-266 |
| Fe | 3 | ... | 5 | ... | \odot'' | ... | 10 | | |
| ? | ... | ... | 4 | ... | \odot'' | ... | 6 | | 3545-333 |
| Yt | 6 | ... | 2 | ... | M \odot'' | 1 | 1 | 3549-147 | 3549-145 |
| Fe | 2 | ... | 3 | ... | \odot'' | ... | 7 | | 3550-006 |
| Fe | 9 | R | 8 | ... | M \odot | 3 | 4 | 3558-674 | 3558-670 |
| Ti } | 2 | ... | 4 | d? | \odot'' | ... | 12 | | 3564-680 |
| Fe } | 1 | | | | | | | | |
| Fe | 10 | R | 12 | ... | M | 6 | 4 | 3565-530 | 3565-528 |
| Fe†† | 20 | R | 20 | ... | M | 8 | 4 | 3570-253 | 3570-226 |
| Fe | 10 | ... | 10 | ... | M | 1 | 1 | 3570-412 | 3570-402 |
| Fe | 30 | R | 40 | ... | M \odot_1 | 9 | 6 | 3581-344 | 3581-344 |
| Fe? | 2 | ... | 4 | ... | \odot'' | ... | 12 | | 3583-483 |
| Yt | 6 | ... | 2 | ... | M | 1 | 1 | 3584-662 | 3584-662 |
| O§§ | 2 | ... | 1 | ... | M | 8 | ... | 3585-992 | 3590-523 |
| C | ... | ... | 2 | ... | M | 2 | ... | 3586-041 | |
| C | ... | ... | 3 | ... | M | 7 | ... | 3590-523 | 3597-192 |
| Fe | 5 | ... | 4 | ... | \odot'' | ... | 12 | | |

* The metal measured was Fe.

† Strongest line of group of six lines.

‡ Also the strongest line in a group of six lines.

§ There is a Co line near this towards the red.

|| Red component of a double.

¶ Violet component of a double. Other component was not measured.

** A strong compound bismuth line also comes here.

†† Violet component of a double.

‡‡ Red component of a double. There is also another Fe line towards the red.

§§ First line in the second head of the carbon band.

||| First line in the first head of carbon band.

| Elements. | IN ARC. | | IN SUN. | | Kind of Stand-ard. | WEIGHT. | | Wave-length in Arc. | Wave-length in Sun. |
|-------------|-------------|--------------|-------------|--------------|--------------------|---------|---------|---------------------|---------------------|
| | Inten-sity. | Appear-ance. | Inten-sity. | Appear-ance. | | In Arc. | In Sun. | | |
| Yt (Fe) ... | 10-? | ... | 4 | ... | M \odot " | 1 | 1 | 3600-884 | 3600-880 |
| Yt ... | 6 | ... | 2 | ... | M \odot | 1 | 1 | 3602-065 | 3602-061 |
| Cr* ... | 10 | R | 4 | ... | M \odot_1 | 1 | 2 | 3605-497 | 3605-483 |
| Fe* ... | 5 | ... | 7 | d | M \odot_1 | 2 | 2 | 3605-621 | 3605-635 |
| Fe† ... | 4 | ... | 6 | ... | M | 2 | 2 | 3606-836 | 3606-831 |
| Fe ... | 15 | R | 15 | ... | M \odot | 11 | 10 | 3609-015 | 3609-015 |
| Yt ... | 7 | ... | 3 | ... | M \odot | 1 | 1 | 3611-196 | 3611-193 |
| Fe ... | 4 | ... | 4 | ... | \odot " | 1 | 15 | 3612-237 | 3612-217 |
| Ca } † ... | ... | ... | 2 | d | M \odot_1 | 1 | 1 | 3617-939 | 3617-920 |
| Fe } ... | 4 | ... | 3 | | | | | | |
| Fe ... | 20 | R | 20 | ... | M \odot_1 | 11 | 10 | 3618-922 | 3618-924 |
| Yt ... | 3 | ... | 1 | ... | M | 1 | 1 | 3621-096 | 3621-122 |
| Fe ... | 4 | ... | 4 | ... | M \odot | 2 | 2 | 3621-616 | 3621-606 |
| Fe ... | 4 | ... | 4 | ... | M \odot_h | 2 | 3 | 3622-161 | 3622-147 |
| Fe ... | 4 | ... | 4 | ... | M \odot " | 1 | 14 | 3623-338 | 3623-332 |
| Fe§ ... | 2 | ... | 3 | ... | \odot " | ... | 10 | ... | 3623-608 |
| Yt ... | 3 | ... | 2 | ... | M \odot | 1 | 1 | 3623-853 | 3623-853 |
| Fe ... | 20 | R | 20 | ... | M \odot_1 | 11 | 10 | 3631-616 | 3631-619 |
| Yt ... | 5 | ... | 3 | d | M | 1 | 1 | 3633-277 | 3633-259 |
| Ti ... | 10 | R | 3 | ... | M \odot' | 3 | 1 | 3635-615 | 3635-616 |
| Fe ... | 5 | ... | 5 | ... | M \odot_1 | 1 | 1 | 3638-454 | 3638-435 |
| Pb¶ ... | 50 | R | 1 | ... | M | 4 | ... | 3639-728 | |
| Cr } † ... | 2 | ... | 5 | ... | M \odot " | 1 | 14 | 3640-545 | 3640-536 |
| Fe } ... | 5 | | | | | | | | |
| Fe ... | 10 | R | 10 | ... | M \odot | 10 | 11 | 3647-995 | 3647-905 |
| Co ... | 5 | R | 3 | ... | \odot " | ... | 5 | ... | 3652-692 |
| Ti ... | 10 | R | 4 | ... | M \odot' | 2 | 7 | 3653-639 | 3653-639 |
| Mn } ... | 2 | ... | 2 | ... | \odot " | ... | 7 | ... | 3658-688 |
| Fe } ... | 2 | | | | | | | | |
| Fe ... | 5 | ... | 3 | ... | \odot " | ... | 13 | ... | 3667-397 |
| Fe ... | 8 | R | 8 | ... | M \odot | 8 | 7 | 3680-064 | 3680-064 |
| Co ... | 9 | } | ... | ... | \odot " | 1 | 13 | 3683-209 | 3683-202 |
| Fe ** ... | 3 | | | | | | | | |
| Va } ... | 4 | | | | | | | | |
| Pb ... | 60 | R | 1 | ... | M | 5 | ... | 3683-622 | |
| Fe ... | 5 | ... | 6 | ... | \odot " | 1 | 14 | 3684-268 | 3684-259 |
| Fe ... | 10 | R | 8 | ... | M \odot | 8 | 6 | 3687-609 | 3687-607 |
| Yt ... | ... | ... | 3 | ... | M \odot | 1 | 1 | 3694-351 | 3694-349 |
| Fe ... | 5 | ... | 5 | ... | \odot " | 1 | 11 | 3695-208 | 3695-194 |
| Fe†† ... | 7 | R | 8 | ... | M \odot | 7 | 5 | 3705-715 | 3705-711 |
| Fe ... | 5 | ... | 5 | ... | \odot " | 1 | 11 | 3707-201 | 3707-186 |
| Fe ... | 10 | R | 10 | ... | M \odot_1 | 6 | 4 | 3709-395 | 3709-397 |
| Yt ... | 10 | ... | 3 | ... | M \odot | 1 | 1 | 3710-442 | 3710-438 |

* In the solar spectrum these belong to a group of several lines. Of the three most prominent, the middle line is Cr, with possibly a weak line on its red edge; and the red one is a close double, the violet component of the double being Fe. (J.)

† The solar line is a group of four lines. The third from the violet side is the brightest and is Fe.

‡ Metal measured was Fe.

§ There is a faint line on the red side.

¶ Red component of double.

¶ In the solar spectrum this is the red component of a double, the other being cobalt.

** The metallic line measured was Fe.

†† Violet component of a double.

| Elements. | In Arc. | | In Sun. | | Kind of Stand-ard. | WEIGHT. | | Wave-length in Arc. | Wave-length in Sun. |
|--------------|-------------|--------------|-------------|--------------|--------------------|---------|---------|---------------------|---------------------|
| | Inten-sity. | Appear-ance. | Inten-sity. | Appear-ance. | | In Arc. | In Sun. | | |
| Fe | 4 | ... | 7 | ... | ⊙ | 1 | 12 | 3716.601 | 3716.585 |
| Fe | 40 | R | 50 | | ⊙ | 11 | 10 | 3720.082 | 3720.086 |
| Ni | 4 | ... | 10 | d | ⊙ | 7 | 5 | 3722.712 | 3722.691 |
| Fe-Ti } * | 8 5 | ... | 7 | ... | M | 5 | 3 | 3727.768 | 3727.763 |
| Fe | 6 | R | 7 | ... | ⊙ | 1 | 15 | 3732.549 | 3732.542 |
| Fe | 5 | ... | 5 | ... | ⊙ | 5 | 3 | 3733.467 | 3733.467 |
| Fe | 6 | R | 7 | ... | ⊙ | 8 | 7 | 3735.012 | 3735.014 |
| Fe | 40 | R | 50 | ... | ⊙ | ... | 2 | | 3736.969 |
| Ni | 6 | ... | 3 | d | ⊙ | 2 | 3 | 3737.081 | 3737.075 |
| Mn } | 2 | ... | 5 | ... | ⊙ | 7 | 8 | 3737.280 | 3737.282 |
| Ca | 4 | R | ... | ... | ⊙ | 4 | 2 | 3743.506 | 3743.502 |
| Fe | 25 | R | 30 | ... | M | 8 | 6 | 3745.708 | 3745.701 |
| Ti } | 3 | ... | 2 | t | M | 6 | 5 | 3746.048 | 3746.054 |
| Fe } * | 5 | ... | 6 | ... | ⊙ | 1 | 9 | 3747.082 | 3747.095 |
| Cr } | 3 | ... | 2 | ... | ⊙ | 7 | 8 | 3748.410 | 3748.409 |
| Fe† | 10 | R | 10 | ... | ⊙ | 7 | 8 | 3749.633 | 3749.633 |
| Fe | 7 | R | 7 | ... | ⊙ | ... | 12 | | 3754.664 |
| Fe } * | 9 | ... | 7 | d | ⊙ | ... | 12 | | 3756.211 |
| ? } | ... | ... | 2 | ... | ⊙ | 8 | 7 | 3758.380 | 3758.379 |
| Fe | 10 | R | 10 | ... | M | 9 | 8 | 3763.939 | 3763.942 |
| Fe | 15 | R | 15 | ... | M | 9 | 8 | 3767.342 | 3767.344 |
| Fe | 9 | R | 10 | ... | ⊙ | ... | 12 | | 3770.130 |
| Fe | 7 | R | 8 | d? | ⊙ | 1 | 1 | 3774.478 | 3774.480 |
| Fe | 3 | ... | 4 | ... | M | 1 | ... | 3775.869 | 3780.646 |
| Yt? | 6 | ... | 3 | ... | ⊙ | ... | 15 | | 3781.330 |
| Th | 40 | R | ... | ... | ⊙ | ... | 15 | | 3783.674 |
| ? | ... | ... | 4 | ... | ⊙ | 3 | 3 | 3788.029 | 3788.032 |
| Fe | 2 | ... | 3 | ... | ⊙ | ... | 15 | | 3794.014 |
| Ni | 10 | R | 6 | ... | M | 3 | 4 | 3795.148 | 3795.150 |
| Fe | 7 | R | 8 | ... | ⊙ | ... | 2 | | 3798.662 |
| Fe-Cr ... | 1 1 | ... | 3 | ... | ⊙ | ... | 2 | | 3799.698 |
| Fe† | 8 | ... | 8 | ... | ⊙ | ... | 15 | | 3804.153 |
| Fe | 7 | ... | 7 | ... | ⊙ | ... | 15 | | 3805.487 |
| Fe | 8 | ... | 8 | ... | ⊙ | 4 | 3 | 3815.984 | 3815.985 |
| Fe | 2 | ... | 3 | ... | ⊙ | 4 | 4 | 3820.566 | 3820.567 |
| Fe-Di ... | 4 ? | ... | 6 | ... | ⊙ | ... | 10 | | 3821.318 |
| Fe | 20 | R | 20 | ... | ⊙ | ... | 10 | | 3823.651 |
| Fe | 30 | R | 30 | ... | ⊙ | 4 | 4 | 3826.024 | 3826.024 |
| Fe | 5 | ... | 6 | ... | ⊙ | 1 | 1 | 3827.973 | 3827.973 |
| Mn (Cr) ... | 5 1 | R | 5 | ... | ⊙ | ... | 2 | | 3829.505 |
| Fe | 20 | R | 20 | ... | M | ... | 2 | | 3832.446 |
| Fe | 8 | R | 8 | ... | ⊙ | ... | 8 | | 3836.226 |
| Mg | 20 | R | 8 | ... | ⊙ | 1 | 1 | 3836.638 | 3836.652 |
| Mg | 30 | R | 10 | ... | M | ... | 2 | | 3838.430 |
| ?-O | ... | ... | 4 | ... | ⊙ | ... | 2 | | |
| Os | ... | ... | 5 | d | ⊙ | ... | 2 | | |
| Mg | 40 | R | 20 | ... | ⊙ | ... | 2 | | |

* The metallic line measured was Fe.

† Violet portion of broad solar double is composed of three lines, the red line is Fe and the middle one Co. (J.) ‡ There is a Va line towards the violet.

§ Central line of symmetrical group in carbon band.

| Elements. | IN ARC. | | IN SUN. | | Kind of Stand. ard. | WRIGHT. | | Wave-length in Arc. | Wave-length in Sun. |
|-------------|-------------|--------------|-------------|--------------|---------------------|---------|---------|---------------------|---------------------|
| | Inten-sity. | Appear-ance. | Inten-sity. | Appear-ance. | | In Arc. | In Sun. | | |
| Fe | 7 | R | 7 | ... | M | 2 | 2 | 3840.589 | 3840.584 |
| Fe | 4 | ... | 5 | ... | ⊙ | ... | 8 | | 3843.406 |
| Fe | 6 | ... | 7 | ... | M | 1 | 2 | | 3856.517 |
| Fe | 10 | R | 10 | ... | M⊙ ₁ | 2 | 3 | 3860.050 | 3860.048 |
| O* | ... | ... | 3 | ... | ⊙' | ... | 8 | | 3864.441 |
| O† | ... | ... | 4 | ... | M | 4 | 4 | 3871.527 | 3871.528 |
| V } | ... | ... | 3 | ... | ⊙ | ... | 15 | | 3875.224 |
| O† | ... | ... | 7 | ... | M⊙ ₁ | 5 | 3 | 3883.479 | 3883.472 |
| O§ | ... | ... | ... | ... | M⊙ ₁ | ... | 8 | 3883.523 | 3883.548 |
| Or | ... | ... | 1 | ... | ⊙ | ... | 12 | | 3883.773 |
| Fe | 15 | R | 9 | ... | M⊙ ₁ | 7 | 6 | 3886.421 | 3886.427 |
| Fe | 3 | ... | 4 | ... | ⊙' | ... | 12 | | 3897.599 |
| Si | 10 | R | 10 | ... | M | 4 | 4 | 3905.670 | 3905.666 |
| Fe | 3 | ... | 3 | ... | ⊙' | 1 | 12 | 3916.886 | 3916.875 |
| Ti | 6 | ... | 4 | ... | ⊙' | ... | 15 | | 3924.669 |
| Fe } | 1 } | ... | 4 | ... | ⊙' | ... | 15 | | 3925.345 |
| Va } | 2 } | ... | 4 | ... | ⊙ | ... | 13 | | 3925.792 |
| Fe } | 3 } | ... | 4 | ... | ⊙ | ... | 13 | | 3925.792 |
| Fe } I. ... | 5 } | ... | 4 } | d | ⊙' | ... | 12 | | 3926.123 |
| ? } | ? } | ... | 4 } | d | ⊙ | ... | 15 | | 3942.559 |
| Fe | 10 | R | 8 | ... | M | 1 | 3 | 3928.000 | 3928.071 |
| K Ca¶ .. | 75 | R | 300 | ... | M | 6 | 5 | 3933.809 | 3933.809 |
| Fe | 3 | ... | 4 | ... | ⊙' | ... | 8 | | 3937.474 |
| F-Co ... | 4 4 | ... | 5 | ... | ⊙ | 1 | 15 | 3941.034 | 3941.021 |
| ? } **. | ? } | ... | 2 } | d | ⊙ | ... | 15 | | 3942.559 |
| Fe } | 5 } | ... | 4 } | d | ⊙ | ... | 15 | | 3942.559 |
| Al | 20 | R | 10 | ... | M⊙ ₁ | 7 | 7 | 3944.165 | 3944.159 |
| Ca†† .. | 4 | ... | 2 | ... | M | 1 | 2 | 3949.070 | 3949.034 |
| Fe | 4 | ... | 4 | ... | ⊙'' | ... | 15 | | 3950.101 |
| Yt | 10 | ... | 2 | ... | ⊙ | ... | 13 | | 3950.497 |
| Fe | 2 | ... | 2 | ... | ⊙' | ... | 13 | | 3954.001 |
| Fe-Ca .. | 5 6 | ... | 6 | ... | ⊙' | 1 | 2 | 3957.228 | 3957.180 |
| Fe | 3 | ... | 3 | ... | ⊙'' | ... | 11 | | 3960.429 |
| Al | 30 | R | 15 | ... | M⊙ ₁ | 7 | 8 | 3961.680 | 3961.678 |
| H Ca¶ .. | 70 | R | 200 | ... | M | 7 | 5 | 3968.617 | 3968.620 |
| H†† | ... | ... | ... | ... | M | ... | ... | 3970.05 | ... |
| Fe§§ .. | 5 | ... | 4 | ... | ⊙' | ... | 11 | | 3971.478 |
| Ca .. | 5 | ... | 3 | d | M | 1 | 2 | 3973.881 | 3973.836 |
| Fe | 5 | ... | 4 | ... | ⊙'' | ... | 15 | | 3977.891 |

* One of the lines in the carbon band.

† Second head of carbon band.

‡ First line of first head of carbon band.

§ Edge of first head of carbon band.

¶ 0.87 apart.

¶ The solar line is doubly reversed and spread out into broad shading for 6.000 or 7.000 on either side. In each case the second reversal is slightly eccentric with respect to the other, being displaced towards the red. (J.)

** Components 0.85 apart.

†† Red component of a triple.

‡‡ Value determined by Dr. Ames.

§§ Red component of a double.

|| Red component of double, the violet component being Fe. There is also a Ni line close to violet side.

| Elements. | In Arc. | | In Sun. | | Kind of Stand-ard. | Weight. | | Wave-length in Arc. | Wave-length in Sun. |
|--------------|-------------|--------------|-------------|--------------|--------------------|---------|---------|---------------------|---------------------|
| | Inten-sity. | Appear-ance. | Inten-sity. | Appear-ance. | | In Arc. | In Sun. | | |
| Fe-Ti ... | 6? | ... | 4 | ... | ⊙ | ... | 14 | | 3981-914 |
| Cr } * ... | 5 | } | 6 | d | ⊙ | ... | 9 | | 3984-078 |
| Fe } ... | 3 | | | | | | | | |
| ? } † ... | ? | } | 7 | d | ⊙ | ... | 9 | | 3986-903 |
| Mn } ... | 4 | | | | | | | | |
| ? } † ... | ? | } | 6 | t | ⊙ | ... | 4 | | 3987-216 |
| Mn } ... | 4 | | | | | | | | |
| Co ... | 2 | } | 3 | ... | ⊙ | ... | 9 | | 4003-916 |
| Co-Fe-Ti ... | 4 1 2 | | | | | | | | |
| Fe-? ... | 10 | ... | 10 | ... | ⊙ | ... | 3 | | 4005-305 |
| Fe ... | ... | ... | 3 | ... | ⊙" | ... | 7 | | 4016-578 |
| Fe } ... | 2 | } | 4 | ... | ⊙" | ... | 10 | | 4029-796 |
| Zr } ... | 2 | | | | | | | | |
| Mn } ... | 30 | R | 7 | ... | M | 3 | 4 | 4030-919 | 4030-914 |
| Mn } ... | 25 | R | 6 | ... | M | 3 | 4 | 4033-230 | 4033-225 |
| Mn } ... | 20 | R | 5 | ... | M | 3 | 4 | 4034-642 | 4034-641 |
| Mn } ... | 7 | ... | 3 | ... | M | ... | ... | 4035-88 | 4035-88 |
| K ... | 50 | R | 1 | ... | M | 2 | 2 | 4044-301 | 4044-293 |
| Fe ... | 20 | R | 20 | ... | M ⊙ ₁ | 7 | 7 | 4045-975 | 4045-975 |
| K ... | 40 | R | 1? | ... | M | 2 | ... | 4047-373 | |
| Zr } ... | 1 | } | 6 | d | ⊙ | ... | 13 | | 4048-893 |
| Mn } ** ... | 8 | | | | | | | | |
| Or } ... | 2 | } | 5 | ... | ⊙" | ... | 13 | | 4055-701 |
| Mn ... | 8 | | | | | | | | |
| Fe ... | 5 | ... | 5 | ... | ⊙" | ... | 8 | | 4062-602 |
| Fe ... | 15 | R | 15 | ... | M ⊙ ₁ | 7 | 7 | 4063-755 | 4063-756 |
| Fe ... | 10 | ... | 10 | ... | M ⊙ ₁ | 7 | 9 | 4071-903 | 4071-904 |
| Fe ... | 4 | ... | 4 | ... | ⊙" | ... | 14 | | 4073-920 |
| Sr ... | 50 | R | 8 | ... | M ⊙ ₁ | 5 | 6 | 4077-876 | 4077-883 |
| Fe } ... | 2 | } | 2 | d | ⊙ | ... | 7 | | 4083-767 |
| Mn } ... | 5 | | | | | | | | |
| Fe ... | 2 | ... | 2 | ... | ⊙ | ... | 7 | | 4083-928 |
| Fe ... | 2 | ... | 2 | ... | ⊙" | ... | 8 | | 4088-716 |
| Si } ... | 3 | } | 6 | ... | ⊙" | ... | 10 | | 4103-101 |
| Mn } ... | 1 | | | | | | | | |
| Fe ... | 5 | ... | 5 | d? | ⊙" | ... | 12 | | 4107-646 |
| Fe ... | 3 | ... | 4 | ... | ⊙" | ... | 14 | | 4114-600 |
| Cr } †† ... | 1 | } | 3 | ... | ⊙ | 1 | 12 | 4121-476 | 4121-481 |
| Co } ... | 10 | | | | | | | | |
| Fe-Or ... | 3 1 | ... | 3 | ... | ⊙' | ... | 13 | | 4121-968 |
| Fe ... | 4 | ... | 3 | ... | ⊙" | ... | 17 | | 4157-948 |
| C ... | ... | ... | ... | ... | M | ... | ... | 4158-2 | |
| Fe ... | 4 | ... | 3 | ... | ⊙" | ... | 20 | | 4185-063 |
| Cl†† ... | ... | ... | 1 | ... | M ⊙ | 5 | 6 | 4197-256 | 4197-251 |

* Components about '060 apart.

† Hazy line shaded to red. Shading is due to a Mn line on red side.

‡ Triple line. Central line is brightest.

§ Seven or eight lines. The brightest and most of the others are due to Fe.

|| Violet component of double, being itself double or reversed in Sun. The other component is weak.

¶ Red component of double, being itself double or reversed in Sun. The other component is weak.

** An unequal double, violet component being much the weaker.

†† Cobalt line was measured.

‡‡ First line of second head of carbon band.

| Elements. | IN ARC. | | IN SUN. | | Kind of Stand-ard. | WEIGHT. | | Wave-length in Arc. | Wave-length in Sun. |
|------------|-------------|--------------|-------------|--------------|--------------------|---------|---------|---------------------|---------------------|
| | Inten-sity. | Appear-ance. | Inten-sity. | Appear-ance. | | In Arc. | In Sun. | | |
| Zr } ... | 2 | ... | 5 | ... | ○" | 2 | 22 | 4199-257 | 4199-263 |
| Fe } ... | 5 | ... | ... | ... | ○' | 2 | 4 | 4202-187 | 4202-188 |
| Fe } ... | 8 | ... | 5 | ... | ○ | ... | 2 | ... | 4215-616 |
| Fe } ... | 2 | 2 | ... | d | ... | ... | 18 | ... | 4215-667 |
| Sr } ... | 40 | R | 4 | ... | M○ | 6 | 3 | 4215-688 | 4215-687 |
| O* } ... | ... | ... | 1 | ... | M○ | 4 | 2 | 4216-133 | 4216-137 |
| Fe } ... | 2 | ... | 4 | ... | ○" | 1 | 22 | 4222-396 | 4222-381 |
| g Ca } ... | 50 | R | 10 | ... | M○ | 9 | 10 | 4226-898 | 4226-892 |
| Fe } ... | 4 | ... | 5 | ... | ○' | 1 | 1 | 4250-300 | 4250-290 |
| Fe } ... | 5 | ... | 7 | ... | ○ | 4 | 3 | 4250-949 | 4250-956 |
| Cr } ... | 20 | R | 7 | ... | M○" | 2 | 15 | 4254-494 | 4254-502 |
| Fe } ... | 6 | R | 7 | ... | ○ | 4 | 3 | 4260-647 | 4260-638 |
| ? } ... | ? | ... | 1 | d | ○ | ... | 12 | ... | 4267-958 |
| Fe } ... | 1 | ... | 2 | ... | ... | ... | ... | ... | ... |
| Fe } ... | 10 | R | 8 | ... | M○ | 8 | 9 | 4271-920 | 4271-924 |
| Cr } ... | 15 | R | 5 | ... | M○ | 1 | 2 | 4274-954 | 4274-958 |
| Oa } ... | 5 | R | 3 | ... | M○ | 2 | 4 | 4283-175 | 4283-170 |
| Ca } ... | 4 | R | 3 | ... | M○ | 3 | 5 | 4289-527 | 4289-523 |
| Cr } ... | 10 | R | 4 | ... | M○ | 2 | 2 | 4289-884 | 4289-881 |
| ? } ... | ... | ... | 4 | d | ○' | ... | 14 | ... | 4293-249 |
| Ca } ... | 3 | R | 2 | ... | M○ | 3 | 5 | 4299-153 | 4299-152 |
| Ca } ... | 6 | R | 4 | ... | M | 5 | 7 | 4302-690 | 4302-689 |
| Sr } ... | 8 | ... | 2 | ... | M | 1 | ... | 4305-636 | ... |
| Ti } ... | 10 | R | 4 | ... | M○ | 4 | 4 | 4306-071 | 4306-071 |
| Oa } ... | 4 | R | 2 | ... | ○ | 3 | 3 | 4307-906 | 4307-904 |
| G } ... | ... | ... | ... | d | ○ | ... | 3 | ... | 4308-034 |
| Fe } ... | 7 | R | 5 | ... | ○ | 8 | 10 | 4308-072 | 4308-071 |
| Ca } ... | 4 | R | 3 | ... | M○" | 3 | 16 | 4318-816 | 4318-818 |
| f Fe } ... | 10 | R | 8 | ... | M○' | 8 | 15 | 4325-932 | 4325-940 |
| Cr } ... | 2 | ... | 1 | d? | ○ | ... | 11 | ... | 4343-387 |
| Fe } ... | 2 | ... | 2 | ... | ○ | ... | ... | ... | ... |
| Fe } ... | 4 | ... | 3 | ... | ○" | 1 | 17 | 4352-908 | 4352-903 |
| Ni } ... | 3 | ... | 1 | ... | ... | ... | ... | ... | ... |
| Cr } ... | 4 | ... | 3 | t | ○ | ... | 10 | ... | 4359-778 |
| Zr } ... | 5 | ... | 1 | ... | ... | ... | ... | ... | ... |
| Fe } ... | 4 | ... | 5 | ... | ○" | 1 | 14 | 4369-948 | 4369-943 |
| Fe } ... | 5 | ... | 5 | ... | ○" | 1 | 17 | 4376-108 | 4376-103 |
| d Fe } ... | 15 | R | 10 | ... | M○' | 10 | 11 | 4383-721 | 4383-721 |
| Fe } † ... | 2 | ... | 3 | ... | ○ | ... | 14 | ... | 4391-149 |
| Ti } ... | 1 | ... | 1 | ... | ... | ... | ... | ... | ... |
| Fe } ... | 10 | R | 8 | ... | M○ | 10 | 11 | 4404-928 | 4404-927 |
| Va } ... | 9 | R | 2 | d | ○ | ... | 19 | ... | 4407-850 |
| Fe } ... | 3 | ... | 3 | ... | ... | ... | ... | ... | ... |
| Od } ... | 6 | ... | 6 | ... | M | 3 | ... | 4413-181 | ... |
| Fe } ... | 4 | R | 4 | ... | M○ | 9 | 7 | 4415-298 | 4415-299 |
| Oa } ... | 5 | R | 4 | ... | M○" | 5 | 7 | 4425-616 | 4425-609 |
| Ca } ... | 5 | R | 4 | ... | M○ | 5 | 5 | 4435-133 | 4435-132 |
| Ca } ... | 4 | R | 3 | ... | M○" | 5 | 6 | 4435-856 | 4435-852 |
| Fe } ... | 8 | ... | 5 | ... | ○" | 2 | 18 | 4447-912 | 4447-899 |
| Ca } ... | 6 | R | 6 | ... | M○ ₁ | 6 | 6 | 4454-949 | 4454-950 |

* First line in first head of carbon band.

† Unequal double, components being about '050 apart.

‡ There is a faint side line towards the red.

§ There is a faint line close to violet side.

| Elements. | In Arc. | | In Sun. | | Kind of Stand-ard. | WEIGHT. | | Wave-length in Arc. | Wave-length in Sun. |
|-------------|-------------|--------------|-------------|--------------|--------------------|---------|---------|---------------------|---------------------|
| | Inten-sity. | Appear-ance. | Inten-sity. | Appear-ance. | | In Arc. | In Sun. | | |
| Ca* | 3 | R | 2 | ... | M | 5 | 3 | 4456.055 | 4456.047 |
| Ca | 1 | ... | 1 | ... | M ⊙ ₁ | 2 | 2 | 4456.791 | 4456.793 |
| Fe | ... | ... | 5 | ... | ⊙'' ₁ | 1 | 18 | 4494.756 | 4494.735 |
| Cr } | 5 | ... | 4 | ... | ⊙ ₁ | ... | 14 | | 4497.041 |
| Zr } | 2 | ... | 1 | ... | ⊙'' | ... | 8 | | 4499.070 |
| Mn } | ... | ... | 2 | d | ⊙' | ... | 7 | | 4499.315 |
| ? } | ... | ... | 1 | ... | ⊙' | ... | 18 | | 4501.444 |
| Ti..... | 6 | ... | 5 | ... | ⊙' | ... | 17 | 4502.6 | 4508.456 |
| O | ... | ... | ... | ... | ⊙'' | ... | 17 | | 4508.456 |
| Ti? | ... | ... | 4 | ... | ⊙'' | ... | 17 | | 4508.456 |
| In..... | ... | ... | ... | ... | M | 4 | ... | 4511.474 | |
| In..... | ... | ... | ... | ... | M | 3 | ... | 4513.883 | |
| Ba | 70 | R | 7 | ... | M ⊙'' | 6 | 8 | 4554.212 | 4554.213 |
| Ti..... | 4 | ... | 6 | ... | ⊙'' | ... | 13 | | 4563.939 |
| Mg | 3 | ... | 5 | ... | ⊙'' | 1 | 14 | 4571.281 | 4571.277 |
| Ti..... | 5 | ... | 6 | ... | ⊙'' | ... | 14 | | 4572.157 |
| Ca-Ti | 3 1 | N | 4 | ... | ⊙'' | 1 | 14 | 4578.807 | 4578.731 |
| Or? | ... | ... | 4 | ... | ⊙'' | ... | 14 | | 4588.384 |
| Ti? | ... | ... | 4 | ... | ⊙'' | ... | 15 | | 4590.129 |
| Fe | 2 | ... | 4 | ... | ⊙'' | ... | 20 | | 4602.183 |
| Lit | 50 | R | ... | ... | M | 1 | ... | 4602.25 | |
| Ct | ... | ... | ... | ... | ... | ... | ... | 4606.6 | |
| Sr..... | 50 | R | 2 | ... | M ⊙' | 5 | 4 | 4607.506 | 4607.509 |
| ? } | ? | ... | 2 | ... | ⊙ ₁ | ... | 11 | | 4611.453 |
| Fe } | 4 | ... | 6 | d | ⊙ ₁ | ... | 11 | | 4611.453 |
| Ti } | 4 | ... | 5 | ... | ⊙' | ... | 13 | | 4629.515 |
| Co } | 5 | ... | 5 | ... | ⊙' | ... | 13 | | 4629.515 |
| Fe | 3 | ... | 4 | ... | ⊙' | ... | 14 | | 4637.683 |
| Fe | 3 | ... | 4 | ... | ⊙' | ... | 14 | | 4638.194 |
| Fe | 2 | ... | 4 | ... | ⊙'' | ... | 17 | | 4643.645 |
| Ni | 6 | R | 3 | ... | M ⊙ | 1 | 1 | 4648.833 | 4648.835 |
| ? } | ? | ... | 2 | d | ⊙' | ... | 11 | | 4668.303 |
| Fe } | 3 | ... | 5 | ... | ⊙' | ... | 11 | | 4668.303 |
| Cd | ... | ... | 4? | ... | M | 3 | 3 | 4678.339 | 4678.353 |
| Fe | 3 | ... | 6 | ... | ⊙' | ... | 12 | | 4679.028 |
| Zn | ... | ... | 2 | ... | M | 1 | ... | 4680.319 | |
| Fe | 2 | ... | 3 | ... | ⊙'' | ... | 13 | | 4683.743 |
| Ni | 4 | ... | 4 | ... | ⊙'' | ... | 12 | | 4686.395 |
| ? | ... | ... | 4 | ... | ⊙' | ... | 14 | | 4690.324 |
| Ti } | 3 | ... | 2 | d | ⊙ ₁ | ... | 11 | | 4691.581 |
| Fe } | 3 | ... | 4 | ... | ⊙ ₁ | ... | 11 | | 4691.581 |
| Mg† | 5 | ... | 9 | ... | ⊙'' | 1 | 11 | 4703.249 | 4703.180 |
| Ni | 3 | ... | 3 | ... | ⊙'' | ... | 13 | | 4703.986 |
| Ni** | 9 | R | 6 | d? | M ⊙ | 1 | 1 | 4714.598 | 4714.599 |
| Zn | 4 | ... | 4 | ... | M ⊙'' | 2 | 2 | 4722.339 | 4722.349 |
| Fe } | 2 | ... | 4 | d | ⊙ | ... | 11 | | 4727.628 |
| Mn } | 7 | ... | 3 | ... | ⊙ | ... | 11 | | 4727.628 |

* Red component of a double. Other line is Mn.

† First line in first head of blue carbon band.

‡ Strong line with fine line very close to violet side and another farther to violet.

§ Besides the double line measured there is another fine line near the red side.

|| The Mg line is of the nature of a band, shaded toward the red. It coincides with the solar line when there is very little material in the arc. (R.)

¶ Solar line is shaded towards the violet, probably owing to a close side line.

** Much the same in character as the red lithium line. (J.)

| Elements. | IN ARC. | | IN SUN. | | Kind of Stand-ard. | WEIGHT. | | Wave-length in Arc. | Wave-length in Sun. |
|------------------|-------------|--------------|-------------|--------------|--------------------|---------|---------|---------------------|---------------------|
| | Inten-sity. | Appear-ance. | Inten-sity. | Appear-ance. | | In Arc. | In Sun. | | |
| Mn | 15 | R | 6 | ... | ⊙'' | ... | 11 | | 4754-226 |
| Mn | 10 | R | 6 | ... | M⊙'' | 1 | 1 | 4783-607 | 4783-601 |
| Cd | ... | ... | ? | ... | M | 3 | ... | 4800-097 | |
| ? } | ? | ... | 1 | d | ⊙ ₁ | ... | 3 | | 4805-253 |
| Ti } | 1 | ... | 4 | | | | | | |
| Zn | ... | ... | 3 | ... | M⊙'' | 1 | 1 | 4810-725 | 4810-723 |
| Mn | 10 | ... | 6 | ... | M⊙'' | 1 | 12 | 4823-715 | 4823-697 |
| Fe? | ... | ... | 4 | ... | ⊙'' | ... | 11 | | 4824-325 |
| Fe? | 4 | ... | 5 | ... | ⊙'' | ... | 14 | | 4859-934 |
| F H | ... | ... | 15 | ... | ⊙' | ... | 5 | | 4861-496 |
| Fe | 7 | ... | 7 | ... | ⊙'' | ... | 11 | | 4890-945 |
| Ti* | 4 | ... | 2 | d | ⊙' | ... | 11 | | 4900-098 |
| Yt* | ... | ... | 2 | | | | | | |
| Cr } | 2 | ... | 6 | d? | ⊙'' | ... | 14 | | 4903-488 |
| Fe } | 5 | | | | | | | | |
| Pb | ... | ... | ... | ... | M | 1 | ... | 4905-634 | |
| Fe | 6 | ... | 7 | ... | ⊙'' | ... | 4 | | 4919-183 |
| Fe† | 9 | ... | 9 | ... | M⊙'' | 1 | 7 | 4920-676 | 4920-682 |
| Fe | 2 | ... | 4 | ... | ⊙'' | ... | 13 | | 4924-109 |
| Fe | 3 | ... | 2 | ... | ⊙'' | ... | 12 | | 4924-955 |
| Ba† | 60 | ... | 7 | d? | M⊙ | 1 | 10 | 4934-237 | 4934-247 |
| Fe | ... | ... | 6 | ... | M⊙ ₁ | ... | 3 | | 4957-482 |
| Fe | ... | ... | 8 | ... | M⊙ ₁ | ... | 3 | | 4957-786 |
| Neb** | ... | ... | ... | ... | ... | ... | ... | 4959-02 | |
| Ti } | 1 | ... | 3 | ... | ⊙'' | ... | 10 | | 4973-274 |
| Fe } | 3 | | | | | | | | |
| ? } \$ | ... | ... | 1 | d? | ⊙'' | ... | 8 | | 4978-782 |
| Fe } | 3 | ... | 3 | | | | | | |
| Ni } \$ | 5 | ... | 3 | d | ⊙ | ... | 5 | | 4980-362 |
| ? } | ? | ... | 1 | | | | | | |
| Ti | 10 | ... | 4 | ... | ⊙ | 1 | 10 | 4981-893 | 4981-915 |
| Fe | 3 | ... | 4 | ... | ⊙'' | ... | 7 | | 4994-316 |
| Ti-La] ... | 10 10 | R N | 4 | ... | M⊙ | ... | 8 | 4999-668 | 4999-693 |
| Pb | ... | ... | ... | ... | M | 5 | ... | 5005-634 | |
| Fe | 3 | ... | 4 | ... | ⊙' | ... | 10 | | 5005-904 |
| Fe† | ... | ... | 6 | ... | ⊙'' | ... | 8 | | 5006-903 |
| Ti } | 10 | R | 4 | d | ⊙'' | ... | 10 | | 5007-431 |
| Fe } | 3 | ... | 3 | | | | | | |
| Neb** | ... | ... | ... | ... | ... | ... | ... | 5007-05 | |
| Mg b d t t | ... | ... | ... | ... | M | 3 | 10 | 5007-473 | |
| (Ni) Ti } | ? | ... | 3 | d | M⊙' | ... | 10 | 5014-412 | 5014-422 |
| Ti } | 5 | ... | 4 | | | | | | |
| Ti | 7 | ... | 3 | ... | ⊙' | ... | 8 | | 5020-210 |
| Ti } | 6 | ... | 3 | d | ⊙' | ... | 8 | | 5036-113 |
| Ni } | 3 | ... | 2 | | | | | | |
| Ca | 3 | N | 2 | ... | M | 2 | 1 | 5041-867 | 5041-795 |

* A Ba line comes between these and does not coincide with either.

† Shaded, and has a faint line towards the red.

‡ A very difficult double with a fine line towards the violet. (J.)

\$ There is a faint line towards the red.

|| Ti line was measured.

¶ There is a faint side line towards the violet.

** Values determined by J. E. Keeler from his measurements at the Lick Observatory using the values of the Pb, Fe, and Mg lines given in this table.

†† Commencement of the head of Mg band.

| Elements. | In Arc. | | In Sun. | | Kind of Stand-ard. | Wright. | | Wave-length in Arc. | Wave-length in Sun. |
|---------------------------|-------------|--------------|-------------|--------------|--------------------|---------|---------|---------------------|---------------------|
| | Inten-sity. | Appear-ance. | Inten-sity. | Appear-ance. | | In Arc. | In Sun. | | |
| Fe | 5 | ... | 5 | ... | ⊙'' | ... | 12 | | 5050-008 |
| Fe | 2 | ... | 2 | ... | ⊙' | ... | 15 | | 5060-252 |
| Ti | 10 | ... | 3 | ... | ⊙' | ... | 12 | | 5064-833 |
| Fe | 4 | ... | 4 | ... | ⊙'' | ... | 14 | | 5068-946 |
| Fe | 4 | ... | 3 | ... | ⊙'' | ... | 9 | | 5083-525 |
| Od | ... | ... | ? | ... | M | 1 | ... | 5086-001 | |
| Fe | 3 | ... | 2 | ... | ⊙'' | ... | 9 | | 5090-959 |
| Fe [†] | 3 | ... | 2 | ... | ⊙ ₁ ' | ... | 7 | | 5097-176 |
| Fe(Cu) ... | 3? | ... | 3 | ... | ⊙ ₁ ' | ... | 12 | | 5105-719 |
| Fe | 3 | ... | 2 | ... | ⊙'' | ... | 11 | | 5109-825 |
| ? } | ? | ... | 2 | ... | ⊙' | ... | 11 | | 5110-570 |
| Fe } | 4 | ... | 3 | d | ⊙' | ... | 11 | | 5110-570 |
| Ni | 5 | ... | 2 | ... | ⊙'' | ... | 9 | | 5115-558 |
| Ni } | 2 | ... | 1 | ... | ⊙ ₁ | ... | 9 | | 5121-797 |
| Co | 3 | ... | 3 | d | ⊙ ₁ | ... | 9 | | 5126-369 |
| Fe | 4 | ... | 4 | ... | ⊙'' | ... | 9 | | 5127-530 |
| Fe } | 1 | ... | 6 | d | ⊙'' | ... | 12 | | 5133-871 |
| ? } | ? | ... | 6 | ... | ⊙ | ... | 4 | | 5139-437 |
| Fe } | 4 | ... | 6 | d | ⊙ | ... | 4 | | 5139-539 |
| Fe † ... | 5 | ... | 6 | ... | ⊙ | ... | 4 | | 5139-645 |
| Fe | 2 | ... | 3 | ... | ⊙'' | ... | 5 | | 5141-916 |
| Ni | 5 | ... | 2 | ... | ⊙ ₁ | ... | 1 | | 5142-967 |
| Fe } | 3 | ... | 4 | d | ⊙ ₁ | ... | 5 | | 5143-042 |
| Ni } | 5 | ... | 3 | ... | ⊙ ₁ | ... | 2 | | 5143-106 |
| ? } | ? | ... | 3 | ... | ⊙'' | ... | 10 | | 5146-664 |
| Fe } | 4 | ... | 3 | d | ⊙ | ... | 9 | | 5151-026 |
| Mn † ... | 2 | ... | 1 | ... | ⊙ | ... | 9 | | 5151-026 |
| Ti? Co? .. | ... | ... | 2 | ... | ⊙'' | ... | 10 | | 5154-237 |
| Ni | 6 | ... | 2 | ... | ⊙'' | ... | 10 | | 5155-937 |
| F ? | ... | ... | 2 | ... | ⊙'' | ... | 11 | | 5159-240 |
| Fe | 4 | ... | 4 | ... | ⊙'' | ... | 13 | | 5162-448 |
| C ₂ | ... | ... | 1 | ... | M | 2 | 1 | 5165-241 | 5165-190 |
| Fe | 2 | ... | 2 | ... | ⊙'' | ... | 10 | | 5165-588 |
| Mg } | 20 | R | 8 | ... | M ⊙ ₁ | 2 | 3 | 5167-488 | 5167-501 |
| b ₁ Fe } | 6 | ... | 6 | d | ⊙ | ... | 7 | | 5167-572 |
| Fe } | 3 | ... | 4 | ... | M ⊙ ₁ | 2 | 3 | 5167-664 | 5167-686 |
| b ₂ Fe } | 3 | ... | 4 | d | ⊙'' | ... | 3 | | 5169-066 |
| Fe } | 3 | ... | 4 | ... | ⊙'' | ... | 5 | | 5169-161 |
| Fe ... | 5 | ... | 5 | ... | ⊙'' | ... | 3 | | 5169-218 |
| b ₃ Mg | 35 | R | 10 | ... | M ⊙'' | 2 | 9 | 5171-783 | 5171-783 |
| | | | | | | | | 5172-866 | 5172-871 |

* The fine line near to violet side belongs to Ni ?

† There is a Cr line near to red side.

‡ The Mn line is a faint side line towards the red from the Fe line.

§ Measurements in the arc spectrum were on the first line of the first head of the green carbon band; measurements in the solar spectrum were probably on the brightest of a group of faint lines near the head of carbon band (J.). Much of the band can be seen on my map of the solar spectrum extending to the left (R.).

|| Components about 0.180 apart on photographic plates. (J.)

¶ Components about 0.138 apart as measured by Rowland in solar spectrum and 0.150 apart as measured on photographic plates. (J.)

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F

| Elements. | IN ARC. | | IN SUN. | | Kind of Stand-ard. | WEIGHT. | | Wave-length in Arc. | Wave-length in Sun. |
|------------------------|-------------|--------------|-------------|--------------|--------------------|---------|---------|---------------------|---------------------|
| | Inten-sity. | Appear-ance. | Inten-sity. | Appear-ance. | | In Arc. | In Sun. | | |
| Ti..... | 10 | R | 3 | ... | ⊙'' | ... | 11 | | 5173-912 |
| b ₁ Mg..... | 40 | R | 20 | ... | M⊙'' | 2 | 11 | 5183-791 | 5183-792 |
| Ti..... | 2 | ... | 4 | ... | ⊙'' | ... | 3 | | 5188-863 |
| *..... | ... | ... | ... | d | ⊙'' | ... | 7 | | 5188-948 |
| Ca..... | 6 | ... | 4 | ... | M⊙'' | 1 | 3 | 5189-019 | 5189-020 |
| Ti..... | 8 | ... | 3 | ... | M⊙'' | 2 | 8 | 5193-134 | 5193-139 |
| Fe..... | 3 | ... | 4 | ... | ⊙'' | ... | 10 | | 5198-885 |
| ?..... | ? | ... | 2 | ... | ⊙'' | ... | 11 | | 5202-483 |
| Fe..... | 4 | ... | 3 | ... | ⊙'' | ... | 11 | | 5202-483 |
| Cr..... | 8 | R | 4 | ... | ⊙'' | ... | 10 | | 5204-708 |
| Fe..... | 3 | ... | 3 | d | ⊙'' | ... | 10 | | 5204-708 |
| Ti..... | 10 | R | 3 | ... | M⊙'' | 2 | 12 | 5210-549 | 5210-556 |
| Fe..... | 3 | ... | 4 | ... | ⊙'' | ... | 10 | | 5215-352 |
| Fe..... | 3 | ... | 4 | ... | ⊙'' | ... | 10 | | 5217-559 |
| Fe..... | 2 | ... | 2 | ... | ⊙'' | ... | 10 | | 5225-690 |
| Fe..... | 4 | ... | 4 | ... | ⊙'' | ... | 8 | | 5230-014 |
| Fe..... | 7 | ... | 8 | ... | ⊙'' | ... | 9 | | 5233-124 |
| Fe..... | 3 | ... | 3 | ... | ⊙'' | ... | 10 | | 5242-662 |
| Fe..... | 2 | ... | 2 | ... | ⊙'' | ... | 11 | | 5250-391 |
| Fe..... | 3 | ... | 3 | ... | ⊙'' | ... | 11 | | 5250-825 |
| Fe..... | 2 | ... | 3 | ... | ⊙'' | ... | 12 | | 5253-649 |
| Ca..... | 2 | ... | 1 | ... | M⊙ ₁ | 1 | 5 | 5260-556 | 5260-557 |
| Ca..... | 6 | ... | 3 | ... | ⊙ | 1 | 12 | | 5261-880 |
| Or..... | 2 | ... | 3 | ... | ⊙ | 1 | 12 | | 5261-880 |
| ?..... | ... | ... | 1 | ... | M⊙ ₁ | ... | 1 | | 5262-341 |
| Ca..... | 6 | ... | 2 | d | ⊙ | 2 | 5 | 5262-408 | 5262-391 |
| Cr..... | 4 | R | 3 | ... | ⊙ | ... | 3 | | 5264-327 |
| †..... | ... | ... | 6 | ... | ⊙'' | ... | 2 | | 5264-371 |
| Ca..... | 6 | ... | 3 | ... | M⊙ | 2 | 3 | 5264-408 | 5264-395 |
| Ca..... | 8 | ... | 3 | ... | ⊙ | 1 | 2 | 5265-725 | 5265-727 |
| }..... | ... | ... | 5 | ... | ⊙ | ... | 2 | | 5265-789 |
| (Ni?)..... | ... | ... | ... | ... | ⊙ | ... | 1 | | 5265-884 |
| Cr..... | 4 | R | 2 | ... | ⊙ | ... | 1 | | 5265-884 |
| Fe..... | 6 | ... | 6 | ... | ⊙'' | 1 | 8 | 5266-733 | 5266-729 |
| E ₂ Fe..... | 8 | ... | 8 | d? | ⊙'' | 1 | 16 | 5269-714 | 5269-722 |
| Ca..... | 10 | ... | 4 | ... | M⊙ | 2 | 3 | 5270-446 | 5270-448 |
| E ₁ | ... | ... | ... | d | ⊙'' | ... | 12 | | 5270-495 |
| Fe..... | 6 | ... | 4 | ... | M⊙ | ... | 3 | | 5270-533 |
| Fe..... | 3 | ... | 3 | ... | ⊙'' | ... | 6 | | 5273-344 |
| }..... | ... | ... | ... | d | ⊙' | ... | 5 | | 5273-443 |
| Fe..... | 3 | ... | 3 | ... | ⊙'' | ... | 8 | | 5273-554 |
| ?..... | ? | ... | 2 | ... | ⊙'' | ... | 11 | | 5276-205 |
| Cr..... | 5 | ... | 2 | t | ⊙'' | ... | 11 | | 5276-205 |
| Co..... | 3 | ... | 1 | ... | ⊙'' | ... | 11 | | 5281-968 |
| Fe..... | 4 | ... | 5 | ... | ⊙'' | ... | 11 | | 5281-968 |

* Components about 0.155 apart on photographic plates. (J.)

† Another set of measurements on photographic plates gives the components as 0.083 apart.

‡ Components about 0.088 apart on photographic plate. It is an exceedingly difficult double and it is possible that this doubleness of E₂ is really a case of the reversal of line in the Sun. (J.)

§ Components 0.077 apart as determined by another short series (R.); 0.130 on photographic plates (J.).

|| Components of double about 0.075 apart on photographic plates. The fine side line to red is about 0.110 from the red component of double. (J.)

| Elements. | IN ARC. | | IN SUN. | | Kind of Stand-ard. | WEIGHT. | | Wave-length in Arc. | Wave-length in Sun. |
|------------------|-------------|--------------|-------------|--------------|--------------------|---------|---------|---------------------|---------------------|
| | Inten-sity. | Appear-ance. | Inten-sity. | Appear-ance. | | In Arc. | In Sun. | | |
| Fe | 5 | ... | 6 | ... | ○" | ... | 11 | | 5283·803 |
| Fe | 2 | ... | 2 | ... | ○" | ... | 12 | | 5288·708 |
| Cr | 6 | R | 4 | ... | ○" | ... | 12 | | 5298·873 |
| Cr | 2 | ... | 3 | ... | ○" | ... | 9 | | 5300·918 |
| Fe | 3 | ... | 4 | ... | ○" | ... | 10 | | 5307·546 |
| Fe? | ... | ... | 4 | ... | ○" | ... | 1 | | 5316·790 |
| 1474 } * | ... | d | 6 | d | ○" | ... | 7 | | 5316·870 |
| Co? | 2 | ... | 3 | ... | ○" | ... | 1 | | 5316·950 |
| Fe | 9 | ... | 8 | ... | ○" | ... | 8 | | 5324·373 |
| Fe? | 3 | ... | 4 | ... | ○" | ... | 9 | | 5333·092 |
| Ca | 7 | ... | 5 | ... | M ⊙ | 1 | 4 | 5349·599 | 5349·623 |
| Th† | 75 | t? | ... | ... | M ⊙ | 2 | ... | 5350·870 | |
| Fe-Ni } | 3 | 3 | 4 | ... | ○ ₁ | ... | 8 | | 5353·592 |
| ? | ... | ... | 2 | ... | ○" | ... | 7 | | 5361·813 |
| Fe(Co) } § | 1 | 3 | 1 | ... | ○" | ... | 5 | | 5363·011 |
| ? | ? | ... | 3 | d | ○" | ... | 1 | | 5363·056 |
| Fe | 4 | ... | 6 | ... | ○" | ... | 8 | | 5367·670 |
| Fe | 4 | ... | 6 | ... | ○" | ... | 8 | | 5370·165 |
| Ni } | 2 | ... | 2 | ... | ○ ₁ | ... | 8 | | 5371·686 |
| Fe-Cr } | 9 | 2 | 7 | d | ○" | ... | 9 | | 5379·776 |
| Fe | 2 | ... | 3 | ... | ○" | ... | 11 | | 5383·576 |
| Fe | 6 | ... | 6 | ... | ○" | ... | 11 | | 5389·683 |
| Fe | 3 | ... | 4 | ... | ○" | ... | 11 | | 5393·378 |
| Fe | 4 | ... | 5 | ... | ○" | 1 | 12 | 5397·319 | 5397·346 |
| Fe | 7 | ... | 7 | ... | ○" | 1 | 14 | 5405·979 | 5405·987 |
| Fe | 7 | ... | 7 | ... | ○" | ... | 7 | | 5410·000 |
| Cr | 10 | R | 5 | ... | ○" | ... | 12 | | 5415·421 |
| Fe } | 4 | ... | 6 | ... | ○" | ... | 10 | | 5424·284 |
| Va } | 4 | ... | 7 | ... | ○" | ... | | | |
| Va } | 3 | ... | | | | | | | |
| Fe } | 5 | ... | | | | | | | |

* The distance apart of the components of this 1474 line measured accurately is 0·146 by Crew, and 0·141 by Rowland. The coincidences with Fe and Co are very doubtful. The Co line comes more nearly between the two rather than coinciding with either. (R.)

A trial of substances in the arc gave the following results:—iron, manganese, chromium, titanium, and two different specimens of meteoric stones showed two faint lines having the same relative intensities with respect to each other as the components of 1474 in the solar spectrum, and either coincided with the components of 1474 or nearly so. When cobalt and nickel were tried, the lines were the same distance apart but the relative intensities were reversed, the red component being much the stronger.

With the best definition 1474 is a triple, or rather a double the red component of which has a weak side line to violet. The components as measured on a photographic plate are respectively 0·120 and 0·050 apart. The main components as determined by a series of measurements on photographic plates are 0·170 apart.

Probably the violet component of the double is iron and the weak side line of the red component is cobalt, but the red component is unknown. (J.)

† With but little material in the arc this is a difficult triplet. The violet component is very strong, the red component about half as strong, and between them, but nearer the red component, is a very narrow line much weaker than either of the others. (J.)

‡ There are some fine lines near to red side.

§ Components about 0·110 apart on photographic plates. (J.)

|| Red component itself is an exceedingly difficult double. (J.)

| Elements. | In Arc. | | In Sun. | | Kind of Stand-ard. | WEIGHT. | | Wave-length in Arc. | Wave-length in Sun. |
|---------------|-------------|--------------|-------------|--------------|--------------------|---------|---------|---------------------|---------------------|
| | Inten-sity. | Appear-ance. | Inten-sity. | Appear-ance. | | In Arc. | In Sun. | | |
| Fe | 5 | ... | 6 | ... | ⊙'' | 1 | 9 | 5434-725 | 5434-742 |
| Fe * | 7 | ... | 7 | ... | ⊙'' | 1 | 9 | 5447-116 | 5447-130 |
| Fe? } | ... | ... | 3 | ... | ⊙' | ... | 1 | | 5455-666 |
| Fe } | 6 | ... | 6 | ... | ⊙' | ... | 8 | | 5455-759 |
| Ni | 3 | ... | 1 | ... | ⊙' | ... | 1 | | 5455-826 |
| Fe | 3 | ... | 4 | ... | ⊙' | ... | 7 | | 5462-732 |
| Fe | 3 | ... | 4 | ... | ⊙'' | ... | 9 | | 5463-174 |
| Fe | 3 | ... | 3 | ... | ⊙'' | ... | 10 | | 5463-493 |
| Ni | 15 | R | 4 | ... | ⊙'' | ... | 10 | | 5466-608 |
| Fe | 2 | ... | 3 | ... | ⊙'' | ... | 5 | | 5477-128 |
| Fe | 3 | ... | 4 | ... | ⊙'' | ... | 8 | | 5487-968 |
| Fe | 5 | ... | 4 | ... | ⊙'' | ... | 8 | | 5497-731 |
| Fe | 5 | ... | 4 | ... | ⊙'' | ... | 8 | | 5501-685 |
| Ca | 5 | N | 3 | ... | ⊙'' | ... | 8 | | 5507-000 |
| Mg† | 10 | ... | 7 | ... | ⊙'' | 1 | 8 | 5513-127 | 5513-207 |
| Fe | ... | ... | 2 | ... | ⊙'' | 4 | 8 | 5528-672 | 5528-636 |
| Fe | 3 | ... | 2 | ... | ⊙'' | ... | 8 | | 5535-073 |
| Fe | 3 | ... | 2 | ... | ⊙'' | ... | 8 | | 5543-418 |
| Fe | 3 | ... | 2 | ... | ⊙'' | ... | 9 | | 5544-158 |
| Fe† | 4 | ... | 3 | ... | ⊙' | ... | 8 | | 5555-113 |
| Fe | 6 | ... | 5 | ... | ⊙'' | ... | 8 | | 5569-848 |
| Fe | 5 | ... | 4 | ... | ⊙'' | ... | 7 | | 5576-319 |
| Ca | 6 | ... | 4 | ... | ⊙'' | 2 | 9 | 5582-204 | 5582-195 |
| Ca | 10 | R | 6 | ... | ⊙'' | 2 | 9 | 5588-977 | 5588-980 |
| Ca | 5 | ... | 4 | ... | ⊙'' | 2 | 5 | 5590-352 | 5590-342 |
| Ca | 7 | R | 5 | ... | ⊙ | 2 | 5 | 5594-689 | 5594-695 |
| Fe | 3 | ... | 2 | ... | ⊙' | 1 | 2 | 5598-563 | 5598-555 |
| Ca | 7 | ... | 4 | ... | ⊙' | 2 | 4 | 5598-712 | 5598-715 |
| Ca | 5 | ... | 4 | ... | ⊙'' | 2 | 4 | 5601-502 | 5601-501 |
| Fe } | 2 | ... | 2 | ... | ⊙' | ... | 10 | | 5603-097 |
| Ca } § | 6 | ... | 3 | ... | ⊙' | ... | 10 | | 5615-526 |
| Fe } | 5 | ... | 5 | ... | ⊙' | ... | 10 | | 5615-879 |
| Fe | 2 | ... | 2 | ... | ⊙'' | ... | 12 | | 5624-253 |
| Fe-Va | 5 2 | ... | 4 | ... | ⊙'' | ... | 14 | | 5624-768 |
| Fe | 2 | ... | 3 | ... | ⊙'' | ... | 5 | | 5634-167 |
| Fe | 2 | ... | 3 | ... | ⊙'' | ... | 10 | | 5641-661 |
| Si | ... | ... | 2 | ... | ⊙ | ... | 9 | | 5645-835 |
| Fe | 2 | ... | 4 | ... | ⊙' | ... | 9 | | 5655-707 |
| Yt? | 1 | ... | 4 | ... | ⊙'' | ... | 9 | | 5658-096 |
| Fe | 3 | ... | 5 | ... | ⊙'' | ... | 9 | | 5662-745 |
| Ti | 3 | ... | 2 | ... | ⊙ | ... | 8 | | 5675-648 |
| Fe | 2 | ... | 3 | ... | ⊙'' | ... | 8 | | 5679-249 |
| Na | 3 | ... | 4 | ... | ⊙'' | ... | 9 | | 5682-861 |

* A difficult double. (J.)

† This Mg line is shaded to one side when there is much Mg in the arc and is therefore a poor metallic standard. The solar line corresponds to the extreme edge of this band-like line. (R.)

‡ There is a side line towards the violet.

§ This triplet is made up of close double and a line close to red stronger than either component of double; wave-length of components about 5602-995; 5603-080 and 5603-180 as measured on a photographic plate. (J.)

|| Lines used by Peirce in his determinations of absolute wave-lengths.

| Elements. | IN ARC. | | IN SUN. | | Kind of Stand-ard. | WEIGHT. | | Wave-length in Arc. | Wave-length in Sun. |
|--------------------------|-------------|--------------|-------------|--------------|--------------------|---------|---------|---------------------|---------------------|
| | Inten-sity. | Appear-ance. | Inten-sity. | Appear-ance. | | In Arc. | In Sun. | | |
| Na | ... | ... | 6 | ... | ○" | ... | 7 | | 5688-434 |
| Fe | 4 | ... | 5 | ... | ○" | ... | 8 | | 5701-789 |
| Si | ... | ... | 5 | ... | ○" | ... | 4 | | 5708-620 |
| Fe | ... | ... | 6 | d | ○ | ... | 6 | | 5709-616 |
| Ni | 5 | ... | 5 | | ○ | ... | 8 | | 5709-780 |
| Mg* | ... | ... | 6 | ... | M⊙ | 4 | ... | 5711-374 | 5711-318 |
| Ni | 5 | } | 5 | ... | ○" | ... | 10 | | 5715-309 |
| Fe-Ti } | 3 | | | | | | | | |
| Fe | ... | ... | 5 | ... | ○" | ... | 10 | | 5731-973 |
| Fe | ... | ... | 3 | ... | ○ | ... | 10 | | 5742-066 |
| Fe | ... | ... | 4 | ... | ○" | ... | 10 | | 5752-257 |
| Fe | ... | ... | 5 | ... | ○" | ... | 10 | | 5753-342 |
| Ni } | ... | ... | 5 | ... | ○" | ... | 9 | | 5754-384 |
| ? | ... | ... | | | | | | | |
| Fe† | ... | ... | 7 | ... | ○ | ... | 8 | | 5763-215 |
| Si | ... | ... | 5 | ... | ○ _h | ... | 6 | | 5772-360 |
| Fe | ... | ... | 5 | ... | ○" | ... | 9 | | 5775-304 |
| Cu?Co? | ... | ... | 7 | d? | ○" | ... | 9 | | 5782-346 |
| Cr | 6 | ... | 4 | ... | ○" | ... | 9 | | 5784-081 |
| Cr | 7 | ... | 5 | ... | ○" | ... | 13 | | 5788-136 |
| Cr } | 10 | ... | 7 | d? | ○" | ... | 16 | | 5791-207 |
| Fe } | | | | | | | | | |
| ? | ... | ... | 4 | ... | ○" | ... | 10 | | 5798-087 |
| Fe | ... | ... | 5 | ... | ○" | ... | 9 | | 5798-400 |
| Ni | 7 | ... | 5 | ... | ○" | ... | 8 | | 5805-448 |
| Fe | ... | ... | 5 | ... | ○" | ... | 7 | | 5806-954 |
| Fe | ... | ... | 5 | ... | ○" | ... | 14 | | 5809-437 |
| Fe† | ... | ... | 6 | ... | ○ | ... | 14 | | 5816-594 |
| Ni | 3 | ... | 3 | ... | ○ ₁ | ... | 6 | | 5831-832 |
| Ba | 10 | ... | 5 | ... | ○" | ... | 14 | | 5853-903 |
| Ca§ | 10 | ... | 7 | ... | ○ ₁ | ... | 14 | | 5857-672 |
| Fe | ... | ... | 6 | ... | ○" | ... | 15 | | 5859-810 |
| Fe | ... | ... | 6 | ... | ○" | ... | 16 | | 5862-580 |
| D ₂ HeI | ... | ... | ... | ... | ... | ... | ... | | 5875-982 |
| Fe } | ¶ | ... | 6 | d | ○ ₁ | ... | 11 | | 5884-048 |
| A(wv) } | | | | | | | | | |
| A(wv) } | ... | ... | 3 | ... | ○ ₁ | ... | 8 | | 5889-854 |
| D ₂ Na | ... | ... | 15 | ... | ○ | ... | 20 | | 5890-182 |
| Ni** | 3 | d? | 4 | ... | ○ | ... | 14 | | 5893-098 |

* This Mg line is shaded on one side, especially when there is much Mg in the arc and therefore should not be used for a metallic standard. (R.)

† There is a fine line near to violet side.

‡ There is a line close to violet side.

§ There is a Ni line near to red.

¶ This value of the wave-length of D₂ is the result of three series of measurements made with a grating having 20,000 lines to the inch, and is accurate to perhaps 0.02.

Observations were made in the first spectrum on both sides of the Sun. The line does not occur as a dark line in the solar spectrum; but is sometimes, if not always, present as a very weak bright line. This is shown by a study of the best photographs of this region of the solar spectrum. (J.)

¶ A water-vapour line is toward the red about 0.080 from the Fe line and ordinarily forms a double with it.

** An exceedingly close equal double when there is very good definition. There is also a solar line near to the violet side, and a water-vapour line near to the red. (J.)

| Elements. | IN ARC. | | IN SUN. | | Kind of Stand-ard. | WRIGHT. | | Wave-length in Arc. | Wave-length in Sun. |
|----------------|-------------|--------------|-------------|--------------|--------------------|---------|---------|---------------------|---------------------|
| | Inten-sity. | Appear-ance. | Inten-sity. | Appear-ance. | | In Arc. | In Sun. | | |
| D. Na | ... | ... | 10 | ... | ⊙" | ... | 20 | | 5896-154 |
| A(wv) | ... | ... | 3 | d? | ⊙ ₁ | ... | 10 | | 5898-395 |
| Fe? } | ... | ... | 1 | | ⊙ ₁ | ... | 13 | | 5901-681 |
| A(wv) } | ... | ... | 5 | | ⊙ ₁ | ... | 15 | | 5905-895 |
| Fe? } | ... | ... | 1 | d | ⊙" | ... | 17 | | 5914-384 |
| Fe * | ... | ... | 5 | ... | ⊙" | ... | 16 | | 5916-475 |
| Fe * | ... | ... | 4 | d | ⊙" | ... | 12 | | 5919-855 |
| ?-(wv) } | ... | ... | 5 | ... | ⊙" | ... | 14 | | 5930-410 |
| Fe * | ... | ... | 5 | ... | ⊙" | ... | 13 | | 5934-883 |
| A(wv) ... | ... | ... | 6 | ... | ⊙" | ... | 14 | | 5948-761 |
| Fe * | ... | ... | 6 | ... | ⊙" | ... | 12 | | 5956-925 |
| Fe * | ... | ... | 6 | ... | ⊙" | ... | 12 | | 5975-570 |
| Fe * | ... | ... | 6 | ... | ⊙" | ... | 13 | | 5977-005 |
| A(wv) ... | ... | ... | 2 | ... | ⊙ _h | ... | 1 | | 5977-254 |
| Fe * | ... | ... | 6 | ... | ⊙ _h | ... | 6 | | 5985-044 |
| Fe * | ... | ... | 6 | ... | ⊙" | ... | 7 | | 5987-286 |
| Fe * | ... | ... | 6 | ... | ⊙" | ... | 7 | | 6003-245 |
| Fe * | ... | ... | 4 | ... | ⊙" | ... | 3 | | 6008-190 |
| Fe * | ... | ... | 6 | ... | ⊙" | ... | 6 | | 6008-782 |
| Mn 10 | ... | ... | 6 | ... | ⊙" | ... | 5 | | 6013-717 |
| Mn 10 | ... | ... | 6 | ... | ⊙" | ... | 8 | | 6016-856 |
| ? } † | ... | ... | 3 | d | ⊙ ₁ | ... | 6 | | 6020-347 |
| Fe } | ... | ... | 5 | | ⊙" | ... | 6 | | 6022-017 |
| Mn 10 | ... | ... | 5 | | ⊙" | ... | 8 | | 6024-280 |
| Fe * | ... | ... | 6 | ... | ⊙" | ... | 7 | | 6027-265 |
| Fe * | ... | ... | 4 | ... | ⊙" | ... | 8 | | 6042-316 |
| Fe * | ... | ... | 4 | ... | ⊙" | ... | 9 | | 6056-232 |
| Fe * | ... | ... | 5 | ... | ⊙" | ... | 13 | | 6065-708 |
| Fe * | ... | ... | 7 | ... | ⊙" | ... | 13 | | 6078-709 |
| Fe * | ... | ... | 5 | ... | ⊙" | ... | 12 | | 6079-223 |
| Fe * | ... | ... | 3 | ... | ⊙" | ... | 4 | | 6102-408 |
| Fe * | ... | ... | 4 | ... | ⊙" | ... | 9 | | 6102-941 |
| Ca } ‡ | 10 | R | 6 | ... | ⊙" | ... | 8 | | 6103-449 |
| Fe } | ... | ... | 4 | d | ⊙ ₁ | ... | 8 | | 6103-812 |
| ? } | ... | ... | 1 | | ⊙ ₁ | ... | 8 | | 6103-812 |
| Li 20 | ... | ... | ... | ... | M | 4 | ... | 6103-812 | 6103-812 |
| Ni 5 | ... | ... | 6 | ... | ⊙" | ... | 8 | | 6108-338 |
| Ni 4 | ... | ... | 3 | ... | ⊙' | ... | 8 | | 6111-287 |
| Fe 5 | ... | ... | 6 | ... | ⊙" | ... | 8 | | 6116-415 |
| Ca 15 | R | ... | 9 | ... | ⊙" | ... | 11 | | 6122-428 |
| Fe * | ... | ... | 8 | ... | ⊙' | ... | 9 | | 6136-834 |
| Fe-Ba ... ?-15 | ... | ... | 7 | ... | ⊙" | ... | 9 | | 6141-934 |
| Na * | ... | ... | 3 | ... | ⊙" | ... | 5 | | 6154-431 |
| Na * | ... | ... | 5 | ... | ⊙" | ... | 4 | | 6160-970 |
| Ca 15 | R | ... | 10 | ... | ⊙" | ... | 9 | | 6162-383 |
| Ca 6 | ... | ... | 6 | ... | ⊙" | ... | 4 | | 6169-260 |
| Ca 7 | ... | ... | 7 | ... | ⊙" | ... | 8 | | 6169-775 |

* Components about 0.100 apart. Red component is partly solar and partly water-vapour. (J.)

† Components about 0.200 apart.

‡ Components 0.100 apart.

| Elements. | IN ARC. | | IN SUN. | | Kind of Stand-ard. | WEIGHT. | | Wave-length. in Arc. | Wave-length. in Sun. |
|-------------|-------------|--------------|-------------|--------------|--------------------|---------|---------|----------------------|----------------------|
| | Inten-sity. | Appear-ance. | Inten-sity. | Appear-ance. | | In Arc. | In Sun. | | |
| Fe | ... | ... | 6 | ... | ○'' | ... | 8 | | 6173-554 |
| Ni | 5 | ... | 6 | ... | ○'' | ... | 8 | | 6177-028 |
| Fe | ... | ... | 6 | ... | ○'' | ... | 8 | | 6180-419 |
| Ni | 4 | ... | 6 | ... | ○'' | ... | 9 | | 6191-397 |
| Fe | ... | ... | 8 | ... | ○'' | ... | 10 | | 6191-770 |
| Fe | ... | ... | 6 | ... | ○'' | ... | 10 | | 6200-533 |
| Fe | ... | ... | 6 | ... | ○'' | ... | 9 | | 6213-646 |
| Fe | ... | ... | 6 | ... | ○'' | ... | 10 | | 6219-493 |
| Fe-Va.... | 7-6 | ... | 7 | ... | ○'' | ... | 12 | | 6230-946 |
| ? | ... | ... | 4 | ... | ○'' | ... | 8 | | 6237-529 |
| Fe | ... | ... | 7 | ... | ○'' | ... | 9 | | 6246-530 |
| Fe | ... | ... | 7 | ... | ○'' | ... | 9 | | 6252-776 |
| Fe* | ... | ... | 7 | ... | ○'' | ... | 9 | | 6254-454 |
| Ni } | 7 } | ... | 6 | ... | ○'' | ... | 8 | | 6256-574 |
| Fe } | ? } | ... | 6 | ... | ○'' | ... | 8 | | 6256-574 |
| Ti | 5 | ... | 2 | ... | ○'' | ... | 9 | | 6261-316 |
| Fe | ... | ... | 5 | ... | ○'' | ... | 11 | | 6265-347 |
| Fe | ... | ... | 3 | ... | ○'' | ... | 10 | | 6270-439 |
| αA(O)† .. | ... | ... | 4 | d | ○'' | ... | 9 | | 6278-289 |
| A(O) | ... | ... | 2 | ... | ○' | ... | 7 | | 6281-374 |
| A(O)‡ | ... | ... | 2 | ... | ○' | ... | 5 | | 6289-608 |
| A(O)§ | ... | ... | 3 | ... | ○ | ... | 6 | | 6293-152 |
| A(O) | ... | ... | 3 | ... | ○'' | ... | 7 | | 6296-144 |
| Fe | ... | ... | 7 | ... | ○'' | ... | 7 | | 6301-719 |
| Ni | 6 | ... | 4 | ... | ○'' | ... | 7 | | 6314-874 |
| Fe | ... | ... | 3 | ... | ○ _h | ... | 5 | | 6315-541 |
| Fe-(Ca) .. | ... | ... | 6 | ... | ○ _h | ... | 14 | | 6318-242 |
| Fe | ... | ... | 5 | ... | ○'' | ... | 13 | | 6322-912 |
| Fe | ... | ... | 6 | ... | ○'' | ... | 12 | | 6335-550 |
| Fe | ... | ... | 6 | ... | ○'' | ... | 12 | | 6337-042 |
| Fe | ... | ... | 5 | ... | ○'' | ... | 6 | | 6344-370 |
| Fe¶ | ... | ... | 5 | ... | ○ | ... | 8 | | 6355-259 |
| Fe | ... | ... | 6 | ... | ○'' | ... | 8 | | 6358-902 |
| Ni | 5 | ... | 2 | ... | ○ _h | ... | 2 | | 6378-461 |
| Fe | ... | ... | 4 | ... | ○ _h | ... | 6 | | 6380-951 |
| Fe | ... | ... | 7 | ... | ○'' | ... | 9 | | 6393-818 |
| Fe | ... | ... | 8 | ... | ○ ₁ | ... | 5 | | 6400-200 |
| Fe | ... | ... | 3 | ... | ○ ₁ | ... | 6 | | 6400-509 |
| Fe | ... | ... | 6 | ... | ○'' | ... | 8 | | 6408-231 |
| Fe | ... | ... | 7 | ... | ○'' | ... | 10 | | 6411-864 |
| Fe | ... | ... | 5 | ... | ○'' | ... | 8 | | 6420-171 |
| Fe** | ... | ... | 6 | ... | ○ | ... | 10 | | 6421-569 |
| Fe | ... | ... | 6 | ... | ○'' | ... | 10 | | 6431-063 |
| Cd | ... | ... | ... | ... | M | 1 | ... | 6438-680 | |
| Ca | 10 | R | 7 | ... | ○'' | ... | 11 | | 6439-298 |
| Ca | 5 | ... | 6 | ... | ○'' | ... | 6 | | 6450-029 |

* This is a difficult double or there is a side line close to violet.

† Chief line in the α group. It is a very close atmospheric double with some weak atmospheric lines towards the red and a faint water-vapour line near to violet side. (J.)

‡ First line of the first pair of lines in the tail of the α group.

§ Second line in the second pair of the tail of α. Faint line to violet.

¶ There is a side line towards the red.

¶ There is a faint line near to red side.

** There is a Ni line towards red side.

| Elements. | IN ARC. | | IN SUN. | | Kind of Stand-ard. | WEIGHT. | | Wave-length in Arc. | Wave-length in Sun. |
|--------------|-------------|--------------|-------------|--------------|--------------------|---------|----------|---------------------|---------------------|
| | Inten-sith. | Appear-ance. | Inten-sity. | Appear-ance. | | In Arc. | In Sun. | | |
| Ca } ... | 10 | R | 9 } | d | ○" | ... | 9 | | 6462-835 |
| Fe } ... | ? | ... | 3 } | ... | ○" | ... | 7 | | 6471-881 |
| Ca 5 | ... | ... | 5 | ... | ○" | ... | 6 | | 6480-264 |
| A(wv) ... | ... | ... | 1 | ... | ○" | ... | 8 | | 6482-099 |
| ? 8 | ... | ... | 4 | ... | ○" | ... | 10 | | 6494-001 |
| Ca 8 | ... | ... | 6 | ... | ○" | ... | 9 | | 6495-209 |
| Fe 5 | ... | ... | 7 | ... | ○" | ... | 10 | | 6499-871 |
| Ca 5 | ... | ... | 5 | ... | ○" | ... | 7 | | 6516-315 |
| ? 6 | ... | ... | 4 | ... | ○" | ... | 10 | | 6518-594 |
| Fe 5 | ... | ... | 4 | ... | ○' | ... | 7 | | 6532-546 |
| A(wv) ... | ... | ... | 1 | ... | ○" | ... | 12 | | 6534-173 |
| ? 3 } | ... | ... | 3 | ... | ○" | ... | 11 | | 6546-486 |
| Ti } ... | 3 } | ... | 6 | ... | ○" | ... | 6 | | 6552-840 |
| Fe } ... | ? | ... | 2 | ... | ○ | ... | 13 | | 6563-054 |
| A(wv) ... | ... | ... | 30 | ... | ○" | ... | 13 | | 6569-461 |
| OH 6 | ... | ... | 6 | ... | ○" | ... | 6 | | 6572-312 |
| ? 2 | ... | ... | 1 | ... | ○ | ... | 5 | | 6574-477 |
| Fe* 4 | ... | ... | 2 | ... | ○ | ... | 7 | | 6575-179 |
| Fe 5 | ... | ... | 4 | ... | ○' | ... | 11 | | 6593-161 |
| Fe 4 | ... | ... | 4 | ... | ○" | ... | 12 | | 6594-115 |
| Fe 4 | ... | ... | 4 | ... | ○" | ... | 9 | | 6609-354 |
| Fe† 3 | ... | ... | 3 | ... | ○" | ... | 7 | | 6633-992 |
| Ni 5 | ... | ... | 5 | ... | ○" | ... | 10 | | 6643-882 |
| ? 1 } | ... | ... | 1 } | d | ○" | ... | 4 | | 6663-525 |
| Fe 4 } | ... | ... | 4 } | ... | ○" | ... | 6 | | 6663-696 |
| Fe 5 | ... | ... | 5 | ... | ○" | ... | 10 | | 6678-232 |
| ? 2 | ... | ... | 2 | ... | ○ | ... | 10 | | 6703-813 |
| ? 3 | ... | ... | 3 | ... | ○ | ... | 12 | | 6705-353 |
| Li† 75 | t? | ... | ... | ... | M | 3 | 6708-070 | | 6717-934 |
| Ca§ 10 | ... | ... | 5 | ... | ○ | ... | 10 | | 6722-095 |
| ? 3 | ... | ... | 3 | ... | ○ | ... | 10 | | 6726-923 |
| Fe 3 | ... | ... | 3 | ... | ○ | ... | 7 | | 6750-412 |
| Fe 4 | ... | ... | 4 | ... | ○" | ... | 12 | | 6752-962 |
| Fe 2 | ... | ... | 2 | ... | ○" | ... | 7 | | 6768-044 |
| Ni 5 | ... | ... | 4 | ... | ○" | ... | 9 | | 6772-565 |
| Ni 2 | ... | ... | 3 | ... | ○' | ... | 10 | | 6787-137 |
| Fe 1 | ... | ... | 1 | ... | ○ | ... | 5 | | 6807-100 |
| Fe 2 | ... | ... | 2 | ... | ○' | ... | 6 | | 6810-519 |
| Fe 3 | ... | ... | 3 | ... | ○" | ... | 8 | | 6820-614 |
| Fe 2 | ... | ... | 2 | ... | ○' | ... | 5 | | 6828-850 |
| Fe 3 | ... | ... | 3 | ... | ○' | ... | 7 | | 6841-591 |
| Fe 3 | ... | ... | 3 | ... | ○' | ... | 6 | | 6843-908 |
| Fe 3 | ... | ... | 3 | ... | ○' | ... | 5 | | 6855-425 |
| A[O] ... | ... | ... | 3 | ... | ○' | ... | 10 | | 6867-461 |

* There is a water-vapour line near to violet side.

† There is a faint line near to each side.

‡ With but little material in the arc this is a difficult triplet. The violet component is very strong, the red component about half as strong, and between them but nearer the red component is a very narrow line much weaker than either of the others. (J.)

§ There is a side line towards the violet.

|| This line and the following one are at the beginning of the head of B. There is a fine line midway between them.

| Elements. | IN ARC. | | IN SUN. | | Kind of Stand-ard. | W ^{RIGHT} . | | Wave-length in Arc. | Wave-length in Sun. |
|---------------|-------------|--------------|-------------|--------------|--------------------|----------------------|---------|---------------------|---------------------|
| | Inten-sity. | Appear-ance. | Inten-sity. | Appear-ance. | | In Arc. | In Sun. | | |
| A[O]* ... | ... | ... | 3 | ... | ⊙' | ... | 11 | | 6867-800 |
| A[O] ... | ... | ... | 1 | ... | ⊙ ₁ | ... | 2 | | 6868-124 |
| A[O] ... | ... | ... | 6 | d | ⊙ | ... | 2 | | 6868-393 |
| Δ(O) ... | ... | ... | 1 } 3 } | d | ⊙ ₁ | ... | 3 | | 6868-779 |
| Δ(O) } ... | ... | ... | 4 } | d | ⊙' | ... | 5 | | 6869-141 |
| Δ(O) } ... | ... | ... | 4 } | d | ⊙ | ... | 5 | | 6869-347 |
| BA(O)† ... | ... | ... | 4 } | d | ⊙" | ... | 12 | | 6870-186 |
| Δ(O) ... | ... | ... | 5 | ... | ⊙' | ... | 6 | | 6871-179 |
| Δ(O) ... | ... | ... | 5 | ... | ⊙' | ... | 6 | | 6871-527 |
| Δ(O) ... | ... | ... | 5 | ... | ⊙" | ... | 5 | | 6872-493 |
| Δ(O) ... | ... | ... | 5 | ... | ⊙" | ... | 4 | | 6873-076 |
| Δ(O) ... | ... | ... | 5 | ... | ⊙" | ... | 5 | | 6874-039 |
| Δ(O) ... | ... | ... | 5 | ... | ⊙" | ... | 5 | | 6874-884 |
| Δ(O) ... | ... | ... | 5 | ... | ⊙" | ... | 9 | | 6875-826 |
| Δ(O) ... | ... | ... | 5 | ... | ⊙" | ... | 7 | | 6876-957 |
| Δ(O) ... | ... | ... | 5 | ... | ⊙" | ... | 7 | | 6877-878 |
| Δ(O) ... | ... | ... | 5 | ... | ⊙" | ... | 11 | | 6879-294 |
| Δ(O) ... | ... | ... | 3 | ... | ⊙" | ... | 11 | | 6880-176 |
| Cr 1 | ... | ... | 1 | ... | ⊙ | ... | 5 | | 6881-970 |
| Cr 2 | ... | ... | 1 | ... | ⊙ | ... | 5 | | 6882-772 |
| Cr 3 | ... | ... | 1 | ... | ⊙ | ... | 5 | | 6883-318 |
| Δ(O)† ... | ... | ... | 4 | ... | ⊙" | ... | 13 | | 6884-083 |
| 1 { Δ(O) ... | ... | ... | 5 | ... | ⊙" | ... | 12 | | 6886-008 |
| 1 { Δ(O) ... | ... | ... | 5 | ... | ⊙" | ... | 12 | | 6886-987 |
| 2 { Δ(O) ... | ... | ... | 5 | ... | ⊙" | ... | 5 | | 6889-194 |
| 2 { Δ(O) ... | ... | ... | 5 | ... | ⊙" | ... | 5 | | 6890-149 |
| 3 { Δ(O) ... | ... | ... | 6 | ... | ⊙" | ... | 5 | | 6892-614 |
| 3 { Δ(O) ... | ... | ... | 6 | ... | ⊙" | ... | 5 | | 6893-559 |
| 4 { Δ(O) ... | ... | ... | 6 | ... | ⊙" | ... | 7 | | 6896-292 |
| 4 { Δ(O) ... | ... | ... | 6 | ... | ⊙" | ... | 8 | | 6897-195 |
| 5 { Δ(O) ... | ... | ... | 6 | ... | ⊙" | ... | 6 | | 6900-199 |
| 5 { Δ(O) ... | ... | ... | 6 | ... | ⊙" | ... | 8 | | 6901-113 |
| 6 { Δ(O) ... | ... | ... | 6 | ... | ⊙" | ... | 5 | | 6904-358 |
| 6 { Δ(O) ... | ... | ... | 6 | ... | ⊙" | ... | 5 | | 6905-263 |
| 7 { Δ(O) ... | ... | ... | 6 | ... | ⊙" | ... | 5 | | 6908-785 |
| 7 { Δ(O) ... | ... | ... | 6 | ... | ⊙" | ... | 9 | | 6909-675 |
| 8 { Δ(O) ... | ... | ... | 5 | ... | ⊙" | ... | 5 | | 6913-454 |
| 8 { Δ(O) ... | ... | ... | 5 | ... | ⊙" | ... | 4 | | 6914-328 |
| Ni 5 | ... | ... | 3 | ... | ⊙' | ... | 4 | | 6914-819 |
| 9 { Δ(O) ... | ... | ... | 2 | ... | ⊙' | ... | 5 | | 6916-957 |
| 9 { Δ(O) ... | ... | ... | 4 | ... | ⊙" | ... | 5 | | 6918-363 |
| 10 { Δ(O) ... | ... | ... | 4 | ... | ⊙" | ... | 9 | | 6919-245 |
| 10 { Δ(O) ... | ... | ... | 3 | ... | ⊙" | ... | 8 | | 6923-557 |
| 11 { Δ(O) ... | ... | ... | 3 | ... | ⊙" | ... | 11 | | 6924-420 |
| 11 { Δ(O) ... | ... | ... | 2 | ... | ⊙' | ... | 5 | | 6928-992 |
| 12 { Δ(O) ... | ... | ... | 2 | ... | ⊙' | ... | 8 | | 6929-838 |
| 12 { Δ(O) ... | ... | ... | 1 | ... | ⊙ | ... | 4 | | 6934-646 |
| 12 { Δ(O) ... | ... | ... | 1 | ... | ⊙ | ... | 5 | | 6935-530 |

* This line and the preceding one are at the beginning of the head of B. There is a fine line midway between them.

† The principal line in the head of B. It is a difficult double.

‡ Single line at the beginning of the tail of B.

| Elements. | In Arc. | | In Sun. | | Kind of Stand-ard. | WRIGHT. | | Wave-length in Arc. | Wave-length in Sun. |
|-----------|-------------|--------------|-------------|--------------|--------------------|---------|---------|---------------------|---------------------|
| | Inten-sity. | Appear-ance. | Inten-sity. | Appear-ance. | | In Arc. | In Sun. | | |
| A(wv?)... | ... | ... | 8 | ... | ⊙" | ... | 10 | | 6947-781 |
| A(wv?)... | ... | ... | 2 | ... | ⊙ | ... | 10 | | 6953-838 |
| A? | ... | ... | 1 | d | ⊙ ₁ | ... | 4 | | 6956-700 |
| A(wv)... | ... | ... | 8 | ... | ⊙" | ... | 12 | | 6959-708 |
| A(wv?)... | ... | ... | 3 | ... | ⊙ | ... | 10 | | 6961-518 |
| A(wv?)... | ... | ... | 6 | ... | ⊙ | ... | 12 | | 6978-655 |
| ? | ... | ... | 2 | ... | ⊙ | ... | 5 | | 6986-832 |
| A(wv)... | ... | ... | 5 | ... | ⊙' | ... | 10 | | 6989-240 |
| A(wv?)* | ... | ... | 5 | ... | ⊙ | ... | 7 | | 6999-174 |
| A(wv?)† | ... | ... | 5 | d? | ⊙ ₁ | ... | 6 | | 7000-143 |
| ? | ... | ... | 4 | ... | ⊙ | ... | 3 | | 7006-160 |
| ? | ... | ... | 5 | ... | ⊙ ₁ | ... | 5 | | 7011-585 |
| ? | ... | ... | 3 | ... | ⊙ | ... | 6 | | 7016-279 |
| A(wv?)... | ... | ... | 3 | ... | ⊙ ₁ | ... | 5 | | 7016-690 |
| A(wv?)... | ... | ... | 6 | ... | ⊙ ₁ | ... | 9 | | 7023-225 |
| ? | ... | ... | 4 | ... | ⊙ ₁ | ... | 1 | | 7023-747 |
| ? | ... | ... | 3 | ... | ⊙ ₁ | ... | 7 | | 7024-988 |
| ? | ... | ... | 3 | d? | ⊙ ₁ | ... | 2 | | 7027-199 |
| ? | ... | ... | 1 | ... | ⊙ | ... | 1 | | 7027-726 |
| ? | ... | ... | 3 | ... | ⊙ | ... | 7 | | 7035-159 |
| ? | ... | ... | 6 | ... | ⊙' | ... | 8 | | 7038-470 |
| ? | ... | ... | 2 | ... | ⊙ | ... | 6 | | 7040-058 |
| ? | ... | ... | 4 | ... | ⊙ | ... | 10 | | 7090-645 |
| ? | ... | ... | 4 | ... | ⊙' | ... | 5 | | 7122-491 |
| ? | ... | ... | 6 | ... | ⊙' | ... | 5 | | 7147-942 |
| ? | ... | ... | 1 | ... | ⊙ | ... | 4 | | 7148-427 |
| ? | ... | ... | 7 | ... | ⊙' | ... | 4 | | 7168-191 |
| ? | ... | ... | 3 | ... | ⊙ | ... | 5 | | 7176-347 |
| A(wv?)... | ... | ... | 3 | ... | ⊙ | ... | 6 | | 7184-781 |
| A(wv?)... | ... | ... | 4 | ... | ⊙ | ... | 7 | | 7186-552 |
| A(wv?)... | ... | ... | 5 | d | ⊙ | ... | 6 | | 7193-921 |
| A(wv)... | ... | ... | 7 | ... | ⊙ | ... | 3 | | 7200-753 |
| A(wv)... | ... | ... | 10 | ... | ⊙ | ... | 5 | | 7201-468 |
| A(wv)... | ... | ... | 10 | ... | ⊙ | ... | 5 | | 7216-812 |
| A(wv?)... | ... | ... | 6 | ... | ⊙ | ... | 4 | | 7223-930 |
| ? | ... | ... | 8 | ... | ⊙ | ... | 5 | | 7227-765 |
| ? | ... | ... | 6 | ... | ⊙ | ... | 4 | | 7232-509 |
| ? | ... | ... | 3 | ... | ⊙ | ... | 3 | | 7233-171 |
| ? | ... | ... | 8 | ... | ⊙ | ... | 4 | | 7240-972 |
| A(wv)... | ... | ... | 4 | ... | ⊙ | ... | 5 | | 7243-904 |
| A(wv)... | ... | ... | 15 | ... | ⊙ | ... | 4 | | 7247-461 |
| A(wv?)... | ... | ... | 4 | ... | ⊙ | ... | 2 | | 7264-861 |
| A(wv?)... | ... | ... | 8 | ... | ⊙ | ... | 3 | | 7265-833 |
| A(wv?)... | ... | ... | 8 | ... | ⊙ | ... | 3 | | 7270-205 |
| ? | ... | ... | 3 | d | ⊙ | ... | 2 | | 7273-256 |
| A(wv?)... | ... | ... | 8 | ... | ⊙ | ... | 4 | | 7287-689 |
| A(wv?)... | ... | ... | 6 | ... | ⊙ | ... | 3 | | 7290-714 |
| A(wv)... | ... | ... | 10 | d? | ⊙ | ... | 3 | | 7300-066 |
| A(wv)... | ... | ... | 4 | ... | ⊙ | ... | 3 | | 7304-475 |
| A(wv?)... | ... | ... | 7 | ... | ⊙ | ... | 4 | | 7318-818 |
| A(wv?)... | ... | ... | 5 | d? | ⊙ | ... | 4 | | 7321-056 |
| ? | ... | ... | 2 | ... | ⊙ | ... | 3 | | |

* There is a line towards the violet.

† There is a line close to violet side.

| Elements. | IN ARC. | | IN SUN. | | Kind of Stand-ard. | WEIGHT. | | Wave-length in Arc. | Wave-length in Sun. |
|-------------|-------------|--------------|-------------|--------------|--------------------|---------|---------|---------------------|---------------------|
| | Inten-sity. | Appear-ance. | Inten-sity. | Appear-ance. | | In Arc. | In Sun. | | |
| ? | ... | ... | 2 | ... | ... | ... | 3 | | 7331-206 |
| ? | ... | ... | 7 | ... | ... | ... | 2 | | 7389-696 |
| ? | ... | ... | 6 | ... | ... | ... | 2 | | 7409-554 |
| ? | ... | ... | 6 | ... | ... | ... | 3 | | 7446-038 |
| ? | ... | ... | 6 | ... | ... | ... | 2 | | 7462-609 |
| ? | ... | ... | 6 | ... | ... | ... | 3 | | 7495-351 |
| ? | ... | ... | 6 | ... | ... | ... | 3 | | 7511-286 |
| ? | ... | ... | 3 | ... | ... | ... | 1 | | 7545-921 |
| A(O)* | ... | ... | ... | ... | ... | ... | 4 | | 7594-059 |
| A(O)† | ... | ... | 10 | ... | ⊙ | ... | 5 | | 7621-277 |
| 1 { A(O) . | ... | ... | 12 | ... | ⊙ | ... | 4 | | 7623-526 |
| 1 { A(O) . | ... | ... | 12 | ... | ⊙ | ... | 4 | | 7624-853 |
| 2 { A(O) . | ... | ... | 14 | ... | ⊙ | ... | 3 | | 7627-232 |
| 2 { A(O) . | ... | ... | 14 | ... | ⊙ | ... | 3 | | 7628-585 |
| 7 { A(O) . | ... | ... | 14 | ... | ⊙ | ... | 3 | | 7659-658 |
| 7 { A(O) . | ... | ... | 14 | ... | ⊙ | ... | 3 | | 7660-778 |
| 10 { A(O) . | ... | ... | 8 | ... | ... | ... | 3 | | 7665-265 |
| 10 { A(O) . | ... | ... | 8 | ... | ... | ... | 3 | | 7666-239 |
| 11 { A(O) . | ... | ... | 7 | ... | ... | ... | 3 | | 7670-993 |
| 11 { A(O) . | ... | ... | 7 | ... | ... | ... | 3 | | 7671-994 |
| ? | ... | ... | 7 | ... | ... | ... | 1 | | 7699-274 |
| ? | ... | ... | 4 | ... | ... | ... | 1 | | 7714-686 |

* Beginning of the head of A. Outside edge.

† Single line at the beginning of the tail of A.

V. On the Drawing of Curves by their Curvature.

By C. V. BOYS, A.R.S.M., F.R.S.*

[Plate I.]

WHILE giving a course of lectures to working men on Capillarity at the R. School of Mines in 1891, I wished to explain the principles upon which the form of a water-drop depends, and to show that an accurate scale-drawing could actually be produced by following Lord Kelvin's rule (Proc. R. Inst. Jan. 29, 1886); but found that the procedure was so cumbersome as to be in no way adapted to popular exposition. In my attempt to simplify the operation I devised a method of carrying it out which has the double advantage that any of these capillary surfaces of revolution can be drawn with a facility which cannot be approached by following Lord Kelvin's instructions explicitly, while the accuracy of any curve thus determined is so great

* Communicated by the Physical Society: read May 12, 1893.

that it may be used for the purpose of approximate numerical calculation when, as is often the case, the equation cannot be solved. The accuracy is certainly considerably in excess of that which can be attained by the same degree of care, using rule and compasses according to his instructions. I hope therefore that though there is no principle involved which is not perfectly well understood, the practical character of the modification and its utility more especially to teachers are such as to render it worthy of the attention of the Physical Society.

Lord Kelvin's rule for drawing the generating curve of any capillary surface of revolution is as follows:—"Through any point, N, fig. 1 (Pl. I.) of the axis draw a line, NP, cutting it at any angle. With any point, O, as centre on the line NP, describe a very small circular arc through PP', and let N' be the point in which the line of OP' cuts the axis. Measure NP, N'P', and the difference of levels between P and P'. Denoting this last by δ , and taking α as a linear parameter, calculate the value of

$$\left(\frac{\delta}{\alpha^2} + \frac{1}{OP} + \frac{1}{NP} - \frac{1}{N'P'} \right)^{-1}.$$

Take this length on the compasses, and putting the pencil-point at P', place the other point at O' on the line P'N', and with O' as centre describe a small arc, P'P''. Continue the process according to the same rule, and the successive very small arcs so drawn will constitute a curved line, which is the generating line of the surface of revolution inclosing the liquid, according to the conditions of the special case treated."

This can be explained to those not already familiar with the principle in a few words. At any depth below the plane surface level of a liquid there is a hydrostatic pressure which is proportional to the depth. At every point of the surface of a drop this is balanced by the surface-tension which is constant over the surface multiplied by the total curvature. The total curvature at any point P in a surface of revolution is defined as being equal to $\frac{1}{OP} + \frac{1}{NP}$, where OP is the radius of curvature of the generating curve at the point P, and NP is the distance normal to the curve from P to the axis of revolution.

Since at any depth the curvature of the tense surface withstands the hydrostatic pressure and since the hydrostatic pressure is proportional to the depth, it is clear that the total curvature measured as defined above must be proportional to the depth, being concave to the liquid below and

convex above the plane surface level. At any depth d the curvature c must equal $\frac{\Delta d}{t}$, where Δ is the density of the liquid (or difference of density of the two liquids if one forms a drop in the other), and t the surface-tension measured in gravitation units. Thus if Δ means grains per cubic inch, t is grains per linear inch. If a bubble is formed on a ring or between two rings, the effect of gravity is so minute that the curvature is practically the same at all levels, and the curves that are formed are the well-known roulettes of the foci of the conic sections, whose equations are known.

In order to avoid the loss of time which results from the perpetual finding of reciprocals in order to determine the new radius of curvature of each small step in the curve, I have divided a rule so that the distances of the divisions from the beginning of the scale are the reciprocals of the numbers attached to them. Such a rule is adapted to measure the smallness of a thing just as an ordinary rule measures its bigness or size. Thus a large thing since it has very little smallness is found by the rule to be measured by a very small number, while a very little thing having a considerable smallness is measured in the same way by a very large number. The curvature of a line is measured by the reciprocal or the smallness of its radius, and so the curvature of a line is read off immediately by the rule. The curvature of a surface is measured by the smallness of two lines which start at the same point and in the same or in opposite directions, and so the curvature of a surface of revolution is found by inspection of the two curvatures upon the rule. In order to be equally ready to deal with the case when the lines are measured in opposite directions, and with a further object not yet apparent, I place the zero of the scale, marked ∞ , somewhere about the middle and divide it each way. Then, if the two radii are found on the same side of the ∞ or centre, their values are to be added, and if on the opposite side one is to be subtracted from the other in order immediately to find the total curvature. The only gain apparent at present is the great saving of time resulting from an obvious construction. The increase in accuracy depends upon the abolition of all accumulated errors of compass setting, which are of three kinds:—(1) The compass may not be set to the exact radius required; (2) the pencil- or pen-point may not be placed exactly upon the end of the line just drawn, producing a step; and (3) the needle-point may not be set exactly upon the former radius-line, producing an angle invisible no doubt, but still existent in the curve. The first of these applies to the method of this paper,

but in less degree; the second and third are as nearly perfectly eliminated as is possible. These, though they may be individually too minute to be observed, yet tend to be cumulative, so that as the number of steps employed is increased with the view to obtain accuracy, so do these accumulated errors tend to increase when the ordinary method is followed. It is on the elimination of these that the accuracy of the method of curve-drawing, which forms the subject of this paper, mainly depends. The increase in facility is also of importance, as the operator is not tempted to make his steps unduly long; it is brought about as follows. I make the rule of a thin strip of transparent celluloid with a small hole at the centre of the scale marked ∞ . A small brass tripod with three needle-feet (fig. 2) is placed so that two feet just penetrate into the paper and the third rests on the longitudinal straight line of the strip (which of course passes through the small hole), and just pricking into it forms a temporary but rigid and stable centre of rotation for the strip. A pencil-point or a capillary glass pen made short and fastened with wax or a spring clip into its place at ∞ will then draw an arc of a circle of which the curvature is equal to the reading on the strip at the place where the needle-point presses. Now it will be clear that at every stage the two numbers which represent the two parts of the curvature are always visible to the eye, there is no necessity to rule any of the normals to the curve, and no necessity to set compasses. Supposing for simplicity that a curve of constant total curvature (unduloid, nodoid, or catenoid), that is where hydrostatic pressure need not be considered, is to be drawn through any point and normal to any definite direction. Then all that has to be done is to set the strip with its longitudinal line in this direction and with its central hole at the point. *E.g.*, let the point be 6 inches from the axis, let the line through the point to which the curve is to be normal be perpendicular to the axis, and let the total curvature be arbitrarily chosen as $\cdot 5$. Then when the strip is placed in position the reading on the scale where it crosses the axis will be $\cdot 16$. The difference between $\cdot 5$ and $\cdot 16$ is $\cdot 3$. The needle-point must therefore be set on the scale at $\cdot 3$, and on the side of ∞ towards the axis. A very short arc must then be drawn with the pencil or pen piercing the hole at ∞ . The reading on the axis will now be found very slightly less (the distance being greater), say $\cdot 16$, the needle-point must now be transferred to the $\cdot 34$, care being taken to hold the strip firmly upon the paper to prevent its moving. A new short arc may now be drawn and the process continued. As soon

as the curve becomes notably inclined to the axis the change of reading on the axis between the two ends of a short arc even may be more than appreciable, so that if the process were carried out exactly as described the needle-point would be on the whole too late in making its move; *i. e.* where the radius is increasing it would be too small, and *vice versa*. To avoid this it is convenient to choose such a small arc as shall change the axial reading by any small number of divisions at a time and to move the needle-point through a corresponding number at a time also, but so that the needle-point is placed always at that division which corresponds with the intermediate one of the axial divisions. The curve can in this way be carried on very rapidly by very small steps without ever even looking to see where the pencil or pen is being taken, and it in no way suffers from the small errors of each resetting of an ordinary compass. It is not even necessary to draw the curve at all. The process can be carried out as described, and the curve will be traced as in imagination by the hole at ∞ . The perfection of the result which is obtainable, whether the compass or the reciprocal rule method is employed, depends of course upon the fact that whereas a very fair representation of a curve may be made by means of a polygon with a very great number of very short sides, each making very nearly an angle of two right with its neighbour, a vastly more perfect result is produced by a corresponding series of small arcs of circles, each having the necessary radius of curvature and making no angular break at each stage. The small discontinuity is one of curvature only, not of direction. The gain in smoothness and accuracy is still very great when the steps are made larger, so that a polygon of the same number of sides would cease to fairly represent the curve. Where the curvature is a maximum or a minimum the contact of the circle of curvatures is of the third instead of the second order, and at these parts a much longer step may be taken without impairing the accuracy of the curve. Similarly, if instead of the arc of curvature being used for each small step some curve of curvature and change of curvature could be employed, a still closer approximation would result, or still larger steps could be safely employed.

Going back now to the curve which has been chosen (a nodoid), it will be found that the point on the axis gets gradually farther away until the end of the rule is reached at .05 in the case of the rule exhibited. The needle-point will now be at division .45. For the next two or three steps the strip will be rapidly approaching parallelism with the axis, so that the axial reading is equally rapidly approaching 0; *i. e.* at an infinite distance. During these steps the axial

reading cannot be directly observed; but since by the time that the rule is parallel to the axis the needle-point must have reached, in the particular case chosen, the division $\cdot 5$, the two or three steps required may be made with more than sufficient accuracy by moving the needle-point a few divisions at a time so as to arrive at this point when parallelism is being reached; in fact at this stage equal angular changes correspond to equal changes on the scale. As soon as this position is passed the central line of the strip cuts the axis on the other side, and so now these readings have to be added to the total curvature $\cdot 5$ in order to find the remaining readings upon which the needle-point should rest. In fig. 2 one complete loop of this particular nodoid has been drawn, and the second one has been carried to the stage at which $\cdot 16$ is the axial reading, and $\cdot 34$ the reading of the temporary centre of curvature. Unduloids may be drawn in a similar way, but in this case the needle-point has to move off to an infinite distance, when the axial reading is equal to the total curvature. The length of line for which the centre of curvature is beyond the end of the rule is generally very small, and this may be drawn so that no error can be detected by alternately moving the needle from one end to the other, each for a very small arc. The catenary may of course be set out in the same way and with still greater ease and accuracy, for the infinite values do not come into any finite part of the curve. The axial reading and that on which the needle-point rests must be kept the same, but on opposite sides of the tracing-point.

It will be evident that if the little tripod is just pressed sufficiently upon the paper to make small impressions of the needle-feet, it may afterwards be taken over the same course and the third needle-point pressed upon the paper, and thus a series of points on the evolute determined. In fig. 2 the evolute is shown dotted. The points of most importance on this are the cusps a, b , corresponding to the places on the curve where the curvature is a minimum or a maximum, the distance ab being the half period of the curve, and the maxima or minima c, c , which are the ordinates of the curve where the abscissa is a minimum or a maximum. By means of these and the curve itself the geometrical constants of any curves drawn in this way may be determined more accurately than from the curve itself alone. Prof. Greenhill has given me the formula by which, with the use of tables of elliptic integrals, the chief constants of the unduloid and nodoid may be calculated. Miss Stevenson, a student of the College of Science, has drawn a large series of these curves, and we have found that while

they can be drawn each in a few minutes only, it is possible to set them out correctly to the thickness of a fairly fine pencil-line; and so they do more than give a general idea of the shape, they serve to make a true scale-drawing.

In the case of capillary surfaces of revolution, in which the fluids on the opposite sides of the surface are of different density, *e. g.* water and air as already explained, the curvature of the surface must be zero at the plane surface level, and must be proportional to the distance above or below this level, being — or convex to the denser liquid above, and + or concave below. The readiest way to determine the curvature when drawing one of these generating curves is to work on a sheet on which a series of equidistant lines have been ruled parallel to the plane surface level, and at such a distance apart that the hydrostatic pressure due to this distance is balanced by a curvature of .01 or some small and simple number. These lines, then, give by inspection, especially if each fifth and tenth line is a little darker, a scale of curvature, and exactly the same process that was followed when describing the curves of constant curvature may be as readily applied when the curvature is constantly varying. In the case of water this distance is,

using the formula already given, $d = \frac{ct}{\Delta} = .0128$ for cur-

vature $c=1$, or .000128 for $c=.01$. If, therefore, the drop or other capillary surface is drawn to ten times the true scale, to effect which the vertical scale of curvature must be multiplied 100-fold, the dimensions are such as to allow of considerable accuracy. I am able to show a very beautifully executed series of capillary curves for alcohol and water drawn to a scale of 10, which Miss Stevenson has been good enough to prepare; but as Prof. Perry has constructed a large number which are printed in the Royal Institution Proceedings, to which reference has been made, there is no occasion to publish them. He, however, would have been able to draw his in as many hours as he required weeks had he made use of the method described in this paper.

In order to originate the reciprocal rule I used a screw-cutting lathe as a dividing-engine, and scratched the wax off a strip of plate glass with a fine point at the places where divisions were required. Of course as the distance from ∞ increases and the readings become smaller, the distance between marks corresponding to a regular series of figures becomes greater, and new subdivisions are with advantage added, as is usual where a scale is not one of equal parts. The glass scale was etched, and the divisions transferred to a strip of celluloid by means of the well-known method with a

Phil. Mag. S. 5. Vol. 36. No. 218. July 1893.

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radius-bar or tube to which two needles are fastened. Fig. 3 is a full-size copy of a portion of the glass scale, on which, to avoid fractions, the numbers are all multiplied by 10. The inch unit was chosen instead of the centimetre, as the leading screw had eight threads to the inch.

It is evident that any curves in which simple relations exist between the radius of curvature and the normal, the coordinates, or other easily observed function of the curve, may be readily drawn in the same way, but in general a scale of equal parts is preferable to the reciprocal scale. The gain in accuracy and perfect evenness and smoothness of the curve over what is obtainable by the use of compasses is the same as that which was found in the case of the capillary curves of revolution, but the saving in time will of course, though still considerable, be less. I am able to show as examples the catenary $\rho = -n$, the undulating and the looped elastica $\rho = \pm \frac{a^2}{y}$, the particular elastica $\rho = \frac{1}{2}n$, the cycloid $\rho = 2n$ with its identical evolute, the tractrix $\rho = \frac{a^2}{n}$ with its evolute the catenary and the evolute of the catenary, the parabola $\rho = 2n$ with its evolute, and all the conic sections (including the parabola) $\rho = \frac{n^2}{r}$.

It is, moreover, evident that the further use which Lord Kelvin has made of the method of drawing curves from their curvature in order to solve certain dynamical problems is one to which the procedure described in this paper may be applied with advantage.

I must in conclusion express my obligation to Miss Stevenson, who has assisted me in the construction of these rules, and who has spared no pains in setting out the beautifully drawn curves which I am able to exhibit.

VI. A New Photometer. By ALEXANDER P. TROTTER*.

IN the course of my investigations on the distribution and measurement of illumination †, which led to the examination of the lighting of several streets and public places in London during the winter of 1891-92, I used illumination-photometers of different kinds. The final form consisted of

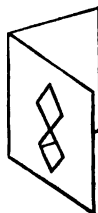
* Communicated by the Physical Society: read June 9, 1893.

† "The Distribution and Measurement of Illumination," Proc. Inst. Civil Engineers, vol. cx. pt. iv. Paper No. 2619.

a horizontal screen of white cardboard, or of paper mounted on glass, having a clear star-shaped hole in the middle. Below this and enclosed in a box was an inclined white screen illuminated by a small glow-lamp. By adjusting the illumination of the lower screen until the star-shaped hole more or less completely disappeared, the illumination of the horizontal screen was measured. After trying several different methods, the illumination of the lower screen was adjusted by altering its inclination to the glow-lamp. I greatly prefer this arrangement of screens to a Bunsen Photometer, first, because there is only one spot to examine instead of a pair of images, and secondly, because, under favourable conditions, an almost complete disappearance of this spot may be effected, instead of a similarity between two images, as with a Bunsen spot. A Bunsen screen with which the spot disappears on both sides simultaneously is rare. I understand that by warming the grease-spot the edge may be softened, and that simultaneous disappearance may be secured. I have never seen such a screen, and am inclined to think that the disappearance is illusory, and that such softening is probably accompanied by decreased rather than by increased precision.

I have recently applied my arrangement of screens to ordinary light-photometry (as distinguished from illumination-photometry). My first plan consisted of two screens (fig. 1), each inclined at 45° to the direction of the lights and to the eye. One screen was immediately behind the other; the front screen was perforated, and was mounted on a sliding-carriage on a photometer-bar. The lights were placed, the one a little in front and the other a little behind the plane of intersection of the screens. The back of the perforated screen was blackened and was shaded from the light which illuminated the back screen. The edge of the perforation was bevelled, to assist the complete disappearance of the hole. The hole consisted of two lozenge-shaped apertures one over the other, point to point, the object being to concentrate attention on a vertical line. The screens were held in a frame capable of rotation round a vertical axis through a small angle, for the purpose of producing small and rapid variations. But although one screen thus received more light and the other less, the cosine-law of illumination caused the former to increase but slightly in brightness while the latter diminished considerably. It should be observed that this arrangement of screens, although developed from a Bunsen photometer, turns out to be a modification of the Thompson-Starling

Fig. 1.

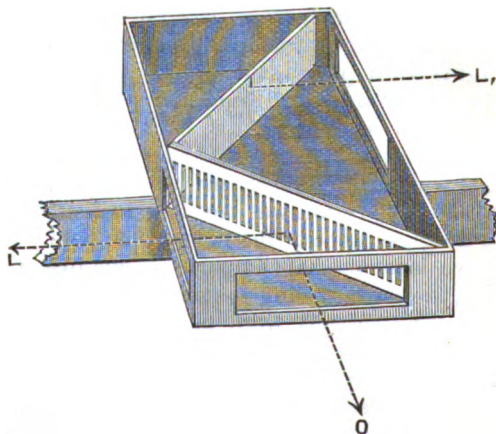


photometer, in which two screens at 45° to the lights* and to the eye are used, but side by side, instead of one behind the other.

I showed an extemporized photometer of this kind to Mr. Crompton and to Mr. Swinburne on March 26, 1893. Mr. Crompton suggested the use of zinc for the screens, and this gave me the hint to try perforated zinc, to abandon a definite vertical line of uniform tone, and to select a line or band of uniformity on a screen provided with a number of perforations. I mentioned the idea to Mr. Swinburne on March 27, but had no opportunity of trying it for more than a week. In the meantime Mr. Crompton had thought of a similar expedient, and had used with considerable success a pair of screens, the front one of which was perforated with horizontal slots, and he observed the shading of the slots, say, from bright to dark, and of the bars from dark to bright. Before I had heard of this modification I had tried vertical bars or slots and perforated screens.

The photometer is shown in fig. 2. It consists of a box mounted on a sliding-carriage on a photometer-bar. A slotted screen and a plain screen are fixed inside, and are observed through an opening from the direction O. The lights fall on the screens through two openings from the directions L and L_1 . The lights are arranged exactly

Fig. 2.



opposite the middle of each side opening, and not in the plane of the photometer-bar as is usual. The lower edge of

* See Note at end of the Paper.

the front opening or diaphragm carries a sight or pointer, and the back screen is provided also with a pointer, preferably at its upper edge. The photometer may be examined from a distance, say six or eight feet, and moved by cords. The two sights should be brought in a line with each other, and the carriage is to be moved until the band of uniform tone is bisected by the pointers. If the carriage be moved slowly it will be seen that the band of uniform tone remains fixed relatively to the scale on the photometer-bar. Readings might be taken by noting the position of the band over the scale, but I prefer to follow the usual custom in photometry, and to keep the scale hidden until an adjustment has been made, to avoid any bias. The operation of estimating the bisection of the band by the pointers is, I think, easier and therefore more conducive to precision than the estimation of the similarity of two images as in the Bunsen, or of two tones as in most other photometers.

I will now give details of the development of this photometer for the guidance of those who may wish to construct them.

Perforated zinc of the ordinary pattern having holes about 0.08 inch diameter and $\frac{1}{8}$ inch pitch, although countersunk on the back and painted dead white on the front, was found to be of no use, probably because the area of the holes was considerably less than that of the remaining metal. Half-inch holes punched in thin card at 0.6 inch pitch gave on the whole a better result than $\frac{1}{4}$ -inch or $\frac{1}{8}$ -inch wooden slips, bevelled, glued to a frame at a distance apart equal to their width, and painted dead white. I then tried a number of different patterns of perforated zinc and other screens, 30 centim. long by 6 centim. high. Circular perforations of 4 millim. and 6 millim. diameter, about half the metal being removed, were less satisfactory than zinc with holes 13 millim. diameter, rather more than half the metal being removed. A fancy pattern was tried, but without good results. The suitability of the screens was compared in some cases by comparison of the "mean error of a single observation" calculated in the ordinary way from ten measurements, two similar glow-lamps being used, sometimes 2 metres apart, and sometimes 3 metres.

Finding that thinness of edge and perfect flatness were very important, I made several screens of card and of paper stretched while wet on wooden frames. The coarsest of these consisted of strips of two-sheet Bristol board 8 millim. wide and 8 millim. apart, 18 such strips, with an 8 millim. space at each end, making 30 centim. The strips were cut with sharp scissors to avoid any burr on the edge. Another

screen has strips 5 millim. wide, and a third has 48 strips 3 millim. wide. White foolscap paper was used, soaked in hot water to remove the glaze; it was mounted whole, and cut on glass when dry, the knife being held slanting as in mount-cutting, to bevel the edge. These screens I find, and my opinion is confirmed by friends who are for the most part unfamiliar with photometers, to be easy to use.

The advantage of vertical strips is that perfect symmetry is attained, a condition which I find to be important in photometry. When perforations are used, dark holes on a light ground are seen at one end of the screen, and light holes on a dark ground are seen at the other end. The balance is indicated by a strip at which these two patterns become confused. I have not succeeded in getting a definite easily-bisected strip of uniform tint with such screens. When, however, strips are used, the spaces being equal to the width of the strips, the appearance of the screen is perfectly symmetrical, and the effect is improved by the use of a diaphragm cutting off from the observer the edges of the screens. When lights of similar colour are compared, the light strips and dark spaces at one end are almost indistinguishable from the dark strips and light spaces at the other end. With 8 c. p. lamps 3 metres apart, and with the 8 millim. strips, one strip or one space can generally be made to disappear; that is to say, its edges become invisible when examined from a distance of 6 or 8 feet. At a shorter distance, one eye only must be used. With the 3 millim. strips, a nearly uniform grid is seen, paling a little towards the middle, and showing a band about 15 millim. wide, including, say, three strips which are indistinguishable from the two spaces between them. When lights differing in colour are used, the narrow strips are distinctly preferable: disappearance is nowhere complete, but the differently coloured strips and spaces seem to blend at a definite place on the screen.

As screens 30 centim. long and requiring a box about 50 centim. by 30 might be considered cumbersome, I have made a photometer with screens $22\cdot5 \times 3\cdot7$ centim. effective; these are contained in a box measuring about $22 \times 32 \times 6$ centim. deep. The diaphragm facing the observer is $15 \times 3\cdot5$ centim. The screens are placed at 45° to the lights and to the observer. I have tried other inclinations, but there is no difficulty in getting a surface sufficiently dead-white to work well at this angle.

I find that a distance of 3 metres between two 8 c. p. glow-lamps is rather great for easy reading of the photometer. A

distance of 2 metres is perhaps a little too small; that is, if a greater distance conduces to greater precision, it might be worth while to employ an intermediate distance. Again, a distance of 3 metres seems suitable for comparing a pair of 16 c. p. lamps. This question may be considered from the point of view of a gradient or fall of illumination; and it is not unlikely that for any one observer, the "mean error of a single observation" is a function of the gradient of illumination at the photometer-screen.

With an 8 c. p. lamp at 1.5 metre, the illumination is 3.56 times a candle-metre; that is, it is 3.56 times the illumination which would be given by one candle at one metre. The gradient is 0.0474 candle-metre per centimetre. With a 2-metre photometer-bar and a pair of 8 c. p. lamps, the illumination due to one lamp is 8 candle-metres, and the gradient is 0.16 candle-metre per centimetre. With a 16 c. p. lamp on a 3-metre bar, the gradient at the middle, *i.e.* 1.5 metre, is 0.948 candle-metre per centimetre. My experience with the form of photometer described in this paper goes to show that a gradient of less than 0.1 candle-metre per centimetre is not desirable. It should be observed that the illumination on a screen inclined at 45° to the light is about 0.7 of that of a screen turned full to the light.

To graduate a photometer-bar of unit length, and having a unit light at one end, I have used the formula:—

$$l = \frac{1}{1 + \sqrt{n}}$$

where l is a length measured on the bar, and n is proportional to the light to be measured. With a 3-metre bar a displacement of 3.9 millim. from the middle is equivalent to a difference of 1 per cent. in the candle-power of the two lights. Since the band of uniformity with the 3 millim. strips may be said to be about 15 millim. wide, and 15.6 millim. are equivalent to 4 per cent., it is only by bisection of this band that a precise measurement can be made. In using the 8 millim. strips, if the middle of one strip or space is the actual point of balance, and by error the space or strip on one side of it be taken as the one indicating the balance, the error is ± 2 per cent. Out of several series of 12 observations, the mean error of a single observation has frequently fallen below this. Among some results which I consider satisfactory, compared with my experience with other photometers, are mean errors of 0.85 and of 1.48 per cent. calculated from sets of 12 readings.

Note added June 5, 1892.

In further tests with this photometer the mean errors have generally fallen below 1 per cent.

At first I tried other angles than 45° . For whitewashed metal screens this angle appears to be suitable. I find, however, that it is preferable with paper screens to use an angle of incidence of 35° , and I understand that this angle is used in the Thompson-Starling photometer.

When the light to be measured is subject to small variations, the direction and the magnitude of the variations are plainly visible by the movement of the band of uniform tone. This photometer has been chiefly used for such measurements, and seems to be well adapted for them.

VII. *On the Nature of certain Solutions, and on a New Means of Investigating them.* By M. CAREY LEA*.

THE three strong acids with which we are best acquainted have this in common, that they all form two classes of compounds,—the one perfectly neutral and perfectly stable in solution, the other class instantly decomposing when it is attempted to dissolve them in water. As types of the first class may be taken the alkaline salts. Of the second, mercuric sulphate, bismuth nitrate, and stannous chloride offer examples, as also the thallic salts of all three.

Between these limiting cases are certain intermediate ones as to which our knowledge of the form which the salts take in solution is not very exact. It need scarcely be mentioned that what has been said does not refer to dissociation into anions and kathions, but into separation of free acid and basic salt, an entirely different question.

In the case of sulphates—to a consideration of which this paper will be devoted—we know that the number of salts of the metals which give a purely neutral reaction with litmus is comparatively small; that all the normal sulphates of the heavy metals show an acid reaction even after any number of recrystallizations, although these may be made from solutions rendered alkaline by the addition of free alkali, and that all the normal sesquisulphates have an acid reaction. The question is as to the meaning of this acid reaction, and whether in any or all cases free acid is present.

The uncertainty that exists depends partly upon the imperfect nature of our indicators. Litmus, which is perhaps

* Communicated by the Author.

the best, is reddened by the contact of any substance which will deprive it of its alkali. Methyl orange, which is by some considered more sensitive than litmus, has this disadvantage, that it seems to be decomposed by some metallic salts, so that its colour is rendered lighter by them instead of darker, although free acid may be present. This tendency greatly diminishes its usefulness.

Another method has been proposed for the detection of free sulphuric acid in the presence of combined. The solution is heated to 100° , and evaporated to dryness in the presence of a small quantity of organic matter, which is blackened if free sulphuric acid is present. As what we want is to determine the nature of the *solution* at ordinary temperatures, such a method is quite worthless.

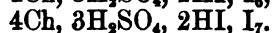
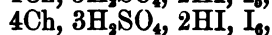
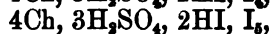
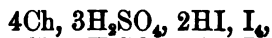
But by means of a new reaction the conditions of such solutions can be examined, and free sulphuric acid can be detected in the presence of sulphates with great accuracy and sharpness, even when only a trace is present.

The method is as follows:—Taking the well-known polarizing-salt discovered by Herapath, the sulphate of iodoquinia, it is possible to remove the whole of the sulphuric acid without breaking up the molecule. This may be done with either barium carbonate or barium hydroxide. The mode of operation is as follows. The barium compound is placed in a beaker and covered with weak alcohol of about 70 per cent. Into this the crystallized herapathite is dropped. In cold alcohol of this strength it is but very slightly soluble; but in the presence of the barium compound it dissolves with facility, and in large quantity, forming a deep sherry-wine coloured liquid. This solution, when allowed to dry spontaneously, leaves an amber-coloured varnish without a trace of crystallization. If, however, we add to this solution a minute quantity of sulphuric acid, there is left behind, on evaporating, a characteristic bluish-black film and isolated crystals of iodoquinia sulphate. In forming this reagent it is more convenient to employ barium carbonate, as the decomposition is effected equally well, and with it we are certain that the solution contains no barium compound. Barium carbonate decomposes iodoquinia sulphate with slow disengagement of carbonic anhydride; it seems therefore probable that the resulting solution contains a free base.

From this solution the sulphate is regenerated with great facility by free, but not by combined sulphuric acid. And as the herapathite thus formed is a well-characterized substance, we obtain a most useful means of deciding as to whether sulphuric acid in certain solutions is free or combined. It is

not necessary that the combined sulphuric acid should be united to a strong base, neutral sulphates of weak bases are wholly without action. Thus neither brucia nor quinia sulphate causes formation of herapathite; the sulphuric acid in these salts has no more tendency to bring about the reaction than, for example, that in sodium sulphate. The fact that quinia sulphate does not form herapathite with the test indicates that there is no free iodine present, thus confirming the view that the iodoquinia molecule is not broken up.

Space cannot be spared here to go with detail into the chemistry of iodoquinia compounds. The whole series of acid persulphates has been most thoroughly studied by Jörgensen *, who distinguishes seven compounds of quinia, sulphuric acid, and iodine, of which four belong to the herapathite type; that is, they contain three molecules of sulphuric acid to four of quinia and two of hydriodic acid, with increasing amounts of iodine. Putting Ch for $C_{20}H_{24}N_2O_2$, the composition of these four salts may be taken as



The first of which series is herapathite. All are isomorphous (*l. c.* p. 253). Jörgensen's view of the constitution of herapathite is that it is "half superiodide, half sulphate;" he gives as its rational formula—



It appears, however, that the sulphuric acid may be removed not only by barium carbonate, but by its hydrate, without breaking up the molecule. It is easily shown that the solution of herapathite, after treatment even with barium carbonate, contains no sulphuric acid. This may be proved by adding to the solution after the treatment ammonia till it becomes pale yellow, evaporating to dryness, and then warming with very dilute hydrochloric acid. An aqueous solution of barium chloride then gives no precipitate, nor even any troubling by standing. It seems perhaps doubtful if a substance having the constitution indicated by the rational formula above cited could have its molecule subsist unbroken after the removal of the sulphuric acid.

The application of this test leads to the following conclusions :—

* *Journal für praktische Chem.* (2) xiv. p. 213 ff.

1. SULPHATES OF THE TYPE R'_2SO_4 , OR $R''SO_4$

I find that these salts dissolve in water and exist in solution as such and absolutely without separation of sulphuric acid even in those cases in which the solution is acid to litmus. The substances examined were the alkaline sulphates and the sulphates of Mg, Zn, Cd, Cu, Ni, Co, Mn, Tl; also the sulphates of morphia, quinia, strychnia, and brucia. To this series of reactions there is a single exception of an interesting character.

A solution of ferrous sulphate invariably contains free acid, no matter how often recrystallized or under what circumstances prepared. A small flask was filled with freshly distilled water and was well boiled, corked, and set aside to cool. In this ferrous sulphate was dissolved and potash was added in quantity sufficient to precipitate a considerable proportion of oxide. Even this solution gave the reaction indicating the presence of free acid. So, too, the double salts of ferrous oxide with ammonia and with magnesia, their solutions always contain free acid, no matter how often they may be recrystallized or purified by precipitation of their solutions in water by alcohol. This exceptional behaviour probably results from the great tendency of ferrous solutions to rapid absorption of oxygen from the air, and, as will presently appear, sesquisulphates are dissociated in solution.

With this one exception, the heavy metallic sulphates above mentioned dissolve in water without decomposition, although their solutions redden litmus. The alkaloids mentioned yield sulphates, which, after suitable purification, are perfectly neutral to litmus.

To explain this contrast it is necessary to remember that a salt reddens litmus whenever the affinity of its acid for the potash in litmus is not held in check by two affinities which oppose it, that of the base for its acid, and that of the litmus dye for its potash. If the base is sufficiently weak, the affinity of its acid for potash preponderates*. The whole question therefore reduces itself to that of the strength of the base with which the acid is united; and it consequently follows irresistibly that even very weak alkaloids are stronger bases than such metallic oxides as those of zinc, copper, cobalt, &c.

Although this deduction seems clear, it may be supported

* It is of interest to observe that the reaction may be changed by the presence of an additional substance, although the latter may be quite neutral. Thus mercuric chloride is faintly acid to litmus, but not after the addition of potassium chloride. The tendency to form a double salt changes the balance of affinities.

by additional evidence. As bases, the alkaloids vary very greatly in strength. A few which contain no oxygen are bases approximating to ammonia in strength. Such are nicotia and conia. Among those which contain oxygen there is much difference in strength: morphia and codeia are strong bases, and are known to precipitate iron, copper, cobalt, and nickel salts. The weaker alkaloids do not seem to have been examined in this respect, and one therefore was selected for examination.

Brucia is one of the weaker alkaloids. It is precipitated from its saline solutions by morphia, strychnia, &c. It forms a neutral and an acid sulphate, both crystallizing well. The alkaloid itself is very sparingly soluble in cold water; it is therefore convenient to operate with solutions raised to a temperature of 50° or 60° C. The sulphates of zinc, cadmium, copper, manganese, nickel, and cobalt proved to be readily precipitated by brucia. The reaction is always easily obtained and well marked. It is particularly so in the case of cobalt, the rose-red solution of which becomes quickly filled with blue flocks of oxide.

That weak bases, such as the oxides of zinc, cadmium, and copper, should be precipitated by a weak alkaloid like brucia is not surprising; but the case is somewhat different with stronger bases like manganous oxide and the oxides of nickel and cobalt. These two last are classed by Mendeléeef as "fairly energetic" bases. This, however, can be understood only by comparison; no base can be considered as a strong one whose neutral salts redden litmus.

When brucia is added to a solution of magnesium sulphate, there is no precipitation. Magnesia is a stronger base and its salts are neutral to litmus, not because the acids are more fully saturated by it, but because the potash of the litmus is unable to detach the acids from the base.

2. SESQUISULPHATES.

Chromic sulphate.—The violet salt was obtained free from green salt by acting on the nitrate with sulphuric acid. It was freed from excess of acid by repeated precipitation with alcohol and thorough washing. It had a pale violet colour and satiny lustre. In solution it always gave, when examined with the test liquid, marked indications of the presence of free sulphuric acid.

Aluminium sulphate.—This was purified from excess of acid in the same manner as the preceding, and gave a similar reaction.

Glucinum sulphate.—Same treatment as the preceding and similar reaction.

Ferric sulphate.—Same reaction.

In all these cases the reaction was extremely well marked. It indicates that these sulphates do not exist as such in solution, but that a portion of their acid is set free.

3. ALUMS.

The alums, as might be expected, show reactions similar to those of the sesquisulphates, with one notable exception.

Potash alumina alum is always dissociated in solution. A specimen made by combining pure aluminium sulphate with potassium sulphate was recrystallized ten times with thorough washing of the crystals. The presence of free sulphuric acid was as evident after the last recrystallization as before.

Ammonia ferric alum is also dissociated by solution.

Potash chrome alum.—This alum differs remarkably from the others. After two or three recrystallizations, which of course must be made at low temperatures, the crystals may be dissolved in water without dissociation. The test liquid indicates that there is no free sulphuric acid present.

It appears therefore that this alum alone of its congeners exists as an alum in solution.

The alums consequently form a series with varying properties, according to the nature of the sesquisalt present. At the head stands chrome alum, perfectly stable in solution; next alumina alum, dissociated in solution but re-forming itself by crystallization with the utmost facility; next ferric alum, also dissociated and also reforming itself by crystallization, but with less facility. And finally manganese alum, whose violet octahedra are so completely dissociated by solution in pure water that they cannot be reproduced by crystallization.

4. ACID SULPHATES.

At one time it was considered to be an established fact that the acid salts of the alkaline bases were completely decomposed by solution in water into neutral salt and free acid. In a review of this subject Berthelot* quotes Andrews, and Favre and Silbermann, as expressing this opinion positively and without question. His own investigation led him to the conclusion that the separation was never complete, that a certain proportion of acid sulphate was always present, diminishing in proportion to the amount of water present, increasing in proportion to the amount of free acid. The

* *Mech. Chem.* ii. p. 318.

formation of acid sulphate was always endothermic, was accompanied by the absorption of 1.05 cal. in the case of NaHSO_4 . He especially remarks that when a very small proportion of acid is added, the tendency is to a complete combination in the form of acid salt*.

This last-mentioned result is contrary to that which I have been able to observe, and I will therefore mention my reactions with some particularity.

I invariably found that when a trace of sulphuric acid was added to the solution of a neutral alkaline sulphate, it reacted as free acid. The matter was examined especially in the following manner. To 40 cub. centim. of distilled water 2 drops of sulphuric acid were added; the liquid was divided into two equal parts, in one of which was dissolved a gramme of neutral sodium sulphate. These two liquids were then examined with the test solution, and the detection of the acid was found to be fully as easy in the presence of the large excess of sodium sulphate as in the case of the acid alone.

It is true that this result is open to the following criticism. Alcohol extracts sulphuric acid from solid acid sodium sulphate, showing thereby, as Mendeléef remarks, the extremely weak affinity which unites it to the neutral salt. In the present examination the test can only be used in alcoholic solution. It may be said that the alcohol first precipitates the solid acid sulphate, and then abstracts free acid from it. There is force in this objection, but I think it may be answered in the following manner. We first reduce sulphuric acid nearly to the limit of dilution and quantity at which it can be detected. We then find that the addition of a comparatively large quantity of neutral sulphate makes absolutely no change in the reaction. It seems therefore legitimate to conclude that no combination has taken place, because otherwise it would be necessary to admit that alcohol can abstract all the acid united with the solid neutral sulphate, which is highly improbable. The weight of the evidence seems therefore to favour complete decomposition by solution into neutral salt and free acid.

When herapathite is dehydrated either by long keeping over oil of vitriol, or by exposure to a temperature of 100°C . for several hours, its colour changes from green to dark brown and its lustre is lost. In this condition it dissolves sparingly in boiling absolute alcohol, and separates by cooling in blackish particles which show little trace of crystallization.

When the brown substance is placed in a vial with barium

* *Mech. Chim.* ii. p. 323.

carbonate also dried, and absolute alcohol, scarcely a trace of action ensues. The liquid, even if kept warm, scarcely colours, and the brown colour of the salt is retained. The addition of a little water brings on rapid action. The dull brown colour changes to bright metallic green, and solution goes on steadily as the sulphuric acid is removed by the barium carbonate.

We thus have the curious result that two substances, both entirely insoluble in water, scarcely act on each other until water is present, and then a rapid decomposition results.

The question naturally presents itself whether it is necessary to first form and then decompose herapathite, or whether a suitable test solution could not be obtained by simply acting on quinia with iodine. An iodine solution instantly produces in one of quinia a bulky precipitate of a light yellowish-brown colour, quickly redissolving if the solutions are not too strong, and the liquid thus obtained, if the iodine is not in excess, immediately forms herapathite on the addition of sulphuric acid.

But the reaction is not a delicate one ; a trace of sulphuric acid cannot be detected as with the solution obtained from herapathite. The reason appears to be as follows :—When pure herapathite is used, the resulting solution contains absolutely no excess of either quinia or iodine. But however carefully we may attempt to mix quinia and iodine, we shall always have a slight excess of one or the other, and in either case the delicacy of its reaction is lost. If quinia is present in excess a trace of sulphuric acid is required to saturate it, and it has been already mentioned that the test solution will not take sulphuric acid from quinia or from any other alkalioid. On the other hand, if iodine is present in excess, the first action is to form one of the more highly iodized bases, more soluble than herapathite and crystallizing less well. So that in either case a trace of sulphuric acid is consumed before the proper reaction occurs, and if only a trace is present the reaction may fail.

It is better therefore to prepare herapathite in the first place, and a convenient means of obtaining it will be here given.

In a Griffin's beaker place 100 cub. centim. of alcohol of 95 per cent., add 5 grammes of quinia sulphate and 40 cub. centim. of acetic acid of 50 per cent. Take dilute sulphuric acid containing one tenth by weight of acid and add of this 7 cub. centim. Place the beaker in a water-bath and apply heat till the alcohol begins to boil gently, then add with con-

stant stirring 20 cub. centim. of a ten per cent. solution of iodine. Turn off the heat, cover the beaker with a glass plate, and allow it to cool slowly with the bath. Next day throw the crystals on a filter and wash with 70 per cent. alcohol. Press between blotting-paper and dry at ordinary temperature.

Herapathite appears to be a very permanent substance. Some that I prepared over thirty years ago has been kept in a stoppered, but not sealed, white glass bottle and freely exposed to light during this time. It appears to be quite unchanged, and was used in part of the work just described.

In preparing the test solution time is gained by using the barium carbonate in considerable excess and by frequent shaking. The herapathite should be in fine powder. After the green particles have entirely disappeared, which will usually take a day or two, the solution must be filtered off and be placed in contact with a fresh portion of barium carbonate, with frequent shaking for several days. The complete removal of the last traces of sulphuric acid cannot be judged of, as might be supposed, by allowing a portion to evaporate and examining for the crystals of herapathite. A specimen may dry up to a yellow varnish and yet may contain sulphuric acid, as may be shown by evaporating to dryness with a little ammonia, exhausting the residue with very dilute hydrochloric acid, and adding a drop of barium-chloride solution. But there is a very much simpler and at the same time more effective means of testing. A solution is allowed to evaporate spontaneously after adding a drop or two of solution of oxalic acid. Then, if there is the slightest trace of herapathite present, it will show itself in extremely characteristic crystals, either small rosettes of black prisms or in thin, light brown, transparent plates, which are black when crossed. A great many acids have this property of forcing out a crystallization; for example acetic, citric, tartaric, malic, and even arsenic. On the other hand, hydrochloric, hydrobromic, and nitric acids have not this power.

The explanation appears to be this. Iodoquinia is a colloid, and when present in large excess is able to prevent the crystallization of the relatively small proportion of herapathite present. The addition of either of the first-named series of acids appears to convert the colloid base into a crystalline salt, which of course no longer interferes with the crystallization of the herapathite.

Method of applying the test.—After having ascertained in the above-mentioned manner that the test solution is absolutely free from herapathite, a few drops of the liquid to be

tested are to be placed in a small porcelain basin, a little alcohol added, and then a few drops of test solution. When the quantity of sulphuric acid is something more than a trace, an immediate black precipitate is formed. If the quantity is something less no immediate result is visible; but as the alcohol evaporates, it leaves behind a film of dark crystals which under a lens are easily recognizable. In this way a quantity of sulphuric acid amounting only to $\cdot 000015$ gramme, about $\frac{1}{66}$ of a milligram, can be detected with certainty, provided the test solution is not used in too great excess. To detect so small a quantity, however, requires some familiarity with the reaction.

With larger quantities of free sulphuric acid, the characteristic violet-black crystalline precipitate falls immediately. In dealing with quantities too small to cause precipitation, it is advantageous to gently warm the basin beforehand; in this way a crystallization is obtained within two or three minutes, and the danger of secondary reactions, such as might be caused by the presence of oxidizing acids, is diminished*.

The conclusions derived from the foregoing investigations may be briefly summed up as follows:—

1. The solution of iodoquinia affords the means of detecting free sulphuric acid even in traces in presence of combined sulphuric acid.

2. The salts of heavy metallic protoxides do not owe their acid reaction to dissociation. The solutions of their sulphates contain no free sulphuric acid. To this there is one exception. Solutions of ferrous sulphate always contained free sulphuric acid.

3. Sesquisulphates, as far as examined, are always dissociated in solution.

4. Alums are always dissociated in solution with a single notable exception. Chrome alum exists as such in solution.

5. Acid salts are dissociated in solution. The dissociation is very great and may perhaps be complete.

* Very faint traces of free sulphuric acid are detected as follows. If the test liquid dries up without showing indications, 1 or 2 cub. centim. of alcohol are poured into the basin and slowly washed round. As the yellow film dissolves it may leave behind it a violet-black film of hercynite, which, being much less soluble, resists the action of the alcohol longer. This is a test of very great delicacy and the treatment with alcohol should never be omitted.

VIII. *Exercises in the Calculation of Errors.*
By Professor F. Y. EDGEWORTH, M.A., D.C.L.*

AN attempt to estimate and reduce the errors in the calculation of *correlations* between organs † may prove not only useful to those who cultivate that branch of exact biology, but also interesting to the less specialized student of Probabilities, in virtue of some precepts of general application.

As shown in former papers, the calculation of correlations consists of three stages. We begin with the coefficients called by Mr. Galton r , and by the present writer $\rho_{12}, \rho_{13}, \&c.$; which determine the correlation between the members of each pair of organs; for the probability of any two deviations x and y (each measured from the corresponding average, in units of the proper modulus) being associated is equal to a constant raised to a power denoted by the following expression:

$$\frac{1}{\sqrt{1-\rho_{12}^2}}x^2 - 2\frac{\rho_{12}}{\sqrt{1-\rho_{12}^2}}xy + \frac{1}{\sqrt{1-\rho_{12}^2}}y^2.$$

The conclusion sought is the quantic of the second degree which forms the exponent of the expression for the probability that particular values of all the organs should be associated; which in the case of three variables is of the form

$$ax^2 + by^2 + cz^2 + 2fyz + 2gxz + 2hxy.$$

This result affords answers to questions like the following:—(1) Given the values of one or more of the variables, what are the values of the remaining variables which are most probably associated with the given ones? (2) Given the values of one or more of the variables, what is the dispersion of each of the other variables about its most probable value ‡?

Intermediate between the first and last stage of the calculation is the determination of the *proportionate* values of the coefficients $a, b, c, f, g, \&c.$; by which we are able to answer questions of the first kind, but not of the second §.

I propose to estimate for each of these three computations the *error* to which it is liable; that is the extent to which the results obtained from a given number of specimens are likely to differ from the results which would be obtained from an indefinitely large number of specimens.

I. The ρ -coefficients which come first are each liable to errors of two or three kinds:—

* Communicated by the Author.

† See papers by the present writer in *Phil. Mag.*, Aug., Nov., Dec. 1892, and Jan. 1893.

‡ See *Phil. Mag.* Jan. 1893.

§ *Ibid.*

(a) One source of error is at the origin or centre from which are measured the deviations, x , y , &c., which form the data for determining the required coefficients. The error in the determination of the centre will depend upon the method of determining it. For the purpose in hand I recommend the sort of method which Mr. Galton has pursued: the use of "percentiles," together with some process of "smoothing"*. The simplest variety of this generic principle is to use the *observed* quartiles and median in order to determine the *most probable* values of those points consistent with the condition that the median should be midway between the two quartiles. Thus, if q_1 , q_3 , m be the observed quartiles and median respectively, and the sought ones Q_1 , Q_3 , M ; we have to determine the latter, under the condition that the expression

$$w_1(Q_1 - q_1)^2 + w(M - m)^2 + w_3(Q_3 - q_3)^2 + 2\lambda(Q_1 + Q_3 - 2M)$$

should be a maximum; where λ is an undetermined factor, w is the *weight* pertaining to the determination of the median by putting the observed median (m) for the real one (M); and w_1 , w_3 are the corresponding weights for the quartiles respectively. Whence

$$Q_1 = q_1 - \frac{\lambda}{w_1}; \quad Q_3 = q_3 - \frac{\lambda}{w_3}; \quad M = m + \frac{2\lambda}{w}.$$

And, to determine λ , we have

$$q_1 + q_3 - \frac{\lambda}{w_1} - \frac{\lambda}{w_3} = 2m + \frac{4\lambda}{w}.$$

Now the error committed in taking the *observed* as the *real* median has for modulus $\sqrt{\frac{\pi}{2n}}$, as Laplace has proved.

And, as the present writer following his method has reasoned, the error committed in taking each observed quartile for the real one has for modulus $\sqrt{\frac{\pi}{1.7n}}$ †. Accordingly $\frac{2\lambda}{w}$, the

* Proc. Roy. Soc. vol. xlv. p. 140.

† Phil. Mag. 1886, vol. xxii. p. 375.

The scruples expressed in the passage referred to are groundless. Laplace's method is justified by the presumption that a variable, such as the position of the median, depending on a number of independent agencies, obeys the law of error (see Phil. Mag. Nov. and Dec. 1892). Also the displacements of the two quartiles are independent of each other and of that of the median; as follows from the theory that each displacement is of the order $\frac{1}{\sqrt{n}}$ (with reference to unit of modulus). This consideration shows how many percentiles—quartiles, octiles, &c.—ought to be utilized in order to employ the generic principle to the most advantage. At least

correction of m ,

$$= \frac{q_1 + q_2 - 2m}{3 \cdot 2};$$

the corrected value of m

$$= \frac{1 \cdot 2m + q_1 + q_2}{3 \cdot 2};$$

and the modulus of the error incident to this determination

$$= \sqrt{1 \cdot 44\pi \div 2 + 2\pi \div 1 \cdot 7 + 3 \cdot 2} \sqrt{n} = \cdot 77 \div \sqrt{n}.$$

Thus by the use of the principal percentiles, the median and the quartiles, with a simple process of smoothing, a result is obtained which is better than that combination of observations which has been thought to be the best, viz., the Arithmetic mean; for which

the modulus of error is $\frac{1}{\sqrt{n}} \left(> \frac{\cdot 77}{\sqrt{n}} \right).$

The error which has been attributed to the determination of the centre affects of course each deviation which is measured from that centre as origin. But the influence which the error of the observed deviations x and y has upon the coefficient of correlation ρ_{12} cannot be estimated, until the method of combining the former in order to determine the latter has been assigned. The methods which present themselves may be classified as (1) the most accurate, (2) the more convenient; each introducing an error additional to those which have been indicated under the heading (a).

(β) (1) Regarding each assigned, or "subject" * x divided into the associated, or "relative," y , as affording an observation-equation $\frac{y}{x} = \rho_{12}$, we see that the best combination of these data is obtained by affecting each observation $\frac{y}{x}$ with a weight inversely proportional to its modulus-squared. Now by hypothesis every y , whatever the x with which it is associated, has for the modulus of its fluctuation $\sqrt{1 - \rho_{12}^2}$ †.

as many as suffer independent displacements may with advantage be admitted; probably at least the octiles and deciles in general.

It is important to observe that the principle may be extended to "discordant" observations which do not range under a single probability-curve; in which case the w 's are to be determined according to first principles, from the height of the ordinate in each neighbourhood (Phil. Mag. *loc. cit.*).

* See Galton, Proc. Roy. Soc. 1888, p. 140.

† See the formula on p. 98 above.

Accordingly the modulus of $\frac{y}{x}$ is inversely proportional to x ; and the weight of $\frac{y}{x}$ is directly proportional to x^2 . The best value of ρ_{12} is $Sxy \div Sx^2$; and the error of this determination has for modulus

$$\sqrt{Sx^2(1-\rho^2)} \div Sx^2 = \sqrt{1-\rho^2} \div \sqrt{Sx^2} = \sqrt{1-\rho^2} \div \sqrt{\frac{1}{n}}$$

(the modulus of x being unity by hypothesis)

$$= \sqrt{2} \times \sqrt{1-\rho^2} \div \sqrt{n}$$

(n being the number of observations utilized).

The laborious multiplication which the formula $Sxy \div Sx^2$ involves may be abridged by grouping the x 's in small fascicules*.

(2) More convenient methods of utilizing the data are (i.) that which I have recommended in a former paper†: dividing the sum of the assigned deviations Sx into the sum of the associated deviations Sy ; and (ii.) the method to which Mr. Galton's statistics lend themselves‡: arranging the observations in small groups, taking the quotient $Sy \div Sx$ for each group, and the arithmetic mean of all these quotients as the value of ρ .

(i.) The modulus of the error incident to the expression $Sy \div Sx$ (x assigned and y observed to be associated) is

$$\sqrt{n(1-\rho^2)} \div Sx = \sqrt{n} \sqrt{1-\rho^2} \div \sqrt{n}$$

(the modulus for the deviation x being unity); worse than the best method in the degree $\sqrt{\pi} : \sqrt{2}$, or 1.25 times.

This result may be improved by omitting some of the data; in virtue of the following general theorem:—

When, instead of the proper weights of a set of observations p_1^2, p_2^2 , &c., another set of weights, q_1^2, q_2^2 , are used as more convenient, it is in general advantageous to reject some of the given observations; the last observation admitted, say x_m , being determined by the equation

$$q_{m+1}^2 \times S_1^m q^2 = 2p_{m+1}^2 \times S_1^m \frac{q^4}{p^2}.$$

This equation is derived from the condition that we should stop taking in new observations as soon as the modulus of the

* The principles which should regulate this sort of approximation may be gathered from the present writer's paper on the "Determination of the Modulus" in the Philosophical Magazine, 1886, vol. xxi. p. 500.

† Phil. Mag. Aug. 1892.

‡ Proc. Roy. Soc. vol. xlv. p. 189.

weighted mean ceases to become smaller by the addition of a new observation ; that is, when

$$S_1^{m+1} q^4 \sigma^2 \div (S_1^{m+1} q^2)^2$$

begins to be greater than

$$S_1^m q^4 \sigma^2 + (S_1^m q^2)^2, \quad \left(\text{where } \sigma^2 = \frac{1}{p^2} \right).$$

Expanding, and neglecting terms of an inferior order, we have the equation above written.

To apply this principle to the case before us, we may, without loss of generality, regard the given values of x as ranged on one branch of a probability-curve from zero to infinity. Each x divided into the associated y gives a value for ρ , of which the true weight is x^2 and the weight used in the method under consideration is x . Putting $p^2 = x^2$ and $q^2 = x$ in the general formula, we have for the limiting condition :

$$x_{m+1} \times S_1^m x \text{ begins to be greater than } 2x_{m+1}^2 \times S_1^m 1,$$

or

$$x_{m+1} \text{ begins to be less than } \frac{1}{2} S_1^m x \div n.$$

Now, as we move outwards from the centre towards infinity, the right-hand member of the above inequality converges to a constant $\frac{1}{\sqrt{\pi}}$, while the left-hand member increases indefinitely. There is therefore no upper limit.

To determine the lower limit, putting u for x_{m+1} , find a point on the x -axis of a probability-curve (of unit modulus), distant u from the origin such that u = half the distance from the origin of the centre-of-gravity of the area which is intercepted by the axis of abscissæ, the ordinate at the point u , and the curve. In symbols,

$$u = \frac{1}{2} \int_u^\infty x e^{-x^2} dx + \int_u^\infty e^{-x^2} dx,$$

$$u \times 4 \times e^{-u^2} \times \int_u^\infty e^{-x^2} dx = 1.$$

Taking logarithms, and using the second of the tables appended to De Morgan's "Calculus of Probabilities" (*Encyc. Métrop.* vol. ii.), I find a value for u between '4 and '45 ; which is presumably the solution.

But, as it may be suspected that this result is exaggerated by the prolongation of the curve to infinity in theory, though not in fact, I have verified the solution by substituting for the centre of gravity the Median of the tract outside the ordinate

at the required point. This calculation being not disturbed by the leverage of a limb stretching to infinity, affords an inferior limit to the true value : say u' , determined from the equation

$$\int_{u'}^{\infty} \frac{1}{\sqrt{\pi}} e^{-x^2} dx = 2 \int_{2u'}^{\infty} \frac{1}{\sqrt{\pi}} e^{-x^2} dx.$$

The root of this equation is found from the Tables to lie between .35 and .4. Concluding, then, that the limit is in the neighbourhood of .4, we ought to reject about *two fifths* of the observations (that being the proportion of the deviations which fall within a distance of .38 from the centre).

The gain in accuracy is seen by comparing the modulus of error before correction, viz.

$$\sqrt{\pi} \sqrt{1-\rho^2} + \sqrt{n},$$

with the modulus after correction, that of the expression $Sy \div Sx$ integrated between limits ∞ and (say) .4. Each y , as before, being liable to an error whose modulus is $\sqrt{1-\rho_{12}^2}$, we have for the modulus of error incident to ρ_{12} ,

$$\begin{aligned} & \sqrt{1-\rho_{12}^2} \left[n \times \frac{2}{\sqrt{\pi}} \int_{.4}^{\infty} e^{-x^2} dx \right]^{\frac{1}{2}} \div n \frac{2}{\sqrt{\pi}} \int_{.4}^{\infty} x e^{-x^2} dx \\ &= \sqrt{1-\rho_{12}^2} \times \sqrt{n} \sqrt{.572} \div \frac{n}{\sqrt{\pi}} e^{-.16} \\ &= \sqrt{1-\rho_{12}^2} \sqrt{\frac{\pi}{n}} \times .756 \times e^{+.16} = \sqrt{1-\rho_{12}^2} \times \sqrt{\frac{\pi}{n}} \times .89 \text{ nearly.} \end{aligned}$$

Thus the modulus of the purified observations is about ten per cent. smaller than the modulus of the whole set. To this slight gain in accuracy is to be added a considerable saving of trouble. As compared with the best possible method, the corrected second-best is very much less troublesome and very little less

accurate—the modulus of the former being $\sqrt{\frac{1-\rho_{12}^2}{n}} \sqrt{2}$,

the modulus of the latter $\sqrt{\frac{1-\rho_{12}^2}{n}} 1.55$.

(ii.) We have next to consider the method of treating the statistics to which Mr. Galton's tables in the paper already cited lend themselves. For each degree or small difference, *e.g.* a tenth (of the unit modulus), on the axis x take the mean of the corresponding y 's ; and put the latter, divided by the former, as a value of the *quæsitum* ρ_{12} : *e.g.*,

$$\rho'_{12} = \frac{S'y}{s} \div x' + \cdot 05 ;$$

where $S'y$ is the sum, and s' the number, of the y 's corresponding to values of x which are between x' and $x' + \cdot 1$. Determine similarly ρ_{12}'' , ρ_{12}''' , &c. for other degrees or differences on the axis x ; and take the Arithmetic Mean of ρ_{12}' , ρ_{12}'' , &c. as the value of ρ_{12} . As each little group of observations has the same weight in this combination, it follows that there is assigned to each observation a weight inversely proportional to s_r , the size of the group to which the observation belongs. But as the values of x are distributed in conformity with a probability-curve with modulus unity, the number s_r is proportional to e^{-x^2} ; and accordingly the weight used is proportional to e^{+x^2} .

To determine the accuracy of this method uncorrected by the rejection of observations, we have for the modulus of the weighted mean

$$\sqrt{1 - \rho_{12}^2} \left[n \frac{2}{\sqrt{\pi}} \int_0^{\infty} e^{-x^2} \times e^{2x^2} dx \right]^{\frac{1}{2}} \div n \int_0^{\infty} \frac{2}{\sqrt{\pi}} e^{-x^2} \times e^{+x^2} dx,$$

which is infinite. There is, then, evidently in this case an upper limit.

To determine the limits at which to begin rejecting observations, we have the datum that, while the weight used for each observation of the form $\frac{y}{x}$ is e_r^x the true weight is x_r^2 .

Applying the general formula above given (recollecting that the values of x are distributed in conformity with a probability-curve whose modulus is unity), we have for the upper limit, say v ,

$$\frac{1}{v^2} e^{v^2} = 2 \int_u^{\infty} \frac{1}{x^2} e^{x^2} dx \div (v - u), \text{ where } u \text{ is the lower limit;}$$

and a similar equation for the lower limit, u .

To obtain an approximate solution of these equations, we may reason thus:—Observing that the curve $y = \frac{1}{x^2} e^{x^2}$ has a minimum ordinate at the point $x=1$, let us, in order to approximate to u , make abstraction of the observations outside that point, and determine a limit u' from the equation

$$\frac{1}{u'^2} e^{u'^2} = 2 \int_1^{u'} \frac{1}{x^2} e^{x^2} dx \div (1 - u').$$

The value of u' thus determined is less than the true value of u . For it may be shown that some of the observations

above the point $x=1$ had better be taken in ; and accordingly, if they are omitted, the modulus of the weighted mean is greater than if they were taken in. But, if the same weighted observations are incorporated with two averages, one of which has a larger modulus than the other, the limit at which it will cease to be advantageous to take in a new observation will be reached sooner in the case of the smaller modulus. Thus, as we move inwards towards the centre, we shall reach u sooner than u' ; in other words, u' is an inferior limit to u .

To determine u' , in the absence of tabulated integrals for the function $\frac{1}{x^2}e^{x^2}$, I have adopted a method which is in fact more appropriate to the case in hand—where the observations are broken up into little bundles :—I have plotted the ordinate of the curve $y = \frac{1}{x^2}e^{x^2}$ for the points $x=1, \cdot 9, \cdot 8, \cdot 7, \&c.$; and, joining their tops, observed the point at which $y \times (1-x)$ begins to be greater than twice the area contained between the ordinate at the point x , the abscissa, the ordinate at the point 1, and the locus joining the tops of the ordinates. This limit proves to be about $\cdot 3$. Accordingly at least all the observations below this value of x are to be rejected.

By similarly operating on the observations above the point $x=1$, I find for v' , a limit superior to v , the point $x=2$; and conclude that at least all the observations above that point are to be rejected.

(γ) A third source of error affecting the computation arises from the imperfect graduation of our instruments and senses, by which we are compelled to put for the true value of any object measured a value in the neighbourhood equal to an integer number of degrees, *e. g.*, tenths of an inch. Assuming that the difference between the apparent and real value is more likely to fall short of than to exceed half a degree, and is very unlikely to exceed a whole degree,—the modulus of the error from this source affecting each observation is much less than a degree ; and is therefore small, if the degree is small, as in the case of *stature*, if the degree be a tenth of an inch ; the unit in which x is measured being $3\cdot 6$ inches. In the case of the *cubit* the unit is smaller, the error from source γ greater.

In computing the errors investigated above, and for other problems, the following notation will be convenient. Let the symbol *plus* written in full [and similarly *minus*] connecting *probable errors* or *moduli* denote the cumulation of the errors,

with attention *if necessary* to their *sign*. Thus, e , e_1 , e_2 being the moduli of independent errors,

$$e_1 \text{ plus } e_2 = \sqrt{e_1^2 + e_2^2},$$

$$e_1 \text{ minus } e_2 = \sqrt{e_1^2 + e_2^2}.$$

But $(e_1 \text{ plus } \lambda e) \text{ plus } (e_2 \text{ minus } \mu e)$

$$= \sqrt{e_1^2 + e_2^2 + (\lambda - \mu)^2 e^2}.$$

To exemplify the combination of the errors with which ρ is affected, let us select out of the methods comprised under heading (β) that which is most easily handled, namely, the uncorrected form of $\beta(2)$ ((i.)); according to which $Sy \div Sx$ is put for ρ_{12} , the summation extending from positive to negative infinity. Since the ordinate of the centre from which the y 's are measured is liable to the error $\cdot 77 + \sqrt{n}^*$, Sy is liable to the error $\cdot 77 \times \sqrt{n}$. By parity Sx is liable to the error $\cdot 77 \times \sqrt{n}$. Also $Sy = n \div \sqrt{\pi}$ (nearly) $= Sx$ (nearly); since each set of observations ranges under a probability-curve of which the modulus is unity. Accordingly the error of ρ_{12} derived from source (α)

$$\begin{aligned} &= \frac{1}{Sx} \text{error } Sy \text{ minus } \frac{Sy}{(Sx)^2} \text{error } Sx \\ &= \left[\frac{\cdot 58 \pi}{n} + \frac{\cdot 58 \pi}{n} \right]^{\frac{1}{2}}. \end{aligned}$$

To this is to be superadded the error from source (β) †;

$$\begin{aligned} &\sqrt{\frac{1 \cdot 16 \pi}{n}} \text{ plus } \sqrt{\frac{(1 - \rho_{12}^2) \pi}{n}} \\ &= \sqrt{\frac{(2 \cdot 16 - \rho_{12}^2) \pi}{n}}. \end{aligned}$$

An illustration of this reasoning is afforded by the computation of correlation ‡ between *stature*, *cubit*, and *knee-height*, referred to in the *Philosophical Magazine* for December 1892, p. 523, note. There different values were obtained for each ρ , according as the positive or the negative deviations were operated on; and according as the formula used for ρ was $Sy \div Sx$ (x being taken as "subject," and y relative §) or $Sx \div Sy$ (*vice versa*).

* Above, p. 100.

† Above, p. 101.

‡ The statistical materials were supplied by Mr. Francis Galton, F.R.S. and the arithmetical work by Mrs. Bryant, D.Sc.

§ Above, p. 100.

| | 1. | 2. | 3. | 4. |
|-------------------|---------------------|---------------------|-------------------------------|-------------------------------|
| | Positive deviation. | Negative deviation. | $\frac{x}{\text{"subject."}}$ | $\frac{y}{\text{"subject."}}$ |
| ρ_{12} | ·80 | ·80 | ·75 | ·83 |
| ρ_{23} | ·87 | ·82 | ·81 | ·87 |
| ρ_{31} | ·86 | ·87 | ·93 | ·80 |

Each of these results is based upon two sets of 150 observations ; but these sets are not *independent*. For instance, the basis of the "positive deviations" (column 1) consists of 150 observations (for *e. g.*, ρ_{12}) of the form $\frac{y}{x}$, and 150 of the form

$\frac{x}{y}$; taking the average of the two values (of ρ_{12}) respectively determined from the two sets of 150 observations. Now the error under head (α) affecting the sum of these is,—if e_1 is put for the error of the abscissa of the Median, and e_2 for that of its ordinate—

$$\sqrt{\frac{\pi}{n}} (e_2 \text{ minus } e_1) \text{ plus } \sqrt{\frac{\pi}{n}} (e_1 \text{ minus } e_2);$$

that is, zero. The result therefore is affected only with the error (β), that is,

$$\sqrt{\frac{\pi(1-\rho_{12}^2)}{n}};$$

or, putting $\rho = \cdot 8$, and $n = 300$, ·06. This result again has to be diminished by about ten per cent.; considering that in the calculation the *corrected* method ((i.)) was employed*. Similar remarks apply to the "negative deviation"—the results in the second column of the table. The *probable error* of the difference between these two results is

$$\cdot 06 \times \cdot 9 \times \sqrt{2} \times \cdot 477, \text{ or } \cdot 04 \text{ nearly.}$$

Similarly the basis of the results in the third column is one set of 150 positive observations and another set of 150 negative observations. The errors under head (α) which affect each of these sets cut each other out; and accordingly the probable error of the difference between an entry in column 3 and the corresponding entry in column 4 is the

* Above, p. 101.

same as that for the differences between the entries in columns 1 and 2, namely .04.

To these estimates an addition is to be made in virtue of the error of the species (γ). It will be found that the errors of this species are nearly cancelled in both 1 and 2, but not so in 3 or 4; a circumstance which perhaps accounts for the considerable divergence between 3 and 4 as compared with that between 1 and 2.

The differences actually occurring are 0, .01, .05, .06, .07, .08.

II. We have next to consider the errors incident to the *proportional* values of the coefficients a, b, c, f, g, h —the case of three variables being taken as an example. It will be recollected that these proportions are thus obtained. The

ratios $\frac{a}{\Delta}, \frac{b}{\Delta}, \frac{c}{\Delta}$ are respectively equal to the principal minors,

and the ratios $\frac{f}{\Delta}, \frac{g}{\Delta}, \frac{h}{\Delta}$ to the other minors, of the determinant

$$\begin{vmatrix} 1 & \rho_{12} & \rho_{31} \\ \rho_{12} & 1 & \rho_{23} \\ \rho_{31} & \rho_{23} & 1 \end{vmatrix}$$

Accordingly the first set of results, the proportional coefficients of the squares of the variables, have the least possible relative error when the ρ 's are all zero (the deviations of the organs independent); and the greatest possible relative error when the ρ 's are each unity (the correlation a case of simple law unmixed with chance). Contrariwise, the relative error of $\frac{f}{\Delta}, \frac{g}{\Delta}, \frac{h}{\Delta}$, the proportional coefficients of the products yz, zx, xy , is greater, the less the coefficients ρ are.

The relative error of $\frac{f}{\Delta}, \frac{g}{\Delta}$, &c. is apt to be greater than that of the ρ 's from which they are calculated. For, put e_{12}, e_{23} , &c. as the absolute errors of ρ_{12}, ρ_{23} , &c. Then the relative errors of ρ_{12}, ρ_{23} , &c. are $e_{12} \div \rho_{12}, e_{23} \div \rho_{23}$, &c.; while the relative error of, for example, $\frac{f}{\Delta}$ ($= \rho_{12}\rho_{13} - \rho_{23}$) is

$$(\rho_{12}e_{13} \text{ plus } \rho_{13}e_{12} \text{ minus } e_{23}) \div (\rho_{12}\rho_{13} - \rho_{23});$$

which is made up of three terms, each of which seems as likely as not to be of the same order as $e_{23} \div \rho_{23}$ (it being recollected that all the ρ 's are proper fractions).

III. We pass to the *absolute* values of the coefficients by

multiplying each of the proportional coefficients above written by Δ , the determinant of the quantic

$$ax^2 + by^2 + cz^2 + 2fyz + 2gzx + 2hxy.$$

The relative error of the divisor $\frac{1}{\Delta}$ has the following elegant expression :—

$$2[f e_{23} \text{ plus } g e_{31} \text{ plus } h e_{12}].$$

The relative error—or briefly *r. e.*—of any of the principal coefficients a

$$\begin{aligned} &= r.e. \left(\frac{a}{\Delta} \div \frac{1}{\Delta} \right) = r.e. \frac{a}{\Delta} \text{ minus } r.e. \frac{1}{\Delta} \\ &= \left(\text{since } \frac{a}{\Delta} = 1 - \rho_{23}^2 \right) - \frac{\Delta}{a} 2\rho_{12}e_{12} \text{ minus } r.e. \frac{1}{\Delta} \\ &= (\text{by the formula of last paragraph}) \\ &2 \left[\left(f + \frac{\Delta\rho_{12}}{a} \right) e_{23} \text{ plus } g e_{31} \text{ plus } h e_{12} \right]. \end{aligned}$$

If the ρ 's are determined as above on p. 104, the α element of error disappears altogether, and the γ element in part. Accordingly, putting $f + \frac{\Delta\rho_{12}}{a} = k$, and expanding, we have

$$r.e. a = 2\sqrt{\frac{\pi}{n}} \left[k \sqrt{1 - \rho_{23}^2} \text{ plus } g \sqrt{1 - \rho_{31}^2} \text{ plus } h \sqrt{1 - \rho_{12}^2} \right] \text{ nearly.}$$

Put as approximate values $\rho_{12} = .8$, $\rho_{23} = .8$, $\rho_{31} = .9$; and evaluate the coefficients $a, b \dots h$. They are approximately $a = c = 6$, $f = h = 1$, $b = 3$, $g = 4$. Substitute these values in the expression for *r.e. a*; and we have, when $n = 300$, modulus of *r.e. a* = about .5. The probable error for the difference between two determinations = $.5 \times .477 \times \sqrt{2} = .33$, nearly.

The relative errors of the other coefficients may be similarly determined, and may be expected to be equally precarious while the number of observations is limited to 300.

This anticipation is fully borne out by the following experience. From each of the four sets of ρ 's above cited there has been calculated* the exponential quantic of the second degree, or ellipsoid of equal probability. The comparative results are exhibited in the following Table.

* By Mrs. Bryant.

TABLE showing Coefficients of Correlation obtained from four batches of 300 observations each.

| | ρ_{12^*} | ρ_{23^*} | ρ_{31^*} | <i>a.</i> | <i>b.</i> | <i>c.</i> | <i>f.</i> | <i>g.</i> | <i>h.</i> |
|---|---------------|---------------|---------------|-----------|-----------|-----------|-----------|-----------|-----------|
| Positive and negative observations; <i>x, y, z</i> respectively "subjects." | .75 | .81 | .93 | 7.401 | 2.907 | 9.419 | -6.943 | -2.637 | + .07105 |
| Positive and negative observations; <i>y, z, x</i> respectively "subjects." | .83 | .87 | .80 | 3.494 | 5.177 | 4.472 | -1.122 | -2.962 | -1.927 |
| Positive observations only. | .80 | .87 | .86 | 4.024 | 4.306 | 5.962 | -2.716 | -3.014 | -.861 |
| Negative observations only. | .80 | .82 | .86 | 4.733 | 3.752 | 5.195 | -1.371 | -1.905 | -2.944 |

Taking a and c as each nearly 6, we should expect *à priori* (according to the last paragraph but one) the probable error between any two determinations of each coefficient to be about 2; and, *à posteriori*, we observe that of the six differences presented by the four values of a , three are within and three without 2. A similar statement is true of the six values of c .

The precariousness of the results becomes much greater, as the number of the variables is increased, as may be seen by considering the expression for $\frac{1}{\Delta}$ in the case of four, compared with that of three, variables.

I do not think it necessary to exhibit the work in full. What has been proved of arithmetical observations may be true also of algebraic formulæ—a better general result is sometimes obtained by not working up all the particulars.

To sum up: we have estimated the error incident to each coefficient employed in determining the correlation between organs. We have shown how this error becomes greater with the number of the organs; the instability of the construction increases rapidly with its height.

In reaching these conclusions respecting correlated averages, we have come upon two principles of wider application. (1) When observations are combined according to a system of weights different from that which is known to be the best, it is in general advantageous to *reject* a certain class of the given observations.

(2) When, as usual, the observations range under a probability-curve, the median m corrected by the quartiles q_1 and q_2 affords a formula for the Mean, viz. $(1.2m + q_1 + q_2) \div 3.2$, which is more accurate than that method of combining such observations which has hitherto been supposed to be the most accurate, viz. the Arithmetic Mean. The principle may be applied with great ease and advantage to Discordant Observations*.

IX. The Hydrates of Hydrogen Bromide.

By SPENCER U. PICKERING, F.R.S.†

IN the various criticisms which have appeared in this Magazine of the conclusions which I drew from my study of the properties of sulphuric-acid solutions, no allusion has been made to one of the strongest of the arguments adduced in favour of the reality of the changes of curvature

* See the papers by the present writer in the 'Philosophical Magazine' for 1886 and 1887.

† Communicated by the Author.

shown by these properties, and of the existence of the hydrates thus indicated, namely the isolation of a hitherto unknown hydrate ($\text{H}_2\text{SO}_4, 4\text{H}_2\text{O}$), which, on the strength of its being indicated by changes of curvature, had been stated to exist in solution. It may have been thought that this was but a lucky coincidence, although, as I showed (*Chem. Soc. Trans.* 1890, p. 340) that the chances against such a coincidence were considerable: the multiplication of instances of a similar character must, however, render any such explanation untenable, and I have already published accounts of three other instances of a still more striking character. Kolb's values for the densities of nitric-acid solutions, when plotted out, showed two breaks of a very marked character indicating the existence of two unknown hydrates with H_2O and $3\text{H}_2\text{O}$ respectively; and on examining the solutions by cooling them to low temperatures, these two hydrates, and these two only, were obtained in a solid crystalline condition (*Chem. Soc. Trans.* 1893, p. 436). Similarly Kolb's and also my own values for the densities of hydrogen-chloride solutions showed a break of a most unmistakable character at the composition of a trihydrate; and this hydrate, hitherto unknown, was isolated from the solution by cooling it. In this case the break in the densities was particularly well marked, since these formed a very nearly straight line from 0 to 40 per cent., whereas from 40 to 44 per cent. the deviation from straightness was very considerable (see fig. 1, A C)*. It was, therefore, thought probable that breaks of a similar character might be found in the case of hydrogen-bromide solutions. The results, however, disappointed this expectation: the breaks which were observed were of a very feeble character, but, though feeble, they have proved to be satisfactory otherwise, for I have succeeded in isolating the two hydrates which they indicate.

Topsoë's values for the densities of this acid (*Ber.* 1870, p. 404) when plotted out indicate a change of curvature at about 28.5 per cent.; but this corresponds to a hydrate containing as much as $11\text{H}_2\text{O}$, the isolation of which in a crystalline condition would be improbable. His values extend up to solutions of 48 per cent. strength only (or $\text{HBr} + 5\text{H}_2\text{O}$), and, therefore, do not cover the region where isolable hydrates would most probably exist. I consequently resolved to make determinations with stronger solutions. These results, which are given in Table I., extend from 65.2 per cent. downwards, the determinations in the region already covered by Kolb's results being comparatively sparse.

* In the case of nitric acid the breaks were equally well marked, owing to the rectilineal character of a large portion of the figure.

Owing to the large gaseous tension of very strong solutions of the acid, it is impossible to make them up to definite strengths by diluting the strongest acid with weighed quantities of water. The strength of each solution had to be determined separately after its density had been taken, for which purpose the contents of the density-bottle were emptied into a large weight of water, and portions of the solution obtained titrated. Three or four titrations of each solution were made, and from the variation in the values obtained the average mean error of the results was deduced to be 0.0466 per cent. HBr , corresponding to a mean error of 0.00045 in the densities. This error is, of course, far larger than the error in the density-determinations themselves; indeed the latter is practically negligible in comparison with it. From 44 per cent. downwards the results are more accurate, the solutions having been made up to the required strength by weighing.

The very strong solutions of the acid cannot be made and kept without developing a considerable amount of free bromine. This renders the titrations somewhat uncertain, and has the effect of making the densities appear too high; it may also affect the apparent position of any changes of curvature which exist, though in what direction it is impossible to say, for when the strength of the solution is determined by titration, any bromine which is present will be reckoned as water, and too low a value for the relation of acid water really present may thus be obtained; but, on the other hand, the bromine may really be dissolved in and combined with some of the acid, leaving a smaller amount than the total found by titration operative, or combined with the water present. We must, therefore, not expect the position of any breaks to coincide very exactly with definite molecular proportions as based on the results of titration. The weaker solutions might have been obtained nearly free from bromine; but as the main consideration in the present determinations was concordance of consecutive results, and not their absolute accuracy, it was necessary to use similar solutions throughout the series.

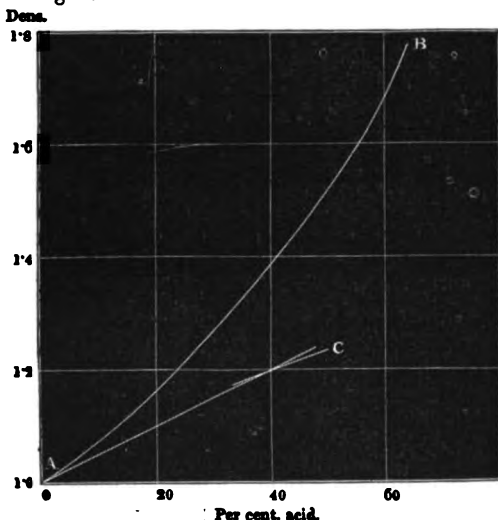
The results when plotted out form a figure illustrated by *AB* (fig. 1). This figure, unlike that representing the densities of hydrogen-chloride solutions, exhibits very considerable curvature as far as about 47 per cent., and afterwards is but slightly curved; the position of this general change, not necessarily a definite change of curvature, corresponds with the strength at which the solutions cease to give off water on exposure to air and begin to give off acid (Roscoe, *Quart. Journ. Chem. Soc.* xiii. p. 157). There seem to be indications

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of some change of curvature at about 30 per cent. similar to that indicated by Topsøe's values, though the present determinations are not sufficiently numerous to establish it satisfactorily*. (I have not attempted to indicate the changes of curvature in the woodcut, owing to the restricted scale of plotting necessarily adopted.)

Fig. 1.—Densities of HBr and HCl solutions.



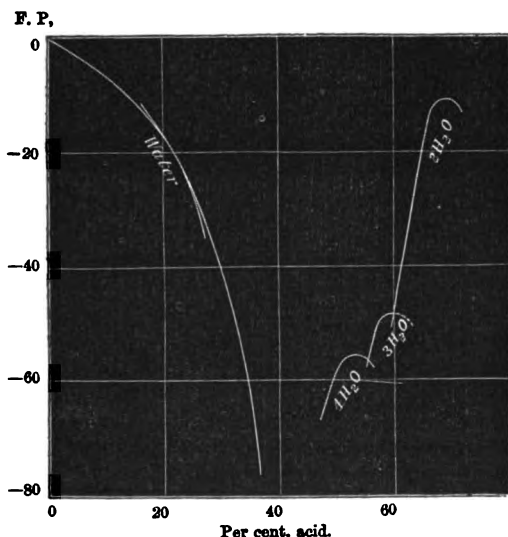
The more numerous results with stronger solutions, 44 to 65 per cent., suggested the existence of two breaks at 52 and 60 per cent. respectively, neither of which, however, were at all well marked. To examine them more fully I first determined the mean error of the results by my graphic method (*Ber.* xxiv. p. 3332, and xxv. p. 1100): this gave 0.000735, a value greater than that deduced from the titrations, as was to be expected, owing to two different samples of acid (containing rather different amounts of free bromine) having been used in making the two series of determinations. When the drawing representing the existence of the two above-mentioned breaks was examined in the manner already described in these pages (*Phil. Mag.* 1892, xxxiii. p. 438), it was found to represent the mean error of the points, and also their "total" error, to be 0.9 time that of the known experimental error, and it must, therefore, be regarded as agreeing very well with this error; whereas a drawing as a single

* Both Berthelot's and Thomsen's values (the latter especially) for the heat of dissolution show strong indications of some break between 20 and 40 per cent., but they are not numerous enough to give its exact position.

curve obliterating the breaks showed an error 3·5 times larger than the experimental error. Again, a drawing of the results which placed breaks at points other than those above mentioned, namely at 56 and 63 per cent. instead of at 52 and 60 per cent., gave an error twice as large as the latter, and 1·7 times larger than the known experimental error. These results, therefore, justify the conclusions drawn from the inspection of the figure.

Although the breaks thus indicated were of a minor character only, it was deemed advisable to investigate the freezing-points of the solutions to see whether hydrates corresponding to them could be isolated, and, as a matter of fact, both the hydrates indicated were isolated. Two series of determinations (of which the second is the fuller) were performed in the same manner as in my recent work on the Amines (Chem. Soc. Trans. 1893, p. 141): these are given in Table II. and illustrated in fig. 2. I need only say in explanation of

Fig. 2.—Freezing-points of Solutions of Hydrogen Bromide.



the figure that whenever the freezing-points of solutions rise, attain a maximum, and again fall, their doing so is a proof that the crystallizing substance is a compound of the two substances forming the solutions, and that the surest means of determining the composition of this compound is to ascertain the position of the maximum freezing-point, which must necessarily coincide with the composition of the pure compound (see *loc. cit.* p. 142). Perhaps it may also be well to

remark that although there must of course be a change of curvature at the point where one crystallization gives place to another, yet these changes are totally different from those previously discussed, and do not necessarily imply any special changes in the solutions at the points where they occur; they are changes in the actual phenomena occurring, whereas the others are changes in the rate at which one particular phenomenon or property is influenced by changes of strength of the solution.

The strongest solution used contained nearly 69 per cent. of acid, and was made by passing the gas into some of its solution cooled in a freezing-mixture. (The solubility of the gas, I may mention by way of parenthesis, is but very slightly affected by temperature.) The whole liquid soon solidified into a mass of transparent gritty crystals. These could not be melted (in order to take their melting-point) without giving off a small amount of gas, so that the melting-point determined is slightly below that of the pure crystals. Adding more and more water, the series of freezing-points shown by the curve marked $2\text{H}_2\text{O}$ was obtained. The maximum of the curve, as determined by drawing a smoothed curve through the experimental points with a bent lath, is at about 69 per cent., and the hydrate is, therefore, the dihydrate, which contains 69.23 per cent. This hydrate was obtained by Berthelot (*Ann. Chim. Phys.* [5] xiv. p. 369), and examined by Roozeboom (*Rec. Chim. des Pays-Bas*, iv. p. 331), who gives its melting-point as $-11^{\circ}3$. The present determinations give it as $-11^{\circ}2$.

At about 60 per cent. the appearance of the crystallization suddenly changes, the crystals being now much finer and less gritty than those of the dihydrate; the freezing-points at the same time cease to fall rapidly, and form a new curve marked $3\text{H}_2\text{O}$ in the figure. This curve has not been followed on the right-hand side beyond its maximum, owing to the crystallization of the dihydrate interfering with doing so, but the maximum can be located with a fair amount of certainty by a bent-lath curve drawn through the experimental points, and is thus found to be at 59.6 per cent., corresponding to $\text{HBr}, 3.05\text{H}_2\text{O}$. This new hydrate is, therefore, the trihydrate (containing 60.00 per cent.), the existence of which was indicated by the break in the densities. Its melting-point is -48° .

At 65 per cent. the crystallization again changes in a very marked manner, the crystals now being larger and more transparent: the freezing-points rise at first and then fall. The position of the maximum in this case is at 53 per cent.,

which represents $3.99\text{H}_2\text{O}$, and the crystallizing substance is, therefore, the tetrahydrate, the existence of which was indicated by the other break in the densities. Its freezing-point is $-55^\circ.8$.

From 47° to 38° per cent. no freezing-points were obtained at temperatures about -80° , nor, in the case of a 43 per cent. solution, even at -95° . If it is permissible to venture a conjecture, this gap might perhaps, if adequate cooling were adopted, be filled up by the crystallization of a pentahydrate. No definite break was observed, it is true, in the densities at the point, and the determinations would have had to have been a good deal more accurate than they were in order to indicate one here as well as at 56 per cent.; but there was a general change in direction somewhere in the neighbourhood. The chief ground, however, for imagining a pentahydrate to exist is that a solution of that composition (47.4 per cent.) possesses remarkable stability, its composition is affected to but a very slight degree (1 per cent.) by boiling under considerable ranges of pressure (750 to 1950 millim.), and also that in the case of a solution of hydrochloric acid which behaves in a similar manner, though to a less marked extent, there is independent evidence to show that this behaviour is due to the presence of a definite hydrate (*Ber.* xxvi. pp. 279, 282).

At 38 per cent. the crystallization of water begins, and the freezing-points gradually rise to 0, the only feature of interest in this curve being the existence of a break at 25 to 30 per cent. agreeing with that indicated by both Topsoë's and my own density results.

The two new isolated hydrates here described form the fifth and sixth instances of hydrates isolated in cases where the only grounds for regarding their existence as probable were that they were indicated by changes of curvature in the figures representing the properties of the solutions. The isolation of so many predicted hydrates would, even if no other arguments existed, be sufficient to place the reality and significance of these breaks beyond doubt, and the two special instances here described are of particular importance in that neither of the breaks were of at all a marked character, this showing that minor breaks have the same significance as the more marked ones*.

* It must be noticed, however, that in comparison with results such as those in the case of sulphuric-acid densities the experimental error here is very large, and that these breaks might be very prominent if more exact determinations were possible. They are, on the other hand, decidedly minor breaks in comparison with those indicating the isolated hydrates of nitric and of hydrochloric acid.

It will be of interest to give the following table, comparing the various hydrates isolated, together with their melting-points, in the case of the three haloid acids, though in doing so I am anticipating the publication of the results which I have obtained with hydrogen iodide. The monohydrate of hydrogen bromide was obtained in small quantities under pressure by Roozeboom, and he also obtained indications of the existence of a similar hydrate of hydrogen chloride: no experiments have been made yet to ascertain whether the iodide forms a monohydrate or not. As far as can be seen, there appears to be no simple relationship between the freezing-points of the various hydrates.

| | m.p. | | m.p. | | m.p. | | m.p. |
|-------------------------|------|------------------------|-------|------------------------|-------|------------------------|-------|
| HCl, H ₂ O ? | | HCl, 2H ₂ O | -17.4 | HCl, 3H ₂ O | -24.8 | | |
| HBr, H ₂ O ? | | HBr, 2H ₂ O | -11.2 | HBr, 3H ₂ O | -48 | HBr, 4H ₂ O | -55.8 |
| | | HI, 2H ₂ O | -43? | HI, 3H ₂ O | -48 | HI, 4H ₂ O | -36.5 |

TABLE I.—Densities of Solutions of Hydrogen Bromide at 15°. Water at 4°=1.

| Per cent. HBr. | Density. | Per cent. HBr. | Density. |
|-------------------|----------|-------------------|----------|
| FIRST SERIES. | | SECOND SERIES. | |
| 65.186 | 1.784496 | 64.757 | 1.776244 |
| 63.931 | 1.762986 | 59.499 | 1.680514 |
| 63.465 | 1.752372 | 58.582 | 1.664665 |
| 62.310 | 1.733345 | 57.613 | 1.648607 |
| 61.545 | 1.720028 | 56.648 | 1.632845 |
| 60.507 | 1.700394 | 55.761 | 1.618365 |
| 59.478 | 1.681383 | 53.949 | 1.587695 |
| 58.798 | 1.669405 | 53.029 | 1.574158 |
| 57.691 | 1.651415 | 52.010 | 1.558199 |
| 56.458 | 1.628475 | 51.443 | 1.545971 |
| 55.701 | 1.616653 | 50.640 | 1.535617 |
| 54.813 | 1.601491 | 49.490 | 1.515815 |
| 53.936 | 1.587476 | 48.225 | 1.498193 |
| 52.723 | 1.567934 | 47.227 | 1.483630 |
| 51.494 | 1.548080 | 46.431 | 1.472454 |
| 48.987 | 1.509520 | 45.372 | 1.457340 |
| 46.986 | 1.479224 | 44.340 | 1.441741 |
| 44.7985 | 1.449141 | | |
| 42.9777 | 1.423322 | | |
| 41.2954 | 1.400219 | | |
| 39.3818 | 1.374766 | | |
| 34.7356 | 1.318402 | | |
| 31.4824 | 1.278364 | | |
| 25.7661 | 1.216692 | | |
| 20.5357 | 1.165279 | | |
| 18.8511 | 1.122792 | | |
| 10.2258 | 1.075679 | | |
| 5.4590 | 1.038674 | | |
| 0 | 0 | | |

TABLE II.—Freezing-points of Aqueous Solutions of Hydrobromic Acid.

FIRST SERIES.

| Per Cent. HBr. | Freezing-point. | Per Cent. HBr. | Freezing-point. |
|---|-----------------|----------------------------|-----------------|
| <i>HBr, 2H₂O Crystallizes.</i> | | <i>Water Crystallizes.</i> | |
| 65.375 | —27.4 | 38.394 | —73.4 |
| 63.786 | —33.4 | 35.677 | —58.4 |
| 62.149 | —46.9 | 32.864 | —47.9 |
| | | 29.974 | —37.9 |
| | | 27.117 | —30.1 |
| | | 24.437 | —25.1 |
| | | 21.963 | —19.4 |
| | | 19.387 | —15.6 |
| | | 16.280 | —11.6 |
| | | 12.188 | — 6.9 |
| | | 7.277 | — 3.4 |
| | | 4.289 | — 1.65 |
| <i>HBr, 3H₂O Crystallizes.</i> | | | |
| 60.500 | —48.4 | | |
| 58.816 | —50.4 | | |
| 57.180 | —53.8 | | |
| 55.414 | —55.9 | | |
| <i>HBr, 4H₂O Crystallizes.</i> | | | |
| 53.370 | —56.2 | | |
| 51.290 | —58.6 | | |
| 48.878 | —62.9 | | |
| 46.511 | none at —77.4 | | |
| 44.092 | " " —85.4 | | |
| 41.548 | " " —79.4 | | |

SECOND SERIES.

| | | | |
|---|-------|----------------------------|-------------|
| <i>HBr, 2H₂O Crystallizes.</i> | | 44.112 | none at —73 |
| 68.728 | —11.2 | 43.208 | " " —80 |
| 67.396 | —11.9 | 43.039 | " " —95 |
| 65.759 | —16.2 | 41.989 | " " —79 |
| 64.447 | —21.9 | 40.726 | " " —80 |
| 63.069 | —28.8 | 39.112 | " " —80 |
| 61.691 | —38.3 | 37.450 | " " —70 |
| 60.346 | —47.2 | | |
| <i>HBr, 3H₂O Crystallizes.</i> | | <i>Water Crystallizes.</i> | |
| 59.517 | —47.9 | 35.755 | —64.8 |
| 58.415 | —48.4 | 34.692 | —59.4 |
| 57.553 | —49.8 | 33.243 | —53.3 |
| 56.550 | —51.8 | 31.583 | —46.3 |
| 55.699 | —54.6 | 30.216 | —41.8 |
| | | 28.897 | —37.3 |
| | | 27.301 | —32.7 |
| | | 24.812 | —26.6 |
| | | 23.637 | —24.1 |
| | | 21.712 | —20.7 |
| | | 19.940 | —17.5 |
| | | 17.993 | —14.5 |
| | | 15.882 | —11.7 |
| | | 13.749 | — 9.3 |
| | | 11.202 | — 6.8 |
| | | 6.396 | — 3.0 |
| | | 3.490 | — 1.5 |
| <i>HBr, 4H₂O Crystallizes.</i> | | | |
| 54.772 | —56.8 | | |
| 53.932 | —56.3 | | |
| 52.986 | —55.7 | | |
| 52.066 | —56.3 | | |
| 50.935 | —56.7 | | |
| 49.714 | —57.6 | | |
| 48.395 | —62.2 | | |
| 47.069 | —66.5 | | |

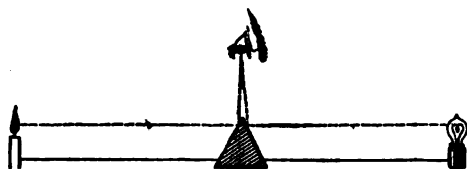
X. *Some Notes on Photometry.*By SILVANUS P. THOMPSON, *D.Sc., F.R.S.**I. *On the use of Two Overlapping Screens as an Isophotal.*

THE employment of two opaque screens placed at an angle with one another, and with the observer's eye, to receive the light from the two sources, was made the basis of a photometric method by the author, in conjunction with Mr. C. C. Starling, in 1881. Their photometer was designed, in the first instance, for electric-light measurements. For this special end any method in which opaque screens are used is to be preferred, in one respect, to those methods in which translucent screens are used; for then it is not necessary to employ coloured glasses when making the comparison, as the opaque screens themselves may be of coloured material, and the choice of opaque coloured material is much more varied than is that of tinted glass.

In the Thompson-Starling photometer the two surfaces for receiving the light met at an angle of about 70° . The pair of screens was constituted by two pieces of card, either white or coloured, or by two surfaces of some brilliantly-tinted fabric mounted on card, each pair being dropped down into position over a wedge-block. The observer, placing his eye opposite the *arête* of the dihedral pair of screens so as to view each surface at the same angle, had to adjust the apparatus until the apparent illumination at the adjacent parts of the two surfaces was equal.

When working with this photometer it was found that the precision of judgment of the eye as to equality of the two illuminations was impaired if by bad workmanship any considerable width of blunted edge intervened between the two

Fig. 1.



surfaces that should have met with precision. There was a similar defect in the original form of the Bouguer photometer, wherein the opaque partition was continued down to the screen and interposed an unilluminated patch equal in breadth

* Communicated by the Physical Society: read June 9, 1893.

to its own thickness between the two illuminated surfaces. In that case the remedy, applied by Foucault in the modified instrument which bears his name, was to shorten the partition so as to permit the two illuminated parts to come just into optical contact. In the case of the oblique opaque screens the author tried to remedy the defect by several modifications, which, though not described at the time, proved useful. In one of these each surface was extended so as partially to overlap the adjacent surface, as indicated in figs. 2 and 3. In

Fig. 2.

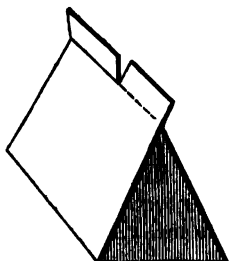
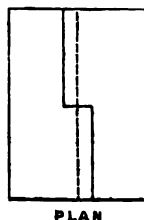


Fig. 3.



another instrument the overlap was given as shown in figs. 4 and 5.

Fig. 4.

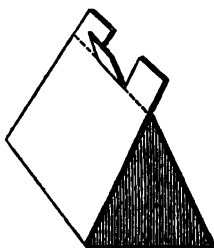
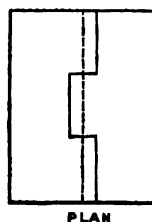


Fig. 5.



The principle of overlap in photometers operating by the diffuse illumination of opaque inclined screens has since been used by Sir John Conroy*, who employed two pieces of white writing-paper, inclined at about 60° to one another. He found, as I did, that 90° is too large a dihedral angle for exact work. Materials such as card and paper are never entirely devoid of specular reflexion. At an incidence of 45° on each surface there is so much specular reflexion of the light as quite to vitiate the observations.

* Phil. Mag. 1883, vol. xv. p. 423.

II. *Periodic Principle in Photometry.*

It is a familiar fact to every person who is accustomed to use the Bunsen photometer that the most convenient way of taking observations is to swing the carriage which supports the screen and mirrors backwards and forwards through a continually-decreasing distance about the position of balance. That position is ultimately found by the eye noting the successive departures from equality produced by rapid small displacements on either side of the position of balance. If these inequalities can be made equal *inter se*, the zero will lie midway; for though the intensity of illumination (assuming the sources of light as points) varies inversely as the square of the distance, the change of intensity for a small change of distance will (irrespective of sign) be the same, to within a small quantity of the next higher order, whether the displacement be toward the standard light or from it. For, taking the initial distance as unity when the illumination is i , then (neglecting small quantities of higher orders), when the distance l is made $1 + \delta r$, the proportional change of illumination is $\mp \frac{2\delta r}{1 \pm 2\delta r}$; or, the change of illumination is approxi-

mately inversely proportional to the distance, and is approximately proportional directly, but with contrary sign, to the displacement.

It is a consequence of the law of fatigue that the eye is much more sensitive to small differences of illumination when these are successively produced than when they are constant in amount. Hence it is easier to estimate the true zero position on the photometer by these successive movements than by simply trying to put the carriage at zero. A difference due to a displacement of two millimetres of the stationary carriage might fail to be perceived. But the eye cannot fail to detect the difference when the carriage is quickly swung to and fro over the distance of two millimetres on either side of the zero; and, judging of the two inequalities on either side, and altering the adjustment until the two inequalities are themselves equal, the zero is determined. As a piece of pure physics, this method of successively approximating to a zero, ill-defined in itself, by means of equal errors on either side, may be compared with the method of Joule for determining the temperature of minimum volume of water.

In the researches of Abney and Festing on the photometry of colour, the same principle of estimating the position of balance by producing rapid movements giving successive

inequalities on either side of the final position was used; and indeed it constitutes the basis of the method of measuring the illuminating effect of any coloured light at different parts of the spectrum. In this case also the motion was produced by hand, by shifting a lever rapidly to and fro.

Indeed it seems probable that, without any specific recognition of its meaning or importance, the method of roughly producing periodic variations in the relative intensities of the two lights has been quite commonly used by many individuals in their work with photometers.

It has seemed to the author worth while to generalize this principle, and to give definition to it, as a recognized principle in photometry. He has therefore essayed to construct a *Vibration-photometer* in which periodic changes in the illumination are deliberately produced, in order thereby to effect systematically that which has hitherto been done unsystematically and by hand.

There are several ways of arriving at the desired result :—

- (1) The “screen” of the photometer may be so mounted on its carriage as itself to vibrate through a small distance, at some convenient frequency.
- (2) The standard light may be moved in some periodic way to and fro through a small distance; though in the case of flame-lamps this is inadvisable.
- (3) The light of the standard lamp may be made to vary by a small percentage in a periodic manner; one way being by revolving in front of it a fan with narrow arms to obscure periodically a portion of its light; another way being to vary periodically the aperture of a Methven slit.
- (4) The light that is to be measured may be made to vary periodically by some known fraction of itself in ways analogous to the preceding.

When any of these things are done the position of balance can be found by simple direct adjustment without the usual delays.

The particular form in which the author has worked out the periodic principle is by mounting upon a spring on the photometer-carriage the paraffin-block translucent “screen” of Dr. Jolly. He finds that a period of $\frac{1}{2}$ of a second is convenient for the purpose. He has also tried an eight-bladed fan, with narrow blades to obscure in passing a fraction of the light. In using with either of these periodic devices the paraffin-block apparatus of Jolly, there is found a curious optical illusion which assists the judgment. As the brightness of the illumination of the two adjacent halves of the

divided block passes through the state of equality, from being brighter on the one side to being brighter on the other, the narrow dark line which divides the two luminous portions appears itself to shift, the apparent displacement being away from the more luminous side. Whether this optical effect arises from irradiation, or from any other cause, it certainly assists the eye in its judgment as to the position of balance.

Some further observations with this device are still in progress.

III. *The Electric-Arc Standard of Light.*

In 1878 experiments were made at Chatham by Abney, Cardew, and others upon the electric arc, in the course of which the practical invariability of the intrinsic illumination of the crater-surface of the positive carbon of the arc was established. Abney and Festing, in their researches on the photometry of colour, have since that period used as a standard of white light the light of the crater of the arc. As pointed out by the writer some years ago, this invariability of whiteness, which implies invariability of temperature, is necessarily due to the constancy of the temperature of volatilization of carbon. The introduction into the substance of the carbons of any material having a lower temperature of volatilization, or of any compound which has a temperature of dissociation lower than that of the volatilization of carbon, necessarily lowers the intrinsic brilliancy of the light. This having once been realized, it seemed only natural to suggest as a standard of light the light emitted from a given area of the crater-surface of a pure carbon. This suggestion was made by the author last year when writing from Rome some remarks for the discussion of the paper of Mr. Trotter on the light of the electric arc, read before the Institution of Electrical Engineers. A similar suggestion was independently made by Mr. Swinburne in the same discussion. For some time past the author has been considering the experimental methods for putting into practice the suggestion then made. The only way to secure a constant effective area of crater is to produce a much larger crater than is required, and cover it by an opaque screen pierced with a suitable aperture of standard dimensions. As this screen must be placed very near the arc, it must be kept cool artificially by circulation of water*.

* M. A. Blondel has recently presented to the Société de Physique of Paris an apparatus denominated *arc normale*, in which is embodied this method of carrying out the proposal of Mr. Swinburne and of the author.

As the intrinsic light of the arc is not far from 70 candles per square millimetre, a circular aperture 1 millimetre in diameter will afford a light of about 55 candles. Hence an aperture smaller than this is preferable in a photometric standard for all ordinary photometric work. For the purpose of a special photometric standard with which to compare other arc lamps, a standard light of 1000 candles or some such magnitude is doubtless advantageous. This would require about 14.3 square millimetres of crater-surface, or a circular aperture of about 4.25 millimetres in diameter. For ordinary photometric work an aperture of 0.674 millimetre diameter would give a light of about 25 candles. It is easy to ensure the illumination of the apparent aperture by employing a magnet to deflect the arc to the front face of the carbon.

There is an advantage in using as a standard source of light one whose light is greater than that of the light under measurement. The light under measurement may obviously be balanced either against a smaller light brought nearer to the screen, or against a greater light placed at a greater distance. But if the greater light at the greater distance be employed, there will, for any given inequality of illumination on the screen, be required a greater actual displacement of the moving part, whether screen or light, in order to arrive at the position of balance. Hence any error in reading the scale will be a lesser fraction of the quantity to be measured.

It might have been supposed, *à priori*, that for a given total length of photometric bench (as in a Bunsen photometer from lamp to lamp) the position of the photometric screen which would make errors a minimum would be the position in the centre; balance being sought between two approximately equal lights. Geometrically it is true that a given displacement along the scale produces a minimum change in the difference of the two illuminations, if the point selected be at the centre of the scale. On the other hand, if the total length of the bench be not fixed, it is obvious that the length of bench which will, for a given change in the difference between the two illuminations, yield the greatest actual displacement along the scale will be an infinite length. But in that case, unless infinite lights are used, the two illuminations will both be zero. In fact there is another element to be considered, namely, that in order to make a satisfactory comparison, the eye requires a certain actual brilliancy of illumination in the two surfaces which are to be compared together. Doubtless the habitual patterns of photometer in use have come by natural selection to be of the size that they

are in consequence of the absolute magnitudes of the standards habitually employed. If a six-foot bench is the right sort of apparatus to satisfy the needs of the eye when the standard is of one or two candle-power, obviously a longer bench will be right when standards of greater power are employed, as giving, on the average, similar absolute illuminations of the working surfaces. If the degree of accuracy implied in the possibility of reading to within 2 millimetres' length of scale can be attained with a Bunsen or Jolly photometer when the standard is a 2-candle Methven slit, or a pair of standard sperm-candles, an accuracy of five times as great ought to be attainable if there is used as a standard a 50-candle light. The bench need not in this case be five times as long as the ordinary bench: the half length only need be elongated five-fold on one side of the screen, the other half remaining as before. In other words, if the standard is of 25-fold brilliancy, it must be placed 5 times as far away from the screen as before in order to balance a given light at the same distance as before on the other side. And, so far as such standard light is concerned, a five-fold accuracy will be attained, since any error or uncertainty in reading the scale will be now but a fifth part of the whole scale-reading.

All the foregoing points, then, to the use of a brighter standard light and a longer photometric bench than heretofore. Such a standard might well be afforded by an arc crater viewed through a circular aperture 1 millimetre in diameter, giving about 0.7854 sq. millimetre of crater-surface, with a light of about 55 candles. This should be placed at one end of a bench some five metres in length; the graduations of the scale being, of course, reckoned from the edge of the aperture*.

One not unimportant advantage of the use of such a pin-hole standard is that it may with real propriety be treated as a luminous point; whereas no one can maintain that the flame standards habitually used are even approximately points relatively to the distances at which they are set from the screen. For these the law of inverse squares cannot possibly be true; though it is never the practice to make any corrections for the errors arising from the size of the flame.

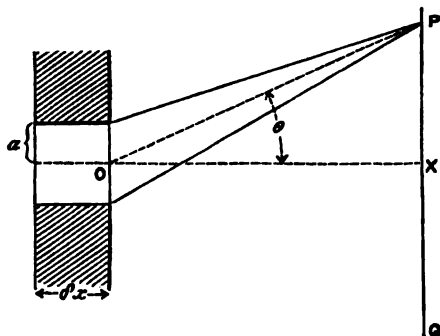
In contemplating the use of circular apertures pierced in metal diaphragms, it becomes necessary to inquire how far

* It is curious to note in this respect that there is usually an erroneous instruction observed with the use of the Methven slit; the distance of the photometric screen being reckoned from the flame behind the slit instead of from the slit itself.

the thickness of the metal will interfere with the illumination of the screen in directions not absolutely in line with the axis of the aperture.

Let the screen PQ (fig. 6) be at a distance $x=OX$ from

Fig. 6.



the diaphragm at O ; the thickness of the diaphragm being called δx , and the radius of the circular aperture in it a . It is required to find the illumination at a point P on the screen at a distance $PX=y$ from the point X which is on the axis of the aperture. Let the angle POX be called θ . Then the apparent aperture as viewed from P will be bounded by two portions of ellipses (the front and back edges of the hole viewed in perspective), having each as semi-major axis a , and as semi-minor axis $a \cos \theta$. These two ellipses will overlap, their centres being displaced by an amount equal to $\delta x \sin \theta$. If we represent the ratio of the thickness of the metal to the radius of the aperture as $\delta x/a = \tan \phi$, then we may write the following expression for A , the effective area of the hole, as visible in the direction OP , as follows:—

$$A = 2a^2 \left\{ \cos \theta \cdot \left[\frac{\pi}{2} - \sin^{-1}(\tan \phi \cdot \tan \theta) \right] - \tan \phi \cdot \tan \theta \sqrt{1 - \tan^2 \phi \cdot \tan^2 \theta} \right\}.$$

Hence, since the real hole has area $= a^2 \pi$, the ratio η of the illumination at P to the central illumination at X will be

$$\eta = \frac{2}{\pi} \left\{ \cos \theta \cdot \left[\frac{\pi}{2} - \sin^{-1}(\tan \phi \cdot \tan \theta) \right] - \tan \phi \cdot \tan \theta \sqrt{1 - \tan^2 \phi \cdot \tan^2 \theta} \right\}.$$

Case (i). To get some idea of the magnitudes involved, let us take a concrete case. Suppose the aperture to be a hole 1 millimetre in diameter and the diaphragm $\frac{1}{2}$ millimetre thick; so that $\tan \phi = 1$. What will the ratio be of the oblique to the central illumination for a point P 2.5 centimetres from the centre X of a screen which is itself at a distance OX = 50 centimetres from the aperture? As a Bunsen disk is seldom more than 5 centimetres in diameter, this is rather an extreme case. Here $\tan \theta = 2.5 \div 50 = 0.05$. So $\theta = 2^\circ 52'$, and $\cos \theta = 0.9975$. Whence $\eta = 0.935$.

Case (ii). Suppose the hole in the diaphragm to be still 1 millimetre in diameter, but the diaphragm to be 2.5 millimetres thick. Here $\tan \phi = 5$. Taking θ as before, we get $\eta = 0.684$.

Case (iii). Suppose, on the other hand, that the hole is made in metal foil only 0.1 millimetre thick, or that, having been pierced through thicker metal the edge has been cut away by countersinking, leaving only a narrow rim 0.1 millimetre in thickness. In this case $\tan \phi = 0.2$. In the case where thin foil is used there is a considerable risk of the metal buckling with heat: and it would be quite possible, from this cause alone, that the axis of the aperture should become oblique by as much as 10° from the axis of the photometer. Assuming then $\theta = 10^\circ$, the ratio of the central illumination, as thus perturbed by the error of centering, to its unperturbed value will be $\eta = 0.940$.

From all this it may be concluded that unless due care be taken in the selection and proper centering of the diaphragm, errors of several per cent. may arise in the photometric measures executed with its means. The errors arising from thickness of the diaphragm diminish, whilst those arising from defect of centering are increased, as the distance from the photometer-screen to the aperture is increased. In the above investigation no account has been taken of the effects of diffraction, which in the case of very minute apertures might become important.

XI. On the Theory of Stellar Scintillation.

By Lord RAYLEIGH, Sec. R.S.*

ARAGO'S theory of this phenomenon is still perhaps the most familiar, although I believe it may be regarded as abandoned by the best authorities. According to it the momentary disappearance of the light of the star is due to accidental interference between the rays which pass the two halves of the pupil of the eye or the object-glass of the telescope. When the relative retardation amounts to an odd multiple of the half wave-length of any kind of light, such light, it is argued, vanishes from the spectrum of the star. But this theory is based upon a complete misconception. "It is as far as possible from being true that a body emitting homogeneous light would disappear on merely covering half the aperture of vision with a half wave-plate. Such a conclusion would be in the face of the principle of energy, which teaches plainly that the retardation in question would leave the aggregate brightness unaltered"†. It follows indeed from the principle of interference that there will be darkness at the precise point which before the introduction of the half wave-plate formed the centre of the image, but the light missing there is to be found in a slightly displaced position‡.

The older view that scintillation is due to the actual diversion of light from the aperture of vision by atmospheric irregularities was powerfully supported by Montigny§, to

* Communicated by the Author.

† *Enc. Brit.*, "Wave Theory," p. 441.

‡ Since the remarks in the text were written I have read the version of Arago's theory given by Mascart (*Traité d'Optique*, t. iii. p. 348). From this some of the most objectionable features have been eliminated. But there can be no doubt as to Arago's meaning. "Supposons que les rayons qui tombent à gauche du centre de l'objectif aient rencontré, depuis les limites supérieures de l'atmosphère, des couches qui, à cause de leur densité, de leur température, ou de leur état hygrométrique, étaient douées d'une réfringence différente de celle que possédaient les couches traversées par les rayons de droite; il pourra arriver, qu'à raison de cette différence de réfringence, les rayons rouges de droite détruisent *en totalité* les rayons rouges de gauche, et que le foyer passe du blanc, son état normal, au vert; Voilà donc le résultat théorique parfaitement d'accord avec les observations; voilà le phénomène de la scintillation dans une lunette rattaché d'une manière intime à la doctrine des interférences" (*l'Annuaire du Bureau des Longitudes pour 1852*, pp. 423, 426).

That the difference between Arago's theory and that followed in the present paper is fundamental will be recognized when it is noticed that, according to the former, the colour effects of scintillation would be nearly independent of atmospheric *dispersion*. Arago gives an interesting summary of the views held by early writers.

§ *Mém. de l'Acad. d. Bruxelles*, t. xxviii. (1856).

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whom we owe also a leading feature of the true theory, that is, the explanation of the chromatic effects by reference to the different paths pursued by rays of different colours in virtue of *regular* atmospheric dispersion. The path of the violet ray lies higher than that of the red ray which reaches the eye of the observer from the same star, and the separation may be sufficient to allow the one to escape the influence of an atmospheric irregularity which operates upon the other. In Montigny's view the diversion of the light is caused by total reflexion at strata of varying density.

But the most important work upon this subject is undoubtedly that of Respighi*, who, following in the steps of Montigny and Wolf, applied the spectroscope to the investigation of stellar scintillation. The results of these observations are summed up under thirteen heads, which it will be convenient to give almost at full length.

(I.) In spectra of stars near the horizon we may observe dark or bright bands, transversal or perpendicular to the length of the spectrum, which more or less quickly travel from the red to the violet or from the violet to the red, or oscillate from one to the other colour; and this however the spectrum may be directed from the horizontal to the vertical.

(II.) In normal atmospheric conditions the motion of the bands proceeds regularly from red to violet for stars in the west, and from violet to red for stars in the east; while in the neighbourhood of the meridian the movement is usually oscillatory, or even limited to one part of the spectrum.

(III.) In observing the horizontal spectra of stars more and more elevated above the horizon, the bands are seen sensibly parallel to one another, but more or less inclined to the axis of the spectrum, passing from red to violet or reversely according as the star is in the west or the east.

(IV.) The inclination of the bands, or the angle formed by them with the axis (? transversal) of the spectrum depends upon the height of the star; it reduces to 0° at the horizon and increases rapidly with the altitude so as to reach 90° at an elevation of 30° or 40° , so that at this elevation the bands become longitudinal.

(V.) The inclination of the bands, reckoned downwards, is towards the more refrangible end of the spectrum.

(VI.) The bands are most marked and distinct when the altitude of the star is *least*. At an altitude of more than 40° the longitudinal bands are reduced to mere shaded streaks, and

* *Roma, Atti Nuovi Lincei*, xxi. (1868); *Assoc. Française, Compt. Rend.* i. (1872) p. 169.

often can only be observed upon the spectrum as slight general variations of brightness.

(VII.) As the altitude increases, the movement of the bands becomes quicker and less regular.

(VIII.) As the prism is turned so as to bring the spectrum from the horizontal to the vertical position, the inclination of the bands to the transversal of the spectrum continually diminishes until it becomes zero when the spectrum is nearly vertical; but the bands then become less marked, retaining, however, the movement in the direction indicated above (III.).

(IX.) Luminous bands are less frequent and less regular than dark bands, and occur well marked only in the spectra of stars near the horizon.

(X.) In the midst of this general and violent movement of bright and dark masses in the spectra of stars, the black spectral lines proper to the light of each star remain sensibly quiescent or undergo very slight oscillations.

(XI.) Under abnormal atmospheric conditions the bands are fainter and less regular in shape and movement.

(XII.) When strong winds prevail the bands are usually rather faint and ill defined, and then the spectrum exhibits mere changes of brightness, even in the case of stars near the horizon.

(XIII.) Good definition and regular movement of the bands seems to be a sign of the probable continuance of fine weather, and, on the other hand, irregularity in these phenomena indicates probable change.

These results show plainly that the changes of intensity and colour in the images of stars are produced by a momentary real diversion of the luminous rays from the object-glass of the telescope; that in the neighbourhood of the horizon rays of different colours are affected separately and successively, and that all the rays of a given colour are momentarily withdrawn from the whole of the object-glass.

Most of his conclusions from observation were readily explained by Respighi as due to irregular refractions, not necessarily or usually amounting (as Montigny supposed) to total reflexions, taking place at a sufficient distance from the observer. The progress of the bands in one direction along the spectrum (II.) is attributed to the diurnal motion. In the case of a setting star, for instance, the blue rays by which it is seen, pursuing a higher course through the atmosphere, encounter an obstacle somewhat later than do the red rays. Hence the band travels towards the violet end of the spectrum. In the neighbourhood of the meridian this cause of a progressive movement ceases to operate.

The observations recorded in (III.) are of special interest as establishing a connexion between the rates with which various parts of the object-glass and of the spectrum are affected. Since the spectrum is horizontal, various parts of its width correspond to various horizontal sections of the objective, and the existence of bands at a definite inclination shows that at the moment when the shadow of the obstacle thrown by blue rays reaches the bottom of the glass the shadow at the top is that thrown by green, yellow, or red rays of less refrangibility. When the altitude of the star reaches 30° or 40° , the difference of path due to atmospheric dispersion is insufficient to differentiate the various parts of the spectrum. The bands then appear longitudinal.

The *definite* obliquity of the bands at moderate altitudes, reported by Respighi, leads to a conclusion of some interest, which does not appear to have been noticed. In the case of a given star, observed at a given altitude, the linear separation at the telescope of the shadows of the same obstacle thrown by rays of various colours will of necessity depend upon the distance of the obstacle. But the definiteness of the obliquity of the bands requires that this separation shall not vary, and therefore that the obstacles to which the effects are due are sensibly at one distance only. It would seem to follow from this that, under "normal atmospheric conditions," scintillation depends upon irregularities limited to a comparatively narrow horizontal stratum situated overhead. A further consequence will be that the distance of the obstacles increases as the altitude of the star diminishes, and this according to a definite law.

The principal object of the present communication is to exhibit some of the consequences of the theory of scintillation in a definite mathematical form. The investigation may be conducted by simple methods, if, as suffices for most purposes, we regard the whole refraction as small, and neglect the influence of the earth's curvature. When the object is to calculate with accuracy the refraction itself, further approximations are necessary, but even in this case the required result can be obtained with more ease than is generally supposed.

The foundation upon which it is most convenient to build is the idea of James Thomson*, which establishes instantaneously the connexion between the curvature of a ray travelling in a medium of varying optical constitution and the rate at which the index changes at the point in question. The following is from Everett's memoir :—

* Brit. Assoc. Rep. 1872. Everett, Phil. Mag. March 1873.

"Draw normal planes to a ray at two consecutive points of its path. Then the distance of their intersection from either point will be ρ , the radius of curvature. But these normal planes are tangential to the wave-front in its two consecutive positions. Hence it is easily shown by similar triangles that a very short line dN drawn from either of the points towards the centre of curvature is to the whole length ρ , of which it forms part, as dv the difference of the velocities of light at its two ends is to v the velocity at either end. That is

$$dN/\rho = -dv/v,$$

the negative sign being used because the velocity diminishes in approaching the centre of curvature. But, since v varies inversely as μ , we have

$$-dv/v = d\mu/\mu.$$

Hence the curvature $1/\rho$ is given by any of the four following expressions :—

$$\frac{1}{\rho} = -\frac{1}{v} \frac{dv}{dN} = -\frac{d \log v}{dN} = \frac{1}{\mu} \frac{d\mu}{dN} = \frac{d \log \mu}{dN}. \quad (1)$$

"The curvatures of different rays at the same point are directly as the rates of increase of μ in travelling along their respective normals." If θ denote the angle which the ray makes with the direction of most rapid increase of index, the curvatures will be directly as the values of $\sin \theta$. In fact, if $d\mu/dr$ denote the rate at which μ increases in a direction normal to the surfaces of equal index, we have

$$\frac{d\mu}{dN} = \frac{d\mu}{dr} \sin \theta,$$

and therefore

$$\pm \frac{1}{\rho} = \frac{1}{\mu} \frac{d\mu}{dr} \sin \theta = \frac{d \log \mu}{dr} \sin \theta. \quad (2)$$

Everett shows how the well-known equation

$$\mu p = \text{const.} \quad (3)$$

can be deduced from (2), p being the perpendicular upon the ray from the centre of *spherical* surfaces of equal index. In general,

$$\frac{1}{\rho} = \frac{1}{r} \frac{dp}{dr}, \quad \sin \theta = \frac{p}{r},$$

and thus

$$-\frac{1}{r} \frac{dp}{dr} = \frac{p}{r} \frac{d \log \mu}{dr},$$

giving (3) on integration.

At a first application of (2) we may find by means of it a first approximation to the law of atmospheric refraction, on the supposition that the whole refraction is small and that the curvature of the earth may be neglected. Under these limitations θ in (2) may be treated as constant along the whole path of the ray; and if $d\psi$ be the angle through which the ray turns in describing the element of arc ds , we have

$$d\psi = \frac{d \log \mu}{dr} \sin \theta ds = \tan \theta d \log \mu.$$

If we integrate this along the whole course of the ray through the atmosphere, that is from $\mu=1$ to $\mu=\mu_0$, we get, as the whole refraction,

$$\psi = \log \mu_0 \tan \theta = (\mu_0 - 1) \tan \theta, \quad \dots \quad (4)$$

for to the order of approximation in question $\log \mu_0$ may be identified with $(\mu_0 - 1)$.

If $\delta\psi$ denote the chromatic variation of ψ corresponding to $\delta\mu_0$, we have from (4)

$$\delta\psi/\psi = \delta\mu_0/(\mu_0 - 1). \quad \dots \quad (5)$$

According to Mascart * the value of the right-hand member of (5) in the case of air and of the lines B and H is

$$\delta\mu_0/(\mu_0 - 1) = \cdot 024. \quad \dots \quad (6)$$

We will now take a step further and calculate the linear deviation of a ray from a straight course, still upon the supposition that the whole refraction is small. If η denote the linear deviation (reckoned perpendicularly) at any point defined by the length s measured along the ray θ , we have

$$\frac{d^2\eta}{ds^2} = \frac{1}{\rho} = \tan \theta \frac{d \log \mu}{ds},$$

so that

$$\frac{d\eta}{ds} = \int \tan \theta d \log \mu = \tan \theta (\mu - 1) + \alpha,$$

α being a constant of integration. A second integration now gives

$$\eta = \tan \theta \int (\mu - 1) ds + \alpha s + \beta, \quad \dots \quad (7)$$

which determines the path of the ray. If y be the height of any point above the surface of the earth, $ds = dy \sec \theta$; so that (7) may also be written

$$\eta = \frac{\sin \theta}{\cos^2 \theta} \int (\mu - 1) dy + \alpha s + \beta. \quad \dots \quad (8)$$

* Everett's C.G.S. System of Units.

The origin of s is arbitrary, but we may conveniently take it at the point (A) where the ray strikes the earth's surface.

We will now consider also a second ray, of another colour, deviating from the line θ by the distance $\eta + \delta\eta$, and corresponding to a change of μ to $\mu + \delta\mu$. The distance between the two rays at any point y is

$$\delta\eta = \frac{\sin \theta}{\cos^2 \theta} \int_0^y \delta\mu dy + \delta\alpha \cdot s + \delta\beta. \quad (9)$$

In this equation $\delta\beta$ denotes the separation of the rays at A, where $y=0$, $s=0$. And $\delta\alpha$ denotes the angle between the rays when outside the atmosphere.

Equation (9) may be applied at once to Montigny's problem, that is to determine the separation of two rays of different colours, both coming from the same star, and both arriving at the same point A. The first condition gives $\delta\alpha=0$, and the second gives $\delta\beta=0$. Accordingly,

$$\delta\eta = \frac{\sin \theta}{\cos^2 \theta} \int_0^y \delta\mu dy \quad (10)$$

is the solution of the question.

The integral in (10) may be otherwise expressed by means of the principle that $(\mu-1)$ and $\delta\mu$ are proportional to the density. Thus, if l denote the "height of the homogeneous atmosphere," and h the elevation in such an atmosphere determined by the condition that there shall be as much air below it as actually exists below y ,

$$\int_0^y \delta\mu dy = \delta\mu_0 h, \quad (11)$$

$\delta\mu_0$ being the value of $\delta\mu$ at the surface of the earth. Equation (10) thus becomes

$$\delta\eta = \frac{\delta\mu_0 h \sin \theta}{\cos^2 \theta}. \quad (12)$$

At the limits of the atmosphere and beyond, $h=l$, and the separation there is

$$\delta\eta = \frac{\delta\mu_0 l \sin \theta}{\cos^2 \theta}. \quad (13)$$

These results are applicable to all altitudes higher than about 10° .

The formulæ given by Montigny (*loc. cit.*) are quite different from the above. That corresponding to (13) is

$$\delta\eta = \delta\mu_0 a \sin \theta, \quad (14)$$

a being the radius of the earth! The substitution of a for l increases the calculated result some 800 times. But this is in a large measure compensated by the factor $\sec^2\theta$ in (13), for at low altitudes $\sec\theta$ is large. According to Montigny the separation at moderately low altitudes would be nearly independent of the altitude, a conclusion entirely wide of the truth.

The value of $(\mu_0 - 1)$ for air at 0° and 760 millim. at Paris is $\cdot 0002927$, so that $\delta\mu_0$ (for the lines B and H) is $\cdot 000007025$. The height of the homogeneous atmosphere is $7\cdot 990 \times 10^5$ centim., and thus $\delta\eta$ reckoned in centim. is

$$\delta\eta = 5\cdot 612 \frac{h \sin \theta}{l \cos^2 \theta} \dots \dots \dots (15)$$

The following are a few corresponding values of θ and $\sin \theta / \cos^2 \theta$:—

| θ . | $\sin \theta / \cos^2 \theta$. | θ . | $\sin \theta / \cos^2 \theta$. |
|------------|---------------------------------|------------|---------------------------------|
| 0° | 0.000 | 60° | 3.46 |
| 20 | 0.387 | 70 | 8.03 |
| 40 | 1.095 | 80 | 32.66 |

Thus at the limit of the atmosphere the separation of rays which reach the observer at an apparent altitude of 10° is 185 centim. Nearer the horizon the separation would be still greater, but its value cannot well be found from (15). Although these estimates are considerably less than those of Montigny, the separation near the horizon seems to be sufficient to explain the vertical position of the bands in the spectrum, recorded by Respighi (I.). The fact that the margin is not very great suggests that the obstacles to which scintillation is due may often be situated at a considerable elevation.

We have now to consider the effect of an obstacle situated at a given point B at level y on the course of the ray. And the first desideratum will be the estimation of the separation at A, the object-glass of the telescope, of rays of various colours coming from the same star, which all pass through the given point B. It will appear at once that no fresh question is raised. For, since the rays come from the same star at the same time, $\delta\alpha = 0$, and thus by (9) $\delta\eta_A = \delta\beta$. The

value of $\delta\beta$ is given at once by the condition that $\delta\eta_B=0$. Thus

$$-\delta\eta_A = \frac{\sin \theta}{\cos^2 \theta} \int_0^y \delta\mu dy = \frac{\delta\mu_0 h \sin \theta}{\cos^2 \theta}, \quad . . . \quad (16)$$

as before. The discussion, already given of (15), is thus immediately applicable.

Equation (16) solves the problem of determining the inclination of the bands seen in the spectra of stars not very low (III.). It is only necessary to equate $-\delta\eta_A$ to the aperture of the telescope. $\delta\mu_0$ then gives the range of refrangibility covered by the bands as inclined. In practice h would not be known beforehand; but from the observed inclination of the bands it would be possible to determine it.

In a given state of the atmosphere h , so far as it is definite, must be constant and then $\delta\mu_0$ must be proportional to $\cos^2 \theta / \sin \theta$. This gives the relation between the altitude of the star and the inclination of the bands.

When θ is small, $\delta\mu_0$ is large; that is, the bands become longitudinal.

As a numerical example, let us suppose that the aperture of the telescope is 10 centim., and that at an altitude of 10° the obliquity of the bands is such that the vertical diameter of the object-glass corresponds to the entire range from B to H. In this case (15) gives

$$h = \frac{10l}{185} = 0.054 l,$$

indicating that the obstacles to which the bands are due are situated at such a level that about $\frac{1}{20}$ of the whole mass of the atmosphere is below them.

The next question to which (9) may be applied is to find the angle $\delta\alpha$ outside the atmosphere between two rays of different colours which pass through the *two* points A and B. Here $\delta\eta_A=0$, and thus $\delta\beta=0$. And further, since $\delta\eta_B=0$, we get

$$-\delta\alpha = \frac{\sin \theta}{s \cos^2 \theta} \int_0^y \delta\mu dy = \frac{\delta\mu_0 h \tan \theta}{y}. \quad . . . \quad (17)$$

If the height of the obstacle above the ground be so small that the density of the air below it is sensibly uniform, then $h=y$, and

$$-\delta\alpha = \delta\mu_0 \tan \theta. \quad . . . \quad (18)$$

In this case the angle is the same as that of the spectrum of

the star observed at A, as appears from (4) and (5). In general, y is greater than h , so that $\delta\alpha$ is somewhat less than the value given by (18).

The interest of (18) lies in the application of it to find the time occupied by a band in traversing the spectrum in virtue of the diurnal motion, according to Respighi's observation (II.). The time required is that necessary for the star to rise or fall through the angle of its dispersion-spectrum at the altitude in question. At an altitude of 10° , this angle will be $8''$, being always about $\frac{1}{10}$ of the whole refraction. The rate at which a star rises or falls depends of course upon the declination of the star and upon the latitude of the observer, and may vary from zero to 15° per hour. At the latter maximum rate the star would describe $8''$ in about one half of a second, which would therefore be the time occupied by a band in crossing the spectrum under the circumstances supposed. In the case of a star quite close to the horizon, the progress of the band would be a good deal slower.

The fact that the larger planets scintillate but little, even under favourable conditions, is readily explained by their sensible apparent magnitude. The separation of rays of one colour thus arising during their passage through the atmosphere is usually far greater than the already calculated separation, due to chromatic dispersion; so that if a fixed star of no apparent magnitude scintillates in colours, the different parts of the area of a planet must *à fortiori* scintillate independently. But under these circumstances the eye perceives only an average effect, and there is no scintillation visible.

The non-scintillation of small stars situated near the horizon may be referred to the failure of the eye to appreciate colour when the light is faint.

In the case of stars higher up the whole spectrum is affected simultaneously. A momentary accession of illumination, due to the passage of an atmospheric irregularity, may thus render visible a star which on account of its faintness could not be steadily seen through an undisturbed atmosphere*.

In the preceding discussion the refracting obstacles have for the sake of brevity been spoken of as throwing sharp shadows. This of course cannot happen, if only in consequence of diffraction; and it is of some interest to inquire into the magnitude of the necessary diffusion. The theory of diffraction shows that even in the case of an opaque screen with a definite straight boundary, the transition of illumination at the edge of the shadow occupies a space such

* The theory of Arago leads him to a directly opposite conclusion (*loc. cit.* p. 381).

as $\sqrt{(b\lambda)}$, where λ is the wave-length of the light, and b is the distance across which the shadow is thrown. We may take λ at 6×10^{-5} centim., and if b be reckoned in kilometres, we have as the space of transition, $\sqrt{(6b)}$. Thus if b were 4 kilometres, the space of transition would amount to about 5 centim. The inference is that the various parts of the aperture of a small telescope cannot be very differently affected unless the obstacles to which the scintillation is due are at a less distance than 4 kilometres.

One of the principal outstanding difficulties in the theory of scintillation is to see how the transition from one index to another in an atmospheric irregularity can be sufficiently sudden. The fact that the various parts of a not too small object-glass are diversely affected seems to prove that the transitions in question do not occupy many centimetres. Now, whether the irregularity be due to temperature or to moisture, we should expect that a transition, however abrupt at first, would after a few minutes or hours be eased off to a greater degree than would accord with the above estimate. Perhaps the abruptness of transition is, as it were, continually renewed by the coming into contact of fresh portions of light and dense air as the ascending and descending streams proceed in their courses. The speculations and experiments of Jevons on the Cirrus form of Cloud* may find some application here. A preliminary question requiring attention is as to the origin of the irregularities which cause scintillation. Is it always at the ground, and mainly under the influence of sunshine? Or may irregular absorption of solar heat in the atmosphere, due to varying proportions of moisture, give rise to transitions of the necessary abruptness? Again, we may ask how many obstacles are to be supposed operative upon the same ray? Is the ultimate effect only a small residue from many causes in the main neutralizing one another? It does not appear that in the present state of meteorological science satisfactory answers can be given to these questions.

A complete investigation of atmospheric refraction can only be made upon the basis of some hypothesis as to the distribution of temperature; but, as has already been hinted, a second approximation to the value of the refraction can be obtained independently of such knowledge and without difficulty. In Laplace's elaborate investigation it is very insufficiently recognized, if indeed it be recognized at all,

* Phil. Mag. xiv. p. 22, 1857. For a mathematical investigation, by the author, see Math. Soc. Proc. xiv. April 1883.

that the whole difficulty of the problem depends upon the curvature of the earth. If this be neglected, that is if the strata are supposed to be plane, the desired result follows at once from the law of refraction, without the necessity of knowing anything more than the conditions of affairs at the surface. For in virtue of the law of refraction,

$$\mu \sin \theta = \text{constant};$$

so that if θ be the apparent zenith distance of a star seen at the earth's surface, and $\delta\theta$ the refraction, we have at once

$$\mu_0 \sin \theta = \sin (\theta + \delta\theta), \quad (19)$$

from which the refraction can be rigorously calculated. If an expansion be desired,

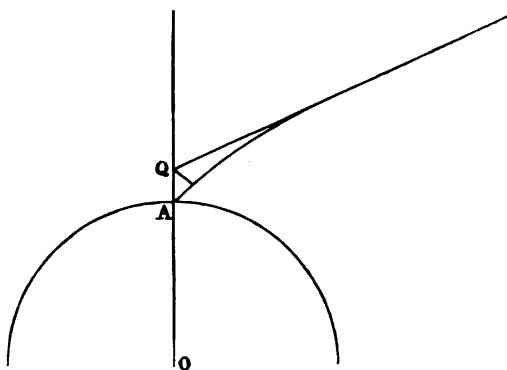
$$\begin{aligned} \delta\theta &= \sin \delta\theta = \tan \theta (\mu_0 - \cos \delta\theta) \\ &= (\mu_0 - 1) \tan \theta \{1 + \tfrac{1}{2}(\mu_0 - 1) \tan^2 \theta\} \quad . . . (20) \end{aligned}$$

is the second approximation.

When the curvature of the earth is retained, so that the atmospheric strata are supposed to be spheres described round O the centre of the earth, the appropriate form of the law of refraction is

$$\mu p = \text{constant}.$$

Thus, if A be the point of observation at the earth's surface



where the apparent zenith distance is θ , and if the original direction of the ray outside the atmosphere meet the vertical OA at the point Q,

$$\mu_0 \cdot OA \cdot \sin \theta = OQ \cdot \sin (\theta + \delta\theta);$$

or if $OA = a$, $AQ = c$,

$$\mu_0 a \sin \theta = (a + c) \sin (\theta + \delta\theta). \quad . . . (21)$$

If c be neglected altogether, we fall back upon the former equations (19), (20). For the purposes of a second approximation c , though it cannot be neglected, may be calculated as if the refraction were small, and the curvature of the strata negligible. If η be the whole linear deviation of the ray due to the refraction,

$$c = \eta / \sin \theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

and, as in (16),

$$\eta = (\mu_0 - 1) l \sin \theta / \cos^2 \theta, \quad . \quad . \quad . \quad (23)$$

so that

$$c = \frac{(\mu_0 - 1)l}{\cos^2 \theta}. \quad (24)$$

By equations (21), (24) the value of $\delta\theta$ may be calculated from the trigonometrical tables without further approximation.

To obtain an expansion, we have

$$\begin{aligned}\delta\theta &= \sin \delta\theta = \frac{\mu_0 \tan \theta}{1 + c/a} - \tan \theta \cos \delta\theta \\ &= \tan \theta \left\{ \frac{\mu_0}{1 + c/a} - 1 + \frac{1}{2}(\delta\theta)^2 \right\} \\ &= (\mu_0 - 1) \tan \theta \left\{ 1 - \frac{\mu_0 c}{(\mu_0 - 1)a} + \frac{1}{2}(\mu_0 - 1) \tan^2 \theta \right\} \\ &= (\mu_0 - 1) \left(1 - \frac{l}{a} \right) \tan \theta \\ &\quad - (\mu_0 - 1) \left(\frac{l}{a} - \frac{\mu_0 - 1}{2} \right) \tan^3 \theta. \quad \dots \quad (25)\end{aligned}$$

To this order of approximation the refraction can be expressed in terms of the condition of things at the earth's surface, and (25) is equivalent to an expression deduced at great length by Laplace.

From the value of l already quoted, and $a = 6.3709 \times 10^8$ centim., we get

$$l/a = 0.0012541. \quad (26)$$

If further we take as the value under standard conditions for the line D

$$\mu_0 - 1 = 0.0002927, \quad . \quad . \quad . \quad . \quad . \quad (27)$$

we find as the refraction expressed in seconds of arc

$$\delta\theta = 60'' \cdot 29 \tan \theta - 0'' \cdot 06688 \tan^3 \theta. \quad (28)$$

In (28) θ is the apparent zenith distance, and it should be

understood that the application of the formula must not be pushed too close to the horizon. If the density of the air at the surface of the earth differ from the standard density (0° and 760 millim.) the numbers in (28) must be altered proportionally. It will be observed that the result has been deduced entirely *à priori* on the basis of data obtained in laboratory experiments.

It may be convenient for reference to give a few values calculated from (28) of the refraction, and of the dispersion, reckoned at $\frac{1}{40}$ of the refraction.

| Apparent zenith distance. | Refraction. | Dispersion (B to H). |
|---------------------------|-------------|----------------------|
| 0 | 0.0 | 0.0 |
| 20 | 21.9 | .5 |
| 40 | 50.5 | 1.3 |
| 45 | 1 0.2 | 1.5 |
| 60 | 1 40.1 | 2.5 |
| 70 | 2 44.2 | 4.1 |
| 75 | 3 41.5 | 5.5 |
| 80 | 5 29.7 | 8.2 |
| 85 | 9 49.2 | 14.7 |

The results of the formula (28) agree with the best tables up to a zenith distance of 75° , at which point the value of the second term is $3''.5$. For 85° the number usually given is about $10' 16''$, and for 90° about $36'$; but at these low altitudes the refraction is necessarily uncertain on account of irregularities such as those concerned in the production of mirage.

XII. *Notices respecting New Books.*

A Memorial of JOSEPH HENRY. Published by Order of Congress.
Washington: Government Printing Office. 1880.

ON the death of Prof. Henry, more than fourteen years ago, the Senate and House of Representatives of the United States of America resolved concurrently that their members, with the Vice-President of the Republic, should take part in a memorial service. It was also resolved that the exercises and other memorial addresses should be printed at public expense, and this book of 528 pages is the result. It contains prayers, sermons, and speeches by eminent clergymen, statesmen, and scientific men; and some of the discourses, notably that of W. B. Taylor, which is given in 221 pages, give an account of Prof. Henry's services to Physical Science and

to his country. We cannot agree with everything which his eulogists have said on his behalf; the occasion was not one on which it was likely that his fame would be depreciated; but it is a wonderful fact that he deserved nearly all the praise which was so lavishly bestowed upon his memory. A hardworking ingenious philosopher, full of love for scientific research, with great natural ability, and not ignorant of the limits of his powers, he had in the sixteen years before 1846 done great services to the world in all departments of Physics, but especially in Electromagnetism and Telegraphy. In 1846 he proceeded to carry out the intentions of Mr. Smithson, of England, who had left by will to the United States more than one hundred thousand pounds for the cause of Science. Till he died, his biography and the history of the Smithsonian Institution were the same. His scientific investigations became more practical; he became a great administrator. We have one or two great men in England who possess the same administrative power, but we can think of no such administrator who was or is also in the front rank of experimental Philosophers. He refused increase in salary; he seemed to think that services to science were like justice, and ought not to be sold for money. Till he died he was ever ready to serve his country, and for her sake he made many interesting experimental researches. As General Garfield said, "the twelve hundred lighthouses that shine on our shores, the three thousand buoys along our rivers and coasts, testify to his faithfulness and efficiency." It is, however, when his colleagues speak of him as a personal friend in some of these memorial addresses that the reader gets an idea of what a great thing it is to the world that such a man as Professor Henry ever lived.

The Fundamental Theorems of Analysis Generalized for Space (1).
(31 pp.)

The Imaginary of Algebra (2). (24 pp.)

THESE are two papers (in pamphlet form) by Dr. A. Macfarlane, Professor of Physics in the University of Texas.

(1) forms a paper read before the New York Mathematical Society (May 7, 1892).

Starting from the fundamental theorem for the cosine and sine of the sum of two angles in terms of the cosines and sines of the component angles, with the aid of Quaternionic analysis, the writer proceeds to give a generalization of it to space and of De Moivre's theorem: he then obtains the product of two angles in space, when expressed in terms of oblique components. On these foundations he builds up generalizations of the exponential theorem (in connexion with this he gives a further generalization in which he arrives at what he calls *quinternions*), of the Binomial, Multinomial, and Logarithmic theorems, and then concludes with generalizations of hyperbolic Trigonometry and of Differentiation. The paper is a fine piece of pure analysis.

(2) is a continuation of the author's 'Principles of the Algebra of Physics.'

It opens with a historical note of the theory and use of $\sqrt{-1}$ by three classes of Analysts, and goes on to applications of quaternions to Spherical Trigonometry, to Circular Spirals, and to Hyperbolic Spirals. *En route* the hyperbolic non-Euclidian Geometry and some other points which have recently occupied attention are touched upon. This paper and the recent Trigonometries by Levett and Davison and by Hayward show how the ideas of De Morgan's *Double Algebra* are coming to the front.

Die Theorie der Beobachtungsfehler und die Methode der Kleinsten Quadrate mit ihrer Anwendung auf die Geodäsie und die Wassermessungen. Von OTTO KOLL. (Berlin, Julius Springer, 1893; pp. viii + 324 and 31 pages of formulæ.)

Mansfield Merriman's 'Textbook of the Method of Least Squares' (Macmillan, 1885) contains 174 pp. + 20 pp. of Appendix and Tables: Dr. Bobek's *Lehrbuch der Ausgleichsrechnung nach der Methode der Kleinsten Quadrate* (Maier, Stuttgart, 1891) has pp. viii + 176; and W. Woolsey Johnson's 'The Theory of Errors and Method of Least Squares' (Wiley, New York, 1892) has pp. x + 174 (and is 12mo, not 8vo).

Now as Prof. Otto's page is much larger than that of any of the above, it is evident that in quantity of matter it "takes the cake."

The first part (pp. 1-42) is devoted to the Errors of Observation, and the remainder, in seven divisions, discusses the Method of Least Squares. The author very rarely cites previous writers, and none of these are familiar to us except Hagen. The simple text is perhaps equal in extent to that of the respective works cited at the commencement, the special feature is the great amount of illustrative examples which are fully worked out. It is this which makes Prof. Koll's work such a practical one. The formulæ at the end will be useful for reference to the student. It only remains to say that the type is very clear, the figures numerous and good, and the arrangement of the page conducive to easy reading.

XIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xxxv. p. 469.]

March 22, 1893.—W. H. Hudleston, Esq., M.A., F.R.S.,
President, in the Chair.

THE following communications were read :—

1. "On the Jaw of a new Carnivorous Dinosaur from the Oxford Clay of Peterborough." By R. Lydekker, Esq., B.A., F.G.S.

2. On a Mammalian Incisor from the Wealden of Hastings." By R. Lydekker, Esq., B.A., F.G.S.

3. "On an Intrusion of Muscovite-biotite-gneiss in the South-eastern Highlands, and its accompanying Thermo-metamorphism." By George Barrow, Esq., F.G.S., of the Geological Survey.

The area to which this paper refers lies in the north-eastern part of Forfarshire, and is drained by the two Esks. The author first describes the distribution, mode of occurrence, and petrological characters of the intrusive masses. In the north-western portion of the area the intrusive rock is always a gneiss, and occurs in thin tongues which permeate the surrounding rocks. Towards the south-east these tongues amalgamate and form large masses, in which the foliation is less marked. Moreover, in this direction the large masses are often fringed with pegmatite, especially on their southern and eastern edges. Where the rock is a gneiss, it is composed of oligoclase, muscovite, biotite, and quartz, but contains no microcline. As the gneissose character becomes less marked, the oligoclase diminishes in amount, and microcline begins to appear, especially towards the margins of the masses. In the most south-easterly of these microcline is greatly in excess of oligoclase.

The differences in structure and composition of these masses are believed by the author to be due to the straining off of the crystals of earlier consolidation during intrusion under great pressure. The still liquid potash-bearing portion of the magma was squeezed out and forced into every plane of weakness in the surrounding rocks; and that portion of it which contained the highest percentage of potash finally consolidated as pegmatite.

Special attention is directed to the distribution of pegmatite. This rock is widely distributed in the Southern Highlands, and cuts across every known system of folding. It is consequently newer than any member of the metamorphic series.

The surrounding metamorphic schists are next dealt with. These are remarkable for their highly crystalline condition, and also on account of the presence of many minerals known to occur in regions where thermometamorphism has taken place. The characters of the more important minerals are described in detail. The rocks of the metamorphic area become less and less crystalline as they are followed towards the Highland border. Three zones, characterized respectively by the minerals sillimanite, cyanite, and staurolite, have been roughly mapped. The more important rocks found in these zones are described in detail, and evidence is given to show that the boundaries between the zones do not in all cases coincide with the strike of the rocks. Thus, a thin bed of quartzite, which retains its character in consequence of the simplicity of its chemical composition, may be followed through all the zones; whereas the bed adjacent to it is in the outer zone a staurolite-schist, in the intermediate zone a cyanite-gneiss, and near the contact with the igneous rock a coarse sillimanite-gneiss. Evidence is given to show that the original rocks formed a sedimentary series.

The phenomena are compared with those of other areas where thermometamorphism has taken place; and the conclusion is reached

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that the differences are of *degree* rather than of *kind*. The special features of the area in question are attributed to the depth at which the change was produced.

April 12th.—W. H. Hudleston, Esq., M.A., F.R.S.,
President, in the Chair.

The following communications were read :—

1. "On some Palæozoic Ostracoda from Westmoreland." By Prof. T. Rupert Jones, F.R.S., F.G.S.

2. "On some Palæozoic Ostracoda from the Girvan district in Ayrshire." By Prof. T. Rupert Jones, F.R.S., F.G.S.

3. "On the Dwindling and Disappearance of Limestones." By Frank Rutley, Esq., F.G.S.

The existence of chert between two sheets of eruptive rocks at Mullion Island seemed to the author to require some explanation. Cherts are usually associated with limestones, and the absence of limestones in many cases where cherts are found points to their removal by underground waters. The older the limestone, the greater the probability of its thickness having dwindled. The thicknesses of the Ordovician, Silurian, Devonian, and Carboniferous Limestones seem to be in the ratio of 1 : 15 : 15 : 100. Many limestones once existing in Archæan rocks may have disappeared, as also limestones in later rocks.

The author comments on the difficulty of distinguishing some cherty rocks from felstones.

Two Appendices are added to the paper, the first on the transference of lime from older to newer deposits, and the second on the formation of nodular limestone-bands.

4. "On some Bryozoa from the Inferior Oolite of Shipton Gorge, Dorset.—Part II." By Edwin A. Walford, Esq., F.G.S.

April 26th.—W. H. Hudleston, Esq., M.A., F.R.S.,
President, in the Chair.

The following communications were read :—

1. "The Origin of the Crystalline Schists of the Malvern Hills." By Charles Callaway, D.Sc., M.A., F.G.S.

This paper is the third of a series of three. In the first of these, published in the Quarterly Journal in 1887, the author contended that many of the gneisses and schists of Malvern were formed out of igneous rocks. In the second, which appeared in the Journal in 1889, he discussed the origin of secondary minerals at shear-zones in the Malvern rocks, and arrived at the conclusion that all the mica and much of the felspar, to say nothing of quartz and other minerals, were of secondary origin. In the present paper the author first pointed out that some of the most important mineral changes described in his second communication—such, for example,

as the conversion of chlorite into biotite—had since been confirmed by independent investigators. He held that, as a whole, the gneisses and schists of Malvern had been formed by the crushing and shearing of consolidated igneous rocks; but he did not deny the possibility that here and there the foliated structure might have been produced in a fused mass. In the first stage of metamorphism the diorite or granite was crushed and decomposed. This slightly compressed rock could be traced step by step into a typical gneiss or schist. The signs of pressure progressively increased, and the mineral and chemical changes became proportionately greater. Reconstruction set in. The process of metamorphism did not always follow the same lines. Felspar was sometimes crushed into seams of fragments, and these, by partial re-fusion and pressure, were converted into gneissose lenticles of quartz and felspar. Intervening chlorite was changed to biotite, or even to muscovite or sericite. Thus a typical gneiss, consisting of quartz-felspar lenticles in a felt-work of mica, was formed out of a diorite. Sometimes the felspar was reconstituted without becoming fragmental; and it was then deposited on, or it included, idiomorphic mica. Or a soda-lime felspar might, by a process of corrosion, be converted into quartz, or a soda-felspar, or both.

In an early stage of metamorphism, the rock was often dirty and rotten through the abundance of chlorite and disseminated iron-oxide. The former being changed to mica, and the latter being either absorbed in the production of biotite, or reconstituted in a crystalline form, a sound clear gneiss was the result. In the completed product, the signs of crushing and shearing were often entirely wanting. Even strain-shadows were rare in it. The metamorphism, however, was demonstrated in numerous localities by tracing the gradations inch by inch, and by the subsequent study of large numbers of microscopic slides, in which the transition was still more clearly seen than in the field.

The classification of the Malvern schists originally proposed was somewhat enlarged, the injection-schists being subdivided into (1) Schists of Primary Injection, in which one rock was injected into another, and (2) Schists of Secondary Injection, formed by the infiltration of secondary minerals along shear-planes.

One of the most important of the chemical changes produced in the conversion of a diorite into an acidic schist was the elimination of magnesia. This was proved by analyses. The recent researches of Mr. Alexander Johnstone had shown that even in the laboratory, and at the ordinary temperatures, carbonated waters were able to remove magnesia from certain of its combinations with silica.

2. "Supplementary Notes on the Metamorphic Rocks around the Shap Granite." By Alfred Harker, Esq., M.A., F.G.S., and J. E. Marr, Esq., M.A., F.R.S., Sec.G.S.

This paper contains some additions and corrections to the work submitted to the Society by the authors on a previous occasion (see Quart. Journ. Geol. Soc. vol. xlvii. p. 266). In the present

communication special attention is paid to the alteration of a group of basic volcanic rocks by the granite.

May 10th.—W. H. Hudleston, Esq., M.A., F.R.S.,
President, in the Chair.

The following communications were read:—

1. "The Felsites and Conglomerates between Bethesda and Llanllyfni, North Wales." By Prof. J. F. Blake, M.A., F.G.S.

The author brought forward fresh evidence in support of the views he had previously expressed as to the Cambrian age of these felsites, and as to the unconformity of the conglomerates on the Purple Slates.

A new tunnel-section at Penrhyn Quarry was described, in which felsite was followed by St. Ann's Grit with a conglomerate-band, and there lying in the midst of the Cambrian Series. After a word or two on the conglomerate on Moel Rhiw-wen, the sections on either side of Llyn Padarn were discussed in detail, and it was shown that the distribution of the rocks on the surface of the country could only be explained by the unconformable position of the conglomerates and grits, which, moreover, lie nearly horizontal.

After a discussion of the conglomerates of Bettws-Garmon, a detailed section of the adit at Moel Tryfaen was given, in which it was shown that there was only a 3 ft. 6 in. band of conglomerate next the Purple Slates, followed by 1350 feet of Banded Slates and Laminated Grits with four distinct intercalated bands of felsite; and it was argued that the conglomerate on the summit, 55 yards across, could scarcely be represented by this thin band. Finally, the distribution of rocks on Mynydd-y-Celgwyn was shown to be satisfactorily explained by unconformity.

Incidentally it was mentioned that a band of rock in the felsite at Llyn Padarn, which had been considered to be a deposited slate, was in reality an intrusive igneous rock.

The conglomerates described were considered to be an overlap of the Bronllwyd Grit.

2. "The Llandovery and Associated Rocks of the Neighbourhood of Corwen." By Philip Lake, Esq., M.A., F.G.S., and Theo. T. Groom, Esq., B.Sc., F.G.S.

The area described forms a part of the northern slope of the Berwyn Hills, and stretches along the southern bank of the Dee from Corwen to Pen-y-glog. The beds of the Berwyns are here thrown into a series of folds which run nearly E.-W.; and the northerly limbs of these folds are long and low, while the southerly limbs are short and steep. The folds are cut through by a number of faults which run nearly E.-W., generally along the crests of the anticlinals, and these invariably throw down towards the north. The southern bank of the Dee Valley is here formed by these faults.

A second series of faults running about 20° W. of N. to 20° E. of S. is of later date. One of these, near Corwen, presents some

peculiar features, since its downthrow in some places is on the east and in others on the west.

The lowest beds present are bluish slates with numerous Bala fossils. These are succeeded immediately by the Corwen Grit of Prof. Hughes. No fossils have been found in this at Corwen; but in a grit occupying a similar position at Glyn Ceiriog numerous fossils have been discovered. The Corwen grit is succeeded by grey slates with grit-bands; and in Nant Cawrddu near Corwen, and Nant Llechog near Pen-y-glog, these slates are followed by banded black shales containing numerous graptolites of the *Monograptus gregarius*-zone. Above these are pale bluish slates; and nothing further is exposed till we reach the Tarannons. The Corwen Grit clearly forms the base of the Llandovery in this area, as suggested by Prof. Hughes.

May 24th.—W. H. Hudleston, Esq., M.A., F.R.S.,
President, in the Chair.

The following communications were read :—

1. "Notes on Dartmoor." By Lieut.-General C. A. McMahon, F.G.S.

The author alludes to Part II. of a memoir on the British Culm Measures recently published by Mr. Ussher, F.G.S., in which the view is advanced that the granite of Dartmoor resulted from the metamorphism of pre-existing rocks which had in a rigid state offered obstruction to a long-sustained N. and S. squeeze, and that their fusion and consequent consolidation were effected *in situ*.

The author gives some of the results of a visit to the western borders of Dartmoor. He details some examples of eruptive granite-veins intruding into Culm beds in the immediate vicinity of the main mass of granite. The latter, in the locality described, is porphyritic down to its boundary, and the veins are also porphyritic. All the circumstances lead the author to believe that these veins are real apophyses from the main mass, and that the view adopted by De la Beche regarding the origin of the Dartmoor granite is the true one. The author alludes to some features in the Meldon granite-dyke not before noted; gives some detailed observations in the bed of the River Tavy, and offers an explanation of the way he thinks the fine-grained marginal variety of the granite, seen in that locality, has been produced.

The author comments on the improbability that a tremendous squeeze sufficient to fuse 225 square miles of a pre-Devonian rock into granite should have left the Culm Measures outside the zone of marginal contact-metamorphism almost untouched.

The author, in conclusion, alludes to the often-observed pseudo-stratification of the Dartmoor granite, and urges that the cause of this is not the one suggested by De la Beche, but that it is due to sub-aerial agencies.

2. "On some Recent Borings through the Lower Cretaceous Strata in East Lincolnshire." By A. J. Jukes-Browne, Esq., B.A., F.G.S.

The borings described in this paper are at Alford, Willoughby, and Skegness, and disclose the existence of an unsuspected anticlinal axis bringing up Lower Cretaceous rocks beneath the Drift. In the Willoughby boring, beneath the Drift, a brown sand was obtained, apparently the 'Roach' division of the Lower Cretaceous, and below it the Tealby Clays (108 feet), oolitic ferruginous beds (18 feet), and sandstone and sand regarded as the Spilsby Sandstone. In the Alford boring the highest solid rock appears to belong to the basal beds of the Red Chalk, and below it is Carstone, and then clay.

The axis of the anticlinal appears to pass between Alford and the border of the Wolds, and is probably continued in a north-westerly direction beyond the village of Claythorpe.

The result of the information now obtained makes it probable that the Chalk tract which lies to the south-east of the Calceby valley is completely isolated from the rest of the Chalk area.

XIV. Intelligence and Miscellaneous Articles.

SOME CORRECTIONS TO A PAPER ON THE LAWS OF MOLECULAR FORCE.

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN,

WITH your permission I should like to make some corrections in my paper on the Laws of Molecular Force, published in the *Philosophical Magazine* for March of this year. In Section 2, page 222, it is stated that the equation for element gases is almost identical with that of Van der Waals but is a little simpler. This is a mistake, for the equation is absolutely that of Van der Waals. At the end of Section 4 and in Section 5 and elsewhere, the term which in the characteristic equation contains the absolute temperature T as a factor is spoken of as the kinetic-energy term, and is assumed to represent kinetic energy. This is an error, for the term includes also the virial of the forces called into play during the collisions of molecules. To anyone who has read my paper on a Kinetic Theory of Solids (*Phil. Mag.* December 1891) the error will appear a strange one, seeing that the Virial of the collisional forces is there treated as of fundamental importance; but the paper on Solids, though published before that on Molecular Force, was written after it, and circumstances prevented my correcting the mistake in the earlier paper before it was read at the Physical Society and published in the *Philosophical Magazine*. Section 5 is so much affected by the error that I wish it to be considered as

cancelled. In Table XXI., Section 6, the ratio k/β for CO_2 is given as 4 instead of 2.5, the logarithm having been copied in place of the number.

Yours obediently,

Melbourne, April 1893.

WILLIAM SUTHERLAND.

ON A REMARKABLE PHENOMENON OF OXIDATION OF PURE ALUMINIUM WHEN IN CONTACT WITH MERCURY. BY E. O. ERDMANN.

As soon as the two metals are in actual contact, snow-white filiform or straw-shaped formations result, growing from the point of contact of the two metals, which in a few minutes acquire a length of 2 to 3 centim. Under the microscope they appear as tube-shaped or plate-shaped veils, of extreme delicacy and perfectly amorphous. If they are detached by tapping or shaking they look like lint. Chemical investigation shows that they consist of pure aluminium hydrate.

It is immaterial for the formation of this oxide whether the contact between the metals is effected by rubbing, or whether the surfaces are purified with hydrochloric acid or caustic soda, and subsequent washing with much water and drying with blotting-paper.

The cause of this peculiar oxidation might be sought for in :—

(1) The formation of an easily oxidizable amalgam of aluminium, which always forms at the surface of contact in the degree in which aluminium oxidizes in moist air.

(2) The electrolytic decomposition of a thin layer of water, which is condensed on the surfaces of the two metals which form the element.

(3) That the highly positive aluminium by contact with mercury acquires a greater affinity for oxygen, in the same manner as, according to Magnus, iron-filings do when hanging to a magnet.—*Physical Society of Berlin*, November 18, 1892; *from Wiedemann's Annalen*, No. 1, 1893.

ON THE PROCESSES WHICH TAKE PLACE AT THE BOUNDARY BETWEEN TWO SOLUTIONS OF DIFFERENT CONCENTRATION WHEN A CURRENT IS PASSED. BY GEORGE H. ZAHN.

The results of these experiments are stated by the author as follows. Besides the well-known formation of hydroxides of magnesium, calcium, and copper above the boundary of a dilute solution over a concentrated one of the same salt when an electrical current passes from the concentrated to the dilute solution, it is possible, when the concentrations are very different, to observe the formation of a solid with barium, strontium, aluminium, iron, manganese, and zinc in combination with several acids. Silver does not exhibit such a behaviour. In each case, even with silver, and with the salts of potassium and of sodium, which form readily

soluble hydrates, an alkaline reaction is observed above the boundary in the dilute solution, even with no great difference of concentration when dimethyl-orange is present, but not with less sensitive reagents. Gmelin* found in the electrolysis of Na_2SO_4 in water, and of CaN_2O_6 in water, in the presence of tincture of mallow, that the formation of acid or of alkali started from the electrode, and proceeded slowly towards the boundary. Davy observed this also with K_2SO_4 in water and solution of litmus.

Observations made using the far more sensitive dimethyl-orange as reagent do not confirm this. A rapid alkalinity is observed about a millimetre above the boundary, and with great differences of concentration the reaction takes place as rapidly above the boundary as at the electrode.

As regards the cause of this deposition at the boundary, which was first observed by Faraday in the case of magnesium sulphate, G. Wiedemann† ascribes it to the different degrees of migration in the solutions. Kohlrausch‡ has objected to this, that a difference-rate of migration of the two solutions can only affect the change of concentration at the boundary, but cannot produce any excess of one ion.

From Hittorf's numbers for the rate of migration, the following conclusions may be formed:—

The influence of dilution on the rate of migration is seen to differ with the nature of the electrolyte. In most cases the migration of the anion decreases with increasing dilution, that of the kation increases in the same degree. With chloride of potassium the rates of migration are independent of the concentration; with the nitrates of silver, potassium, and sodium, the migration of the anion increases with dilution, that of the kation decreases.

If now the processes above the boundary had their origin in the difference of the values for the migration a formation of hydrate might take place in most cases, potassium chloride could show no change above the boundary independent of differences of concentration, or at any rate very small ones, while with nitrates of silver, potassium, and sodium a formation of acid is to be expected. But the experiments, using dimethyl-orange as a reagent, are in disagreement with this; for with the same direction of current chloride of potassium as well as the last-mentioned salts show the same behaviour above the boundary as the other solutions.

Hence there remains so far only Kohlrausch's explanation, which sees in the action of water in electrolysis the cause of the processes at the boundary, and according to which these phenomena must necessarily follow. It would be desirable that the experiments should be made on a sufficiently large scale to examine the products qualitatively and quantitatively.—Wiedemann's *Annalen*, No. 4, 1893.

* Wiedemann's *Electricität*, vol. ii. pp. 599 & 614.

† *Electr.* vol. ii. p. 607.

‡ *Wied. Ann.* vol. xxvi. p. 210, 1885.

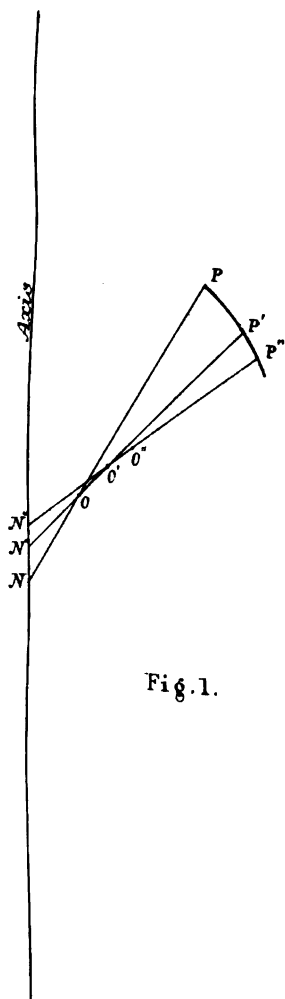
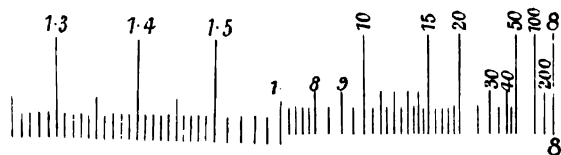


Fig. 1.

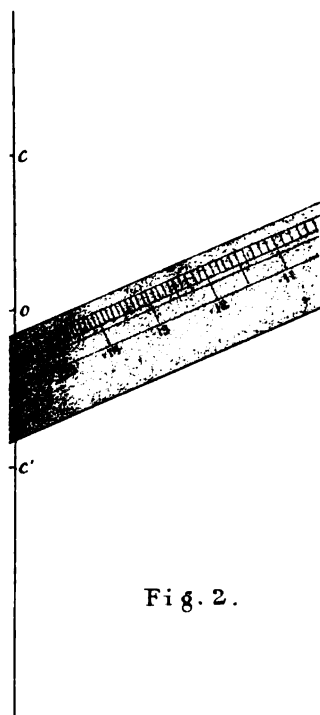


Fig. 2.

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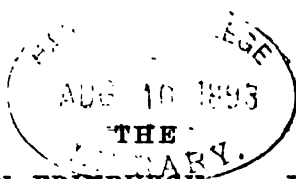
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XV. *Studies of the Phenomena of Simultaneous Contrast-Colour; and on a Photometer for Measuring the Intensities of Lights of different Colours.* By ALFRED M. MAYER*.

IT is often desirable in the study of simultaneous contrast-colours to have large surfaces coloured by contrast, so that we can the better match the colours of these surfaces with rotating coloured disks and thus arrive at quantitative statements of their hues. This is especially desirable in ascertaining the hues of the light of flames, of the Welsbach incandescent lamp, and of the arc electric light when compared with daylight, or when compared one with another. The result of many experiments is the apparatus described in the following section and which is useful for this purpose.

Screen for ascertaining the Hues of Lights and the Contrast-Colours of these Lights.—A ring is formed of white cardboard by cutting out a central opening of 12 centim. in diameter in a disk of 22 centim. in diameter. This ring has a breadth of 5 centim. Another ring is made similar to this one, except that it has four narrow radial arms to support a disk of thin translucent *white* paper† 35 centim. in diameter. This paper disk is placed between the rings, which are then fastened together and screwed to a thin rod, on a stand, as shown in fig. 1.

* Communicated by the Author.

† Trials with many kinds of paper showed that a white linen tracing-paper was the best. It is not possible to describe this so that one may be sure of selecting a similar paper. It was obtained of Keuffel and Esser, Fulton St., N.Y., and sold as "No. 202 Alba tracing-paper."

Phil. Mag. S. 5. Vol. 36. No. 219. Aug. 1893. M

Place the screen, thus formed, in front of a petroleum-lamp and exclude the daylight from the side thus illuminated. The other side of the screen is illuminated by the light of the sky admitted through a distant window. The cardboard ring is thus illuminated on one side only by the lamp, on the other side only by the daylight. The translucent paper transmits the lamp-light to the side facing the window, while it transmits the daylight to the side facing the lamp. On the side of the screen facing the window the cardboard ring appears cyan-blue, while on the side facing the lamp the ring appears orange-yellow.

Hues of the Sides of the Ring.—An idea of the hues and intensities of these colours, which cause astonishment even in those who are experimenters in chromatics, will be given by the description of the following experiments.

By means of a Bunsen-photometer disk I adjusted the distance of the lamp from the screen so that I obtained, as nearly as I could judge, equal illumination of the sides of the screen. I then found that the blue was matched in a rotator by a disk having a sector of 60 parts of the circumference of Prussian blue, with a sector of 10 parts of emerald-green and a sector of 30 parts of white cardboard. The blue was that of one of the many coloured disks given me by Professor O. N. Rood, and was marked "Blue between cyan-blue and the ultramarine of the physicist, but nearer the latter. Near F and on its more refrangible side. Made with Prussian blue." The blue on this disk appeared as saturated in hue as could be made by the pigment.

The match of the colour of the side of the ring facing the lamp, L, in fig. 3, was obtained by placing a silvered mirror, M, so that the reflexion of this side of the ring, S, was seen close to the rotator, R.

The colour of the cardboard ring facing the lamp was matched by the rotation of a disk formed of 50 parts of chrome-yellow, 30 parts of red-lead (red-orange), and 20 parts of white cardboard. Such appears to be the hue of the light

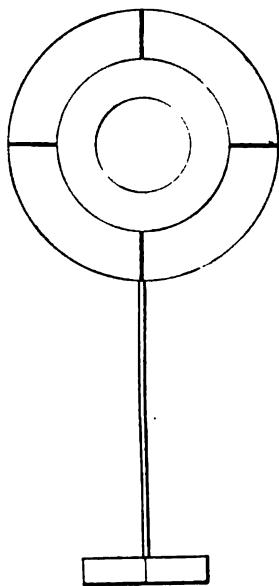


Fig.1

of a petroleum-flame when compared, in this manner, with the light of the sun.

The petroleum-flame used in these experiments was that of a Belgian burner, giving about 35 candles. The daylight was obtained from a window 85 centim. square, the lower half of which, when viewed from the screen, was occupied by the snow-clad surface of an opposite hill. The day was very clear, and the sky very slightly tinted with blue.

The Colours of the Sides of the Ring of the Screen are Complementary.—I combined the Prussian blue, emerald-green, chrome-yellow, and orange-red on a disk on the rotator, and found that when the disk was formed of sectors having 60 parts of Prussian blue, 11 of emerald-green, 19 of chrome-yellow, and 10 of red-lead, I obtained a grey which was exactly matched by a central disk formed of 71 parts of dead ivory-black and 29 of white cardboard (see fig. 2). These measures gave the following equation:—

$$\left\{ \begin{array}{l} 69 \text{ Prussian-blue} \\ \text{Emerald-green} \end{array} \right\} + \left\{ \begin{array}{l} 19 \text{ Chrome-yellow} \\ \text{Red-lead} \end{array} \right\} = \text{Grey } \left\{ \begin{array}{l} 71 \text{ Black} \\ 29 \text{ White} \end{array} \right\}.$$

It is rather difficult to get the exact match on the rotating disk of the hues on the front and back of the cardboard ring of the screen on account of the illumination of these surfaces. The rotator must be placed nearer the window than the screen so that it is well illuminated.

The equation shows that the cyan-blue of 60 parts of Prussian blue + 11 of emerald-green is complementary to an orange-yellow of 19 chrome-yellow + 10 of red-lead. The hue of this orange of the lamp side of the ring, as given by the rotator, was 50 chrome-yellow + 30 red-lead + 20 white, which mixture is approximately in the proportion of 19 to 10. The correspondence of the two experiments is, I suppose, about as near as could be expected from the difficulty of matching the illuminated hues of the ring of the screen.

The small central disk on the rotator gave a grey of 71 parts

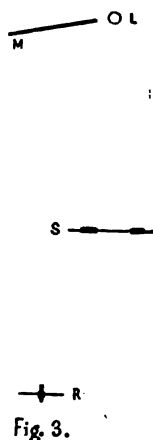


Fig. 3.

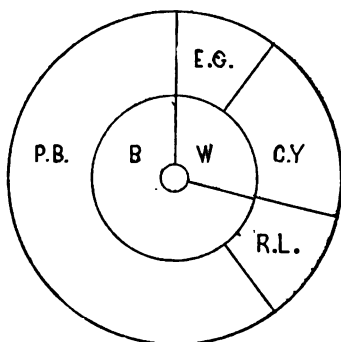


Fig. 2

of ivory-black + 29 of white cardboard, which matched the grey given by 71 parts of cyan-blue + 29 parts of orange. Calling the intensity of the orange 100, we have $100 \times 29 = 711$, which gives for I (the intensity of the cyan-blue) only 40.8 per cent. of that of the orange.

The orange-yellow of the side of the ring facing the lamp and of the side of the translucent paper facing the daylight is complementary to the cyan-blue of the side of the ring facing the daylight and of the side of the translucent paper facing the lamp.

In fig. 4, L is the lamp; S the screen, which in this experiment is deprived of the border of translucent paper; W, the window; M, a silvered mirror which reflects the back of the screen to the eye which looks through an achromatized double refracting calc-spar prism at C.S., and sees two images of the side of the screen reflected from the mirror and two images of the side of the screen facing the window. By suitably inclining and rotating the calc-spar prism, these images may be brought into the positions shown in fig. 5, in which A represents one of the images of the side of the screen facing the window; B, the other image of the same; C is one of the images of the side of the screen facing the lamp and seen by reflexion from the mirror.

The overlapping of these images, when the illumination is properly adjusted, gives the following results, as shown by the letters in fig. 5, where B stands for cyan-blue, Y for



Fig. 4.

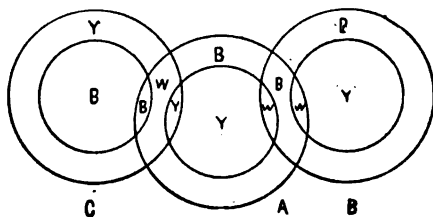


Fig. 5.

orange-yellow, and W for white. The translucent paper Y of B overlaps the ring of A and gives white, and the blue of the ring of B overlaps Y of the translucent paper of A and gives white. In the same manner the orange-yellow of the cardboard ring of C overlaps the blue of the ring of A and gives white. Where the ring of C overlaps the translucent

paper of A there is a more intense orange, and when the blue of the translucent paper of C overlaps the blue of the ring of A we have a more intense blue. On bringing B of the translucent paper of C over Y of the translucent paper of A we have white.

Experiments on the Complementary Colours of Gratings.—

Out of thin cardboard, such as is used for thin visiting-cards, I cut gratings with a dividing-engine (see fig. 6). The widths of the spaces cut out of these gratings exactly equalled the breadths of the cardboard left in the grating. Gratings were thus made having spaces of 1, 2, 3, 4, and 5 millim. The cardboard I rendered opaque by coating one side of it with ivory-black in dilute shellac-varnish. After it has dried, the cardboard is well flattened before it is fastened to the surface of a piece of hard wood on the dividing-engine. The cutting-edge of the cutter for this work must have a very acute angle. I made one by grinding

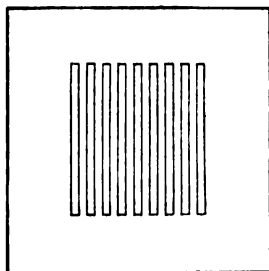


Fig. 6.

down a rod of Stubs' steel. Heating this to a dull cherry-red and then forcing it into a large ball of beeswax gives the edge of the cutter the required temper, without the necessity of subsequently "letting it down." The blackened side of the

gratings was covered with the "Alba tracing-paper." The grating was mounted back of an opening in a black cardboard-screen, so that only the white grating was exposed. Two other black screens, Wh and Y of fig. 7, having openings of the same size as the grating, and covered on the back with the translucent paper, were placed on either side of the grating, G. In fig. 7, L is the lamp. The window is on the other side of G. The screen, S, divides the apparatus so that the light of the window, W, reflected by the mirror, M, on to the screen, Wh, cannot fall on G or on Y, which are only illuminated by the lamp L.

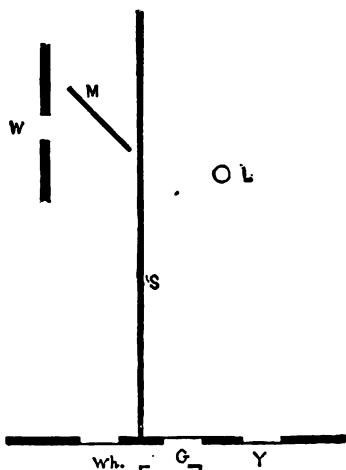


Fig. 7.

The translucent paper of the grating G and of the screen Y appear orange-yellow. The bands of white cardboard of the grating appear cyan-blue. The translucent paper of the screen Wh is white.

Sit a little to one side of the grating so as not to intercept the light from the window, and look at the grating through the calc-spar prism. Rotate it till the blue bands of the grating are superposed on the orange bands, when, if the surface of the grating is equally spaced, the superposed surfaces appear white when compared with the white of the screen Wh. Without the screen Wh the eye has no term of comparison, and may take a yellowish white for white. The illumination of the screen Wh should be made equal that of the superposed images of the grating.

When this experiment is carefully made, with the proper illumination, the effect is surprising when, in favourable conditions, on rotating the prism you see the grating actually obliterated with no bands visible, but only a uniform white surface. The grating with spaces of 3 millim. gave the best results.

In experiments with the screen (fig. 1), formed of the cardboard ring and the translucent disk, it is easy, by altering the relative intensities of the daylight and lamp-light and by changing the distance of the lamp from the screen, to produce great changes in the saturation of the contrast-colours. Indeed I have sometimes thus obtained, towards nightfall, a cyan-blue so saturated in hue that little or no white was required in the disk of the rotator to match the colour on the ring. In the same manner similar changes in colour have been observed in the hue of the ring illuminated by the lamp.

On illuminating one side of the screen by daylight and the other by the white light of a Welsbach incandescent lamp, and then placing coloured glasses or films of coloured gelatine between the screen and the Welsbach lamp, effects of contrast are obtained which are so readily imagined by the physicist as to require no description ; but they are worth viewing.

Increase of the Purity and Luminosity of the Contrast-Colours by a Rotating Screen.—Make a disk of white cardboard of 27 centim. in diameter, with eight sectors cut out of it, and cover it with translucent paper so that the paper extends beyond the disk and makes a border 3 centim. wide. A circle of 8 centim. in diameter is left in the centre of the disk and a ring of $1\frac{1}{2}$ centim. on its border. This disk is shown in fig. 8, but with only six sectors. It should have eight. It is placed between the lamp and the window, and rotated with a velocity of one revolution in about $1\frac{1}{4}$ second,

while it is viewed on the side facing the window. The blue sectors thus take successively the places just before occupied by the sectors of orange-yellow, and the effect is to heighten the contrast-colour in such a remarkable manner that the blue sectors by their more intense colour appear separated from the central circle and rim and appear in a plane farther from the eye than the plane of the centre and rim. On the side

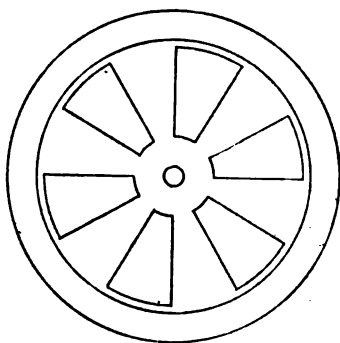


Fig. 8.

of the disk illuminated by the lamp the same effects are produced, only they appear more marked. A change will also be observed in the hue of the advancing and following edges of the sectors, on both sides of the disk, the advancing edges appearing more saturated in hue than the following edges.

A mode of observation by which Contrast-Colours are Intensified.—Simultaneous contrast-colours are generally viewed by placing grey or tinted surfaces on coloured grounds, or by the juxtaposition of coloured surfaces. The effects thus produced are of such constant occurrence in the paintings of artists, and in coloured fabrics, that their study is of great interest. The contrast-colours thus produced have generally been studied by simply placing on a coloured ground smaller grey or tinted surfaces and observing these with the unaided eye. This method has been improved by H. Meyer*, who viewed the grey on the coloured ground when both were covered with white transparent paper.

The mode of observation I have devised for the study of contrast-colours is as follows:—A glass tube of 2·7 centim. in interior diameter and 10 centim. long is coated on the outside with black Japan varnish, so as to have reflexion only from the interior surface of the tube. A ring of 3 centim. in diameter with a central opening of 2 centim. is cut out of grey paper. The grey of this ring was matched on the rotator by a disk having 57 parts of ivory-black and 43 parts of white Bristol board. This ring, placed on a surface of emerald-green, appears of a rose colour. If at the distance of distinct vision we look at the ring through the tube, we shall see the ring by direct vision enclosing a circle of green and surrounded by

* Pogg. Ann. xcv. p. 170.

a ring of emerald-green, and this enclosed by a rose-coloured ring, produced by reflexion from the interior of the tube, and surrounding this ring is another of emerald-green, as shown in fig. 9, in which R and R are the red rings and G, G, and G the circle and the two rings of emerald-green.

The hue of the rose-coloured rings, as seen through the tube, is much more intense than the hue of the ring viewed on the emerald ground with the unassisted eye. Experiments made with the aid of an achromatized calc-spar prism, and by matching on a rotating disk the colours of the grey ring on an emerald-green ground showed that the intensity of the contrast-colour, as seen with the reflecting-tube, is nearly double of what it is when viewed by the eye alone. The colour of the ring when viewed by the unassisted eye was matched on the rotator by a disk having 30 parts of Chinese vermilion + 7 of "Hoffman's violet R.R.R." + 34 parts of ivory-black + 29 of white Bristol board. As seen through the reflecting-tube the match appeared to be given by 57 of Chinese vermilion + 15 of "Hoffman's violet R.R.R." + 28 of white Bristol board.

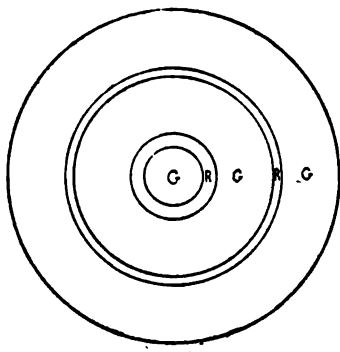


Fig. 9.

Another tube, 4.5 centim. in diameter and 18 centim. long, gave excellent results, with two reflected rings, and on nearer vision, with four reflected rings. A tube, suitable for these experiments, is selected by closing one of its ends by a disk of cardboard having a pin-hole at its centre. When the end with the pin-hole faces the sky and we look through the other end, we see bright rings caused by the reflexion of the light of the pin-hole from the interior surface of the tube. If these rings are circular and concentric, the tube is of circular section and its axis is a right line.

The value of this mode of observation is shown by the following experiments:—Place the ring of grey paper, or a circle of grey paper, about $1\frac{1}{2}$ centim. in diameter, on a surface painted with cobalt-blue, not too saturated. The grey ring or circle appears of an orange tint. Place a similar grey ring or circle on a surface lightly washed with emerald-green, it appears pinkish. The difference between the hues of the ring when viewed on the cobalt-blue and on the emerald-

green, though decided, is not strongly marked ; but if viewed through the reflecting-tube the ring on the cobalt-blue appears of a rather intense orange, and the ring on the emerald-green appears of a rose-colour. When so viewed the difference in these hues is strongly marked.

Pieces of cardboard, painted with the following colours, were arranged in pairs. Orange-yellow on the less refrangible side of D, and orange-yellow on the more refrangible side of D. Greenish-yellow and yellowish-green, both made with gamboge and Prussian blue. Purple of violet end of spectrum with added red, made with Hoffman's violet R.R.R., and violet between G and H, Young and Müller's fundamental colour. Place a pair of the colours, as given above, side by side and on each put a grey ring, with a reflecting-tube over each ring. When viewed by the unassisted eye the differences in hue are slight and difficult to define ; but when viewed in rapid succession through the adjoining tubes the differences in hue are decided and may be readily matched in colour with disks on the rotator.

The Duration of the Time of Vision necessary to perceive Contrast-Colour.—A square screen was made, as shown in fig. 10, with a square of cardboard in its centre, 8 centim. on the side, surrounded by a square of translucent white paper, 35 centim. on the side. This screen was placed between the petroleum-flame and the window so that its sides were equally illuminated. On the side facing the window the central square appeared cyan-blue. One half of this square was covered by a strip of paper so tinted with orange-yellow that it appeared grey when in juxtaposition with the other blue half of the square.

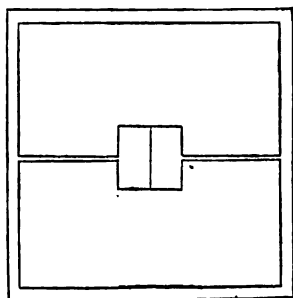


Fig.10.

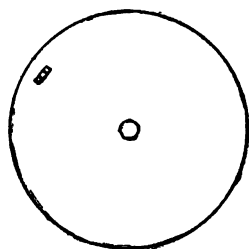


Fig.11.

On a rotator were placed two superposed black disks of the same diameter (25 centim.). Near the periphery of each disk was cut out an annular slot, 4 centim. long and 6 millim. wide, as shown in fig. 11. By turning one of these disks on the other the opening of this slot could be varied from 4 centim. to nothing.

The rotator is so made that the time of a rotation of the disk can be held uniform and also accurately measured. On gradually narrowing the opening in the slit, the duration of vision of the blue and grey square was reduced to $\frac{1}{1600}$ of a second, when the blue half of the square could not be distinguished from the grey half.

When the screen was illuminated by a more orange light, obtained by placing a sheet of orange gelatine between the lamp and the screen, the grey and blue were not distinguishable when the duration of vision was $\frac{1}{1300}$ of a second.

In these experiments I only got 11·6 flashes of light from the screen in a second, while the number of flashes required to banish all flickering from the screen was accurately measured as $\frac{1}{46}$ of a second with the illumination of the lamp alone, and $\frac{1}{42}$ of a second when the lamp-light traversed the orange gelatine film. These experiments show, what is well known, viz., that as the intensity of the light diminishes the duration of no perceptible change in the intensity of the residual impression increases. I found that the light from a white cloud, seen, near noon, through a north window on a clear day lasts only $\frac{1}{48}$ of a second before the residual effect diminishes.

A grey ring was placed on an emerald-green ground facing the light from a bright white cloud. When viewed through the opening in the rotator the ring appeared pink on the green ground till the duration of the vision of the ring was reduced to $\frac{1}{8380}$ of a second, when the ring ceased to be visible on the emerald-green ground; but so long as it was visible the contrast-colour was visible. I found that 43 flashes per second were necessary to render the vision of the pink ring and green ground steady, without the least flickering, while only 11·6 flashes per second were obtained in determining the $\frac{1}{8380}$ of a second as the time when contrast-colour ceased to be visible. The fact that the contrast-colour of the ring remained till the ring could not be distinguished from the green ground gave the opinion that I ceased to obtain contrast-colour because the narrow slit used gave too little light to the eye. On doubling the width of the slit and doubling the velocity of rotation, the contrast-colour of the ring reappeared, though the duration of vision was the same as in the former experiment.

Experiments on simultaneous Contrast-Colours produced by the flash of the Electric Discharge.—The foregoing experiments having proved insufficient to form any opinion as to the time of vision necessary to perceive simultaneous contrast-colour, I made the following experiments with the light obtained by the discharge of a Holtz induction-machine.

The grey ring was placed on the emerald-green ground near a Holtz machine, which gave a very bright flash of 8 centim. long. The condensing surface on the two jars connected with the electrodes of this machine equalled 135 square centimetres. Professor O. N. Rood* measured the duration of the flash of Leyden jars of 738 and 71 square centimetres of surface, charged by an inductorium. The durations of the discharges of these jars were respectively $\frac{1}{5,700,000}$ second and $\frac{1}{25,000,000}$ of a second. From these measures I infer that the duration of the flash of the Holtz machine did not exceed the $\frac{1}{10,000,000}$ of a second. With short striking distances between the electrodes the flash is formed of several separated acts, as shown by Henry†, Feddersen‡, Rood§, and Mayer||. In the case of the discharge of a large inductorium the writer(||) has shown that when the striking distance between brass ball electrodes is only one millimetre, with a Leyden jar of 242 square centim. of surface in the circuit, the discharge lasts $\frac{1}{24}$ of a second and is formed of over 120 separate sparks; but as the striking distance is increased the discharge is formed of fewer and fewer components, till at a striking distance between 1 and 2 centim. the discharge is reduced to a single flash. In the following experiments the striking distance is 8 centim., and a single flash was given, whose duration we may safely assume was less than $\frac{1}{1,000,000}$ of a second.

In a dark room, at night, the flash of this machine gave vivid contrast-colours,—the grey ring appearing bright pink on an emerald-green ground, and of a bright yellow on an ultramarine ground. The after-images of these effects lasted about $\frac{1}{2}$ of a second.

A rod was placed in front of a white cardboard screen and the shadow of the rod was formed on the screen by a candle. The distance of the candle was such that the white cardboard appeared equally brilliant when illuminated only by the candle, or, only by the electric flash. At the moment of the flash the appearance presented was very remarkable. From the shadow of the candle appeared suddenly to shoot a dark screen, which had superposed the shadow of the candle, and which shot to the side of the shadow and appeared of a bright golden orange, while the apparently uncovered shadow of the candle appeared of a brilliant cobalt-blue; to my eye exactly as though an opaque screen had been suddenly removed from a

* Amer. Journ. Sci. Sept. 1871.

† Pogg. Ann. vol. cxvi. p. 132.

|| Amer. Journ. Sci. Dec. 1874.

† Proc. Amer. Phil. Soc. 1842.

§ Amer. Journ. Sci. Oct. 1872.

slit in the shutter of a darkened room, which slit was covered by a piece of cobalt glass.

A square of thin green glass, 4 centim. by 6 centim., was placed on a piece of thin silvered glass, 4 centim. by 12 centim., so that the edges of the green glass and of the silvered glass coincided. This arrangement gave a surface, half of silvered mirror, half of green glass. This apparatus was so placed that the electrodes of the machine and the flash were reflected from it to the eye. The room was dark. At the moment of the flash its reflexion appeared as in fig. 12. On

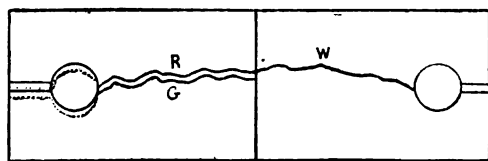


Fig. 12.

the mirror the line of the discharge was white; W in the figure. The continuation of this line on the surface of the green glass appeared red (R in figure), though really white. In front of and parallel to this line was a green line, G, produced by the light of the flash reflected from the surface of the silvered mirror, and having traversed twice the thickness of the green glass. In this experiment we obtain contrast colours in the source of light itself.

The explanation of the phenomena of simultaneous Contrast-Colours, as generally given in works on chromatics, is that they are due to "error of judgment," to "deception of judgment," or to "fluctuation of judgment." The reasoning given may be convincing if all the conditions really exist which the writers assume to exist in their explanations of these phenomena. One of these conditions is that a judgment can be formed in the minute interval of time only necessary in which to perceive contrast-colours. In the experiments just described with the electric flash we have *apparently* instantaneous perception of the contrast-colours in the grey ring placed on the green and ultramarine grounds, in the candle and electric light shadows and even in the very flash itself when this is seen reflected from the top surface of a green glass and from the mirror on which the green glass rests.

Many careful experiments made by me and others, using as chronometer three pairs of forks of the octave of UT₂, giving respectively 10, 12, and 15 beats per second, showed that certainly the interval between the flash and the per-

ception of the colours was much less than $\frac{1}{15}$ of a second. Indeed, on viewing the flash and the illuminated surfaces at the same time, or, hearing the discharge and viewing only the illuminated ring, *no interval could be detected* by this mode of observation as existing between the instant of the flash and the perception of the colours, and we certainly could have detected a shorter interval than $\frac{1}{15}$ of a second had it existed.

Incidentally, I will here state that when different geometrical or irregular figures cut out of white paper and placed on an ivory-black ground were illuminated by the electric flash, the observer, so far as I could ascertain, formed conclusions as to the forms of the pieces of paper in an interval of time less than the $\frac{1}{10}$ of a second. Certainly the interval of time required to reach a conclusion as to the contrast-colour was less than the $\frac{1}{15}$ of a second. Professor Mendenhall in 1871 (*Amer. Journ. Sci.*) gives 0.292 sec. for the time required by an observer to respond, by means of an electric chronograph, to the appearance of a white card. When the observer responds by touching the circuit-key with one hand when a white card appears, and with the other hand when a red card appears, Professor Mendenhall finds 0.443 sec. as the time required for the response. Subtracting the first number from the last he obtains .151, or $\frac{1}{6}$ sec., as the time to form a judgment between white and red. Similar experiments gave him 0.202, or $\frac{1}{5}$ sec., as the time to judge whether a circle or a triangle appeared to the observer. The intervention of the operation of brain, nerve, and muscle before the response is recorded involves complex operations, and the action of right or left sides of brain when the two hands are used. It appears that the plan of eliminating these actions, and thus obtaining a residual time which is attributed to the interval required to form a judgment of colour or of form, is faulty. I am sure that if estimation of the time required for such mental operations is made by the *continuous indications* of the beats of forks, such intervals as $\frac{1}{6}$ and $\frac{1}{5}$ of a second will at once appear much in excess of the time respectively required to form a conclusion as to whether a white or red colour or a circle or triangle has been presented to our vision.

It is here to be noted that although the after-images of the contrast-colours seen in the light of the electric flash lasted about $\frac{1}{2}$ of a second, yet the most careful scrutiny could detect no change in sensation at and immediately following the flash. The contrast-colours, so far as I and others observed, appeared at the moment of the flash. After the instant the image of the flash is formed on the retina there exists, no doubt, an interval of time before we are conscious of the stimulus, whose effects are seen rapidly to rise and then more gradually

to fall, falling with two oscillations in intensity, so that all the events of the phenomenon take place in about $\frac{1}{2}$ of a second. However, no vague impression of surfaces merely differing in illumination and then suddenly changing into a colour and its contrast-colour could be detected. I think that this interval of no colour-sensation, if it exist, must be of exceeding short duration; but such a period of light without colour cannot be detected, and if it cannot be perceived, then, so far as we are concerned, it appears to me that there can be no hesitation in the perception of the colours, and no "fluctuation of the judgment" and "dividing between two images the difference in colour which really exists" before the mind reaches its conclusion as to the character of the colours.

The following experiments were separately made on three persons between whom no communication had passed as to the nature of the experiments to be tried on them. I placed a grey ring on a ultramarine disk in front of the Holtz machine and requested the observer, who had implicit confidence in my truthfulness, to describe to me as accurately as possible the exact hue of the pink, or rose colour, or red he would see on a green ground at the instant of the electric flash. Each observer at once said: "It is not pink, the ring appears yellow on a blue ground." Now in each of these experiments the observer was prepared, by my pardonable lying, to see red on a green ground, and to see yellow on a blue ground, his mental condition of anticipation to see red on a green ground was first removed, then a new departure was taken and a judgment formed which resulted in his seeing yellow on a blue ground, and all that in a minute interval of time.

I do not know if psychologists have come to a conclusion as to the smallest interval of time necessary to form a judgment, either true or false, or in which to have a "fluctuation of the judgment," or in which "to exercise judgment and divide between two colours the difference in colours which really exist." If such mental operations can be performed in the millionth, the thousandth, or even in a few hundredths of a second, then the explanations of these phenomena, as generally given, may be convincing.

Von Bezold in his 'Theory of Colour,' Boston, 1876, in explaining the fact that a rod seen by reflexion from a piece of green glass laid on a mirror gives two images, one green the other red, says:—"As the observer does not *know* which of the two images is the coloured one he exercises his judgment, and divides between the two images the difference in colour which really exists." Now this experiment is similar in its conditions and in its effects of contrast-colour to the

one I made on the contrast-colours of the electric flash, when the same colours were distinctly seen apparently at the moment of the discharge. Can one "exercise his judgment and divide between the two images the difference in colour which really exists" in an interval of time which is less than $\frac{1}{15}$ of a second?

In the experiment of the coloured shadows cast by the candle and by daylight, these colours are explained by Von Bezold (pp. 152, 153), as follows:—"The spot occupied by the blue shadow is illuminated by the *white daylight*, the larger white surface by *daylight and by candle-light*, the other shadow by candle-light only. It might be presumed, therefore, that one of the shadows would appear white, the other yellow. This is not the case, however; for *knowing* the surface to be white we still take it to be white after it has really received the yellow light of the candle. Our judgment is led astray regarding white, and hence we believe the place occupied by the second shadow to be blue, although it is actually white." Helmholtz ('Lectures,' London, 1873, p. 267), says:—"Thus in the experiment described above of coloured shadows thrown by daylight and candle-light, the doubly illuminated surface of the paper being the brightest object seen gives a false criterion for white. Compared with it, the really white but less bright shadow thrown by the candle looks blue." These explanations assume knowledge and conditions which are not essential. If this knowledge and these conditions were necessary to see the phenomena then these explanations of the phenomena might be convincing; but the conditions they assume are not necessary. The following experiments show that there is no necessity at all in "knowing the surface to be white" or to see "the doubly illuminated surface of the paper."

The experiment of the coloured shadows cast by the candle and by daylight was arranged behind a screen, so that no one could divine what was there. A tube blackened on the inside went obliquely through the side of the screen and was so adjusted that the circular field of view through the tube was entirely filled by equal portions of the two shadows, which formed two semicircles, one coloured orange the other blue. The two persons on whom I experimented were ignorant of the phenomena of contrast-colour, and, moreover, were misled as to what they would see on looking into the tube, and I was specially careful not to speak to them about colour. These persons were strangers to each other, and neither knew that the other had been the subject of my experimenting. The first observer at once reported:—"I see a circle half yellow and half blue." The other said:—"I see a golden

band next to a sky-blue band and the golden band is rather deeper in colour where it is next to the blue," which is certainly a very good description.

Having in mind the facts established by the foregoing experiments, it seems to me that we have either to regard the phenomena of simultaneous contrast-colour as psychical phenomena of which no satisfactory explanation has been given, or we must discard the Young-Helmholtz hypothesis of colour-sensation and adopt one similar to that of Hering, which gives a direct physiological explanation of contrast-colour effects without the psychological considerations which those who adopt the Young-Helmholtz hypothesis are obliged to resort to in their explanation of these phenomena; and which explanations, as I have attempted to show, are faulty, and have to be modified to be convincing.

According to Hering's hypothesis of colour-sensations, when a portion of the retina is stimulated adjoining portions of the field of view are affected by a sort of inductive action; so that changes are produced which are antagonistic or complementary to those portions of the retina actually stimulated.

M. Foster in his 'Physiology,' Lond. 1891, Part IV., bk. iii., gives an excellent discussion of the relative merits of the Young-Helmholtz hypothesis and Hering's in explaining colour-sensations. In conclusion he writes:—"... so far as we are aware no crucial test between the two has as yet been brought forward. We may now leave the matter with the remark that, while the Young-Helmholtz theory tends to lead us direct from the retinal image to the psychological questioning of the sensations, and seems to offer no bridge between the first step and the last, Hering's theory is distinctly a physiological theory, and at least holds out for us the promise of being able to push the physiological explanation nearer and nearer home before we are obliged to take refuge in the methods of psychology."

A Photometer for Measuring the Intensities of Differently Coloured Lights.

It has already been shown that, in certain conditions of illumination and in certain directions of sight, a screen formed of perforated cardboard covered with translucent paper appears with complementary colours, and that if the screen be in the form of a disk with alternate sectors cut out of it, and is illuminated on one side by daylight and on the other side by lamp-light, that the blue of one side of the disk and the orange of the other appear intensified on slowly rotating the disk. On increasing the velocity of rotation the

complementary colours gradually blend, and when the velocity of rotation has banished all flickering light from the disk it appears nearly white. The side facing the daylight has a slight yellowish tint; the side facing the lamp appears whiter, but is tinted with a feeble bluish hue.

To study more minutely these phenomena I made a disk which could be readily taken apart and mounted with different translucent papers and have attached to it disks and rings of various colours. I shall call this disk the *photometer-disk*. It is made as follows:—

Two disks, 13 centim. in diameter, and having eight sectors cut out, as shown in fig. 13, were made of thin Bristol board. A circle of 2 centim. in diameter was left in the centre of the disk, from which the cardboard sectors radiate. The border of the disk is a ring of $\frac{1}{2}$ centim. wide, which was painted black. Clamps, made of thin hammered brass, held these disks together.

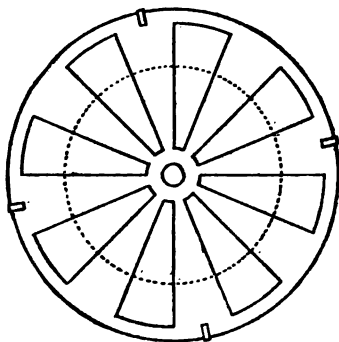


Fig.13.

Between these disks was placed a circle of the same white translucent paper as was used in the construction of the large contrast-colour screen, fig. 1, and the disks were clamped together with the open sectors of the two disks coinciding in position. A black disk of 8.2 centim. in diameter was placed on each side of the photometer disk, thus leaving between it and the black peripheral ring an annular space of 1.9 centim. wide, formed of alternate spaces of cardboard and of translucent paper. The disk was mounted on a rotator and placed opposite two silvered mirrors inclined at an angle of 150° ; an arrangement similar to that of Letheby for observing the disk of Bunsen's photometer. The plane of the disk of the rotator bisected the angle formed by the mirrors, as shown in fig. 14, so that the surfaces of both sides of the disk could be seen simultaneously, or, rather, in rapid succession. On rotating the disk while illuminated by daylight on one side and by lamp-light on the other, the side illuminated by daylight appeared white tinted with yellow; the side facing the lamp

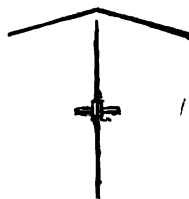


Fig.14.

appeared white tinted with blue. The hues were the same as described in the experiment with the large disk, fig. 8, only the surfaces appeared brighter by contrast with the black centre and border.

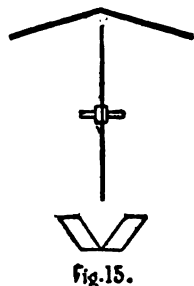
The feeble character of the hues on the photometer-disk led me to hope that I could bring these to the same hue on both sides of the disk by the effects of contrast. To accomplish this I placed on the daylight side of the photometer-disk a compound disk formed of three split disks, one of red lead, one of chrome-yellow, the other of white Bristol board. On the lamp-light side I placed a disk formed of three split disks—coloured ultramarine, emerald-green, and one of white Bristol board. On rotation, the compound disk on the daylight side gave an orange-yellow; on the lamp-light side the disk gave a bluish-green. These colours corresponded in hue to those seen on the respective sides of the ring of the photometer-disk when it is rotated, only the hues were much more saturated. After a few trials I brought, by the contrast effects of these coloured disks, the tints on the two sides of the ring of the photometer to the same hue; the translucent ring appearing white with a very slight orange-yellow tint on both of its sides. The greenish-blue had by contrast effect obliterated the blue tint of the ring and even replaced it by a very feeble orange-yellow; while on the other side of the ring the orange-yellow disk had diminished the orange-yellow tint of the ring to the same feeble orange-yellow as seen on the other side of the ring.

Experiments were now made to test this apparatus as a photometer. Equality of illumination cannot be determined with any precision if the two surfaces compared differ even slightly in hue. Here we had the same hue to deal with on both sides of the ring; which condition is different from the Bunsen photometer, on which we have two colours on each side of the disk. Various methods were tried to render reliable the comparison of the illumination of the two sides.

(1) I used the eye alone, regarding only the portions of the ring on the border near the mirror, as shown in fig. 14.

(2) Two prisms reflected the images of portions of the sides of the ring nearest the mirror to juxtaposition, as shown in fig. 15.

(3) A tube blackened on the inside, with a black screen on the end next the disk, as shown in fig. 16, was used. The



eye was thus shielded from extraneous light and the comparisons of illuminations was made, as in experiments 1 and 2, on the portions of the rings which were nearest the mirror, as shown in fig. 16. Vision through this screened tube gave the best results.



Fig. 16.

After practice in such comparisons, made during several hours on different days, I became more and more skilful and the results of measurements become more concordant; but such methods of photometry do not approach the accuracy of those in which two contiguous surfaces of different degrees of translucency coalesce into one surface of a uniform illumination, as happens on the balance of illuminations on the two sides of a Bunsen-photometer disk when these are illuminated by lights of the same intensity and of exactly the same hue. A photometer for this mode of observation is described in the following section. It has, however, the advantage over the Bunsen photometer in that it serves to measure the intensities of differently coloured lights.

The Rotating-Disk Photometer.—The photometer-disk was taken apart and a ring of thin white linen paper* of the diameter of the disk and $\frac{9}{10}$ centim. wide was laid on one of the disks; this was covered by the circle of thin translucent white paper, and on this was laid another ring of the thin linen paper. The disks were now clamped together. The outer portions of the open sectors of the disk were thus closed by two thicknesses of the thin linen paper with the “alba tracing-paper” between them, *a*, in fig. 17; while the inner portions of the sectors were closed by the tracing-paper alone, *b*, in fig. 17.

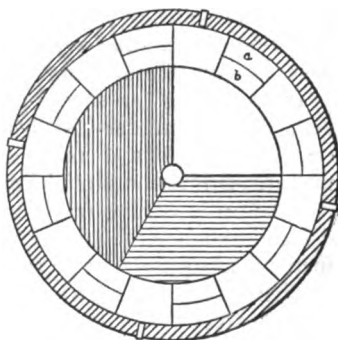


Fig. 17.

On rotating the disk, it was not possible to balance the

* The best paper I have experimented with for this purpose is water-marked “Crane & Co., Dalton, Mass., Bond, No. 21.”

colours of the outer half (*a* in fig. 17) of the ring formed of three thicknesses of paper, with the same central coloured disks, used in the previous experiment, when one side of the disk was illuminated by lamp-light, the other by daylight. But on increasing the saturation of the hues of the central disks and adding peripheral rings of the same hues, I succeeded in making the hues the same on both sides of the photometer-ring. If equality of hue can be obtained when the photometer is illuminated, on one side by lamp-light and on the other by daylight, then the contrast-colours may be brought to the same hue when the photometer is illuminated on one side by a candle or petroleum-flame and on the other side by the electric-arc light or by the whitest Welsbach incandescent lamp.

With a change of distance of the petroleum-flame from the photometer, the differences in the illumination of the portions *a* and *b*, fig. 17, of the ring were changed. When the two sides of the ring were equally illuminated the rings *a* and *b* appeared indistinguishable, fusing into one ring of uniform tint and illumination, of the breadth of *a* + *b*.

With the best Bunsen-photometer disk* I was unable to decide where it received equal illumination on its sides, so difficult was it to judge of equal brightness of the blue and orange on one side when compared with the orange and blue in the same respective positions on the other side of the disk.

With a petroleum-flame of 40 candle-light-giving power on one side of the rotating photometer and a candle on the other, the delicacy of the indications of the rotating photometer equalled, and even slightly excelled, those of the very best Bunsen-photometer disk.

If we bring in succession the translucent sectors of the rotating photometer-disk between two lights we observe that, on certain sectors, *a* and *b* appear as one surface of the same uniform tint and illumination; on other sectors sometimes *a*, sometimes *b*, is the brighter. Rotation of the disk entirely destroys such slight differences, and the disk then acts as if made of absolutely homogeneous material, placed in the same conditions of contact of the layers of paper, in each translucent sector.

The Hue of the Light of "a White Incandescent Welsbach Lamp" compared with Daylight.—When the screen (fig. 1) is illuminated on one side by the Welsbach lamp and on the other by daylight, the side of the ring of the screen facing

* The best Bunsen photometer-disks I have used are those sold by the American Meter Company of N. Y. They are made in England.

the daylight appears a feeble blue decidedly tinged with violet. The side of the ring facing the Welsbach lamp is coloured greenish-orange. This greenish orange was matched in hue, but not in luminosity, by a rotating disk having 41.5 parts of red-lead, 41.5 of chrome-yellow, and 17 of emerald-green, viewed illuminated by daylight. This appears to be the hue of the Welsbach light when compared with daylight.

Experiments in which are compared the Hues of the Light of an Incandescent Welsbach Lamp and of Candle-light.—When “a white-light incandescent Welsbach lamp” is placed on one side of the large screen (fig. 1) and a candle or petroleum-flame on the other side, the cardboard ring of the screen facing the Welsbach light appears of a light bluish-green; the side of the ring facing the candle or petroleum-flame appears of a light carmine.

Matching these hues on the rotator with split disks gave the following results when the two sides of the screen were equally illuminated. The hue of the ring on the side facing the Welsbach lamp was matched by 8 parts of emerald-green, 10 of cobalt-blue, 25 of ivory-black, and 57 parts of white Bristol board, as seen illuminated by the Welsbach lamp, The hue on the side of the ring facing the candle or petroleum-flame was matched by 12 of carmine, 17 of ivory-black, and 71 of white cardboard, as seen illuminated by the petroleum-flame.

Experiments with the Rotating Photometer-disk placed between the Welsbach Lamp and the Petroleum-flame.—On rotating the photometer-disk, without any central disks, between these lights, the same hues as those already described were seen on its sides, only those hues were much less saturated.

The white disks placed on the sides of the rotating photometer made the hues less saturated.

With a white disk on the petroleum-flame side and a black disk on the Welsbach-lamp side, the differences between the hues of the sides of the photometer were more pronounced.

With a disk of cobalt-blue, emerald-green, and white on the Welsbach-light side and a white disk on the petroleum-flame side, the side of photometer facing the Welsbach lamp appeared white and the side facing the petroleum-flame was less carmine, the differences in hue being less than in any of the previous experiments.

By trial I found that when a disk of 33 parts of emerald-green, 42 of cobalt-blue, and 25 of white was placed on the Welsbach-lamp side of the photometer-disk, with a ring of the same hue on the periphery, and a disk of 75 parts of

carmine and 25 of white was on the petroleum-flame side of the photometer-disk, with a ring of the same hue on the periphery of the photometer, that the sides of the photometric ring of the photometer had the same hue; which was white tinged with just a perceptible carmine.

We are now in a condition to make an interesting experiment which shows in a striking manner the effects of the coloured central disks and peripheral rings on the colours of the photometric ring of the photometer. The exact balance of hue on both sides of the photometer has been obtained. Reverse the photometer-disk with its central disks and rings, and rotate the disk in front of the mirrors. We now see the photometric ring with strong contrast of colour on its sides, and the concentric rings *a* and *b* are separately seen, not appearing indistinguishable as in the previous experiment. By the reversal we have, by the effects of the disks and rings, added to the effects produced alone by the lights.

It is to be noted that the colours on the disks and rings of the photometer must not be too saturated in hue. The elementary disks of these compound colour-disks should be made of thin Bristol board, and after they have been painted should be well flattened before they are slit radially. After the proper hues have been obtained for the disks which correct the colour of the photometric ring, the same hues should be painted on single disks, which are subsequently flattened. The thinner the colour-correcting disks and the closer they fit to the photometer-disk, the greater is their contrast colour-effect. The coloured rings must be cut out of the painted cardboard, for if the rings are painted after they are formed it is very difficult to make them flat.

To render easy the making of this photometer, I made experiments so that one could get the proper hues of the correcting disks and rings by mixtures of definite weights of the pigment powders and definite volumes of gum-water; but it is less troublesome to paint a few disks with colours variously saturated and repeat the experiments I have described, and thus furnish oneself with the sets of disks and rings necessary for the photometric measures of the arc electric light, of the Welsbach white burner, &c. when compared with the standard candle or petroleum-flame.

The rotator on which the photometer-disk is revolved should be made as shown in fig. 18, so that the standard, *S*, and the pulley, *P*, which is driven by the wheel, *W*, shade as little as possible the rotating disk.

Photometric Measures with the Rotating-disk Photometer.—On one side of the photometer was placed "a white Welsbach

burner" with a light-giving power of 33 candles, on the other side a standard candle. As the candle was gradually brought nearer the rotating photometer, the illumination and hues of the portions *a* and *b* (fig. 17) of the photometric ring approached equality, and when the candle was at a certain distance the difference of illumination and hues of *a* and *b* become indistinguishable, and only a band with a breadth of *a* + *b* with a uniform surface was observed on the sides of the photometric ring.

The measures of the intensity of the light of the Welsbach lamp in terms of the standard candle were made by a friend. He made sixteen measures with my Rotating-disk Photometer and sixteen with the Bunsen Photometer.

The mean of the series of measures made with the Rotating-disk Photometer differed from the mean of the departure of the maximum and minimum measures from the mean by 1.49 per cent. of the mean intensity of the light of the Welsbach lamp.

The mean of the series of measures made with the Bunsen Photometer differed from the mean of the departure of the maximum and minimum measures from the mean by 5.22 per cent. of the mean intensity of the light of the Welsbach lamp.

Hoboken, N. J., U.S.A.,
April 15, 1893.



Fig. 18.

XVI. *Notes on a Modification of Maxwell's Electrical Theory.*
By ALEX. McAULAY, M.A., *University of Tasmania* *.

1. **I**n the Phil. Trans., 1892, p. 685, I have developed a modification of Maxwell's electrical theory. As frequent mention of this paper will be made below, it will be referred to briefly as 'Electromag.' The principal object of the paper was to free Maxwell's theory from certain difficulties I felt in applying it to gross matter, but I was careful to point out at the beginning that the theory developed might require serious modification for the æther. The principal object of the present paper is briefly to consider what modifications, if any, are required.

2. We shall require a proposition analogous to Prop. I.

* Communicated by the Author.

(p. 690) of 'Electromag.' For brevity I must refrain from redescribing my methods and notation and must constantly refer the reader to the original paper.

PROP. If τ_a, τ_b be fluxes, $V\tau_a\tau_b/D$ is an intensity, D, D' being the densities of matter in the standard and present positions respectively. [In the original paper D was used for electrical density and D_m for material density.] By this is meant that $V\tau_a\tau_b'/D'$ bears the same relation to $V\tau_a\tau_b/D$ as does σ' to σ in equations (5) § 7 of 'Electromag.'

To prove, we have

$$\tau_a' = m^{-1}\chi\tau_a, \quad \tau_b' = m^{-1}\chi\tau_b, \quad D' = m^{-1}D.$$

Hence

$$V\tau_a'\tau_b'/D' = m^{-1}V\chi\tau_a\chi\tau_b/D = \chi'^{-1}V\tau_a\tau_b/D.$$

3. It may be noticed that the investigation in 'Electromag.' is not apparently complete for a perfect dielectric, though in a sense the equations are correct. For such a dielectric ϵ is zero, and it would seem to follow from equation (28) § 50 that since $\epsilon=0$, $\mathbf{d}\nabla l=0$. This, however, is not true, for in this case we have the condition $S\nabla d=0$, which introduces a new term into equation (28). It is easy to see, however, that the case is met by ignoring equation (28) § 50 and putting \mathbf{E} of equation (29) equal to zero; for D and d have now the same meaning, and account has been taken in equation (29) of $S\nabla D=0$. Since in the present paper \mathbf{E} of equation (29) is always zero, we will use \mathbf{E} to stand for the \mathbf{E}_0 of § 61 (except that it is best to *define* it not as \mathbf{RK} but as $-\mathbf{d}\nabla l$, or, what is the same in the present case, $-\mathbf{D}\nabla l$). Thus \mathbf{E}' will have the meaning usually given to \mathbf{E} .

4. For a fluid we have for the l' of § 51,

$$l' = -D'(\rho'^2/2 + w) + (2\pi K'^{-1}D'^2 - \mu'H'^2/8\pi), \quad \dots \quad (1)$$

where w is the ordinary potential energy per unit mass due to compression or rarefaction, and is therefore a function of D' only; and where K', μ' are scalars, which also can only be functions of D' .

Thus

$$\begin{aligned} \mathbf{d}l' &= \mathbf{d}D' \cdot \partial l' / \partial D' = \mathbf{d}(m^{-1}D) \cdot \partial l' / \partial D' \\ &= -\frac{1}{2}\Psi^{-1}D'\partial l' / \partial D' \end{aligned}$$

['Electromag.' § 54, equation (10)]. Hence [ibid. § 54, equation (20)],

$$[\phi'] = D'\partial l' / \partial D',$$

or [ibid. equation (21)]

$$\phi' = -(p + p_e) - 2\pi K'^{-1}D'(\)D' - \mu'H'(\)H'/8\pi, \quad \dots \quad (2)$$

where p is put for the ordinary pressure given by

$$p = (D' \partial / \partial D' - 1)(D' w) = D'^2 \partial w / \partial D'; \quad . \quad . \quad (3)$$

and p_e is an additional pressure due to the variation of K' and μ' with D' given by

$$p_e = D' \partial / \partial D' . (-2\pi K'^{-1} D'^2 + \mu' H'^2 / 8\pi). \quad . \quad . \quad (4)$$

Now in equation (26), § 50, put

$$F = \Phi_f = \Phi' = 0.$$

Thus

$$\begin{aligned} D' \ddot{\rho}' &= -D' \nabla' W + \phi' \Delta' \\ &= -D' \nabla' W - \nabla' (p + p_e) - \frac{1}{2} (D' \Delta' E' + B' \Delta' H' / 4\pi), \end{aligned}$$

where we have substituted E' for $4\pi K'^{-1} D'$ and B' for $\mu' H'$. From these connexions and the equations

$$S \nabla' B' = S \nabla' D' = 0 \quad . \quad . \quad . \quad (5)$$

it is quite easy to prove that

$$\begin{aligned} B' \Delta' H' &= 2 \nabla B' \nabla \nabla' H' - H'^2 \nabla' \mu', \\ D' \Delta' E' &= 2 \nabla D' \nabla \nabla' E' - E'^2 \nabla' K' / 4\pi, \end{aligned}$$

and therefore that

$$\begin{aligned} -\nabla' p_e - \frac{1}{2} (D' \Delta' E' + B' \Delta' H' / 4\pi) \\ = -\nabla (D' \nabla \nabla' E' + B' \nabla \nabla' H' / 4\pi) - D' \nabla' P_e, \end{aligned}$$

where

$$8\pi P_e = E'^2 \partial K' / \partial D' + H'^2 \partial \mu' / \partial D'. \quad . \quad . \quad (6)$$

Hence, putting as usual

$$P = \int (dp / D'), \quad . \quad . \quad . \quad (7)$$

we obtain

$$\ddot{\rho}' = -\nabla' (W + P + P_e) - \nabla (D' \nabla \nabla' E' + B' \nabla \nabla' H' / 4\pi) / D', \quad . \quad (8)$$

which, when the electrical terms are omitted, is the usual hydrodynamical equation of motion.

Put now

$$\dot{\rho}' = \sigma', \quad . \quad . \quad . \quad (9)$$

and let σ be an intensity. Noting that D' , $\nabla \nabla' E'$, B' and $\nabla \nabla' H'$ are all fluxes, and therefore, by § 2 above, that

$$\nabla (D' \nabla \nabla' E' + B' \nabla \nabla' H' / 4\pi) / D'$$

is an intensity, we obtain from equation (8)

$$\chi' \dot{\sigma}' = -\nabla (W + P + P_e) - \nabla (D' \nabla \nabla' E' + B' \nabla \nabla' H' / 4\pi) / D. \quad (10)$$

Now

$$\chi' \dot{\sigma}' = d(\chi' \sigma') / dt - \chi' \sigma' = \dot{\sigma} + \nabla_1 S \sigma_1 \sigma'.$$

Also

$$\nabla \nabla \mathbf{H} = 4\pi \dot{\mathbf{D}}, \quad \nabla \nabla \mathbf{E} = -\dot{\mathbf{B}}; \quad . \quad . \quad . \quad (11)$$

the first being given by equations (36) and (37) of § 50 of 'Electromag.', and the second by equation (20) § 62, and equation (34) § 50. Thus

$$d(\sigma - \nabla \mathbf{D} \cdot \mathbf{D})/dt = -\nabla (W + P + P_e + \sigma^2/2). \quad (12)$$

5. The intensity $\nabla \mathbf{D} \cdot \mathbf{D}$ I shall call the Poynting intensity. For the present position of matter it is parallel to the Poynting flux $\nabla \mathbf{E} \cdot \mathbf{H}/4\pi$. In fact, \mathbf{P} being the Poynting flux and \mathbf{Q} the Poynting intensity,

$$\mathbf{D}' \mathbf{Q}' = v^{-2} \mathbf{P}', \quad . \quad . \quad . \quad (13)$$

where v is the velocity $1/\nu(K'\mu')$ of light in the dielectric. [Note that \mathbf{P} here is not quite the same as the \mathbf{P} of § 103 of 'Electromag.', as that includes $-\phi \chi' \rho' = -\phi \sigma$.]

It will thus be seen that the term $\nabla \mathbf{D} \cdot \mathbf{D}$ is in all ordinary dielectrics utterly insignificant compared with the term σ in equation (12), and probably it would be quite hopeless to detect it by experiment, especially as all fluids are far from perfect.

Operating on equation (12) by $\nabla \cdot \nabla$ we see that the flux $\nabla \nabla (\sigma - \mathbf{Q})$ is a constant for every element of the dielectric. Thus *Helmholtz's theorems concerning vortices must be modified by substituting the velocity—the Poynting intensity for the velocity*. This may be obtained in a different way. Take the line-integral of both sides of eq. (12) between two particles of the fluid. We find that *Lord Kelvin's theorem concerning flow must be modified by making the same change and further adding P_e to the expression $W + P + \sigma^2/2$, which occurs in that theorem*.

6. Though the effect of the Poynting intensity appearing in the equation of motion is insignificant in its influence on the motion of gross matter, it may be quite otherwise *in vacuo*. It was, in fact, by considering the case of the æther that I was led to eq. (12).

Turning now to the æther, we will consider three cases:—

I. The one mentioned in § 2 of 'Electromag.', viz., where the density D is zero and the ordinary potential energy w is also zero.

II. Where D is small (compared with the density of gross matter) but not zero, and where w is still zero.

III. Where D has any value not large and where w (no longer assumed merely a function of D) varies largely with strain except in the neighbourhood of gross matter.

7. Case I. is an extreme one, but seems to me the most natural to make on the theory developed in 'Electromag.'

Before considering this case a word or two of general import will be given.

I cannot see that Maxwell has shown his right to ignore, as he does in considering the propagation of waves, the equation of motion of the medium. It is not hard to show that we may disregard it if we accept his equations as literally true for rapid waves in a medium of ordinary density. But may we do so for the æther, and may we do so in the case of gases where the gross matter present has practically no effect on electrical actions?

By ignoring the equation Maxwell is led to the conclusion that the æther when it is excited by electromagnetic waves exerts a pressure on gross matter. What is the effect of this pressure after it has left the sun and before it has again reached gross matter? It must have some effect on the æther, but the equations expressing that effect are wanting. If we tie ourselves down to a strict dynamical theory these equations appear, and we have to decide what is their meaning. In case I., on the present hypothesis, there is no doubt at all about the meaning. It can be expressed either by the equation

$$\nabla (4\pi \mathbf{D}' \nabla' \mathbf{E}' + \mathbf{B}' \nabla' \mathbf{H}') = 0, \quad . \quad . \quad . \quad (14)$$

or by saying that the Poynting intensity remains constant for every element of the æther. It follows also that there is no ponderomotive action and reaction between the æther and gross matter, which has an obvious bearing on the question of whether or not the æther can exert a pressure on gross matter.

Are these results consistent with an electromagnetic theory of light? I think they are not, but this is not on account of the most obvious apparent consequences. Take, for instance, the fact of the constancy of the Poynting intensity. From this we deduce that if any part of the æther were ever electrically at rest the actual displacement and magnetic force for that part would always be parallel, and if the displacement and magnetic force were for any part of the æther ever not parallel that part could never come electrically to rest.

8. These results are not necessarily inconsistent with a theory of light, for it must be remembered that the æther now contemplated is capable of indefinite expansion or condensation, and that whatever be the amount of this expansion or condensation its electrical constants remain absolutely unaffected. But by indefinite expansion the volume distribution of Poynting intensity is indefinitely diminished, and conversely for condensation. In fact, the æther is capable of

moving, and in case of a forced irregular disturbance would move with velocities comparable with that of light. This will explain how we can on the present hypothesis account for the encroachment with sufficient rapidity of light waves on a previously dark region.

But there is a difficulty I have not been able to surmount. Eq. (14) is not linear in the electromagnetic vectors, and hence in general the superposition of two solutions of our equations does not give a third solution. I will show directly how a single plane wave which is sufficiently arbitrary to leave room for the explanation of polarized light &c. can be borne by our æther, but I have failed in the endeavour to see what the effect on each other of two plane waves inclined to one another would be. It looks as if they must be altered in kind by their encounter, and this is contrary to several optical facts.

9. Without further preface I proceed to the consideration of case I. It may be remarked that a great part of the work below relating to this case is applicable to ordinary dielectrics, so that though I am inclined to reject the case, the work is not thrown away.

Our equations are now (5), (11), and (14). Equations (11) are for present purposes more conveniently written by eq. (23) § 63 of 'Electromag.'

$$\begin{aligned} (4\pi)^{-1} \nabla' \mathbf{H}' &= \partial \mathbf{D}' / \partial t + \nabla \nabla' \mathbf{D}' \sigma' \} \\ - \nabla' \mathbf{E}' &= \partial \mathbf{B}' / \partial t + \nabla \nabla' \mathbf{B}' \sigma' \} \end{aligned} \quad . \quad . \quad (15)$$

the ∇ being unnecessary before $\nabla' \mathbf{H}'$ and $\nabla' \mathbf{E}'$ when \mathbf{K}' and μ' are constant scalars, as we suppose to be the case for the æther. Putting now

$$\mathbf{H}' \nu \mu' = \mathbf{H}_0, \quad \mathbf{E}' \nu \mathbf{K}' = \mathbf{E}_0, \quad v^2 \mu' \mathbf{K}' = 1, \quad . \quad . \quad (16)$$

$$\begin{aligned} v \nabla' \mathbf{H}_0 &= \partial \mathbf{E}_0 / \partial t + \nabla \nabla' \mathbf{E}_0 \sigma' \} \\ - v \nabla' \mathbf{E}_0 &= \partial \mathbf{H}_0 / \partial t + \nabla \nabla' \mathbf{H}_0 \sigma' \} \end{aligned} \quad . \quad . \quad . \quad (17)$$

With this notation eq. (14) becomes

$$\nabla (\mathbf{E}_0 \nabla' \mathbf{E}_0 + \mathbf{H}_0 \nabla' \mathbf{H}_0) = 0. \quad . \quad . \quad . \quad (18)$$

Notice that if σ' is zero equations (17) reduce to Maxwell's. Hence any solution of Maxwell's which also satisfies eq. (18), or, what amounts to the same, when σ' is zero any solution of Maxwell's which renders $\nabla \mathbf{E}_0 \mathbf{H}_0$ constant at every point is a solution also of our problem. We shall be led to such a solution below.

10. The only case I have been able to discuss is a plane wave with \mathbf{E}_0 and \mathbf{H}_0 in the front. Suppose, then, \mathbf{E}_0 and \mathbf{H}_0

are functions of z and t only, which are perpendicular to k [i, j, k taken as usual with reference to the rectangular axes x, y, z]. Thus

$$\nabla' = k\partial/\partial z, \quad (19)$$

and therefore ∇' is commutative with k . Put

$$\mathbf{E}_0 - k\mathbf{H}_0 = 2\alpha, \quad \mathbf{E}_0 + k\mathbf{H}_0 = 2\beta, \quad (20)$$

which give

$$\mathbf{E}_0 = \alpha + \beta, \quad \mathbf{H}_0 = k(\alpha - \beta). \quad (21)$$

Equation (18) now gives

$$S(\alpha\partial\alpha/\partial z + \beta\partial\beta/\partial z) = 0,$$

or

$$\alpha^2 + \beta^2 = -X^2, \quad (22)$$

where X is a function of the time only.

From the constancy of the Poynting intensity we see that it is needless to consider a more general value of σ' than uk , where u is a scalar function of z and t only. Substituting this value and multiplying the second of equations (17) by k and adding it to and subtracting it from the first we obtain

$$\partial\alpha/\partial t + \partial\{(u+v)\alpha\}/\partial z = 0 \quad (23)$$

$$\partial\beta/\partial t + \partial\{(u-v)\beta\}/\partial z = 0 \quad (24)$$

These give at once

$$\alpha = \partial\gamma/\partial z, \quad (u+v)\alpha = -\partial\gamma/\partial t, \quad . . (25)$$

$$\beta = \partial\delta/\partial z, \quad (u-v)\beta = -\partial\delta/\partial t, \quad . . (26)$$

where of course γ, δ , like α, β , are vector functions of z and t only, which are perpendicular to k .

Suppose $\gamma = \gamma_1 i + \gamma_2 j$, where γ_1 and γ_2 are scalars. Since $\partial\gamma/\partial z$ and $\partial\gamma/\partial t$ are parallel, it follows that

$$\frac{\partial\gamma_1}{\partial z} / \frac{\partial\gamma_1}{\partial t} = \frac{\partial\gamma_2}{\partial z} / \frac{\partial\gamma_2}{\partial t}$$

or

$$J\left(\begin{matrix} \gamma_1 & \gamma_2 \\ z & t \end{matrix}\right) = 0. \quad (27)$$

Hence γ_1 and γ_2 and therefore γ are functions of a single scalar function θ of z and t . θ is to a certain extent arbitrary, since any function of θ will serve instead of θ . Thus

$$\gamma = \gamma(\theta), \quad (28)$$

where $\gamma(\theta)$ stands for any vector function of θ which is perpendicular to k . Similarly

$$\delta = \delta(\phi),$$

where ϕ and $\delta(\phi)$ are functions exactly similar to θ and $\gamma(\theta)$.

Equations (25) and (26) now give

$$\partial\theta/\partial t + (u+v)\partial\theta/\partial z = 0, \quad \dots \quad (29)$$

$$\partial\phi/\partial t + (u-v)\partial\phi/\partial z = 0. \quad \dots \quad (30)$$

These show that if a point move in the direction of k faster by v than the æther, θ will for it remain constant, and if a point move in the direction of $-k$ faster by v than the æther, ϕ will for it remain constant. In other words, θ and ϕ are propagated relatively to the æther with the velocity v in the direction of and that opposite to k .

11. We may drop the γ and δ used above by putting

$$\alpha = \alpha(\theta) \cdot \partial\theta/\partial z, \quad \beta = \beta(\phi) \cdot \partial\phi/\partial z, \quad \dots \quad (31)$$

where $\alpha(\theta)$ and $\beta(\phi)$ are vector functions of θ and ϕ which are perpendicular to k . Equations (29), (30), and (31) are exactly equivalent to all the former equations involving α , β , γ , and δ .

On account of the arbitrariness of θ and ϕ they may be chosen so that $\partial\theta/\partial z$ and $\partial\phi/\partial z$ are each unity, or, again, they may be taken as the angles α and β make with i .

The unknown u may of course be eliminated from equations (29) and (30), leaving but one equation, but clearer ideas seem to be obtained by not effecting this elimination.

Let us now confine ourselves to propagations in one direction, and therefore put $\beta = 0$. Take θ so that $\partial\theta/\partial z = 1$, i. e. $\theta = z - Y'$, where Y' is a function of t only. Substituting this value of θ in equation (29),

$$u = \partial Y'/\partial t - v.$$

Hence if the æther be oscillating about a mean position

$$\partial Y'/\partial t = v + \dot{Y}'',$$

where Y'' is a function of t oscillating about the value zero. It follows that $Y' = vt + Y$ or

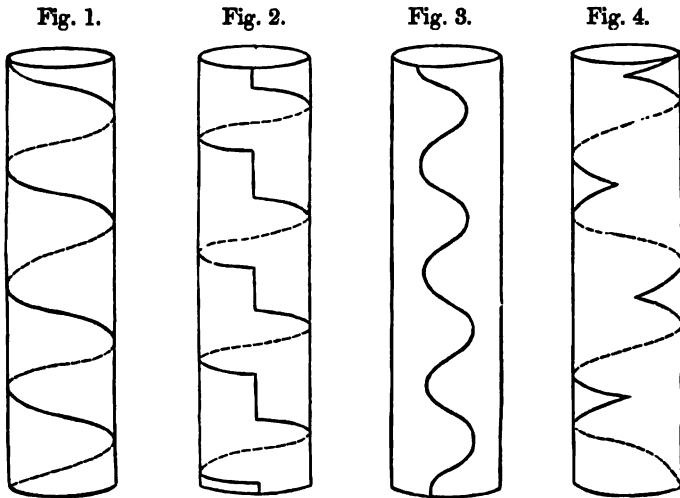
$$\theta = z - vt - Y, \quad \dots \quad (32)$$

where Y is an oscillatory function of t , whose average value is zero.

The solution so far is applicable to an isotropic dielectric, for which K' and μ' are independent of strain. In this aspect it will be returned to later.

12. For the æther at present under consideration we see by equation (22) that α^2 and therefore $\tau\alpha$ is a function of the time only. But it is a function (in the case of waves) of t and z , i. e. it is a constant.

Let Y of equation (32) be zero. Suppose at any instant lines are drawn from all points of the axis of z equal and parallel to the values of α there. Their extremities will lie on a right cylinder with z for axis, and the curve they form will be a complete representation of the wave. Figures 1, 2, 3, 4 thus represent different types of waves that can be borne



by our æther. Fig. 1 is of course a circularly polarized wave. Fig 2 is a wave partly plane-polarized and partly circularly polarized, i. e. elliptically polarized. Fig. 3 would probably appear to us as a plane-polarized, and fig. 4 as ordinary unpolarized light.

All such waves are particular ones of Maxwell's. Now Maxwell asserts that when such waves are incident on gross matter the æther exerts a pressure on that matter. But as we have seen, on the present theory all ponderomotive forces consist of actions and reactions between different parts of gross matter and never between gross matter and æther, and yet for the present case our stress is exactly the same as Maxwell's. The explanation of the apparent discrepancy is contained in § 75 of 'Electromag.' If we find that a certain stress suffices to explain certain experimental facts, there are an infinite number of other stresses that will also do so. We

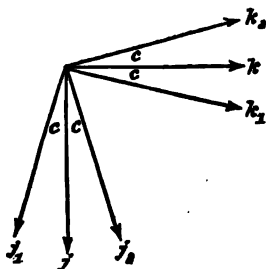
do not therefore conclude that on the present theory this pressure of Maxwell's would not exist, but we do conclude that it does not exist for eight minutes in the æther between the sun and earth, that in fact at the instant when the earth experiences the pressure the sun or some other body experiences the reaction. This is, of course, because in the present theory the conditions of equilibrium are *always* satisfied by the æther.

13. Take θ as the angle that α makes with i . The solution of § 12 with this meaning of θ is

$$\alpha = A(i \cos \theta + j \sin \theta), \quad . \quad . \quad . \quad . \quad (33)$$

where A is a constant and θ is any function of $z-vt$, for instance $2\pi(z-vt)/\lambda$. I will now show that it is impossible for two waves of this type inclined to one another to coexist.

Fig. 5.



Let i be drawn perpendicular to the plane of the paper upwards. Let j, k, j_1, k_1, j_2, k_2 be related as shown in fig. 5. It is required to find whether with σ^1 zero the following equations can be satisfied:—

$$\left. \begin{aligned} \mathbf{E}_0 &= \mathbf{E}_{01} + \mathbf{E}_{02}, \quad \mathbf{H}_0 = \mathbf{H}_{01} + \mathbf{H}_{02}, \\ \alpha_1 &= A_1(i \cos \theta_1 + j_1 \sin \theta_1), \quad \mathbf{E}_{01} = \alpha_1, \quad \mathbf{H}_{01} = k_1 \alpha_1 \\ \alpha_2 &= A_2(i \cos \theta_2 + j_2 \sin \theta_2), \quad \mathbf{E}_{02} = \alpha_2, \quad \mathbf{H}_{02} = k_2 \alpha_2 \end{aligned} \right\}, \quad . \quad (34)$$

where A_1 and A_2 are constants, and θ_1 and θ_2 are functions of z_1 and t and of z_2 and t respectively.

Since σ' is zero these values of \mathbf{E}_0 and \mathbf{H}_0 satisfy equation (17), and we know that in this case equation (18) is equivalent to the equation $\nabla \mathbf{E}_0 \mathbf{H}_0 = \text{a constant throughout time and therefore throughout space}$. We have seen that $\nabla \mathbf{E}_{01} \mathbf{H}_{01}$ and $\nabla \mathbf{E}_{02} \mathbf{H}_{02}$ are such constants, so that it only remains to make if possible $\nabla (\mathbf{E}_{01} \mathbf{H}_{02} + \mathbf{E}_{02} \mathbf{H}_{01})$ a constant. Now

$$\begin{aligned}
 V(\mathbf{E}_0, \mathbf{H}_{02} + \mathbf{E}_{02} \mathbf{H}_{01}) &= V(\alpha_1 k_2 \alpha_2 + \alpha_2 k_1 \alpha_1) \\
 &= A_1 A_2 V\{(i \cos \theta_1 + j_1 \sin \theta_1)(-i \sin \theta_2 + j_2 \cos \theta_2) + (i \cos \theta_2 \\
 &\quad + j_2 \sin \theta_2)(-i \sin \theta_1 + j_1 \cos \theta_1)\} \\
 &= A_1 A_2\{(k_1 + k_2) \cos(\theta_1 - \theta_2) + V j_1 j_2 \sin(\theta_1 - \theta_2)\} \\
 &= A_1 A_2\{2k \cos C \cos(\theta_1 - \theta_2) + i \sin 2C \sin(\theta_1 - \theta_2)\},
 \end{aligned}$$

where $2C$, as indicated in fig. 5, is the angle between j_1 and j_2 and between k_1 and k_2 . Hence when neither $\cos C$ nor $\sin C$ is zero, *i. e.* when the waves are not parallel, we must have both $\cos(\theta_1 - \theta_2)$ and $\sin(\theta_1 - \theta_2)$ constant throughout space and time, *i. e.* $\theta_1 - \theta_2$ must be constant. But since θ_1 involves z_1 and θ_2 involves z_2 , this is impossible. Hence two such waves cannot coexist.

14. This shows that if a wave incident on a reflecting surface be of the present type, it is if in free æther altered in type by the reflected wave.

Even this, however, is not completely condemnatory of the present hypothesis; for

(1) Although such waves will be altered in type we have not shown in what manner, and I am at present unable to do so. They may be only so altered that the alteration does not affect our senses. This, however, I consider extremely improbable.

(2) We have no experimental evidence that in *free æther* such alteration does not occur. In our most perfect vacua the density is such that if they could be assumed continuous material plenums, Maxwell's ignorance of the equilibrium equation would be justifiable. Though we have every reason to believe that they are not such plenums, yet owing to our ignorance of the effect on the æther of the proximity of material atoms, I think we are justified in so regarding them for present purposes. If this assumption be made, Maxwell's theory of light is applicable to all terrestrial experiments. It would still remain on the present hypothesis to be proved that the apparent positions and spectra of the heavenly bodies are not appreciably altered by the interferences just considered. This would seem by no means so difficult as the task just now proposed.

But there is another grave difficulty. We have no guarantee that the velocity of light in space will be practically a constant. If, for instance, there were in the solar system a circulation of the æther whose velocity was comparable with that of light, the apparent positions of the sun and planets would be largely affected.

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15. However this be, our ideas would be greatly simplified if Maxwell's ignorance of the equilibrium equation could be justified by some suitable modification of the fundamental assumptions.

Let us now assume that the æther has a material density sufficiently large to render σ' small compared with the velocity of light. This is case II. of § 6 above. In this case Maxwell's ignorance will be justified.

To fix the ideas let us suppose that a plane-polarized wave with the energy of strong sun-light causes the maximum æther velocity to be b times that of light where b is small. σ' may then be regarded as a small quantity in equations (15) and (17), so that equations (15) reduce to Maxwell's.

Since we now suppose the velocity to be small and oscillatory, the present and standard positions may be assumed to coincide, and we have

$$E\nu K = A_i \cos \{2\pi(z - vt)/a\} = A_i \cos \theta,$$

$$H\nu\mu = A_j \cos \theta,$$

for the wave we contemplate. The energy λ per unit volume is given by

$$\lambda = -(\mathbf{K}\mathbf{E}^2 + \mu\mathbf{H}^2)/8\pi = A^2 \cos^2 \theta / 4\pi.$$

Hence the average value $\bar{\lambda}$ of λ is

$$\bar{\lambda} = A^2/8\pi = 4.225 \times 10^{-5}$$

in ergs per cub. centim., according to the data given in § 793 of Maxwell's 'Electricity and Magnetism.'

The velocity of the æther may be calculated from Maxwell's stress, or written down at once from equation (12) above. For in the present case W , P , and P_z are zero, and σ'^2 may be neglected. Thus

$$\begin{aligned} D\dot{\sigma} &= dVDB/dt = (4\pi v)^{-1} A^2 k d(\cos^2 \theta)/dt \\ &= v^{-1} \bar{\lambda} k d(1 + \cos 2\theta)/dt. \end{aligned}$$

Since σ is to vary about a mean value

$$D\sigma = v^{-1} \bar{\lambda} k \cos 2\theta.$$

Thus

$$b = \sigma_m / kv = \bar{\lambda} / v^2 D,$$

where σ_m is the maximum value of σ . Thus approximately

$$bD = 5 \times 10^{-26}.$$

The lower limit obtained by Lord Kelvin for the density of æther ('Math. and Phys. Papers,' ii. 32) is

$$D = 10^{-22}$$

approximately. In this case $b = 1/2000$. There seems then

no difficulty on the mere ground of requisite density in explaining the justifiability of ignoring the equation of equilibrium. And we see that in all material transparent bodies we are fully warranted.

I have not, however, been able to satisfy myself that in the present case the æther density is stable, *i. e.* that it will not gather itself up round nuclei. If it did so, its density not in the neighbourhood of these nuclei might be too small to enable us to ignore the equation of equilibrium.

16. Case III. seems the most satisfactory one. Suppose the æther absolutely rigid and motionless except in a thin skin coating every atom of matter. Suppose in this skin it has exactly the same freedom as in case I. This is equivalent to supposing that in the æther the terms of l depending only on Ψ vary infinitely rapidly with all variations of Ψ except in the skin, where they are zero. In this case the atoms of matter will be unimpeded in their motion through the æther, the equation of equilibrium can be rigorously ignored for the æther, the electrical equations for the æther reduce to Maxwell's form, and the investigation in § 64 of 'Electromag.' concerning convection currents is made satisfactory.

These assumptions sound highly artificial, so it is well to remark that the mathematical results of a theory apparently different in fundamental assumptions are identical. This theory may be stated in the following different forms:—

(1) The æther is immovable and freely penetrates all atoms offering no resistance to their motion.

(2) The theory of 'Electromag.' is true of matter, but Maxwell's theory is true of free æther.

(3) For matter the theory of 'Electromag.' is true. For space where there is no matter we have in place of the fundamental assumptions of §§ 23 to 31 the following:—For such space the undashed letters have no meaning. The Lagrangian function is the volume-integral of

$$2\pi K_0^{-1}D^2 - \mu_0 H^2/8\pi.$$

$$K=0. \quad S\nabla'D=0. \quad \nabla\nabla'H=4\pi C'=4\pi\partial D/\partial t.$$

In addition certain assumptions must be made with regard to the bounding surface of matter. They are most readily expressed by saying that for a thin skin bounding the matter the assumptions of 'Electromag.' are true, and that for this region the Lagrangian function per unit volume of the standard position is $2\pi K_0^{-1}D^2 - \mu_0 H^2/8\pi$, the outer surface of the skin being motionless and the inner surface moving continuously with the matter.

I have given these three forms to indicate that the theory

is not so artificial as it at first sight appears. For mathematical purposes the first form of the theory is the most convenient.

17. Applying the solution of § 11 to a moving dielectric (constant scalar permeability and capacity) we see that the velocity of light ought on the present theory to be altered by the full value of the velocity of the medium. Thus the theory requires some modification to explain Michelson's results, &c. The last section at once suggests a possible form of such modification, viz. that the theory of 'Electromag.' is true for the interior of material atoms but not for the æther in their immediate vicinity. In 'Electromag.' the individual atoms of matter were not taken into account. To meet the present theory on the lines of 'Electromag.' it would be necessary to make some modification in the fundamental assumptions.

Hobart, April 8, 1893.

XVII. *Further Data on Colour-Blindness.*—No. IV.

By Dr. WILLIAM POLE, F.R.S.*

HERING's *Explanation of the defect.*

EVERYBODY who has had to do with colour-blindness has heard of the connexion with it of the eminent physiologist, Professor Ewald Hering, of Prague; but it is remarkable how little is known here of his actual writings. Between 1872 and 1874 he laid before the Imperial Academy of Sciences of Vienna six communications on the vision of light and colours, which were afterwards published separately †, and have now become classical in the literature of the subject. In 1879 I published in 'Nature' a set of articles giving an abstract of the work, and this abstract has formed, I believe, the only direct account in the English language of Hering's labours in the department of colour-vision, although his writings thereon have been legion.

This work, however, does not refer to colour-blindness, except in a few lines promising a future special treatment of it. The promise was fulfilled in 1880 by an Essay entitled "Zur Erklärung der Farbenblindheit, aus der Theorie der Gegenfarben," published at Prague in a scientific serial called 'Lotos.' Some reprints were circulated, of which I was fortunate enough to get one; but it is very scarce, and is probably little known in England except to the few who interest themselves specially in these foreign scientific views.

* Communicated by the Author.

† *Zur Lehre vom Lichtsinne.* Zweiter Abdruck. Wien, 1878.

As the theory embodied in it is a matter of constant comment whenever colour-blindness comes under discussion, it may not be amiss to give to the English public some account of the author's own manner of stating his opinions, which I am enabled to do with his concurrence.

The title of the paper is "An Essay towards the Explanation of Colour-Blindness by the Theory of Opposite Colours," and it is divided into five sections.

In the *First Section*, headed "Some passages from the Theory," the author explains generally what the theory is, so far as is necessary for the purpose in view, giving particularly an explanation of the term "*Gegenfarben*." He holds that there are essentially six simple visual sensations—white, black, yellow, blue, red, and green, by the mixtures of which, in different proportions, all colour-impressions arise.

The mixture of white and black produces various degrees of grey, which he believes to be present, to some extent, in all colour-impressions. But the result of mixing the other coloured sensations depends on certain relations which the four fundamental colours yellow, blue, red, and green have to each other. It is found that more than two of these can never be recognized in the same mixture, and that certain pairs of them cannot both appear in the same hue. Hence the two colours forming such a pair are called *Gegenfarben*, i. e. opposed, or contrary, or antagonistic colours. There are two such opposed pairs: yellow and blue, in certain definite hues, form one pair; red and green, in certain definite hues, form the other pair. The yellow, for example, may combine with red, forming a new compound colour, in which the yellow and red are both recognizable; or with green, forming a yellow-green in which both yellow and green are recognizable; but it cannot form a new compound colour with its opposite blue; for, put what proportions you will (except the neutralizing ones), the mixture will not give any new hue, but will remain either blue or yellow. Similarly, the red may combine with blue or yellow to form new hues, but cannot do so with green. And so on with the others*.

* This relation of "opposed" colours will be recognized as corresponding to what are usually called "complementary" pairs; but Hering considers that the idea of opposition is more forcible and emphatic; and it is on this principle that, as expressed in the title, his theory chiefly depends.

The precise hues of his four *Urfarben*, or fundamental colours, were, in this publication, left undetermined, but they have since been pretty nearly settled. The yellow and blue pair agree fairly with the ordinary ideas attached to the names, but the fundamental red and green do not do so, both inclining more towards blue; they correspond with the two neutral hues of the red-green blind.

The remainder of this section explains certain physiological or psychophysiological functions of vision by which the author conceives that the colour-sensations may be produced, and their peculiar relations accounted for. For these the earlier Memoir may be referred to. The most relevant proposition is, that in any pair of opposite colours the two sensations are produced by contrary actions on the same excitable substance. The author's views on these points have been much controverted, but the discussions upon them do not immediately affect the general nature of the colour-blind explanations.

The *Second Section* is "On the optical powers (*Valenzen*) of homogeneous and mixed light." It contains the author's views about the spectrum; and for the purpose of making them clear he has taken the German privilege of forming a new word, *Valenz*. It is from the Latin *valens*, powerful, efficacious; and is used to express the recognizable presence of a certain colour in a mixture. Thus the hue of scarlet, compounded of red and yellow, would be said to have both a red and a yellow valenz; crimson, compounded of red and blue, would have a red and a blue valenz, and so on. There is no good English equivalent for the word, and it will be simpler to use the original than a circumlocution.

The author holds that the whole of the spectral colours contain white, and therefore have a white "valenz," which is most distinct in the yellow and yellow-green, but less so in the other parts.

All rays from the extreme red or beginning of the spectrum as far as the pure or fundamental green (*Ur-grün*, or original green, a term borrowed from Preyer) contain also yellow, *i. e.* have a yellow valenz. All rays from that to the violet end contain blue or have a blue valenz. These distinctions divide the spectrum into two parts, one characterized by yellow, the other by blue. At the beginning of the red the yellow sensation is so weak that for the normal eye it is overpowered by the red, and similarly in the strong green it is overpowered by that colour; it is only in a small stripe that the pure yellow is seen, which corresponds to the *Urgelb*. The variations in the blue half are similarly characterized.

The pure yellow divides the yellow half of the spectrum into two quarters, and the pure blue similarly divides the blue half. The four quarters are therefore characterized as follows:—

Valenzen.

| | | |
|--------------------|-----|---------------------------|
| The First quarter | has | Red, yellow, and white. |
| The Pure yellow | „ | Yellow and white. |
| The Second quarter | „ | Yellow, green, and white. |
| The Pure green | „ | Green and white. |
| The Third quarter | „ | Green, blue, and white. |
| The Pure blue | „ | Blue and white. |
| The Fourth quarter | „ | Blue, red, and white. |

The *Third Section* contains “General observations on Colour-blindness.”

After remarking on various possible disturbances of colour-vision, as to which theory can give no account, the author states that it follows definitely from his doctrine that an eye which has no sensation of red can have no sensation of green and *vice versa*; and similarly for yellow and blue.

Now it appears that there are actually eyes for which the rays of light give no red and also no green sensations, while the yellow, blue, and white colour-effects remain, either as in the normal eye, or with modifications. Such eyes are red-green blind. Whether there is a corresponding blue-yellow blindness, with vision of red and green, is uncertain; but there appear to be cases where both pairs fail, *i. e.* blindness to all colour.

The author adds:—“I possess at present too little personal experience on colour-blindness to enable me to give a general theory of it. But my studies for years in the literature of such investigations are sufficient to show me that the phenomena of colour-blindness are irreconcilable with the Young-Helmholtz theory, and they especially convince me that all really red-blind persons are also green-blind, and *vice versa*; and further recent observations render this conclusion continually more probable. When Helmholtz wrote his ‘Physiological Optics’ the circumstances were very different, and the proportionally scarce material at his disposal appeared well calculated to support his theory.”

The *Fourth Section* is devoted to the consideration of “General or total Colour-blindness,” and of a remarkable case of the kind discovered by Becker. By a careful study of this case, the author endeavours to show how difficult the facts of it are to reconcile with the theory of the three sensations, and how consistently it may be explained by his own hypothesis.

The *Fifth Section* treats of *Red-green Blindness*, which is the most usual form of the defect, and with which we have chiefly to do here.

The author points out that if we suppose the red and green elements to be removed from normal vision, the blue, yellow, white, and black sensations remaining as before, then the impressions given by the spectrum will be exactly as they are described in the colour-blind cases. The patient will see the first half of the spectrum a pure yellow, and the second half a pure blue; but both will be modified in different places with different *nuances* and degrees of saturation.

Before reaching the point which corresponds to the normal fundamental green the yellow will gradually fade in the presence of the colourless or white sensation, and beyond this point the blue will enter and gradually increase in a corresponding manner.

Such a colour-blind person will not be actually blind to the pure green of the normal eye; he will see it as a colourless sensation. And on the other hand the rays of the spectral red will be visible to him so far as their yellow and white "Valenzen" are strong enough to make an impression. His spectrum will therefore be divided into a first yellow and a second blue half; and as all the various rays of each half will only be distinguished by various additions of black or white, and not by difference of hue, all his colour-sensations may be imitated by suitable mixtures of yellow or blue with white, black, or grey. Also as his two hues must be complementary, mixtures of the two together in the proper proportions will be colourless.

This description assumes that the yellow, blue, and white effects are the same for the colour-blind as for the normal eye. It is, however, found that these may vary in different colour-blind individuals [as indeed they do in the normal eye], and this has given occasion to divide such patients into two classes which the adherents of the Young-Helmholtz theory separate as red-blind and green-blind. But the author has tried patients of both classes, and has found his explanation equally applicable without exception.

The author then describes experiments he has made with the spectrum. The colourless spot lies, as is well known, between *b* and *F*; it is not always in the same place, but lies sometimes nearer *b* and sometimes nearer *F*. It is possible that an analogous difference of place may exist in normal eyes; for in the place where one person may see a pure green another may see a blue-green or a yellow-green, and so on.

The position of the whole blue and yellow spectrum depends on the position of the neutral spot. The farther this spot lies towards the blue so much farther is the beginning of the yellow spectrum shifted in the same direction, so

beginning with rays of a smaller wave-length than correspond to the extreme red. The longer waves have then little or no yellow effect; and since the white effect is also wanting there, the spectrum appears shortened at the red end.

Kries and Küster found that the red end appeared more saturated than the yellow: so that red-green blind persons can distinguish rightly a saturated red of the hue of the spectral red from yellow; they understand by red a highly saturated yellow. Such persons, if their spectrum is not shortened, probably see, instead of the spectral red, a yellow of higher saturation than normal eyes can ever see. For with the latter the pure yellow hue is strongly mixed with white; and as they go to orange and beyond, the yellow becomes more and more overpowered by the red sensation.

Hering determined the hue of red which red-green blind persons matched with grey. He took a paper of the hue of spectral red, but which to him had clearly a yellow tinge, and he found that this required, to render it neutral, blue in different proportions for different patients; those with full-length spectrum, and the neutral point nearer the line E, required much blue; those with shortened spectrum, and the neutral point nearer F, required less blue.

The red thus obtained, and which the red-green blind eye matches with a certain grey, will appear to a normal eye sometimes more blue and sometimes more yellow. It tends more to purple the farther the neutral point lies towards the green, and more to the spectral red the farther it lies towards the blue. The grey matching red will, for a shortened spectrum, appear to the normal eye much darker than this red.

The neutral green and the neutral red of any red-green blind person may be matched with each other by adding white or black. And their mixture will also produce white for the normal eye, which proves them to be true complementary colours.

The author says:—"I have obtained above 100 equations in this way, with ten different colours, from four red-green blind patients, and have convinced myself that the consequences drawn from the theory of opposite colours are throughout correct. It is shown that these patients see only two colours. That these are yellow and blue is, it is true, not absolutely demonstrated, any more than that two normal persons both see yellow exactly alike. If anyone chooses to assert that one of them sees blue where the other sees yellow, we cannot contradict him, nor can he, on the other hand, prove his assertion. But it is only by the assumption that yellow

and blue are the hues of the red-green blind that congenital colour-blindness comes into analogy with the red-green blindness of the retina periphery, and with acquired red-green blindness, in both which there has been abundant proof that yellow and blue are really seen, as the affected person knows all colours by his own experience. The red-green blind patients always point out pure yellow and blue correctly, and no two colours in which blue on the one hand and yellow on the other hand are prominent, are ever mistaken for each other"*.

Hering then goes on to show, as many others have done, the striking incompatibility, with the observed facts, of the original explanation of colour-blindness by the absence of one of the three fundamental colours of the Young-Helmholtz doctrine. He takes, as an example, the assumed form called green-blindness (implying the normal vision of red and violet), and shows such inconsistencies in it as have almost entirely destroyed its credibility †.

He then alludes to the newer explanation introduced, to save the theory, by assuming that the excitability curves of the red and green have become identical‡. This he considers also unreasonable and inadmissible, as giving up the fundamental principle of Young's theory, and as not deducible from any facts observed. He concludes, on the whole, that if the Young-Helmholtz theory had not been bequeathed to physiologists as a venerable legacy, it would certainly never have been drawn from the examination of the colour-blind.

On the other hand, he calls attention to the fact that all the phenomena of red-green blindness arise quite simply and naturally out of the Theory of Opposed Colours.

Since the above described Essay was written Professor Hering has naturally matured his views, and has published much further interesting matter on the subject: he has engaged in sharp controversies on his colour theories generally; but does not appear to have been led to make any essential modifications in his explanations of dichromic vision.

* The remarkable confirmation by cases of one-eyed red-green blindness had not become prominent at that time: they were noticed fully by Hering at a later date.

† The original words are as follows:—"Ich will das Bild der 'Grünblindheit,' wie es sich nach der ursprünglichen Theorie von Helmholtz ergibt, hier nicht weiter skizziren, denn es glaubt, abgesehen von einigen Nachzüglern, doch Niemand mehr daran."

‡ See *Phil. Mag.* Jan. 1893, p. 55.

On the contrary, the tendency of investigation has been rather the other way; for the most recent conclusions of Helmholtz himself have tended to confirm Hering's views as to the large predominance of the white element in the spectral colours, and to establish almost exactly two of his fundamental colour-sensations.

Athenæum Club, S.W.
June 1898.

XVIII. On a new *Volumenometer*.

By J. E. MYERS, B.Sc.*

THE instrument described below was devised by Professor Stroud some three years ago, with the view of having a volumenometer which should be capable of yielding more accurate results than could be obtained by the older methods. After the instrument was made some preliminary trials showed that considerable difficulties would be encountered in making the instrument air-tight, and in consequence of the pressure of other work the instrument was put on one side till last October, when it was placed in my hands.

Various instruments, the principle of whose action is based on Boyle's law, have been devised with the object of determining the volumes of bodies without immersing them in liquids. The ordinary volumenometer devised by Say is described in textbooks, but a little calculation shows that no great accuracy can be obtained by its use. In Rüchhoff's volumenometer† determinations are made by running out mercury from the cavity of the instrument, thereby increasing the volume until the pressure is reduced to a certain fixed value. After the body has been placed in the cavity of the instrument a precisely similar experiment is performed. From a knowledge of the weights of mercury which run out in the two cases, the volume of the body introduced follows by a simple calculation. In Paalzow's volumenometer‡ measurements are made by increasing the volume of the instrument to a certain fixed limit, first without and then with the body in the cavity. The pressure, recorded by the manometer attached, is noticed in each case, whence the volume required is calculated. Baumhauer's volumenometer§ differs

* Communicated by the Physical Society: read June 23, 1898.

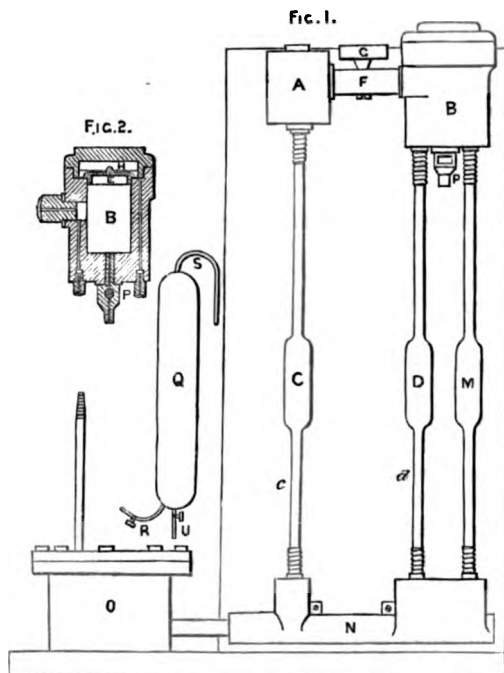
† Wied. Ann. vi. p. 288.

‡ Ibid. xiii. p. 332.

§ Archives Néerlandaises.

only from that due to Paalzow in a detail of construction. Messrs. Gee and Harden* suggest a method of determining the volumes of bodies, depending on the gravimetric estimation of the carbon dioxide occupying a vessel of known volume in which the body whose volume is required is placed. However, since a cubic centimetre of carbon-dioxide gas weighs only '0020 gramme, it is clear that the accuracy attainable in determining small volumes by this method cannot be very great. The volumenometer about to be described has proved itself capable of determining the volumes of bodies with as great expedition and much greater accuracy than any of the instruments above noticed.

Let A, B, C, D represent the volumes of the cavities of the vessels A, B, C, D. A is in connexion with C, and B with D, as indicated in the accompanying figure. Suppose mercury stands at the same level in each of the tubes *c* and *d*, and let



the same pressure applied simultaneously compress volume C into A, and volume D into B. The condition that the mer-

* British Association Report, Newcastle, 1889.

cury shall still be at the same level in both tubes is that the volume-ratios $\frac{A}{B}$ and $\frac{C}{D}$ shall be equal. This principle forms the basis of action of the instrument. The vessel B contains mercury, the quantity of which may be reduced by opening the tap P, and allowing some to run out. In this way the equality of volume-ratios may readily be obtained. The two volumes A and B can be put in communication with each other by means of the iron tube F, which is of small bore and is provided with a tap, G. The main difficulty encountered in using each of the instruments above described arises from the necessity of hermetically closing the cavity of the instrument. This difficulty we have successfully surmounted by providing that the pressures on the under and upper surfaces of the cap employed to close the instrument shall be approximately equal. The device employed will be readily understood by reference to figs. 1 and 2. C, D, and M are glass pipettes, each of about 20 cub. centim. capacity. They differ from ordinary pipettes in one particular, the upper attachments of the bulbs consisting of glass tubes of capillary bore (1 millim. diameter). The top of the pipette C communicates with the cavity of A. By means of the screw-cap E it will be seen that the cavity of B is divided into two compartments, an upper and a lower. The pipette D communicates with the lower, and M with the upper compartment of the cavity of B. It will be clear from this, that as pressure is applied to the mercury in the reservoir it will force the mercury up the pipettes, thus compressing the air both above and below the screw-cap. An approximate balance of pressure is sufficient to guard against leakage.

The lower extremities of the pipettes are connected to an iron portion N, which is in communication with the reservoir O, containing mercury, to which the arrangement for applying pressure Q, is attached.

At the places of juncture of the pipettes and the iron portions, iron pieces whose diameter is equal to the diameter of the pipettes are screwed in. The joints are made air-tight by means of thick-walled indiarubber tubing carefully wired down. The arrangement Q employed for applying, varying, or removing pressure consists of a cylindrical tube closed at both ends, connected with the water-main by means of a narrow tube R, provided with a tap. The tube S serves to effect communication with the reservoir O, and the pressure may be reduced at any time by opening the tap on the tube U. The pipettes C and D with the connecting piece N form a convenient differential manometer.

In making determinations with this instrument, an excess of mercury is placed in the lower compartment of the vessel B. The caps E and H are screwed down to fixed marks, and pressure is then applied. Owing to the excess of mercury in B the volume-ratio $\frac{A}{C}$ will be greater than the ratio $\frac{B}{D}$. In order

to equalize these ratios mercury is run out by opening the tap P. Repeated trials must be made by running out small quantities, removing and then reapplying the pressure after the vessels A and B have been put in communication with each other and with the external atmosphere. The adjustment is complete when the mercury stands at the same horizontal level in both limbs of the manometer, after application of the pressure employed. The instrument is now ready for use.

It is of importance that the pressures in the vessels A and B shall be identical at the commencement of each experiment. This equalization is effected by means of the tap G. The body whose volume is required is placed inside the cavity, the screw-cap replaced, and pressure applied to such an extent that the compression is the same as in the preliminary adjustment, as indicated by the level of mercury in the tube c. Owing to the diminished volume due to the introduction of the body, a further quantity of mercury must be run out in order that the manometer may not indicate any difference of pressure. The quantity which runs out is collected and carefully weighed. Calculation shows that the product of the weight multiplied by the constant of the instrument gives the volume required. For let v represent the volume of B, and let the total internal volume of B and D after the preliminary adjustment has been made $= (n+1)v$. If x is the volume of the body introduced, then the volume originally $(n+1)v$ becomes after compression $\frac{(n+1)v-x}{n+1}$. But if the volume of mercury

withdrawn $= dv$, the same final volume is $v-x+dv$. Equating these expressions, we obtain the simple relation

$$x = \frac{n+1}{n} dv = k \cdot dv,$$

where k is a constant, provided the same compression is employed in all experiments. The constant k may be readily determined by measuring with the instrument the volume of a known weight of mercury.

It is convenient therefore to start with the same initial pressure in all experiments. The initial pressure employed is that of the atmosphere, and in order to ensure that such may

invariably be the case small holes have been drilled through each of the screw-caps E and H, which holes are perfectly closed by means of screws (not shown in the diagram) before the application of pressure in each experiment. The internal volumes of A and B are each approximately 16 cub. centim., and the capacities of C and D as above stated 20 cub. centim.

It is difficult to compare the instrument with those due to Paalzow and Rüdorff under similar conditions. In the present instrument air under about two atmospheres' pressure is employed, while in previous instruments rarefaction has always been resorted to. This alone suffices to produce increased accuracy. Paalzow shows, in the paper above referred to, that with his instrument a difference of pressure of 0.1 millim. involves a change of volume = 0.016 cub. centim. In Professor Stroud's instrument the same pressure-difference requires a change of volume = 0.0023 cub. centim.,—that is, the accuracy is 7 times as great. Rüdorff does not give the dimensions of his instrument, so that comparison cannot be made in this manner. From a series of results which he gives, however, the calculated mean error = 0.008 cub. centim., and this is much larger than the error deduced from any of the series of results given below.

The following are specimens of some of the earlier results which have been obtained. At Prof. Stroud's suggestion the first uncertain figure (or estimation figure) in the result is indicated in small type :—

I. Determination of the Volume of an Iron Cylinder.

$$v = 3.97_6.$$

$$3.97_1.$$

$$3.97_8. \quad \text{Volume deduced from measurement} = 3.97_7.$$

$$3.96_8.$$

II. Determination of Specific Gravity of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Weight of CuSO_4 employed was about 6 grammes.

The following are the results of successive determinations :—

$$\text{S.G.} = 2.28_0. \quad \text{Volume} = 2.64_0 \text{ cub. centim.}$$

$$2.28_8. \quad 2.63_0.$$

$$2.28_4. \quad 2.63_5.$$

$$2.28_6. \quad 2.63_2. \quad \text{Mean error} = .003 \text{ cub.}$$

$$2.28_8. \quad 2.63_2. \quad \text{centim.}$$

$$2.28_4. \quad 2.63_5.$$

$$2.28_0. \quad 2.64_0.$$

III. Determination of Specific Gravity of a piece of Cork.

The volume of cork employed was about 10 cub. centim.

| | |
|--------------------------|---|
| S.G.=.172 ₁ . | Volume=10.17 ₉ cub. centim. |
| .172 ₃ . | 10.17 ₃ . |
| .172 ₁ . | 10.17 ₉ . Mean error=.002 cub. |
| .172 ₃ . | 10.17 ₁ . centim. |

IV. Determination of Specific Gravity of very finely divided Cork Dust.

A value greater than the one above given for cork was of course expected. The cork dust was contained in a small cylindrical glass vessel of about 3 cub. centim. capacity and almost filled it. The experiments prove, however, that the volume actually occupied by the cork was only about 0.569 cub. centim.

| | |
|-------------------------|---|
| S.G.=.95 ₈ . | Volume=.56 ₉ cub. centim. |
| .95 ₄ . | .57 ₁ . |
| .94 ₉ . | .57 ₄ . Mean error=.002 cub. |
| .96 ₃ . | .56 ₈ . centim. |
| .95 ₃ . | .56 ₈ . |
| .95 ₄ . | .57 ₁ . |

A slight difficulty occurs when one is letting out mercury from the vessel by opening the tap, in consequence of the spasmodic change in level of the mercury in the capillary tube. A more accurate method of procedure consists in having the capillary tube graduated, and observing as follows:—Read the position of the mercury column when it is just above or below the standard position, then open the tap to permit a small drop of mercury to escape, which is separately collected and weighed, so that, after reading the position of the mercury column, a simple linear interpolation suffices to calculate the exact quantity of mercury which would have escaped if the equilibrium had been exact.

The following are successive determinations of the volume of an iron cylinder, employing this mode of procedure:—

Volume=6.50₇ cub. centim.

| | |
|---------------------|-------------------------------|
| 6.50 ₈ | |
| 6.50 ₉ . | |
| 6.50 ₈ . | |
| 6.51 ₀ . | Mean error=.0009 cub. centim. |
| 6.50 ₉ . | |

| | |
|---------------------|------------------------------------|
| 6.50 ₇ . | |
| 6.50 ₉ . | Volume of cylinder deduced from |
| 6.50 ₈ . | measurement=6.50 ₉ cub. |
| 6.51 ₀ . | centim. |

Mean=6.50₈₈.

The instrument would probably be very suitable for the accurate determination of the specific gravity of samples of gunpowder.

XIX. The Magnetic Field close to the Surface of a Wire conveying an Electrical Current. By Professor G. M. MINCHIN, M.A.*

AT a meeting of the Physical Society on March 10, 1893†, I gave an expression for the conical ("solid") angle subtended at any point, P, in space by a circle occupying any position.

When the circle is the seat of an electric current, this conical angle is the measure of the magnetic potential produced at P by the current. The conical angle is usually expressed by a series of spherical harmonics, or, rather, by two such series, one of which is to be used when the distance of P from the centre of the circle is less than the radius of the circle, and the other when it is greater. The expression which I have given consists of two complete elliptic integrals of the third kind, which for convenience I reproduce here.

In fig. 1 let A C B be the circular current; P' any point

Fig. 1.

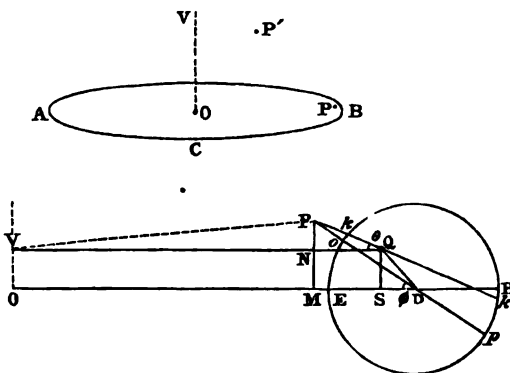


Fig. 2.

in space at which the value of the conical angle subtended by the current is Ω ; O V the central axis perpendicular to the plane of the current; A B the diameter of the current determined by the plane P' O V; ν the sine of the angle P' O V; $\rho = A P'$, $\rho' = B P'$; z the perpendicular from P' on A B. Then, a being the radius O B, and $O P' = r$, we have

$$\Omega = 2\pi - \frac{2z}{\rho r} \left\{ \frac{r-a}{1+\nu} \Pi\left(\frac{-2\nu}{1+\nu}, k\right) + \frac{r+a}{1-\nu} \Pi\left(\frac{2\nu}{1-\nu}, k\right) \right\}, \quad (1)$$

* Communicated by the Physical Society: read June 9, 1893.

† Phil. Mag. April 1893.

where $k^2 = 1 - \frac{\rho'^2}{\rho^2}$, and Π is the symbol for the complete elliptic integral of the third kind, its parameter and modulus, respectively, being the quantities included in the brackets following Π , according to the ordinary notation of such integrals, viz.,

$$\Pi(n, k) = \int_0^{\pi/2} \frac{d\omega}{(1 + n \sin^2 \omega) \sqrt{1 - k^2 \sin^2 \omega}}.$$

If P' lies anywhere in the plane of the circle and *inside* its area, $\Omega = 2\pi$; and if P' lies anywhere in the plane of the circle and *outside* its area, $\Omega = 0$. If P' is taken strictly on the circumference of the circle, and if the circle is a strictly Euclidian curve, i. e. something absolutely devoid of breadth, Ω is necessarily indeterminate. It is well known that all the surfaces of constant conical angle subtended by a circuit of any form, plane or tortuous, contain the circuit as a bounding edge, and that any two surfaces for which $\Omega = \Omega_1$ and $\Omega = \Omega_2$ are inclined to each other at the constant angle whose circular measure is $\frac{1}{2}(\Omega_1 - \Omega_2)$ at all points on this common bounding edge.

When the circuit is not a Euclidian curve, but a wire, and the point in space which we consider is near the surface of the wire, as at P in fig. 1, it becomes necessary to take account of the dimension of the cross-section of the wire, and the conical angle subtended at P is the integrated result of dividing the normal cross-section made by a plane through P into an indefinitely great number of indefinitely small elements of area and breaking up the wire into a corresponding number of circular filaments having these elements of area for cross-sections, these circular filaments having all the same central axis, OV , and their planes being, of course, all parallel.

Our object now is to find the value of Ω when P is very close to the wire both when the current is assumed to be of constant density and when it is assumed to be of variable density in the cross-section. Fig. 2 represents the normal cross-section of the wire (supposed to be a circle) made by a plane through P .

Take any point, Q , in the cross-section, and at Q take an indefinitely small element of area, dS . If i is the total current flowing through the cross-section of the wire, the current

in the first case through dS is $i \frac{dS}{\pi c^2}$, where c is the radius of

the cross-section; and if Ω is the conical angle subtended at P by the circular filament of the wire passing through dS ,

the magnetic potential at P due to the current in the filament is

$$i\Omega \frac{dS}{\pi c^2} \dots \dots \dots (2)$$

Let the radius, QV, of the filament be denoted by α ; let PQ=R; $\angle PQV=\theta$; then in the typical formula (1) we have $\rho'=R$, $r=VP$, $z=PN=R \sin \theta$, R being, of course, very small compared with α .

Although our object is to obtain the value of Ω correctly to the *second* order of the small quantity $\frac{R}{\alpha}$, it will be useful for future reference to express the quantities ν , &c. as far as the third order.

Thus we have

$$r = \alpha \left(1 - \frac{R}{\alpha} \cos \theta + \frac{R^2}{2\alpha^2} \sin^2 \theta + \frac{R^3}{2\alpha^3} \cos \theta \sin^2 \theta \right), \quad (3)$$

$$\frac{1}{\rho} = \frac{1}{2\alpha} \left\{ 1 + \frac{R}{2\alpha} \cos \theta + \frac{R^2}{8\alpha^2} (3 \cos^2 \theta - 1) + \frac{R^3}{16\alpha^3} (5 \cos^3 \theta - 3 \cos \theta) \right\}, \quad (4)$$

$$\frac{1}{r} = \frac{1}{\alpha} \left\{ 1 + \frac{R}{\alpha} \cos \theta + \frac{R^2}{2\alpha^2} (3 \cos^2 \theta - 1) + \frac{R^3}{2\alpha^3} (5 \cos^3 \theta - 3 \cos \theta) \right\}, \quad (5)$$

$$\nu = \frac{R \sin \theta}{r}, \quad (6)$$

$$k' = \frac{R}{\rho}, \quad (7)$$

where k' is the modulus complementary to k .

Now, of the two elliptic integrals in (1) the first is one in which the parameter is negative and nearly equal to -1 , while in the second the parameter is positive and very large.

Observe that $\frac{z}{r} = \sin PVQ = \sqrt{1-\nu^2}$, so that (1) can be written

$$\Omega = 2\pi - \frac{2}{\rho} \left\{ (r-\alpha) \sqrt{\frac{1-\nu}{1+\nu}} \Pi\left(\frac{-2\nu}{1+\nu}, k\right) + (r+\alpha) \sqrt{\frac{1+\nu}{1-\nu}} \Pi\left(\frac{2\nu}{1-\nu}, k\right) \right\}. \quad (8)$$

To deal with the first of these elliptic intervals, let

$$\frac{2\nu}{1+\nu} = 1 - k'^2 \sin^2 \psi, \quad \therefore \sqrt{\frac{1-\nu}{1+\nu}} = k' \sin \psi; \quad (9)$$

and for the second, let

$$\frac{2\nu}{1-\nu} = \cot^2 \chi, \quad \therefore \sqrt{\frac{1+\nu}{1-\nu}} = \frac{1}{\sin \chi}. \quad (10)$$

Hence we have

$$\Omega = 2\pi - 2 \left\{ \frac{r-\alpha}{\rho} \cdot k' \sin \psi \Pi(-1 + k'^2 \sin^2 \psi, k) + \frac{r+\alpha}{\rho} \cdot \frac{1}{\sin \chi} \Pi(\cot^2 \chi, k) \right\}. \quad (11)$$

The values of these complete elliptic integrals of the third kind are well known in terms of integrals of the first and second kinds. Thus (see Hymers's 'Integral Calculus,' section ix., or any treatise on Elliptic Functions) we have the equation

$$\frac{k'^2 \sin \psi \cos \psi}{\Delta(k', \psi)} \{ \Pi(-1 + k'^2 \sin^2 \psi, k) - K \} = \frac{\pi}{2} - K \cdot E(k', \psi) + (K - E) \cdot K(k', \psi). \quad (12)$$

Now

$$E(k', \psi) = E' - \int_{\psi}^{\pi/2} \sqrt{1 - k'^2 \sin^2 \psi} \cdot d\psi,$$

and

$$K(k', \psi) = K' - \int_{\psi}^{\pi/2} \frac{d\psi}{\sqrt{1 - k'^2 \sin^2 \psi}},$$

where E' and K' are the *complete* integrals with modulus k' .

Also it is well known that $KE' + K'E - KK' - \frac{\pi}{2} = 0$. Hence the right-hand side of (12) becomes, by expanding and neglecting powers of k' beyond the second,

$$E\left(\frac{\pi}{2} - \psi\right) - \frac{k'^2}{4} \left(\frac{\pi}{2} - \psi + \sin \psi \cos \psi\right) (2K - E);$$

so that

$$\begin{aligned} & k'^2 \sin \psi \Pi(-1 + k'^2 \sin^2 \psi, k) \\ &= k'^2 \sin \psi \cdot K + E \frac{\frac{\pi}{2} - \psi}{\cos \psi} - \frac{k'^2}{4} \left\{ (2K - E) \sin \psi + \frac{\frac{\pi}{2} - \psi}{\cos \psi} (2K - E \cos 2\psi) \right\} \\ &= E \frac{\frac{\pi}{2} - \psi}{\cos \psi} + \frac{k'^2}{4} \left\{ (2K + E) \sin \psi - \frac{\frac{\pi}{2} - \psi}{\cos \psi} (2K - E \cos 2\psi) \right\}. \quad (13) \end{aligned}$$

Now since $k' = \frac{R}{\rho}$, the first term in brackets in (11) can be written

$$\frac{r-\alpha}{R} \cdot k'^2 \sin \psi \Pi(-1 + k'^2 \sin^2 \psi, k),$$

and we have

$$\Omega = 2\pi - 2 \left\{ \frac{r-\alpha}{R} \cdot k'^2 \sin \psi \Pi(-1 + k'^2 \sin^2 \psi, k) + \frac{r+\alpha}{\rho} \cdot \frac{1}{\sin \chi} \Pi(\cot^2 \chi, k) \right\}, \quad (14)$$

in which the value of the first elliptic integral is to be substituted from (13).

Dealing now with the second elliptic integral, its value is given by the known equation

$$\frac{\Delta(k', \chi)}{\sin \chi \cos \chi} \Pi(\cot^2 \chi, k) = \frac{\pi}{2} + K \{ \tan \chi \Delta(k', \chi) - E(k', \chi) \} + (K - E) \cdot K(k', \chi). \quad (15)$$

But observe that

$$\sin \chi = \frac{R}{2\alpha} \sin \theta \left(1 + \frac{R}{\alpha} \cos \theta \right),$$

so that χ is a small quantity of the same order as k' . Hence, if in the coefficient of K we neglect quantities of the order $\frac{R^3}{\alpha^3}$,

$$\begin{aligned} & \frac{1}{\sin \chi} \Pi(\cot^2 \chi, k) \\ &= \cos \chi \left\{ \frac{\pi}{2} + (K - E) \cdot \chi \right\} \\ &= \left(1 - \frac{R^2}{8\alpha^2} \sin^2 \theta \right) \left[\frac{\pi}{2} + \frac{R}{2\alpha} \sin \theta \left(1 + \frac{R}{\alpha} \cos \theta \right) (K - E) \right]. \quad (16) \end{aligned}$$

The coefficient $\frac{r+\alpha}{\rho}$ to the second order is $1 + \frac{R^2}{8\alpha^2} \sin^2 \theta$, so that we have

$$\frac{r+\alpha}{\rho} \cdot \frac{1}{\sin \chi} \Pi(\cot^2 \chi, k) = \frac{\pi}{2} + \frac{R}{2\alpha} \sin \theta \left(1 + \frac{R}{\alpha} \cos \theta \right) (K - E). \quad (17)$$

Hence

$$\begin{aligned} \Omega = 2\pi - 2 \left\{ \frac{r-\alpha}{R} \left[E \frac{\frac{\pi}{2} - \psi}{\cos \psi} + \frac{k'^2}{4} \{ (2K + E) \sin \psi \right. \right. \\ \left. \left. - \frac{\frac{\pi}{2} - \psi}{\cos \psi} (2K - E \cos 2\psi) \} \right] + \frac{\pi}{2} + \frac{R}{2\alpha} \sin \theta \left(1 + \frac{R}{\alpha} \cos \theta \right) (K - E) \right\}. \quad (18) \end{aligned}$$

In the small term we can put $k' = \frac{R^2}{4a^2}$, $\frac{r-a}{R} = -\cos \theta$, and $\psi = \theta$, so that, neglecting quantities of the order $\frac{R^2}{a^2}$,

$$\Omega = 2\pi - 2 \left\{ \frac{r-a}{R} E \frac{\frac{\pi}{2} - \psi}{\cos \psi} + \frac{\pi}{2} + \frac{R}{2a} (K - E) \sin \theta + \frac{R^2}{16a^2} \left[3(2K - 3E) \sin \theta \cos \theta + \left(\frac{\pi}{2} - \theta \right) (2K - E \cos 2\theta) \right] \right\}. \quad (19)$$

The relation between ψ and θ is given by the equation

$$k' \sin \psi = \sqrt{\frac{1-\nu}{1+\nu}} = \tan \frac{\lambda}{2}, \text{ where } \lambda = \angle PVQ,$$

$$\therefore \sin \psi = \frac{\rho}{R} \tan \frac{\lambda}{2},$$

$$\therefore \sin \psi = \sin \theta \left\{ 1 + \frac{R}{2a} \cos \theta + \frac{R^2}{8a^2} (5 \cos^2 \theta - 1) \right\}, \quad (20)$$

as far as the second order of small quantities; and the series for $\sin^{-1} x$ in terms of x , or rather for x in terms of $\sin^{-1} x$, gives, to the same order,

$$\psi = \theta + \frac{R}{2a} \sin \theta + \frac{R^2}{2a^2} \sin \theta \cos \theta, \quad (21)$$

$$\therefore \cos \psi = \cos \theta - \frac{R}{2a} \sin^2 \theta - \frac{5R^2}{8a^2} \cos \theta \sin^2 \theta. \quad (22)$$

Also

$$\frac{r-a}{R} = -\cos \theta + \frac{R}{2a} \sin^2 \theta + \frac{R^2}{2a^2} \cos \theta \sin^2 \theta; \quad (23)$$

so that (19) becomes expressed entirely in terms of θ . Thus,

$$\frac{r-a}{R} = -\left(\cos \psi + \frac{R^2}{8a^2} \cos \theta \sin^2 \theta \right), \text{ therefore}$$

$$\frac{r-a}{R} \cdot \frac{1}{\cos \psi} = -\left(1 + \frac{R^2}{8a^2} \sin^2 \theta \right)$$

since θ may be put for ψ in the term of the second order; and thus we have now the equation

$$\Omega = 2\pi - 2 \left\{ (1-E) \frac{\pi}{2} + E\theta + \frac{R}{2a} K \sin \theta + \frac{R^2}{16a^2} \left[(2K-E) \left(\frac{\pi}{2} - \theta \right) + (6K-E) \sin \theta \cos \theta \right] \right\}, \quad (24)$$

which is, however, not yet in its simplest form.

Now it is a known result that when k' is small,

$$K = \log \frac{4}{k'} + \frac{k'^2}{4} \left(\log \frac{4}{k'} - 1 \right), \quad . \quad . \quad . \quad (25)$$

$$E = 1 + \frac{k'^2}{2} \left(\log \frac{4}{k'} - \frac{1}{2} \right), \quad . \quad . \quad . \quad . \quad (26)$$

and these enable us to verify the above value of Ω . Thus for any point, P, in the plane of the circle and within its circumference, $\Omega = 2\pi$; and if in (24) we put $\theta = 0$, we get

$$\begin{aligned} \Omega &= 2\pi - (1 - E)\pi - \frac{R^2}{8a^2} (2K - E) \frac{\pi}{2} \\ &= 2\pi, \end{aligned}$$

as we see from (25) and (26), since, to the second order, $k'^2 = \frac{R^2}{4a^2}$. Similarly for any point, P, in the plane of the circle and outside its circumference, $\Omega = 0$; and this we find to be the case by putting $\theta = \pi$.

To find the value of Ω in its final form in terms of R and θ , we must substitute the value of k' in K and E. Now

$$k' = \frac{R}{\rho} = \frac{R}{2a} \left\{ 1 + \frac{R}{2a} \cos \theta + \frac{R^2}{8a^2} (3 \cos^2 \theta - 1) \right\}, \quad . \quad (27)$$

and if we denote $\log \frac{8a}{R}$ by L, we have

$$K = L - \frac{R}{2a} \cos \theta + \frac{R^2}{16a^2} (L + 1 - 4 \cos^2 \theta), \quad . \quad (28)$$

$$E = 1 + \frac{R^2}{8a^2} (L - \frac{1}{2}). \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

Now in (24) K occurs only in terms of the first and second order, and therefore its value need be taken to the first order only, *i. e.*

$$K = L - \frac{R}{2a} \cos \theta; \quad . \quad . \quad . \quad . \quad . \quad (30)$$

and hence we have finally

$$\Omega = 2\pi - 2 \left\{ \theta + \frac{LR}{2a} \sin \theta + \frac{R^2}{16a^2} (6L - 5) \sin \theta \cos \theta \right\}, \quad (31)$$

which is the expression for the conical angle correct to the second order of small quantities.

As a test of the correctness of this value of Ω we should find that $\nabla^2 \Omega = 0$, as far as quantities of the second order. To apply this test, express Ω in terms of the columnar co-ordinates of P. Let the distance of P from the central axis

OV (fig. 2) be ζ . Then we should have

$$\frac{d^2\Omega}{dz^2} + \frac{d^2\Omega}{d\zeta^2} + \frac{1}{\zeta} \frac{d\Omega}{d\zeta} = 0,$$

or if $\zeta = \alpha - \eta$, where $\eta = QN$,

$$\frac{d^2\Omega}{dz^2} + \frac{d^2\Omega}{d\eta^2} - \frac{1}{\alpha - \eta} \frac{d\Omega}{d\eta} = 0.$$

Now the term in brackets in (31) is

$$\tan^{-1} \frac{z}{\eta} + \frac{Lz}{2\alpha} + \frac{z\eta}{16\alpha^2} (6L-5),$$

and, observing that $R^2 = z^2 + \eta^2$,

$$\frac{dL}{dz} = -\frac{z}{R^2}, \quad \frac{dL}{d\eta} = -\frac{\eta}{R^2}, \quad \frac{1}{\alpha - \eta} = \frac{1}{\alpha} + \frac{R}{\alpha^2} \cos \theta,$$

we find $\nabla^2\Omega = 0$.

Before obtaining the effect at P due to the whole current flowing through the cross-section, $pk'Bk$, it is necessary to express α , the radius of the circular filament through Q, in terms of a the radius of the filament through D. If $PD = m$, we have $\alpha = a + R \cos \theta - m \cos \phi$, where $\phi = \angle PDO$; and to the same order of approximation as before, (31) becomes

$$\Omega = 2\pi - 2 \left\{ \theta + \frac{LR}{2a} \sin \theta + \frac{R \sin \theta}{16a^2} [(3-2L)R \cos \theta + 8(L-1)m \cos \phi] \right\}, \quad (32)$$

where $L = \log_e \frac{8a}{R}$.

Resultant Conical Angle.—The element of area of the cross-section at Q being dS , the resultant conical angle subtended by the circuit at P is $\int \Omega dS$, if the density of the current in the cross-section is assumed to be constant. This we shall assume for the present. Let $\angle QPD = \chi$, and take $dS = R dR d\chi$. Then the first two terms in (32) will give $2(\pi - \theta)dS$, or $2(\pi - \phi + \chi)dS$, the integral of which is $2(\pi - \phi) \cdot A$, where A is the area of the cross-section, $pk'Bk$. The term $\int \chi dS$ obviously vanishes, since χ is negative for points Q on the lower side of the line PD.

If the tangent from P to the circle $pk'Bk$ makes the angle ω with PD, the values of χ run from $-\omega$ to ω ; and it is obvious any integral of the form

$$\int_{-\omega}^{\omega} f(\cos \chi) \sin \chi d\chi$$

vanishes, f being any rational symbol of functionality, while

$$\int_{-\pi}^{\pi} f(\cos \chi) \cdot d\chi = 2 \int_0^{\pi} f(\cos \chi) d\chi.$$

Now, the values of χ being understood to range from 0 to ω , and θ being equal to $\phi - \chi$,

$$\begin{aligned} \int \Omega dS = & 2(\pi - \phi)A - \frac{2 \sin \phi}{a} \iint LR^2 dR \cdot \cos \chi d\chi \\ & - \frac{\sin 2\phi}{4a^2} \left[\frac{3}{2} \iint R^3 dR \cdot \cos 2\chi d\chi - \iint LR^3 dR \cdot \cos 2\chi d\chi \right. \\ & \left. + 4m \iint LR^2 dR \cdot \cos \chi d\chi - 4m \iint R^2 dR \cdot \cos \chi d\chi \right]. \quad (33) \end{aligned}$$

If we first perform the integration in each case with respect to R , taking χ constant, we shall have, for example,

$$\iint R^3 dR \cdot \cos 2\chi d\chi = \frac{1}{4} \int (R'^4 - R^4) \cos 2\chi d\chi, \quad (34)$$

where $R' = Pk'$ and $R = Pk$ (fig. 2); but since in integrating throughout the semicircle $pk'BkO$ the values of χ are repeated in the revolution of the radius-vector, Pk' , the values of $d\chi$ being negative as the radius-vector revolves from the position of the tangent from P , it is clear that both terms in the integral at right side of (34) are included in the single expression

$$\frac{1}{4} \int R^4 \cos 2\chi d\chi,$$

R now being a radius-vector from P to a point on the circumference of the circle.

Similarly

$$\iint LR^3 dR \cdot \cos 2\chi d\chi = \int (\frac{1}{4} LR^4 + \frac{1}{16} R^4) \cos 2\chi d\chi.$$

To calculate the double integrals involved in (33), we shall take as the independent variable the angle $k'Dp$, or ψ ; and we have, if c is the radius of the cross-section,

$$R^2 = m^2 + 2cm \cos \psi + c^2, \quad (35)$$

$$R^2 d\chi = c(c + m \cos \psi) d\psi, \quad (36)$$

$$R^2 \cos 2\chi = 2R^2 \cos^2 \chi - R^2 = m^2 + 2cm \cos \psi + c^2 \cos 2\psi. \quad (37)$$

Hence

$$\begin{aligned} \iint R^3 dR \cdot \cos 2\chi d\chi &= \frac{1}{4} \int R^4 \cos 2\chi d\chi \\ &= \frac{c}{4} \int_0^{\pi} (c + m \cos \psi) (m^2 + 2cm \cos \psi + c^2 \cos 2\psi) d\psi = \frac{1}{2} Am^2, \quad (38) \end{aligned}$$

putting A for πc^2 . Similarly

$$\iint R^2 dR \cdot \cos \chi d\chi = \frac{1}{2} A m. \quad (39)$$

To find the integrals which involve the logarithms, observe that by trigonometrical expansion

$$\begin{aligned} \log R^2 &= \log m^2 \left(1 + 2 \frac{c}{m} \cos \psi + \frac{c^2}{m^2} \right) \\ &= \log m^2 + 2 \left(\frac{c}{m} \cos \psi - \frac{1}{2} \frac{c^2}{m^2} \cos 2\psi + \frac{1}{3} \frac{c^3}{m^3} \cos 3\psi - \&c. \right). \end{aligned} \quad (40)$$

Hence

$$\begin{aligned} \iint L R^2 dR \cdot \cos 2\chi d\chi &= \frac{1}{4} \int L R^4 \cos 2\chi d\chi + \frac{1}{16} \int R^4 \cos 2\chi d\chi \\ &= \frac{c}{4} \int_0^\pi L (c + m \cos \psi) (m^2 + 2cm \cos \psi + c^2 \cos 2\psi) d\psi \\ &\quad + \frac{1}{16} \int (c + m \cos \psi) (m^2 + 2cm \cos \psi + c^2 \cos 2\psi) d\psi \\ &= \frac{A}{8} \left(4m^2 L - 2c^2 + \frac{c^4}{3m^2} \right), \quad (41) \end{aligned}$$

where L stands now for $\log \frac{8a}{m}$. Finally

$$\iint L R^2 dR \cdot \cos \chi d\chi = \frac{A}{2} \left(mL - \frac{c^2}{4m} \right). \quad (42)$$

(Of course the integrations in ψ are very simple, since $\int_0^\pi \cos n\psi \cdot \cos n'\psi \cdot d\psi = 0$, except when $n=n'$, and then $\int_0^\pi \cos^2 n\psi \cdot d\psi = \frac{\pi}{2}$. No term in ψ beyond $\cos 3\psi$ contributes to the integral (41).)

Substituting these values in (33), and denoting the resultant conical angle, $\int \Omega dS$, by Θ , we have

$$\begin{aligned} \frac{\Theta}{A} &= 2(\pi - \phi) - \frac{\sin \phi}{a} \left(mL - \frac{c^2}{4m} \right) \\ &\quad - \frac{\sin 2\phi}{16a^2} \left\{ (6L - 5)m^2 - c^2 \left(1 + \frac{c^2}{6m^2} \right) \right\}. \end{aligned} \quad (43)$$

This result is susceptible of verification thus. If the components of magnetic force at P per unit pole per unit current

are X , Z parallel to OD , OV , we have

$$\frac{dX}{dx} + \frac{dZ}{dz} + \frac{dY}{dy} = 0,$$

where $\frac{dY}{dy}$ is the line rate of increase of force at P perpendicular to the plane, POD , of xz . Y is, of course, zero, but we easily see that

$$\frac{dY}{dy} = \frac{X}{a - m \cos \phi},$$

by taking a position of the point, or pole, close to P along the perpendicular at P to the plane xz . Hence we should

have, up to and including terms in $\frac{1}{a^2}$, the result

$$\frac{dX}{dx} + \frac{dZ}{dz} + X \left(\frac{1}{a} + \frac{m}{a^2} \cos \phi \right) = 0. \quad (44)$$

The values of X and Z are best found from $\frac{d\Theta}{dm}$ and $\frac{d\Theta}{md\phi}$, which (neglecting A for the moment) are the components of force along and perpendicular to DP .

Now

$$\frac{d\Theta}{dm} = -\frac{\sin \phi}{a} \left(L - 1 + \frac{c^2}{4m^2} \right) - \frac{\sin 2\phi}{16a^2} \left\{ (12L - 16)m + \frac{c^4}{3m^3} \right\}, \quad (45)$$

$$\frac{d\Theta}{md\phi} = -\frac{2}{m} - \frac{\cos \phi}{a} \left(L - \frac{c^2}{4m^2} \right) - \frac{\cos 2\phi}{16a^2} \left\{ (12L - 10)m - \frac{2c^2}{m} - \frac{c^4}{3m^3} \right\}; \quad (46)$$

$$\text{also} \quad X = -\frac{d\Theta}{dm} \cos \phi + \frac{d\Theta}{md\phi} \sin \phi, \quad (47)$$

$$Z = \frac{d\Theta}{dm} \sin \phi + \frac{d\Theta}{md\phi} \cos \phi, \quad (48)$$

$$\text{and} \quad \frac{d}{dx} = -\cos \phi \frac{d}{dm} + \frac{\sin \phi}{m} \frac{d}{d\phi},$$

$$\frac{d}{dz} = \sin \phi \frac{d}{dm} + \frac{\cos \phi}{m} \frac{d}{d\phi}.$$

The necessary condition (44) is found to be satisfied both for the terms of the first and for those of the second order.

Variable Current-density.—The preceding investigation assumes the current-density to be constant at all points in the

cross-section of the wire. If, however, we assume that at any point, Q (fig. 2), it varies inversely as the distance of the point from the axis OV of the current, its value at Q may be written $\sigma \frac{a}{\alpha}$, where σ is a constant and a and α have the meanings already given to them*. If we put, as before, i for the total current traversing the section, we have

$$\sigma a \int \frac{dS}{\alpha} = i, \dots \dots \dots (48 a)$$

which gives $\sigma = \frac{i}{A}$, where A is the area of the cross-section.

The resultant conical angle subtended now at P will be

$$\frac{i}{A} \int \Omega \frac{a}{\alpha} dS, \dots \dots \dots (48 b)$$

where Ω has the value given in (32); and since, to the second order,

$$\frac{a}{\alpha} = 1 - \frac{1}{a} (R \cos \theta - m \cos \phi) + \frac{1}{a^2} (R \cos \theta - m \cos \phi)^2, \quad (48 c)$$

to the expression for $\int \Omega dS$ given in (43) must be added the correction

$$\int \Omega \left\{ -\frac{1}{a} (R \cos \theta - m \cos \phi) + \frac{1}{a^2} (R \cos \theta - m \cos \phi)^2 \right\} dS. \quad (48 d)$$

The term of the second order in Ω in (32) will, of course, contribute nothing to this correction, while the term of the first order in Ω is to be taken with the term

$$-\frac{1}{a} (R \cos \theta - m \cos \phi)$$

only, so that the expression for the correction is

$$2 \int (\pi - \theta) \left\{ -\frac{1}{a} (R \cos \theta - m \cos \phi) + \frac{1}{a^2} (R \cos \theta - m \cos \phi)^2 \right\} dS \\ + \frac{1}{a^2} \cdot \int L R \sin \theta (R \cos \theta - m \cos \phi) dS. \quad (48 e)$$

Putting $\theta = \phi - \chi$, as before, the only terms of new form that present themselves are

$$2 \iint \left\{ -\frac{\sin \phi}{a} \left(1 + \frac{2m}{a} \cos \phi \right) \cdot R \chi \sin \chi \right. \\ \left. + \frac{R^2}{2a^2} \sin 2\phi \cdot \chi \sin 2\chi \right\} R dR d\chi;$$

* The necessity for considering this case was pointed out to me by Professor Perry.

and it will be found that

$$\iint R^2 dR \cdot \chi \sin \chi d\chi = \frac{1}{3} \int \chi (R^3 - R^3) \sin \chi d\chi = A \frac{c^2}{8m}, \quad (48f)$$

$$\begin{aligned} \iint R^3 dR \cdot \chi \sin 2\chi d\chi &= \frac{1}{4} \int \chi (R^4 - R^4) \sin 2\chi d\chi \\ &= A \frac{c^2}{4} \left(1 - \frac{c^2}{6m^2}\right), \quad (48g) \end{aligned}$$

in which χ has been taken from 0 to ω only, so that in the correction (48e) these must be doubled.

Hence the whole of the correction (48e) amounts to

$$-\frac{\sin \phi}{2a} \frac{c^2}{m} + \frac{1}{16a^2} \left\{ 8c^2(\pi - \phi) - \left(2c^2 + \frac{2c^4}{3m^2}\right) \sin 2\phi \right\},$$

so that (43) is replaced by

$$\begin{aligned} \frac{\Theta}{A} &= 2(\pi - \phi) - \frac{\sin \phi}{a} \left(mL + \frac{c^2}{4m} \right) + \frac{1}{16a^2} \left\{ 8c^2(\pi - \phi) \right. \\ &\quad \left. - \left[(6L - 5)m^2 + c^2 + \frac{c^4}{2m^2} \right] \sin 2\phi \right\}, \quad (48i) \end{aligned}$$

the right-hand side being the value of the resultant conical angle subtended by the circuit at the point P. The magnetic potential at P is therefore this right-hand side multiplied by i , the total current traversing the cross-section of the wire.

It will be found that this value of Θ satisfies, both for the terms of the first order and for those of the second, the condition (44).

If the density of the current at any point Q in the cross-section be assumed to vary as any power of the distance of Q from the axis OV, the conical angle subtended at a point near the wire is found just as easily as in the case in which the density is supposed to vary inversely as the distance. Thus,

if it is proportional to $\frac{1}{a^n}$, (48c) will be replaced by

$$1 - \frac{n}{a} (R \cos \theta - m \cos \phi) + \frac{n(n+1)}{2a^2} (R \cos \theta - m \cos \phi)^2,$$

and we have merely the same terms (48f), &c., as before.

We see then that when small quantities of the first order, indicated by the fraction $\frac{m}{a}$, are taken into account, the magnetic potential, and therefore the magnetic force, at any point are not the same as if the whole current were condensed into an infinitely thin filament traversing the centre of the wire,

D; for, at points, P, close to the wire $\frac{c}{m}$ is nearly unity, and hence the fraction $\frac{c^2}{4m^2}$ is not negligible in comparison with L, unless, indeed, $8a$ is many thousands of times greater than c .

Consider the magnetic force, Z_x , just outside the wire at E. This is obtained by putting $\phi=0$ and $m=c$ in $\frac{1}{A} \frac{d\Theta}{md\phi}$; thus, omitting the factor i ,

$$Z_x = -\frac{2}{c} - \frac{1}{a}(L + \frac{1}{4}) - \frac{c}{16a^2}(12L + 1),$$

while by putting $\phi=\pi$, $m=c$, we obtain the force, Z_x , at B:

$$Z_x = -\frac{2}{c} + \frac{1}{a}(L + \frac{1}{4}) - \frac{c}{16a^2}(12L + 1),$$

whereas the magnetic force at the centre, O, of the circle is of the order $\frac{2\pi}{a}$, and is therefore much less than the force close to the surface of the wire.

Lines of Magnetic Force.—The forms, or approximate equations, of the lines of magnetic force close to the wire may be determined to the second order of small quantities in like manner. Thus, in my previous paper on the Magnetic Field of a Circular Current (Phil. Mag. April 1893, p. 356) I have shown that if at any point in space in presence of a current running in an infinitely thin circular filament G is the vector potential due to the current, we shall have

$$G \cdot \alpha = \text{constant}$$

along the line of force, where α is the distance of the point from the axis of the current (*i.e.*, the perpendicular to its plane drawn at its centre). In the case of a point so close to a wire that the current through its cross-section must be broken up into filaments (as in the previous calculation of Θ), the total vector potential at any point is $\int G dS$, and as α is the same for all the filaments, the equation of a line of force is

$$\int G \cdot \alpha \cdot dS = \text{constant}.$$

But (Phil. Mag. *ibid.*)

$$G \cdot \alpha = \{(1 + k^2)K - 2E\} \rho,$$

and the current-density in the filament through dS being

first supposed constant and equal to $\frac{i}{A}$, the equation of a line of force is

$$\frac{i}{A} \int \{ (1 + k^2) K - 2E \} \rho dS = \text{constant}. \quad (49)$$

With previous notation and approximation, we have

$$K = \log \frac{8a}{R} + \frac{R \cos \theta - 2m \cos \phi}{2a} + \frac{R^2(L - 1 - 2 \cos 2\theta) + 8Rm \cos \theta \cos \phi - 8m^2 \cos^2 \phi}{16a^2}, \quad (50)$$

$$E = 1 + \frac{R^2(2L - 1)}{16a^2}, \quad (51)$$

$$\rho = 2a \left(1 + \frac{R \cos \theta - 2m \cos \phi}{2a} + \frac{R^2 \sin^2 \theta}{8a^2} \right), \quad (52)$$

$$k^2 = \frac{R^2}{4a^2}, \quad (53)$$

where $L \equiv \log \frac{8a}{R}$. Hence (49) becomes

$$\frac{4ai}{A} \iint \left[1 + \frac{R \cos \theta - 2m \cos \phi}{2a} + \frac{R^2 \sin^2 \theta}{8a^2} \right] \left[L - 2 + \frac{R \cos \theta - 2m \cos \phi}{2a} + \frac{R^2(L + 1 - 2 \cos 2\theta) + 8Rm \cos \theta \cos \phi - 8m^2 \cos^2 \phi}{16a^2} \right] R dR d\chi, \quad (54)$$

it being understood that χ ranges from 0 to ω , and therefore ψ from 0 to π , when (as in the calculation of Θ) the independent variable is changed from χ to ψ .

In addition to the integrals (38), (39), (41), (42), the following are now required, and they are easily deduced like the others:

$$\iint LR^3 dR d\chi = \frac{A}{8} \{ L(2m^2 + c^2) - 2c^2 \}, \quad (55)$$

$$\iint R^3 dR d\chi = \frac{A}{4} (2m^2 + c^2), \quad (56)$$

$$\iint LR dR d\chi = \frac{A}{2} L, \quad (57)$$

$$\iint R dR d\chi = \frac{A}{2}, \quad (58)$$

where $L \equiv \log \frac{8a}{m}$.

With these values (54) gives as the equation of a line of force

$$\frac{L}{2} - 1 - \frac{\cos \phi}{4a} \left\{ (L-1)m + \frac{c^2}{4m} \right\} + \frac{1}{16a^2} \left\{ L \left(\frac{m^2}{2} + \frac{c^2}{4} \right) + \frac{m^2}{2} - \frac{c^2}{4} - \cos 2\phi \left(L \frac{m^2}{2} - \frac{c^2}{4} - m^2 + \frac{c^4}{24m^2} \right) \right\} = \text{const.}, \quad (59)$$

to the second power of the small quantity or $\frac{c}{a}$.

As a verification, the curve (59) should be at right angles to the curve $\Theta = \text{const.}$ given by (43), i. e., if we calculate the value of $m \frac{d\phi}{dm}$ for each curve, the one should be the negative reciprocal of the other, as far as small quantities of the second order. This is found to be the case; for, from (59) we have

$$\frac{dm}{m d\phi} = \frac{m}{2a} \sin \phi \left(L - 1 + \frac{c^2}{4m^2} \right) - \frac{m^2}{8a^2} \sin 2\phi \left\{ (L-2)^2 + \frac{c^2}{4m^2} - \frac{7c^4}{48m^4} \right\}$$

which is $-\frac{m d\phi}{dm}$ calculated from the equation $\Theta = \text{const.}$

If we denote the ratio $\frac{c^2}{4m^2}$ by λ , the result (59) may be written

$$\frac{1}{2}L - \frac{m}{4a} (L-1+\lambda) \cdot \cos \phi + \frac{m^2}{16a^2} \left\{ L \left(\frac{1}{2} + \lambda \right) + \frac{1}{2} - \lambda - \left(\frac{1}{2}L - 1 - \lambda + \frac{3}{4}\lambda^2 \right) \cos 2\phi \right\} = \text{const.} \quad (60)$$

Variable Current-density.—Let the current-density now be supposed to vary inversely as the distance from the axis OV. If at any point P in space Γ is the vector potential due to a system of circular currents all having the same axis OV, and if x is the distance of P from this axis, the equation of a line of force is, as has been shown,

$$\Gamma x = \text{constant.}$$

And Γ is the resultant vector potential at P due to a system of currents running in filaments through the wire, the density of the typical current filament through Q (fig. 1) being $\frac{i}{A} \cdot \frac{a}{x}$; therefore

$$\Gamma = \frac{4i}{A} \int \frac{\alpha}{\rho k^2} \{ (1+k^2)K - 2E \} \frac{a}{\alpha} dS; \quad (61)$$

and since x is the same for all the filaments, in taking Γx we may put x under the sign of integration, so that

$$\Gamma x = \frac{i}{A} \int \{ (1 + k^2) K - 2E \} \rho \frac{a}{\alpha} dS. \quad (62)$$

As we require only the terms to be added to (59) by the introduction of the term $\frac{a}{\alpha}$, we may keep only terms of the first order in the expressions for $(1 + k^2) K - 2E$ and ρ . Thus

$$(1 + k^2) K - 2E = L - 2 + \frac{R \cos \theta - 2m \cos \phi}{2a}, \quad (63)$$

$$\rho = 2a \left\{ 1 + \frac{R \cos \theta - 2m \cos \phi}{2a} \right\}. \quad (64)$$

Hence, neglecting the factor $\frac{2ai}{A}$, the correction introduced is

$$\iint \left\{ L - 2 + (L - 1) \frac{R \cos \theta - 2m \cos \phi}{2a} \right\} \left\{ - \frac{R \cos \theta - m \cos \phi}{a} + \frac{(R \cos \theta - m \cos \phi)^2}{a^2} \right\} R dR d\chi. \quad (65)$$

In this the term of the first order is

$$- \frac{1}{a} \iint (L - 2) (R \cos \theta - m \cos \phi) R dR d\chi, \quad (66)$$

which, by putting $\cos \theta = \cos \phi \cos \chi$, is simply $A \frac{\cos \phi}{a} \cdot \frac{c^2}{8m}$.

The term of the second order is

$$\frac{1}{2a^2} \cdot \iint \{ (2L - 4) (R \cos \theta - m \cos \phi)^2 - (L - 1) (R^2 \cos^2 \theta - 3mR \cos \theta \cos \phi + 2m^2 \cos^2 \phi) \} R dR d\chi, \quad (67),$$

$$= \frac{1}{2a^2} \cdot \iint \{ (L - 3) R^2 \cos^2 \theta - (L - 5) mR \cos \theta \cos \phi - 2m^2 \cos^2 \phi \} R dR d\chi, \quad (68)$$

which, by putting $\cos^2 \theta = \frac{1}{2} + \frac{1}{2} \cos 2\phi \cos 2\chi$, &c., reduces to

$$\frac{A}{32a^2} \left\{ -L(2m^2 - c^2) - 7c^2 + \cos 2\phi \left(-c^2 + \frac{c^4}{3m^2} \right) \right\}. \quad (69)$$

[To prevent error, it may be observed that it is not allowable to put $\cos \theta = \cos \phi \cos \chi$ in any of the equations (63), (64), or (65) until, as in (66) or (67), all multiplications introducing powers of $\cos \theta$ have been performed.]

The terms (66) and (69), after neglecting the factor A ,
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when added to (59) give as the equation of a line of force near the wire,

$$\frac{L}{2} - \frac{\cos \phi}{4a} \left\{ (L-1)m - \frac{c^2}{4m} \right\} + \frac{1}{16a^2} \left\{ L \left(\frac{3c^2}{4} - \frac{m^2}{2} \right) + \frac{m^2}{2} - \frac{15c^2}{4} - \cos 2\phi \left(L \frac{m^2}{2} + \frac{c^2}{4} - m^2 - \frac{c^4}{8m^2} \right) \right\} = \text{const.} \quad (70)$$

As before, we can verify this result by showing that the curve (70) is at right angles to the curve (48*i*). Taking, as previously, $\frac{c^2}{4m^2} = \lambda$, this equation is

$$\frac{1}{2}L - \frac{m}{4a}(L-1-\lambda)\cos\phi + \frac{m^2}{16a^2}\{(3\lambda-\frac{1}{2})L + \frac{1}{2} - 15\lambda - (\frac{1}{2}L - 1 + \lambda - \frac{1}{2}\lambda^2)\cos 2\phi\} = \text{const.} \quad (71)$$

It is interesting to observe that the supposition of variable density affects the term of the first order both in the value of Θ and in the constant of the line of force in the same way.

To trace any Line of Force.—With the centre, *D*, of the cross-section of the wire describe a series of circles, fig. 3, their radii being *Df*, *Dg*, *Dh*, . . . Then to trace the particular line of force which passes through *f* (suppose) let *Df* = *m*₀, and let *m* be the radius of any other of the circles. If ϕ is the angle defining the point in which this latter circle is met by the line of force through *f*, we equate the left-hand side of (60) in case of constant density, and of (71) in case of variable density, to the expression which this left-hand side assumes when *m*₀ and 0 are put for *m* and ϕ . Firstly, neglecting the terms of the second order, we have, to determine ϕ , in the case of constant density,

$$\frac{1}{2}L - \frac{m}{4a}(L-1+\lambda)\cos\phi = \frac{1}{2}L_0 - \frac{m_0}{4a}(L_0-1+\lambda_0);$$

and if ϵ is the value of ϕ given by this equation, we can put $2\phi = 2\epsilon$ in the terms of the second order. If the term of the second order, $\frac{m^2}{16a^2}\{ \dots \}$, in (60) is denoted by γ , the more correct value of ϕ is obtained from the equation

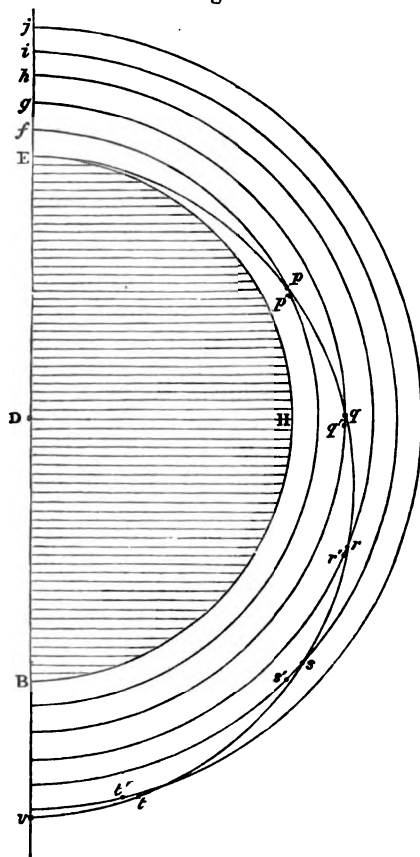
$$\frac{m}{4a}(L-1+\lambda)(\cos\phi - \cos\epsilon) = \gamma - \gamma_0,$$

where in γ we put 2ϵ for 2ϕ , and in γ_0 , of course, $2\phi = 0$.

As a numerical example, let the wire in fig. 1 form a circle 20 millim. in diameter, *i. e.* *OD* in fig. 2 is 10 millim.; and let the diameter of its cross-section be 2 millim. *i. e.* *DB* = 1 millim. in fig. 2.

In fig. 3 let EHB represent half the cross-section of the wire, its centre being D, and let the centre, O (see fig. 1), be in the production of the line DE at a distance 10 millim. above D, while $DE=1$. Let a series of circles be described

Fig. 3.



round D with radii Df, Dg, Dh, \dots equal to 1.1, 1.2, 1.3, 1.4, 1.5 millim., and suppose that we trace the line of force which touches the wire at E. If we calculate the angle ϕ which defines the point in which this line cuts the circle of radius Df , we find, taking only terms of the first order, $\epsilon = EDp'$, or

$$\epsilon = 63^\circ 21'.$$

This gives the point p' ; but taking the terms of the second order the angle becomes $62^\circ 37'$, which gives the true point, p , by means of the angle EDp . Similarly the point, q' , in

Q 2

which, if only terms of the first order were taken account of, the line of force would cut the next circle (of radius Dg) is defined by the value $\epsilon = 90^\circ 14'$, which, being corrected by the terms of the second order, becomes $89^\circ 9'$, and the corresponding point is g .

In like manner the points r', s', t' given by terms as far as the first order correspond to values of ϵ equal to

$$112^\circ 48' ; 134^\circ 26' ; 165^\circ 41',$$

which are corrected into

$$111^\circ 40' ; 133^\circ 13' ; 163^\circ 17',$$

the corresponding points being r, s, t . Thus the line of force which starts from the inner surface of the wire is $Epqrst$, and it is found to cut the diameter EB in a point v such that Dv is about 1.52 millim.

The lines of force at points between B and v are incomplete curves which emanate from various points on the surface EHB of the wire between E and B . The line of force at B itself reduces to a mere point. These lines can, of course, be traced by putting m_0 and π for m and ϕ in (60).

It has been already pointed out that the magnetic effect of a current running in a wire is not the same, at points near the surface of the wire, as if the whole current were concentrated in an infinitely thin filament running along the central line of the wire, although such is sometimes assumed to be the case.

Let us, for example, see what the values of ϕ , or of ϵ , would be in the numerical case just discussed if we assume that c can be put equal to zero, *i. e.* $\lambda = 0$.

The value of ϵ which corresponds to the circle of radius 1.1 millim. (supposing still that we are tracing the line of force which passes through E) is found to be $66^\circ 15'$ instead of $63^\circ 20'$; the value of ϵ which corresponds to the circle of radius 1.4 is 142° instead of $134^\circ 26'$, while that which corresponds to the radius 1.5 is impossible—indicating that, to the first order of small quantities, the line of force does not intersect the circle of radius Dj , but lies within it. Thus there is a notable difference made in the results by assuming that the whole current can be concentrated in a line running through D .

If $a = \infty$, *i. e.*, if the current runs in a straight wire, the conical angle and the constants of the lines of force are the same as if $c = 0$, and therefore *such concentration of a current along the central line of the wire is allowable only when the wire is straight, or when the curve into which it is bent has a very large radius of curvature.*

In the case of variable current-density the equation determining ϵ is

$$\frac{1}{2} L - \frac{m}{4a} (L - 1 - \lambda) \cos \epsilon = \frac{1}{2} L_0 - \frac{m_0}{4a} (L_0 - 1 - \lambda_0);$$

and applying this to the same numerical case, we find that p' , q' , r' , s' are determined by the angles

$$68^\circ 49'; \quad 98^\circ 10'; \quad 123^\circ 4'; \quad 152^\circ 4',$$

while the position of t' becomes imaginary. This shows that the supposition of variable density brings the lines of force closer to the surface, B, of the wire—as we should expect *à priori*. It is not considered necessary to draw a separate figure for the case of variable density, since the forms of the lines of force and the method of drawing are sufficiently illustrated by the case of assumed constant density.

Initial or rapidly alternating Currents.—The magnetic potential and the forms of the lines of force will not be the same when the current has become steady as they were in the initial stage of the current, because, just at starting, the current is confined to the surface of the wire. If we can assume that when the current is entirely superficial its density (or its infinitesimal depth below the surface of the wire) is constant, the magnetic potential at any point P and the constant of the line of force can be obtained by subtracting from the value of the potential in (43) its value when c is replaced by $c - \Delta c$, and a similar subtraction from (59). Thus, the magnetic potential is the right-hand side of (43) multiplied by i , the total current in the cross-section. If δ is the density of this current, $i = \pi c^2 \delta$, and if q is the total superficial current ($= 2\pi c \delta \cdot \Delta c$), the magnetic potential becomes

$$q \left[2(\pi - \phi) - \frac{\sin \phi}{a} \left(mL - \frac{c^2}{2m} \right) - \frac{\sin 2\phi}{16a^2} \left\{ (6L - 5)m^2 - c^2 \left(2 + \frac{c^2}{2m^2} \right) \right\} \right].$$

From (49) it appears that the constant of the line of force due to the current in the whole cross-section is (59) multiplied by i , or by $\pi c^2 \delta$. When this multiplication is effected, the differentiation with respect to c is to be performed, as in the case of the potential.

Of course the preceding discussion applies to the case of a circular vortex ring in a perfect fluid, the velocity of a particle at any point of the fluid being the analogue of the magnetic force. See Basset's 'Hydrodynamics,' vol. ii. chap. xiv. Mr. Basset assumes that for a vortex ring the magnitude of the cross-section is negligible, so that the concentration of

the ring along its core filament is allowable; but, as we have seen, this requires that the ring must be an extremely thin one, and in most cases of the coiling of wires for the conveyance of currents the assumption would be inadmissible; for, the ideal vortex filament required by the assumption (infinitely thin as compared with the radius of its aperture) finds but a very coarse representative in any coil of wire. We have already given the values of the magnetic force at the centre, O , of the curve formed by the wire and at the points, E, B , just outside its surface; these are the analogues of the velocity of the (irrotationally moving) fluid at these points in the case of a vortex ring. The velocity with which the ring itself moves forward is given by Mr. Basset as equal to $\frac{f}{2\pi a} (\log \frac{8a}{c} - 1)$, where f is the strength of the vortex (product of the cross-section and molecular rotation), while the velocity of the fluid at O is $\frac{f}{a}$; so that the ratio of the forward velocity of the ring itself to the velocity of the fluid at the centre, O , of its aperture is

$$\frac{\log \frac{8a}{c} - 1}{2\pi},$$

which, as Mr. Basset says, is "large" in the case supposed (*i. e.*, a very thin ring). We must observe, however, when comparing actual electrical coils with fine vortex rings, that for a vortex ring for which a is 1000 times c (which would ordinarily be considered as a "fine" ring), this ratio is not very large: it amounts only to 1.27; while for a vortex ring the radius of whose aperture is 100 times that of its cross-section, this ratio is only .9, *i. e.*, the ring moves more slowly than the fluid at its centre.

XX. *Long-Distance Telephony.* By Prof. PERRY, *F.R.S.*,
assisted by H. A. BEESTON*.

WHEN resistance, capacity, self-induction, and leakage are taken into account, this subject is one of considerable difficulty. It is given to very few men to be able to discuss complicated mathematical formulæ without making mistakes—the proceedings of Scientific Societies possess many such mistakes detected and undetected—and consequently I instruct my students to experiment with their formulæ, using numerical values for their variables. The consideration of

* Communicated by the Author.

the most general problem of long-distance telephony, involving certain terminal conditions, has been taken up by Mr. Heaviside ; but the ordinary mathematical physicist must find great difficulty in understanding the investigation (Phil. Mag. January 1887). Some of my students have recently obtained numerical results, neglecting the terminal conditions, which seem to me to be very instructive, and I think that the Tables will have a permanent value.

As a matter of fact, the line is supposed to be of infinite length, and we consider the state of a signal as it gets further and further away from the origin.

By comparing the current c at a section x centimetres from the origin with the current at $x+dx$, and properly disposing of the difference, we arrive at the equation :—

$$\frac{d^2c}{dx^2} = kl \frac{d^2c}{dt^2} + (kr + sl) \frac{dc}{dt} + src, \dots (1)$$

where (per unit length of conductor) k is the capacity, r the resistance, l the self-induction, and s the leakage conductivity. The solution which suits telephonic conditions is

$$c = ae^{-hx} \sin (pt - gx),$$

where

$$\sqrt{\frac{kpr}{2}} \sqrt{\sqrt{\left(1 + \frac{p^2 l^2}{r^2}\right) \left(1 + \frac{s^2}{k^2 p^2}\right)} \mp \left(\frac{pl}{r} - \frac{s}{pk}\right)}$$

gives the value of h if the minus sign is taken, and gives the value of g if the plus sign is taken, and $c = a \sin pt$ is the current at the origin. Of course $p = 2\pi f$, where f is the frequency. Any number of such functions of any frequencies may exist simultaneously.

Two conditions must be satisfied in telephony. Taking the shrillest and gravest notes of the human voice as being of frequencies f and f' , and taking therefore currents of these frequencies :—let X be the distance at which the ratio of the amplitudes of the shrill and grave currents is increased by $1/m$ th of itself ; let Y be the distance at which one of the currents has altered in lag behind the other by $1/n$ th of the periodic time of the more rapid one ; then it is easy to see that

$$X = 1 / \{m(h - h')\}^*,$$

$$Y = 2\pi / \left\{np \left(\frac{g}{p} - \frac{g'}{p'}\right)\right\}.$$

* This is approximate. If m is not large, the true expression ought to be used,

$$X = \log_e \left(1 + \frac{1}{m}\right) / (h' - h).$$

The letters with dashes indicate that p' or $2\pi f'$ must be taken instead of p . It is easy to see that X and Y become infinite if $\frac{l}{r} = \frac{k}{s}$.

I do not know what values of m and n would produce confusion of sound in the telephone. But as an exercise we have taken $m=4$ and $n=6$. We have also taken $p=6000$, $p'=600$.

For the first French Atlantic Cable the capacity and resistance were 0.43 microfarad and 2.93 ohms per nautical mile, so that

$$k = 2.3215 \times 10^{-12} \text{ farads per centim.}$$

$$r = 1.582 \times 10^{-5} \text{ ohms per centim.}$$

Mr. Beeston has calculated the distances X and Y , the lesser of which may be taken as the limiting distance for good telephony for various values of l and s .

TABLE I.—Limiting distances X in millions of centimetres for various amounts of leakage and self-induction. (One million centimetres are equivalent to about six miles.)

| Values of $s \times 10^{10}$. | Values of $l \times 10^{10}$. | | | | | | |
|--------------------------------|--------------------------------|--------|--------|--------|---------|------------|--------|
| | 0 | 2.6373 | 26.373 | 79.118 | 131.863 | 184.61 | 263.73 |
| 0 | 0.983 | 1.054 | 1.963 | 5.169 | 10.178 | 17.500 | 33.839 |
| .01 | ... | ... | 1.961 | | | | |
| .10 | ... | ... | 1.969 | | | | |
| 1 | ... | ... | 1.999 | | | | |
| 5 | 1.049 | 1.130 | 2.187 | 6.339 | 13.944 | 41.532 | 75.59 |
| 10 | 1.130 | 1.224 | 2.356 | 8.462 | 21.98 | 59.03 | 328.2 |
| 20 | 1.319 | 1.444 | 3.357 | 18.009 | 128.17 | very large | 131.65 |
| 40 | 1.754 | 1.965 | 6.250 | 390.11 | 67.95 | 18.94 | 8.75 |
| 70 | 2.527 | 2.935 | 17.671 | 39.73 | 7.727 | 4.161 | 2.573 |
| 100 | 3.447 | 4.134 | 72.03 | 10.00 | 0.650 | 2.111 | 1.617 |
| 150 | 5.314 | | | | | | |
| 200 | 7.536 | | | | | | |
| 250 | 10.090 | | | | | | |

TABLE II.—Limiting distances Y in millions of centimetres for various amounts of leakage and self-induction.

| Values of $s \times 10^{10}$. | Values of $l \times 10^{10}$. | | | | | | |
|--------------------------------|--------------------------------|--------|--------|--------|---------|------------|--------|
| | 0 | 2.6373 | 26.873 | 79.118 | 131.863 | 184.61 | 263.73 |
| 0 | 1.459 | 1.484 | 1.778 | 2.665 | 3.719 | 4.996 | 7.239 |
| .01 | ... | ... | 1.783 | | | | |
| .10 | ... | ... | 1.800 | | | | |
| 1 | ... | ... | 1.893 | | | | |
| 5 | 1.889 | 1.927 | 2.424 | 4.142 | 6.674 | 10.472 | 20.29 |
| 10 | 2.426 | 2.482 | 3.297 | 6.639 | 14.130 | 28.88 | 116.36 |
| 20 | 3.752 | 3.874 | 5.796 | 18.700 | 82.59 | very large | 75.12 |
| 40 | 7.292 | 7.649 | 15.152 | 566.36 | 76.55 | 18.184 | 7.214 |
| 70 | 15.216 | 17.342 | 57.965 | 76.304 | 11.493 | 5.266 | 2.815 |
| 100 | 27.078 | 30.147 | 283.49 | 22.70 | 0.354 | 3.267 | 1.810 |
| 150 | 58.35 | | | | | | |
| 200 | 106.43 | | | | | | |
| 250 | 170.36 | | | | | | |

It will be noticed that although X and Y are derived in different ways, by taking certain values for m and n they could be made much the same in value, and altering s or l seems to produce the same sort of effects on X and Y .

Mr. Beeston has drawn curves from the calculated numbers, but these need not be published.

If there is no self-induction, increasing the leakage increases the distance to which we can telephone. If there is no leakage, increasing the self-induction increases the distance.

When the amounts of s and l are not too great, increasing either increases the distance. These and other important facts are visible in the tables.

Without such tables as these and this method of study it would be almost impossible for the average mathematician to make anything of his mathematical results. Thus, for example, when equation (1) applies to such a function as $\sin pt$ it is just the same as

$$\frac{d^2c}{dx^2} = \left(kl - \frac{sr}{p^2} \right) \frac{d^2c}{dt^2} + (kr + sl) \frac{dc}{dt} \quad \dots \quad (2)$$

Hence we see that the effect of leakage is to *diminish* the self-induction by the amount sr/kp^2 , and to increase the

resistance by the amount sl/k . But it is easy to see that if we diminish self-induction or increase resistance we do harm in telephony, and yet this kind of diminution through leakage does good. On going into the matter carefully, it is seen that it is the p being in the denominator of sr/kp^2 which produces the good effect. In fact, if l and s are small, taking $p=6000$, $p'=600$, we find

$$X \propto 1 / \sqrt{kr} \left\{ 1 - 4246 \frac{l}{r} - \frac{s}{3800k} \right\}.$$

So that increasing s or l produces a good effect. Having found the mathematical reason we have not far to go to find the physical reason.

It is evident from the tables that if we had no leakage we could completely get rid of the evil effects of capacity by introducing self-induction. It is also evident that if we had no self-induction, we could completely get rid of the evil effects of capacity by introducing leakage. But when there is some leakage and some self-induction, we can in practice only mitigate the evil effect of capacity; for it is obvious that although certain values of l and s give infinite distances, doubling or halving these values produces enormous diminution in distance, and such a constant of a cable as s may alter very greatly.

About fifteen years ago, with Prof. Ayrton I made many experiments on signalling through bare copper wires lying at the bottom of the water in the moat of Yedo in Japan. Here k and s were both very great. We had much less success than we expected, and we abandoned, perhaps too readily, our idea of a very cheap submarine cable.

The following tables are of general application. Let the numbers given in Table III. be divided by the value of \sqrt{kr} for any cable or conductor of a telephonic line, and let them also be divided by the value of m which is considered suitable*, and they will become the limiting distances X in centimetres for that conductor, for the various values of $\frac{l}{r}$ and $\frac{s}{k}$ given.

Let the numbers in Table IV. be divided by the value of \sqrt{kr} for any conductor of a telephonic line, and let them also be divided by the value of n which is considered suitable, and they will become the limiting distances Y in centimetres for that conductor, for the various values of $\frac{l}{r}$ and $\frac{s}{k}$ given.

* It is more correct to say that the numbers are to be multiplied by $\log_e \left(1 + \frac{1}{m} \right)$.

TABLE III.

| Values of s/k . | Values of $10^5 \times l/r$. | | | | | | |
|----------------------|-------------------------------|----------|----------|----------|----------|----------|----------|
| | 0 | 1.667 | 16.67 | 50 | 83.33 | 116.7 | 166.7 |
| 0 | 0.0267 | 0.0286 | 0.0533 | 0.1404 | 0.2765 | 0.4753 | 0.9191 |
| 215.4 | 0.0285 | 0.0307 | 0.0594 | 0.1722 | 0.3787 | 1.1281 | 2.053 |
| 600 | | | | | | | ∞ |
| 430.8 | 0.0307 | 0.0332 | 0.0640 | 0.2298 | 0.5970 | 1.6034 | 8.913 |
| 857 | | | | | | ∞ | |
| 861.5 | 0.0358 | 0.0392 | 0.0912 | 0.4891 | 3.4732 | 2755.0 | 3.576 |
| 1200 | | | | | ∞ | | |
| 1723 | 0.0476 | 0.0534 | 0.1898 | 10.596 | 1.8455 | 0.5145 | 0.2377 |
| 2000 | | | | ∞ | | | |
| 3015 | 0.0686 | 0.0797 | 0.4799 | 1.0792 | 0.2099 | 0.1130 | 0.0699 |
| 4308 | 0.0936 | 0.1123 | 1.9564 | 0.2717 | 0.0176 | 0.0573 | 0.0439 |
| 6000 | | | ∞ | | | | |
| 60000 | | ∞ | | | | | |

TABLE IV.

| Values of s/k . | Values of $10^5 \times l/r$. | | | | | | |
|----------------------|-------------------------------|----------|----------|----------|----------|----------|----------|
| | 0 | 1.667 | 16.67 | 50 | 83.33 | 116.7 | 166.7 |
| 0 | 0.0531 | 0.0540 | 0.0646 | 0.0969 | 0.1352 | 0.1813 | 0.2833 |
| 215.4 | 0.0687 | 0.0700 | 0.0881 | 0.1506 | 0.2427 | 0.3808 | 0.7379 |
| 600 | | | | | | | ∞ |
| 430.8 | 0.0882 | 0.0903 | 0.1199 | 0.2414 | 0.5139 | 1.0502 | 4.231 |
| 857 | | | | | | ∞ | |
| 861.5 | 0.1364 | 0.1409 | 0.2108 | 0.6800 | 3.0033 | 111056 | 2.732 |
| 1200 | | | | | ∞ | | |
| 1723 | 0.2652 | 0.2781 | 0.4377 | 20.596 | 2.7837 | 0.6613 | 0.2624 |
| 2000 | | | | ∞ | | | |
| 3015 | 0.5533 | 0.6306 | 2.1079 | 2.775 | 0.4179 | 0.1915 | 0.1024 |
| 4308 | 0.9847 | 1.0963 | 0.1031 | 0.826 | 0.0129 | 0.1188 | 0.0658 |
| 6000 | | | ∞ | | | | |
| 60000 | | ∞ | | | | | |

Another way of putting the results in these tables is this :—Let K be the whole capacity of the line in farads, R its resistance in ohms, L its whole self-induction in secohms, S the whole leakage-conductivity in mhos : L/R and S/K are the same as the l/r and s/k of the tables. For given values of these find the number in either table ; square it and divide by any chosen m^2 or n^2 ; this gives the product of the whole capacity K and the whole resistance R of the conductor.

Of course in all lines which have the same values of L/R and S/K , the product KR is constant. I must again draw attention to the fact that we have neglected the terminal conditions.

I have not hitherto said anything about the amplitude of the current ; in fact the receiving apparatus has been supposed to be infinitely delicate. It is obvious that $1/h$ is the distance in which the amplitude becomes $1/e^{\text{th}}$ of its initial amount. If the numbers in the following Table V. be divided by \sqrt{kr} for any line, they give the distances in which a current of frequency 955 per second has its amplitude *halved*.

TABLE V.

| Values of s/k . | Values of $\frac{e}{r} \times 10^4$. | | | | | | |
|----------------------|---------------------------------------|-------|-------|-------|-------|-------|-------|
| | 0 | 1.667 | 16.67 | 50 | 83.3 | 116.7 | 166.7 |
| 0 | .0127 | .0167 | .0197 | .0314 | .0402 | .0476 | .0567 |
| 215.4 | .0124 | .0130 | .0188 | .0283 | .0340 | .0389 | .0331 |
| 430.8 | .0122 | .0128 | .0177 | .0257 | .0295 | .0315 | .0329 |
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| 6462 | .0079 | | | | | | |
| 8616 | .0071 | | | | | | |
| 10770 | .0065 | | | | | | |

The effect of leakage is in every case to diminish the amplitude of the current, making it necessary to have more sensitive receiving-instruments or more powerful sending-instruments.

If some of our clever mathematicians would for a while put aside the ambition to write original papers and would

give us in one paper, however long, an exposition of Mr. Heaviside's views on this subject, he would confer great benefits upon the average electrician. Mr. Heaviside can discover new truths, and we all believe in his results when we understand them, but he seems unable to lower his reasoning to our mathematical levels. Since writing this paper I have tried to understand Mr. Heaviside's numerous papers on this subject, but I am sorry to say that I am not yet able to express a certain opinion as to the practical value, or want of value, of the preceding tables.

XXI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 150.]

June 7th, 1893.—W. H. Hudleston, Esq., M.A., F.R.S.,
President, in the Chair.

THE following communications were read :—

1. "The Bajocian of the Sherborne District: its Relations to Subjacent and Superjacent Deposits." By S. S. Buckman, Esq., F.G.S.

This paper is partly the result of excavations made by Mr. Hudleston, F.R.S., and the author at Sherborne, to determine the position of the so-called 'Sowerbyi-zone.'

The author uses the term 'Bajocian' in a merely conventional sense to denote the lower beds of what has been called 'Upper part of the Inferior Oolite.' He introduces a term *emar* (ἔμαρ) as a chronological subdivision of an 'age,' and considers the beds dealt with in the paper to have been deposited during 12 *emata*, which he calls, in descending order, *fuscum*, *zigzag*, *Truellii*, *Garanti-anum*, *niortense*, *Humphriesianum*, *Sauzei*, *Witchellia* sp., *discites*, *concauum*, *bradfordense*, and *Murchisonæ*.

A line from Stoford, Somerset, through North Dorset to Milborne Wick, Somerset, is the base-line of the district reviewed. Seventeen sections of places close to this line are given to show the relations of the beds, with the different amounts of strata deposited during successive *emata*, and during the same *emar* at different places. By means of Tables he shows that the area of maximum accumulation receded eastwards in the earlier *emata*, and then proceeded westwards during the later *emata*. A similar and corresponding faunal recession and progression is pointed out, though the faunal headquarters always remain west of the great accumulation of deposit. Adding the various maximum deposits together, the author finds as much as 130 feet of strata deposited during the twelve *emata*, = (practically) the 'Inferior Oolite of Dorset.' This is a far greater thickness than has hitherto been allowed to beds of

this age in the district, but the fault lay partly in incorrect correlation.

The Dorset strata are correlated with strata in other districts—namely, with those of Dundry and Leckhampton Hills in this country. Of these the author gives sections, pointing out the emata during which the strata of those localities were deposited, and making some alterations in their correlation.

Passing to Württemberg, the author shows that the equivalent of Waagen's *Sowerbyi*-zone is exactly represented at Sherborne. Returning to Normandy, the author compares his results with the recent work done by Munier-Chalmas, who in some respects has made an even more detailed subdivision of the strata. In a Table he shows the correspondence between his divisions for Dorset and those of Munier-Chalmas in Normandy and Haug in Southern France.

2. "On Raised Beaches and Rolled Stones at High Levels in Jersey." By Andrew Dunlop, M.D., F.G.S.

In this paper the author gives some account of the higher raised beaches examined by him on the south-eastern and eastern coast, but probably found in other parts of the island also, as indicated by the existence of rolled stones &c. These beaches seem to prove submergence (in the case of that at South Hill, to a depth of at least 130 feet below the present level) at the end of the 'first glacier period.'

The brick-clay often lying on raised beach, and containing pebbles, has been compared to loess by the author. He believes that Prof. Prestwich's theory of sudden and rapid upheaval, with a resulting tumultuous sweep of water, may be applied to Jersey; but also, if the sinking took place at the end of the Glacial Period, the peculiar conditions produced by melting ice may have played their part in producing the brick-clays.

Subsequent upheaval above the present sea-level is indicated by submerged forests, sometimes lying on the brick-clay.

No fossils have hitherto been found in the raised beaches; but a bone of *Bos primigenius* (?) has been extracted from the brick-clay.

XXII. Intelligence and Miscellaneous Articles.

ON THE CRITICAL POINT, AND SOME PHENOMENA WHICH
ACCOMPANY IT. BY G. ZAMBIASI.

THIS comprises three sets of experiments:—

I. Application of the O tube of Cailletet and Collardeau to ordinary ether.

II. Production of Cagniard de Latour's phenomenon with plain tubes containing various quantities of ether.

III. Production of the same phenomenon, comparing two or three tubes heated in the same bath.

In the experiment with the O tube the meniscus disappeared at

193°. The two columns of mercury presented a greater or less difference according to the initial difference. The equalization of the mercury-levels took place at 196°. The formula expressing the equilibrium of the two parts of the tube shows that the course of the difference of level corresponds very appreciably to that of the difference between the density of the liquid and that of the vapour.

The phenomenon of Cagniard de Latour was observed in seven tubes, in which the volumes of the liquid and the vapour were, at the temperature of 18°·6, respectively in the following ratios:—

$$\frac{4}{1} \quad \frac{2}{5} \quad \frac{1}{2} \quad \frac{6}{11} \quad \frac{4}{5} \quad \frac{4}{10} \quad \frac{7}{5}$$

From the results obtained the author concludes that, in order that the meniscus can be observed in the tube, the ratio $\frac{v}{v_1}$ of the volume of the liquid to the volume of the vapour at the ordinary temperature must not be below a lower limit comprised between

$$\frac{1}{4} \quad \text{and} \quad \frac{2}{5},$$

nor above a higher limit comprised between

$$\frac{9}{10} \quad \text{and} \quad \frac{7}{5}.$$

Comparative experiments on several tubes heated in the same bath have shown that the temperature at which the meniscus disappears is not constant for the same body, but depends on the quantity of this body compared in a given volume. In the same tube the reappearance was constantly observed at the same temperature as the disappearance.—*Journal de Physique*, June 1893.

THE CRITICAL POINT, AND THE PHENOMENON OF THE DISAPPEARANCE OF THE MENISCUS WHEN A LIQUID IS HEATED UNDER CONSTANT VOLUME. BY G. ZAMBIASI.

The fact established by the author in the above Note, that the temperature t_c at which the meniscus disappears is not constant, but rises when the ratio of the initial volume of the liquid to the volume of the vapour disappears, might have been foreseen from Jamin's experiments, in which the disappearance of the meniscus was obtained by a compression at constant temperature. M. Amagat has demonstrated the same fact in a still more accurate manner in producing, by a slow increase of pressure of carbonic acid, the disappearance at 30°·50, when heat alone produces disappearance at 31°·55. If the temperature t_c was singular, it would be independent of the compression.

It does not increase the tension, which is a maximum; but by condensing the vapour it increases the volume and the mass of the liquid, so that the ratio of the volumes increases.

The densities d and d' and the volumes v and v' of the liquid and the vapour, when a mass m of a body in a closed vessel at constant volume is heated, should at all temperatures satisfy the equations

$$vd + v'd' = m,$$

$$v + v' = V.$$

We have then .

$$\frac{v}{v'} = \frac{m - Vd'}{Vd - m}.$$

Discussing this expression, the author shows that the meniscus disappears at the critical point if V is the volume of the mass worked with.

If a mass of a body is subjected to a gradual heating in a volume near its critical one, though a little lower, it will *successively* reach a condition in which the meniscus disappears; a condition in which its pressure will be equal to the critical pressure, when its temperature is equal to the critical temperature; in fine, to a distinctly gaseous state. From the moment at which the meniscus disappears that pressure is no longer independent of the mass. Between this moment and that at which it reaches the critical temperature the body is in a state which corresponds neither to a mass of gas, nor to a mass of vapour and of gas in juxtaposition. It may be regarded as a mixture or as a solution of the two kinds of matter.

If the constant volume in which the mass in question is enclosed is equal to its critical volume V , the disappearance of the meniscus, the reestablishment of the level of the mercury in the O tubes, the critical pressure, and the critical temperature should be *simultaneously* realized.

In order to be certain that a body has been brought to the critical state, we must be certain that it offers simultaneously two elements characteristic of this state. The disappearance of the meniscus, and the reestablishment of the level in the capillary tubes taken separately are not sufficient indications, for they may take place outside the critical condition. On the contrary, equality of the densities or of the specific volumes of the liquid and of the vapour will be a sufficient datum, since it is equivalent to two critical elements.

In conclusion, in order that the method of heating a body at constant volume shall offer certain indications of the critical conditions, the author proposes to perfect it by providing the O tube with a regulator of volume. By suitably modifying the volume by trials the disappearance of the meniscus and the reestablishment of the level of mercury might be obtained at the *same instant*. The space occupied by the body will then be the critical volume; on the other hand, the temperature and the pressure will then be also those of the critical point.—*Journal de Physique*, June 1893.

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[FIFTH SERIES.]

SEPTEMBER 1893.

XXIII. *On the Hypotheses of Dynamics.* By Prof. J. G. MACGREGOR, D.Sc., Dalhousie College, Halifax, N. S.*

PROFESSOR LODGE'S paper on the Foundations of Dynamics†, in which he criticises an Address of mine on the same subject‡ and replies to criticisms I have made§ on a series of papers by him in this Magazine||, contains so much debatable matter that it would require more space than is available to give it full discussion. There are some points, however, which are of so much importance in the clearing up of our conceptions of the fundamental assumptions of Dynamics, that I venture in as brief a manner as possible to draw attention to them.

(1) *The Relativity of the First and Second Laws of Motion.*

Prof. Lodge completely misunderstands the objection which was urged in my Address against the usual statement of the first and second laws of motion, and which had been previously urged by various writers¶. He states it to be "that

* Communicated by the Author.

† Phil. Mag. current volume, p. 1.

‡ Trans. Roy. Soc. Canada, vol. x. (1892), sec. iii. p. 3.

§ Phil. Mag. vol. xxxv. (1893) p. 134.

|| Vols. viii. (1879) p. 277, xi. (1881) pp. 36 & 529, xix. (1885) p. 432.

¶ The list of writers which Prof. Lodge gives is obviously not intended to be complete. It omits C. Neumann (*Ueber die Principien der Galilei-Newton'schen Theorie*, Leipzig, 1870), Prof. J. Thomson (Proc. R. S. Edin. vol. xii. pp. 568 & 730), Prof. Tait (ibid. p. 743 and 'Properties of Matter,' 1885, p. 92), H. Streintz (*Die physikalischen Grundlagen der Mechanik*,

Phil. Mag. S. 5. Vol. 36. No. 220. Sept. 1893. R

uniform motion is unintelligible or meaningless, unless you specify its direction and velocity with reference to a set of axes," whereas the real objection is that the laws themselves, in their usual form, are unintelligible, unless the axes are specified, to which the uniform motion or acceleration mentioned in them is referred. His criticism is therefore necessarily somewhat wide of the mark. It may be summarized thus:—(1) Uniform motion is perfectly intelligible; and therefore no specification of axes is necessary in the enunciation of the first law. (2) The difficulties in the way of specifying axes are practically insurmountable.

With regard to (1), it will be noted that it rests entirely on the intelligibility of uniform motion, and does not therefore touch the necessity of the specification of axes in the case of the second law* or of the first law in the form which Prof. Lodge has given it himself:—"Without force there can be no acceleration of matter"†. For in neither case is there any reference to uniform motion.

With regard to the intelligibility of uniform motion, while it cannot be admitted that "such notions as axes of reference are not at all necessary for the apprehension of what is meant by a uniform velocity" (seeing that a uniform velocity is one whose magnitude and direction do not change relatively to the axes employed in its specification), it is nevertheless obvious that the specification of particular axes is not necessary for this purpose. But the intelligibility of the first law requires more than the mere apprehension of what is meant by uniformity of velocity. For it is not a mere statement about uniform velocity, but an assertion that a particle in given circumstances must have a uniform velocity. Now a velocity which is uniform with respect to one set of axes may be variable with respect to others. It is therefore at once obvious that, if we employ the ordinary conception of force, the assertion which the law makes cannot hold for all axes, and consequently can have no definite meaning, unless

Leipzig, 1888), L. Lange (*Ber. d. K. Sächs. Ges. d. Wiss. zu Leipzig, Math.-phys. Classe*, Bd. xxxvii. 1885, p. 333, and *Die geschichtliche Entwicklung des Bewegungsbegriffes*, Leipzig, 1886), and Muirhead (*Phil. Mag.* [5] vol. xxiii. 1887, p. 473), the last, however, being mentioned subsequently in a footnote.

* Mach, Streintz, Lange, and other German writers refer to the relativity of the first law merely, because they employ as second law Galileo's law of the "physical independence of forces" (*Unabhängigkeitsprinzip*). The second law to which I refer is Newton's second law.

† 'Nature,' vol. xlviii. p. 62.

we are told what are the axes by reference to which it does hold*.

Much may of course be derived from the first and second laws without specification of axes. The whole science of dynamics bears witness to that fact. But, as Streintz has shown in the work referred to above, much practical inconvenience and much unnecessary complication have arisen from the employment of these laws in their vague form; and I shall have occasion to refer below to one paradox, the absoluteness of rotation notwithstanding the relativity of motion, which receives its solution when the relativity of these laws is recognized.

The specification of axes by reference to which the first and second laws hold, or of what may be called dynamical reference systems, is thus no mere refinement of the pedantic mathematical mind. On the contrary, it satisfies a felt want. The want is not felt indeed in dealing with the simple problems of the common school. For the rough experiments which are usually cited in elementary text-books as suggesting the laws show that it is by reference to axes fixed in the earth that they are supposed to hold; and this tacit specification is quite sufficient for the discussion, *e. g.*, of the inclined plane and the wheel and axle. But when we come to treat the problems of theoretical Astronomy, it is at once obvious that we cannot assume the laws to hold with respect to these axes; and the question forces itself upon the attention: What are the axes by reference to which they must now be considered to hold? And the question having been raised must be answered. The critical student who has seen in his study of kinematics that velocity and acceleration are relative conceptions, will not be convinced by Prof. Lodge's "opprobrious or perhaps complimentary epithets" that they lose their relativity when applied to the motion of bodies.

Turning now to the second criticism, it is obvious that to one who thinks it is proposed to specify axes by means of which the magnitudes and directions of velocities may be described absolutely (p. 8), the difficulties in the way must appear

* Should Prof. Lodge, therefore, endeavour to crush a doubter of the first law, as he tells us he would, by saying to him:—"If the speed and direction of a freely moving body vary they must vary in some definite manner; very well, tell me in what manner they are varying. You cannot, unless you can show me absolutely fixed lines of reference,"—the doubter need be at no loss for a reply. He has but to say:—"If you will kindly tell me what are the axes by reference to which you hold the velocity of the body to be uniform, I will then tell you how I suppose it to vary. But unless we agree upon axes of reference it is impossible for us to compare our respective axioms."

insuperable*. They would be in that case the difficulties attending the solution of an inconceivable problem. That the actual problem has only recently been attacked is due not so much to its difficulty as to the fact that the necessity of its solution has been apparent only since the full recognition of the essential relativity of velocity and acceleration, whether uniform or variable. That there are difficulties, however, is obvious from the fact that only some of the methods employed appear to be sound, and that a number of writers have attacked the problem and left it only half solved†. What the difficulties are may be shown best by a sketch of the efforts made to overcome them.

There would seem to be two legitimate ways of finding dynamical reference systems:—(1) by re-studying the experimental results for the deduction of which the laws of motion were enunciated, and re-formulating these laws; and (2) by assuming that, since the laws of motion in their vague form have been abundantly tested in the hands of men enabled by a kind of dynamical instinct to use them aright, there must be axes by reference to which they hold, and proceeding to determine these axes by the aid of the laws themselves.

The former method, the historical-critical, is that employed by Prof. Mach‡. He points out that Galilei observed the first law to hold, by reference to points fixed in the earth, for motions on the earth's surface of small duration and extent, and that, when Newton came to apply it to bodies moving in space, he generalized it, showing that, so far as could be determined, it held for the motions of the planets by reference to the distant and to all appearance relatively fixed celestial bodies. And he holds that the first law, when referred, so far as space is concerned, to the fixed stars, and, so far as time is concerned, to the earth's rotation, is to be regarded as a sufficient approximation to accuracy for practical purposes, and as forming as close an approximation as it will be possible to obtain until a considerable widening of our experience occurs.

It seems to me that the historical-critical method might carry us farther than this. For we now know that the so-called fixed stars are not fixed; and means have been devised of correcting observations made on this assumption. We also know that the laws of motion do not hold when referred to a time-scale determined by the earth's rotation; and a rough correction has been determined for application

* The fact that Prof. Lodge regards motion with respect to the æther as absolute motion (p. 30) perhaps renders this statement doubtful.

† Neumann, J. Thomson, and Muirhead. See works cited above.

‡ *Die Mechanik in ihrer Entwicklung*; Leipzig, 1889, pp. 217 & 481.

to this time-scale, in the case of motions extending over long periods of time. The first law, when expressed by reference to the fixed stars and the earth's rotation, is therefore no longer regarded as sufficiently accurate for all purposes; and the exact expression of the law, as empirically determined and employed in actual work, changes from day to day or at least from decade to decade. The question therefore arises: Can we put the laws of motion into general forms such that the empirical forms which they may have at any time may be regarded as special cases determined by the state of knowledge of the time?

The latter of the two methods* referred to above is intended

* Mach, though holding, as seen above, to the empirical result of the historical-critical method, gives in his *Mechanik* (p. 218) an interesting "remnant," as he calls it, of his efforts to apply the second method. He holds that, in using the first law in its Newtonian form, we may be regarded as employing the universe, or a sufficiently large portion of it, as our reference system, and on the following grounds:—"Instead of saying the velocity of a mass μ remains constant in space we may also employ the expression, the mean acceleration of the mass μ , relatively to the masses $m, m', \&c.$, at the distances $r, r', \&c.$, is zero, or

$$\frac{d^2}{dt^2} \frac{\sum mr}{\sum m} = 0.$$

The latter expression is equivalent to the former, provided we take into consideration a sufficient number of sufficiently distant and great masses, the mutual influence of the nearer small masses being in that case negligible." If this be so, the first law may be expressed as follows:—The mean acceleration of any particle, relatively to the other particles of the universe, or of a sufficient portion of the universe, is zero, provided the particle is not acted upon by force,—an expression which obviously has not the same vagueness as the Newtonian form of the law, though practically, as Mach points out, it is not more readily applicable, on account of the impossibility of making the summation necessary for the determination of the mean acceleration.

How this result is arrived at, Mach does not say. But it is easy to prove it to be one of the properties of the centre of mass, that the component acceleration, in any direction, of any one particle of a system, relatively to the centre of mass of the system, is equal to the mean component acceleration of this particle, in the same direction, relatively to all the other particles of the system, provided the mass of the particle is small compared with the mass of the system. In making the above statement, therefore, Mach would seem to assume that the uniform velocity contemplated in Newton's form of the first law is a velocity which is uniform relatively to the centre of mass of the universe, or of a sufficiently large portion of it; and if that be so, he assumes a partial specification of a dynamical reference system. It would also appear that the portion of the universe taken into consideration need not consist of numerous and distant particles, but must simply have sufficient mass.

It is obvious that if the above assumption be made, not only may the first law be thrown into the above form, but also the second law may be thrown into a corresponding form. The making of this assumption, however, introduces a complication. If we assume merely that there are axes

to give laws of this kind. Prof. James Thomson may be said to have employed it when he showed how, by observation of successive relative positions of particles given as moving in straight lines, the axes by reference to which their paths are rectilinear may be determined geometrically*. Thomson and Tait may be said to employ it also, when they show, by a deduction from the first law, how we may imagine ourselves as obtaining "fixed directions of reference"†. But these authors make no attempt to give a formal specification of a dynamical reference system.

Lange employed this method in the paper referred to above, basing his suggestion as to specification on a kinematical result, viz. that for three, or fewer than three, points, which are moving relatively to one another in any way whatever, it is always possible to find a system of coordinates, indeed an infinite number of such systems, by reference to which these points will have rectilinear paths; while for more than three such points this is possible only in special circumstances. It follows that the law of the uniformity of the direction of motion of particles free from the action of force is, for three such particles, a mere convention, and that it is a result of experience only in so far as it applies to more than three particles by reference to one and the same system. Hence just as the dynamical time-scale is defined as a time-scale by reference to which a particle free from the action of force moves with a uniform speed, so the dynamical reference system may be defined as a system by reference to which three particles free from the action of force move in rectilinear paths. Following out these considerations he finally proposes to enunciate the first law in the following form:—Relatively to any system of coordinates by reference to which three particles projected from the same point in space and thereafter

by reference to which the first and second laws hold, it may be proved by means of the second and third laws that relatively to these axes the centre of mass of a system of particles will have no acceleration, provided no external forces act on the system. While, therefore, the assumption that the centre of mass of the universe may be employed as the origin of a dynamical reference system is justified, it is obvious (1) that if, in employing Mach's expression of the first law, we restrict ourselves to a part of the universe, it must be a part on which no external forces act; and (2) that since, in obtaining this form of the law and the corresponding form of the second law, we employ the third law of motion, the new laws are not merely new expressions of the old laws, but involve the third law in addition.

* See also Prof. Tait's solution of this problem by Quaternions in the paper cited above.

† 'Treatise on Natural Philosophy,' vol. i. part 1 (1879), § 249.

left free from the action of force, which do not, however, lie in a straight line, describe any three straight lines intersecting in a point (the axes of coordinates for example), the path of any fourth particle free from force will be rectilinear. And relatively to any time-scale, by reference to which one particle free from force will, when its motion is referred to the above axes, move with uniform speed, every other particle free from force will move with uniform speed, if its motion be referred to the same axes.

It was this method also which I employed in my Address, when I had not yet met with Lange's paper, the conclusion reached being, that the 1st and 2nd laws hold relatively to any particle not acted upon by force, as point of reference, and to lines drawn from it to other particles which are unacted on by force and have the same velocity as the first particle, as axes of reference. I showed also that it followed from this, that in dealing with the ordinary problems of the motion of bodies on the earth's surface, axes fixed in the earth might serve practically as a dynamical reference system*.

With regard to all such modes of specifying axes as those referred to, Prof. Lodge asks, "How can we utilize as axes the trajectories of particles free from force, without tacitly assuming the first law continually?" A criticism in the form of a vague question is hard to meet, because indefinite. If the first law is assumed in its own enunciation, when such trajectories are employed in the specification of axes, it should be easy to point out exactly where the assumption seems to be made; and a definite criticism of that kind might be met at once. But, judging from the context, the question is probably suggested by the mistaken notion, that when such trajectories are employed they must be assumed to be straight lines in absolute space,—a notion which springs directly from the belief that the object of specifying axes is the description of velocities absolutely. The object of specifying axes, however, is not "to attempt the impossible." And when the trajectories of particles free from force are employed as axes, or for the specification of axes, no assumption is made as to their form. Indeed it is recognized that they cannot be said to have any definite form except by reference to other axes; and that they may be made to take an infinite number of forms by varying the axes by reference to which their forms are specified. And no assumption being made as to

* I need hardly refer to Prof. Lodge's objection to such statements of the first law on the ground of their complexity. If intelligibility is consistent with simplicity, well and good. But if not, it is of course the simplicity which must be sacrificed.

their form, no assumption of the first law is made in utilizing them.

We are also asked how we can appeal to the experience of the human race with regard to such axes*. It must be admitted that we cannot make any direct appeal. The only dynamical axioms which can make such an appeal are axioms applicable within, but not beyond, the narrow range of direct experience. When we pass from the discussion of the motion of bodies on the earth's surface to the motion of bodies in space, we enter a region which is outside our direct experience; and the human race, if it is interested in such things, must learn that the hypotheses made by philosophers to coordinate dynamical phenomena generally, must be judged solely by the accuracy of the deductions which flow from them.

Possibly Prof. Lodge is not thinking of the human race generally so much as of the race of young students. And it is at once obvious that such an enunciation of the first law as that suggested, for example, by Lange, is not suitable for use in an elementary text-book or before a class of beginners. But no one has proposed to use it in either case. The object of writers who have sought to solve the problem under consideration has been logical, not pedagogical. The beginner deals with simple motions of bodies on the earth's surface. He is led to see from his own experience that, relatively to axes fixed in the earth (the north-south, east-west, and up-down lines, say, at his place of observation), the first and second laws hold for such simple motions. All that is necessary at this stage is to make clear that it is relatively to such axes that in such cases these laws are found to hold. When he reaches such problems as those of theoretical Astronomy, he will see at once that the laws of motion, as first enunciated, are insufficient and that they must be generalized. And by that time he will have learned that axioms are not to be accepted or rejected according as they do or do not appeal directly to his experience, but according as the deductions which flow from them do or do not stand the test of observation.

Mach's objection† to such modes of specifying axes as those just considered is more to the point. While he admits that the first law may be expressed definitely by means of them, he holds that in using them we only apparently avoid

* This objection ought surely not to be urged by a writer who holds to the third law of motion as an axiom, and yet tells us that he is constantly meeting with engineers (whose dynamical experience is of course wider than that of most members of the human race) who refuse to admit it.

† *Die Mechanik*, p. 484.

a reference of motion to the fixed stars and the earth's rotation. No doubt, in practical observation of motions on the earth's surface or in space, we must still employ, immediately, points fixed in the earth, or the fixed stars, respectively, as reference systems, and the earth's rotation as giving us our time-scale, applying to the crude observations, when necessary, the corrections which may have been determined. But the laws as expressed above both give a theoretical justification of this course and indicate the way in which the necessary corrections may be made more and more accurate. If the laws of motion in the form referred to be assumed, it may readily be shown that in the circumstances in which we find ourselves, surrounded on all sides by bodies, at vast distances, which are moving with velocities of apparently the same order of magnitude as our own, these bodies may be employed as a rough reference system; that the earth, constituted and situated as it is, must be rotating with a roughly uniform angular velocity relatively to these bodies, and that therefore we are justified for most practical purposes in using the fixed stars as a reference system and the earth's rotation as a time-scale. Moreover, with this assumption it becomes apparent that the corrections to be applied to the crude observations made relatively to this reference system and this time-scale, must become more accurately known as we acquire increased knowledge of the motions of the stars and of the masses and motions of the members of the solar system*.

It may turn out, of course, that the assumption on which the above method rests is untenable, that in fact there may be no axes by reference to which Newton's laws hold. In that case other axioms will have to be formulated. Meantime the above general form of the laws may be said, at least qualitatively, not only to give us as a particular case the empirical expression which they have at present, but also to account for those of the past and to indicate the lines on which we must work that they may be improved in the future.

I mentioned above two legitimate ways in which dynamical reference systems may be determined. The attempt has been made to determine them in what seems to me an illegitimate way, viz. by assuming *à priori* that such systems must have certain characteristics, notably that they must have no rotation. This is the only kind of method to which Prof. Lodge seems to refer in the paragraph in which he gives a sketch of the difficulties in the way of specifying axes (p. 7). It is

* Thus this mode of expressing the relativity of the laws of motion has, in addition to the advantages just mentioned, that which Mach claims for his, that its tendency is to stimulate the progress of science.

based upon the belief that dynamical reference systems are means of describing velocities absolutely.

This is the method which Streintz employs in the work referred to above. He accepts Newton's conclusion* that it is possible to recognize absolute motion of rotation, and possible, therefore, apart from all reference to surrounding bodies, to recognize a body as not rotating. He consequently assumes that the fundamental body, by reference to which the motion of other bodies must be specified in order that the first law may hold, must be a body which is undergoing no rotation †; and he holds that such a body may be recognized by the application of the Foucault's pendulum test and by other similar experimental tests.

While Streintz's method leads him to a correct, though a particular, result, as tested by the results of legitimate methods, it is based upon an assumption which, when the relativity of the laws of motion is admitted, may readily be shown to be erroneous, viz. that the absence of centripetal forces enables us to recognize a body as being absolutely without rotation. The widespread confidence in the conclusion which Newton drew from the behaviour of his rotating bucket of water seems to me to be an instance of the confusion of thought which has its origin in the non-recognition of this relativity ‡. That a particle which is moving in a curved path must be acted upon by a resultant force which has a component directed towards the centre of curvature, is a deduction from the second law of motion. Without specification of axes the deduction has no definite meaning; for a path which is curved relatively to one set of axes may be differently curved or even straight relatively to others. Obviously, however, the axes by reference to which motion is assumed to be specified are axes by reference to which the second law holds. Fully enunciated, the proposition would therefore read thus:—A particle which, relatively to a dynamical reference system, is moving in a curved path, must be acted upon by a force having a component directed towards the centre of curvature. If, therefore, in any case we can detect the action or the non-action of such force, we may assert that the particle is moving or is not moving, respectively, in a path which is

* *Principia*: Scholium to Definitions.

† Prof. Tait proposes a similar mode of specification (*Properties of Matter* (1885), p. 92).

‡ Writers who accept Newton's conclusion usually deny the possibility of recognizing absolute translation. Yet if we regard the laws of motion as holding for absolute space, which we must do in order to accept his conclusion, it follows that the translational acceleration of a body determined by the second law must be an absolute acceleration.

curved relatively to a dynamical reference system; but we have no means of making any assertion as to the absolute motion of the particle. The rotation of a body about an axis may be regarded as the motion of its particles in circles about that axis. If, therefore, we observe any body which from our point of view seems to rotate about an axis, and if we are able to recognize the non-action of centripetal forces on its particles, we may assert that, relatively to a dynamical reference system, the body is not rotating about this axis; while if we can recognize and measure the centripetal forces, we may be able to assert that relatively to such a system it is rotating about this axis. But we can make no statement about its absolute rotation*.

It follows that the experimental tests which Streintz proposes to apply to his fundamental body would enable him to select a body which was not rotating relatively to a dynamical reference system, but would not enable him to select one which was absolutely without rotation†.

(2) *The Independence of the First Law of Motion.*

Prof. Lodge agrees with me in holding the first law to be a particular case of the second, but imagines that, for reasons I need not quote, I will not seriously adhere to the view that the first law gives us no more useful definition of time than the second. I do, however, seriously adhere to it, for the obvious reason that, if the first law be a particular case of the second, we must be able to obtain from the second all that we can obtain from the first. I quite admit, of course, that for educational purposes it is desirable to give separate enunciation

* The application to the old problem of the rotation of the earth is obvious. By reference to axes fixed in the earth, the fixed stars rotate about the earth's polar axis, while by reference to axes fixed relatively to the stars, it is the earth which rotates. Which is the real motion? Both motions are real, as real as any motions can be. But Foucault's, and other similar experiments, are held to show that it is the earth which is really rotating. According to the above they do not prove this; but they do prove that relatively to a dynamical reference system it is the earth and not the system of fixed stars which is rotating. Motion when specified relatively to such a system is no more real than when specified otherwise. But when it is specified in this way, we find that we are able to represent our dynamical experience by means of simpler formulæ than when we specify it otherwise. And thus we come to regard motion specified in this way as being real.

† On absolute rotation, see Prof. J. Thomson (Proc. R. S. E. vol. xii. p. 577), Prof. Mach (*Die Mechanik*, p. 216), L. Lange (*Bewegungsbegriff*, p. 64), Muirhead (*loc. cit.* p. 476), and Prof. K. Pearson (Grammar of Science, Appendix, note 1).

to the first law. But that is quite consistent with a denial of its logical independence*.

(3) *The asserted Deduction of the Third Law of Motion.*

The question of the possibility of deducing the third law from the first seems to me of such importance† that I shall discuss it at some length.

The common belief that the deduction is possible arises probably from the fact that Newton is supposed to have made it‡. I can best examine Newton's argument§ by writing it

* Prof. Minchin is reported in 'Nature' (vol. xlviii. p. 166) as not admitting the first law to be a particular case of the second, on the ground that "unless force was postulated (the function of the first law), the second became a mere definition, and not a law." Obviously, if the first law be regarded merely as a postulate it cannot be a particular case of a law. But Prof. Minchin states that it gives also "the criterion of the presence of force;" and it is this aspect of the law which is held to be a particular case of the second. Prof. Henrici is reported (*ibid.*) as saying that "in passing from geometry to kinematics the idea of time presented itself, and the appropriate axiom was contained in Newton's first law." He would thus make the first law a kinematical axiom, though why such an axiom should be expressed in terms of dynamical conceptions is not apparent. It would follow, however, from this position that the first law ought not to be enunciated among the dynamical axioms, in which case the question of dependence or independence would not arise.

† Prof. Lodge now considers it of minor importance. But he has insisted upon the possibility of deducing this law, not only in his book on Mechanics, but also in papers in this Magazine and in 'The Engineer.' Indeed he still considers the deduction so important for the conversion of examination candidates and engineers as to justify us in pretending, as it were, to make it, by means of a non-rigorous proof (p. 10).

‡ "That Newton really regarded himself as having deduced the third law from the first is rendered extremely doubtful by the fact that he retained this law as one of his axioms. But it seems clear that he regarded part of what we now consider to be included in the third law to be capable of deduction. That Newton regarded the third law as less general in its applicability *as an axiom* than we do may be gathered from his comments on it. He illustrates it by reference to the finger pressing a stone, a horse hauling a stone by means of a rope, and bodies impinging upon one another,—all cases of palpably contact-actions. And he concludes his illustrative comments by saying:—"This law holds also in cases of attraction, as will be proved in the following Scholium." The fact that his third law states action and reaction to be equal and opposite but says nothing as to their being in the same straight line, forms corroborative evidence that he regarded his law as applicable directly to contact-actions only. For in such actions it would follow, from the opposition of action and reaction, that they must be in the same straight line. It would thus appear that Newton regarded the application of the third law to attractions as capable of deduction."—My Address, p. 10.

§ "In attractionibus rem sic breviter ostendo. Corporibus duobus quibuscumvis A, B se mutuo trahentibus, concipe obstaculum quodvis interponi, quo congressus eorum impediatur. Si corpus alterutrum A magis trahitur versus corpus alterum B, quam illud alterum B in prius A,

out in detail. If I understand it aright (it is so condensed as to be somewhat obscure) it is as follows :—Let A and B be two mutually attracting bodies, and let F and F' be the attractions on A and B respectively. Imagine any obstacle, O, interposed between them so as to prevent their approach. Then, provided the attractional stress between A and B be independent of the existence of other stresses between them and other bodies (assumption No. 1, the “physical independence” of stresses), F and F' will still be the attractions on A and B respectively. Let R and R' be the action on A and the reaction on O, respectively, of the contact stress between A and O; and let R_1 and R_1' be the corresponding forces for B and O respectively. Since there are no external forces acting on the system of A, B, and O, it follows from the law of the conservation of the motion of the centre of mass* (assumption No. 2, which we may call the generalized first law of motion), that the centre of mass of A, B, and O will move uniformly. If A, B, and O be rigid bodies (this restricts the argument to the case of attracting bodies kept at a constant distance from one another) O's motion will also be uniform. Hence the resultant force on O must, by the first law of motion, which is a particular case of the generalized first law, be zero. But, by the law of the composition of forces, which is a deduction from the second law of motion (assumption No. 3), this resultant force is $R' + R_1'$ †. Hence $R' = -R_1'$. Now, by the third law of motion regarded as applicable to contact stresses (assumption No. 4) we have $R = -R'$ and $R_1 = -R_1'$. Hence $R = -R_1$. But the motions of A and B must be uniform for the same reason as that of O. Hence by the first and second laws as above, $F + R = 0$ and $F' + R_1 = 0$. Hence also $F = -F'$.—If this is a correct statement of Newton's argument it is obvious that it does not make the deduction which is claimed for it ‡.

obstaculum magis urgebitur pressione corporis A quam pressione corporis B; proindeque non manebit in æquilibrio. Prævalebit pressio fortior, facietque ut systema corporum duorum et obstaculi moveatur in directum in partes versus B, motuque in spatiis liberis semper accelerato abeat in infinitum. Quod est absurdum et legi primæ contrarium. Nam per legem primam debet systema perseverare in statu suo quiescendi vel movendi uniformiter in directum, proindeque corpora æqualiter urgebunt obstaculum, et idcirco æqualiter trahentur in invicem.”—*Principia*: Scholium to Axiomata.

* Newton had previously (Cor. 4 to Axiomata) proved this law, assuming, in the proof, the third law as applicable to all stresses.

† I assume, as Newton does, for simplicity, that the forces are all in one straight line.

‡ See Lange, *Bewegungsbegriff*, p. 57.

Maxwell's version of Newton's argument*, which he regards as "a deduction of the third law of motion from the first," may, as I showed in my Address (p. 12), be attacked on two grounds. First, it assumes that the attraction between the mountain and the remainder of the earth is the only stress between them, ignoring the stress at their surface of contact, an inequality in the action and reaction of which might obviously neutralize the "residual force" due to the assumed inequality in the action and reaction of the attraction. Secondly, the conclusion, thus illogically obtained, is not the third law of motion. For the former asserts the equality and opposition of the action and reaction of the stress between two parts of a body, to which body, *as a whole*, the first law has been assumed to apply, while the latter makes the same assertion for two bodies, *to each of which* the first law is applicable. That this criticism is sound becomes especially apparent, if we reflect that when dealing with rotation and strain we must regard the laws of motion as applicable to particles or elements, the first and second laws being held to apply to each particle, and the third law to the stresses between pairs of particles. Maxwell's deduced law would apply only to the actions and reactions of the stresses between the parts of single particles which, as Prof. Lodge says (p. 11), are "not worth troubling about." It would tell us nothing about the stresses between pairs of particles, and would thus be of no use in the solution of dynamical problems.

Prof. Lodge's version of Newton's argument :—"Jam the bodies apart with a rigid obstacle, then you have reduced their action to contact action" &c., (p. 10), is so condensed that it is hard to analyse. But it is easy to see that its first statement is incorrect. For when we "jam the bodies apart" we do not reduce their action to contact action. The attraction continues. We have simply introduced, in addition, two contact stresses. The premisses, therefore, being thus faulty, the conclusion cannot be warranted.

Prof. Lodge appears to have abandoned the deduction of the third law from the first in its usual form. "Whether," he says, "it is deducible from the first law or not may be

* "If the attraction of any part of the earth, say, a mountain, upon the remainder of the earth, were greater or less than that of the remainder of the earth upon the mountain, there would be a residual force acting upon the system of the earth and the mountain as a whole, which would cause it to move off with an ever-increasing velocity through infinite space. This is contrary to the first law of motion, which asserts that a body does not change its state of motion unless acted upon by external force" ('Matter and Motion', Arts. lvii. and lviii.).

held to depend on how general the terms are in which that law has been stated. If it can be axiomatically asserted that the *centre of mass of a rigid system* moves uniformly until an external force acts on the system, and also that the system does not begin to spin, then the third law is established. For since zero acceleration means zero force, it follows that all the internal forces add up to zero, and have no moment; and since the system can be dissected bit by bit without ceasing to be a system within the scope of the first law, it follows that no stress can contain an unbalanced force or couple." Here, then, we have a new deduction, on which I would make two remarks:—(1) The conclusion is obviously too general. For since the assumptions specified are made for a rigid system only, the "no stress" of the conclusion should clearly be—no stress between the parts of a rigid system. The conclusion would thus become only a particular case of the third law. (2) That even this modified conclusion cannot be obtained without additional assumptions, and, even with them, by the method of dissection, may readily be shown. "All the internal forces add up to zero and have no moment." How do we know this? Only by the aid of familiar deductions from the second law of motion. Thus the second law is assumed. Dissect away one particle from the system. By the second law, as above, the internal forces of the remaining particles now add up to zero and have no moment. But we cannot assert this to have been true before the removal of the particle, unless we assume the physical independence of stresses. If this second additional assumption be made, though we now know that the actions and reactions of the stresses between any one particle and the remaining particles add up to zero and have no moment, we cannot conclude that "no stress can contain an unbalanced force or couple," because they would add up to zero and would have no moment, also, provided any inequality in the action and reaction of one stress, and their resultant moment, were neutralized by inequalities in the actions and reactions of other stresses and by their resultant moment, respectively.

While Prof. Lodge's method of dissection will not give even the modified conclusion, even with the aid of the above additional axioms, the reverse process will give it without his assumption as to spin. For in a system of two particles the conservation of motion of the centre of mass and the second law together tell us that the action and reaction of the single stress in the system are equal and opposite. And in a system of any number of particles, the axiom of the physical independence of stresses tells us that the stress between any two particles is the same as if there were no

others acting, and that, therefore, in the case of all the stresses action and reaction are equal and opposite.

It is at once obvious that this argument will hold also, whether we restrict ourselves to rigid systems or not. Prof. Lodge does so, probably because he feels he cannot appeal to the experience of the human race with regard to the motion of the centre of mass of a non-rigid system. Had he adopted as his axiom the generalized first law (which he would be justified in doing according to my conception of an axiom as a proposition by means of which it is found possible to co-ordinate dynamical phenomena generally), then, with the aid of the second law and the physical independence of stresses, he might have deduced the equality and opposition of the action and reaction of all stresses *. But even then he would have deduced only what is explicitly stated in the third law and not the whole law. For just as the second law, by the generality of its assertion, implies the "physical independence of forces," so the third law implies the physical independence of stresses, at least so far as the equality and opposition of their action and reaction are concerned. This implied part of the third law is assumed in the above deduction.

So much for the asserted possibility of deducing the third law from the first. Prof. Lodge has held also that it may be deduced from the second †. Divested of its "muscles and clothing," his argument is as follows:—Action may be taken to mean simply the whole force applied to the body considered. The reaction of a body is defined as equal to the product of its mass into its acceleration. The second law of motion may be expressed in an equation on the one side of which we have the resultant force on a body or the action, on the other side of which we have its mass multiplied by its acceleration, which we have agreed to call its reaction. Thus action is equal to reaction. After a few paragraphs of explanatory matter he changes the expression of this result, without any attempt at justification, to the following:—The reaction or mass acceleration of a body is equal and opposite to the resultant of all the forces acting on it. It is hardly necessary to discuss this argument. It will be sufficiently obvious that if the definitions of action and reaction be accepted, reaction, if assumed to have direction, must be co-directional with action, not opposite to it, and that there-

* Streintz (*loc. cit.* p. 131) and Muirhead (*loc. cit.* p. 477) point out the possibility of deducing the third law from the generalized first law, but do not perceive the necessity of assuming the physical independence of stresses.

† 'The Engineer,' vol. lix. (1885), pp. 217, 311, 380.

fore the conclusion which ought to be drawn is not even expressed in the same words as the third law. It is also just as obvious that even if the conclusion drawn had been warranted, though expressed in the same words as the third law it would not have been the same law, because the term reaction would be used in entirely different senses in the two laws.

That the above efforts to deduce the third law from the first or second should thus prove futile need not surprise us. For the second law gives us a quantitative statement as to the effect which is produced in a particle by a force; while the third tells us that forces always occur as one-sided aspects of stresses, and gives us the relation between the two forces of which every stress consists. Had these laws been recognized as being thus complementary to one another, efforts to deduce either from the other would have been seen beforehand to be doomed to failure*, and the above dreary refutations would not have been called for.

(4) *Prof. Lodge's Deduction of his Law of Conservation.*

Though Prof. Lodge still holds (pp. 11 & 14) that the conservation of energy (as defined by him) "can be deduced from Newton's third law and from the denial of action at a distance," and indeed gives a new version of this deduction, he admits that his deduction applies only to conservation during transfer, and that conservation during residence or "storage" is incapable of deduction†. How he reconciles

* This seems, at first sight, not to agree with what Mach says (*Mechanik*, p. 226) after having referred to the subject matter of Newton's first and second laws, viz.:—"The third law contains apparently something new. We have already seen, however, that without the correct conception of mass it is unintelligible, and that on the other hand, through the conception of mass, which itself can be obtained only through dynamical experiences, it is rendered unnecessary." As, according to the ordinary interpretation, the idea of mass is given in terms of force by the second law, Mach would seem to hold that the third law is not independent of the second. This is not the case, however. Mach had previously shown that if we interpret Newton's second law by the aid of his definitions, this law does not give us a clear conception of mass. He himself obtains the conception, without reference to force, by an appeal to experience, which takes the place of the appeal made in the third law and thus renders it unnecessary.

† After dismissing, with some hesitation, the "plausible" method of establishing a law of nature by appeal to definition, he suggests that conservation during storage should be adopted as an axiom; but he does not meet the argument given in my Address to show, that if we retain Newton's laws, it is illogical to employ the law of conservation as an axiom, and that if we adopt the latter law as an axiom, Tait's suggestion (*Ency. Brit.*, Art. Mechanics, § 299) is the only logical one, viz., that Newton's laws should be abandoned and the law of transference of energy adopted instead.

the reiteration of his old claim with this admission we are not told.

With regard to my criticism of his earliest mode of making this deduction, he replies that the appeal to experience which I pointed out as having been made in his argument was a mere piece of politeness, which might have been omitted without affecting the argument. I think if he will look into the matter he will find that if he had been less polite his reasoning would have been faulty. It is unnecessary to occupy space in proving this, however, because the new deduction, given in the present paper and referred to below, embodies exactly the same fallacy as the old one.

In reply to my criticism of the law of conservation deduced by the argument of his third paper (quite a different law as I pointed out from that obtained in the earlier paper, though Prof. Lodge does not seem to realize this), viz., that it was of the same nature as the law of the conservation of momentum, his energy as defined in that paper being constant in quantity, because equal quantities of positive and negative energy must always be produced together, he states that his law is deduced from a less obvious assumption than the conservation of momentum. This is possibly true; but it does not affect the nature of the law deduced. The law of the conservation of electrical quantity is obtained in a different way from either, but is nevertheless a law of the same kind.

The new version of the deduction of the conservation of energy from the third law and the assumption of contact-action, is based upon a new definition of energy as "the result of work done," or "the result of activity lasting a finite time." As this is rather vague, work done on a body having a variety of results, Prof. Lodge proceeds to expound his definition and tells us that energy "is a name for the line-integral of a force, considered as a quantity that can be stored"*. Here, again, is the appeal to experience,—that the line-integral of force *may* be considered as a quantity which can be stored. If it is introduced merely out of politeness, it must not be used in the argument. If used in the argument, it forms an unacknowledged assumption.

The argument is as follows :—"Bodies can only act on one another while in contact, hence if they move they must move over the same distance; but their action consists of a pair of equal opposite forces; therefore the works they do, or their activities, are equal and opposite; therefore, by defi-

* His comments show that he should have added here the words "in a body." But this does not affect the present argument.

dition, whatever energy the one loses the other gains. In other words : in all cases of activity, energy is simply transferred from one body to another, without alteration in quantity." Now it is obvious that we cannot pass *by definition* from work done or activity to energy, for energy has been defined as the *result* of work done or activity, the line-integral of a force considered as a quantity which can be stored. We must first pass from the equality and opposition of the works done (or line-integrals of the forces) to the equality and opposition of the *results* of the works done (or of the line-integrals of the forces *considered as quantities which can be stored*). How is this passage made? We are not told. But it is obviously by the assumption that work done on a body is equal to the result of work done, or that the line-integral of a force *may be considered* as a quantity which can be stored. And as obviously, this assumption is the law of the conservation of energy. Thus the conclusion of the argument, which, as in former deductions, is clearly conservation during transference only, is obtained by assuming the law of conservation generally.

It would indeed be a remarkable thing if it were possible, in the case of systems whose parts act upon one another only when in contact or at constant distance, to deduce the conservation of energy during transference from the third law of motion alone. When we make no assumption as to the distance at which action may occur, we require, in order to obtain the law of transference, to obtain first the general law of conservation, for which purpose we have to assume the second law of motion, and some such axiom as the impossibility of the perpetual motion. Having obtained from these axioms the general law of conservation, the third law then gives us the law of transference. Why, then, when we restrict our attention to systems exhibiting constant distance action * only, should it be possible to deduce the law of transference independently of the law of conservation? This is a logical question to which it should be possible to give a clear answer, if it is possible to make the deduction referred to.

(5) *Prof. Lodge's Deduction of Contact-action.*

In former papers † Prof. Lodge claimed to prove the

* Prof. Lodge's argument assumes constant distance action, not specifically contact-action; for "if they move they must move over the same distance" is true of actions at all constant distances, not merely of actions at distance zero.

† Phil. Mag. [5] viii. p. 279, xi. p. 36.

incompatibility of action at a distance (1) with the law of the conservation of energy and the third law of motion, and (2) with the former law alone, and to be able to prove its incompatibility with the third law alone. In my paper (p. 139) I showed that the incompatibility with *the* law of conservation and the third law had not been proved, and that the incompatibility with *his* law and the third law was a necessary consequence of his definitions. I showed also that the argument by which he had sought to prove the incompatibility with *the* law of conservation alone (expressed in the form of the impossibility of the perpetual motion) was not sound. I also called attention to the fact that no attempt to substantiate the third of the above claims, a very important one, had been made. In the present paper he makes no reference to all this, but he makes a dogmatic statement which appears at first sight to be a reiteration of the second claim mentioned above, viz., "Energy is only really conserved under conditions of universal contact-action" (p. 16). Prof. Lodge is obviously under the impression that in making this statement he is taking up a position which is opposed to that of all his "prehistoric" dynamical brethren. In reality, however, any one who holds to the ordinary law of conservation and is able to regard action at constant distance as "practically" contact-action, must admit it; for, subject to the last proviso, it is an obvious deduction from the ordinary law. We may express that law as follows:—In any isolated system of bodies, the sum of their kinetic working-power, the working-power they may possess because of their being individually in a state of strain, and the working-power of the system due to actions between the bodies at variable distance, must be constant. Now the first two kinds of working-power constitute what Prof. Lodge calls energy, and the third must vary with the configuration of the system. Hence Prof. Lodge's energy can be conserved only subject to the condition of action at constant distance. If, therefore, action at constant distance be admitted to be "practically" contact-action, Prof. Lodge's statement is seen to be an immediate deduction from, and therefore merely a particular case of, the ordinary law of conservation.

- (6) *Relative generality and precision of Prof. Lodge's Law of Conservation and the ordinary law; localization of Potential Energy; "Identity" of Energy.*

Prof. Lodge makes no reference to the argument by which I sought to prove that his law of the conservation of energy

is merely a particular case of the ordinary law (p. 137 of my paper.)

In reference to his statement that his law is as axiomatic as the ordinary law, I showed that the latter is the more general in its applicability to dynamical problems. Prof. Lodge declares himself to be in entire agreement with this : but he adds that it is no discredit to "the true law not to lend itself to fictions," and that, while it is often permissible to work in a fictitious or incomplete manner, ignoring communicating mechanism, such "omissions and slurrings" should not be made in laying foundations, and that the habit of thus ignoring unknown essentials may lead to the treatment of fictions as if they were realities. There seems to me to be confusion here between the fictitious and the general*. There is nothing fictitious in the ordinary law of the conservation of energy. Work being said to be done by a body when the body moves (relatively, of course, to a dynamical reference system) against an opposing force, and energy being defined as power of doing work †, the ordinary law asserts that energy is conserved. It is sometimes expressed in terms of the fiction of action at a distance and sometimes also in terms

* It is this confusion, I think, which has led Prof. Lodge, in his comparison of our respective types of mind, to make the entirely erroneous statement that I am willing "to base Physics on action at a distance" (p. 2, footnote). To it is due also the statement of p. 16 in which the ordinary conception of potential energy is ascribed to "the believer in action at a distance."

† Prof. Lodge's extraordinary objections to this definition are easily met.—(1) It is "vague." Doubtless it is to one who can make the statements quoted below. Compare its precision with that of the definitions by which it is to be replaced:—"effect of work done;" "result of work done;" "line-integral of a force considered as a quantity which can be stored." The formal definition of his '*Mechanics*':—"Energy is that part of the effect produced when work is done upon matter, which is not an accidental concomitant, but really owes its origin to the work, and could not, so far as we know, have been produced without it; and which, moreover, confers upon the body possessing it an increased power of doing work,"—would seem to imply that he rightly considers his own definition so vague as to require to be supplemented by the ordinary definition. (2) "Plenty of energy has no power of doing work, at least, no power that we can get hold of." Nor can it have according to the definition. Probably what is meant is that plenty of bodies possess energy which we cannot utilize; but our ability to get hold of power is no criterion of its existence. (3) "A given amount of energy may have an infinite working-power, since it can do work at every transfer without itself diminishing." As just stated, according to the definition, energy cannot be said to have any working-power at all. It is the body or system of bodies possessing the energy which has the power. (4) "It is bold to maintain the conservation of working-power in face of the doctrine of the dissipation of energy." The conservation of power of any kind is quite consistent with diminishing opportunity of exercising it.

of the fiction* of contact-action. But it may be expressed without any reference to such fictions. Moreover, it may be deduced from the second law of motion and the impossibility of the perpetual motion, neither of which axioms involves such fictions. It is thus quite general, involving no assumption as to the distance at which bodies can act on one another, and applying to all cases of action, whether at distance zero, at constant distance, or at variable distance.

It will thus be evident why "the true law" does not lend itself to fictions, and why the ordinary law does. "The true law" does not, because it already embodies a fiction. The ordinary law does, because it embodies none, and is equally applicable, whatever fiction we may find it convenient in the meantime to assume or may ultimately find apparently coincident with fact. It is no discredit to "the true law" not to lend itself to fictions, provided the fiction it embodies assists us in coordinating the whole range of dynamical phenomena†. But discredit must attach to it so long as there are groups of phenomena to which the ordinary law can, while "the true law" cannot, be applied.

It will also be evident that, since the ordinary law involves no fictions, there need be no fear lest the employment of it should lead to the confounding of fictions with realities.

Not only does the ordinary law make no assumption as to the distance at which action may occur, it also assumes nothing as to the mechanism of action, and holds whether bodies be regarded as acting on one another through a medium or not, and if they are, whatever the medium may be through which their action is supposed to be conveyed. To speak of the law as on this account incomplete seems to me to be incorrect. Until we find some hypothesis as to acting mechanism which will enable us to coordinate dynamical phenomena, the science of dynamics must of course be incomplete; and doubtless as soon as possible some such hypothesis should be framed. But no such axiom has yet been suggested which is capable of general application. We cannot therefore help ourselves. The foundations of dynamics must in the meantime remain incomplete, though they are none the less firm on that account. Even, however, when the time of omissions and slurrings shall have passed, the law of the conservation of energy will be no more com-

* As Prof. Rücker has pointed out in 'Nature,' vol. xlviii. p. 126, contact-action is as inconceivable as action at a distance. Both are thus equally fictions.

† Prof. Lodge holds, somewhat inconsistently, that "in a fundamental or theoretical treatment convenient fictions are better avoided" (p. 17).

plete than it is now. We may have acquired more definite conceptions as to the character of certain forms of energy, as to the mode of transference of energy, and as to the place of residence of potential energy ; but as the law of conservation makes no statement on such points which will thereby be completed, our present ignorance with regard to them does not render it incomplete.

While in the event of some hypothesis as to acting mechanism becoming axiomatic there would be some re-adjustment in the ordinary conception of potential energy, there would not be nearly so much as Prof. Lodge supposes; for though his account of this conception (p. 16) is obviously a burlesque, he clearly does believe that it involves an "erroneous localization of energy," that, *e. g.*, in the case of a raised stone, the potential energy must be supposed, nearly all at any rate, to be resident in the stone *. This impression, however, may readily be shown to be erroneous. The potential energy (see the definitions of work done and energy, given above) may be said to belong to the system of earth and stone, because work may be done by the earth or by the stone or by both during the approach of these bodies. That it cannot be said to belong to either, is obvious from the consideration that, if either be held fixed relatively to a dynamical reference system, the work done during approach is then done by the other. How much of the work done during approach is done by the one and how much by the other, when both are in motion, depends upon the forces against which they move and their respective displacements relative to such system. It is thus obvious that according to the ordinary conception we can assert no more than that the potential energy belongs to the system, that this conception therefore involves no localization of the energy in the system, and consequently no erroneous localization.

This of course arises from the fact that the ordinary conception of potential energy involves no assumption as to acting mechanism. Should some sufficiently definite hypothesis of this kind become axiomatic, it would then become possible to localize potential energy. If, *e. g.*, we should come to hold that bodies consist of rigid particles connected by, and acting on one another through, an elastic medium, it

* He objects to the ordinary conception of potential energy as being "a mere receptacle for stowing away any portion of energy which it is not convenient for the moment to attend to," yet admits (p. 24) that his own potential energy belongs to the same "temporary order of ideas." He also defies "any one to realize it as a thing." If he will define "thing" we may perhaps try.

would then be obvious that the potential energy must be considered to be resident in the medium. But until some such hypothesis becomes axiomatic, no localization of potential energy is possible.

It should be noted here that the adoption of the hypothesis of contact-action alone does not enable us to localize potential energy. As an axiom of acting mechanism it is incomplete; and it involves only the residence of energy in some body or other *. If we are to know in what body the energy resides, the axiom of acting mechanism must be made sufficiently complete. Thus, as just stated, if we assume, in addition to mere contact-action, that material bodies consist of rigid particles, and that the medium is elastic, the potential energy in the case of the raised stone must be considered to be resident in the medium. If, however, we assume bodies to consist of elastic particles, then the potential energy must be regarded as possibly resident partly in the medium and partly in the particles of the earth and stone. Prof. Lodge does not seem to realize this; for though he has proposed no hypothesis as to acting mechanism beyond that of contact-action, he has no hesitation in saying dogmatically (for he makes no attempt to justify the assertion) that in the case of the raised stone and in similar cases † the potential energy resides in the medium ‡.

Prof. Lodge claims that the law of the conservation of contact-action energy is more precise and definite than the ordinary law "because it is the law not only of *conservation*, but of *identity*." As to what is meant by its being a law of identity, he gives us two statements, of which we may consider the later first. "My proposition," he says, in his

* I use the word body here in Prof. Lodge's general sense as applicable to a portion of the medium as well as to a material body. When, according to the contact-action conception, potential energy is regarded as resident in a body, the body must be considered to be an elastic body in a state of strain (p. 20). Since it is thus considered to consist of parts capable of relative motion, it is a system of relatively movable parts. Thus, according to Dr. Lodge's conception, potential energy is resident in systems just as truly as it is according to the ordinary conception, only the systems in the one case are small, while in the other they may be large. See Mr. E. T. Dixon's letter to 'Nature,' vol. xlviii. p. 102, and Dr. Lodge's reply, p. 126.

† Prof. Lodge is not so precise in his localization in all cases. In the case of the bent bow, even the ordinary conception of potential energy would admit of our localizing it "in the bow," and in the case of the gunpowder that conception would give us a more definite localization than "in the powder."

‡ Probably my meaning in the statement quoted by Prof. Lodge on p. 16, footnote, will now be clear.

latest paper (p. 30), "amounts to just this, that whatever energy appears in a bounded region must necessarily have passed through the boundary." It is quite obvious that the assumption of contact-action together with the law of the conservation of energy do justify this proposition. It is equally obvious that, with the ordinary conception of energy, this proposition cannot be asserted. It may hold, but we cannot assert that it does. Why this difference? Not because the law of conservation is more precise or definite in the one case than in the other, but because we have a more complete conception of transference. With the ordinary conception of energy the only source of knowledge of transference is the third law of motion. With the other conception, we have both the third law and the axiom of contact-action*; and it is because of the greater definiteness which this latter axiom gives to our conception of transference, that it enables us to assert that if energy appears within a bounded region, it must have been either conveyed or transferred across the boundary†.

The above proposition seems to Prof. Lodge "to confer upon energy the same kind of identity or continuous existence (or, if you please, objectivity) as matter possesses." What kind of identity or continuous existence matter is supposed to possess (we need not refer to anything so metaphysical as objectivity) may be gathered from the earlier of the two statements referred to above, viz. :—"On the new plan we may label a bit of energy and trace its motion and change of form, just as we may ticket a piece of matter so as to identify it in other places under other conditions; and the route of the energy may be discussed with the same certainty that its existence was continuous as would be felt in discussing the

* It should be noted that according to these two conceptions the third law, though expressed in the same words, is not the same law. In the one case it applies to all material bodies, whether in contact or at a distance. In the other it applies to all bodies in contact, whether they are material bodies or elements of the medium.

† It should be noted, however, that the law of conservation during transference which, notwithstanding the reiteration of his old claim, is all that Prof. Lodge now considers himself to have deduced, does not of itself, as he seems to suppose, justify the assertion of the above proposition. For it is consistent with this law that energy may, as he says, "leak away in some silent unobtrusive fashion." If it may thus leak out of observation, it may also leak into observation. Since, then, some of the energy which appears within a bounded region may have got there by this process of unobtrusive leakage, and since the above law can tell us nothing as to how it got there, this law cannot of itself justify the above proposition. It cannot therefore even in this first sense be called a law of identity.

route of some lost luggage which has turned up at a distant station in however battered and transformed a condition" *.

I need not discuss here the question whether even matter can be said to have the kind of identity here specified, whether in fact we can label a bit of it and follow it in its wanderings. We certainly cannot, in general, do so practically. Whether or not we can do so ideally may, I think, be found to depend upon our hypothesis as to the constitution of material bodies.

That energy, however, has this kind of identity seems to me to be a much more definite proposition than the one considered above, and not by any means to be implied in it. Indeed, that the contact-action conception of energy does not confer upon it the capability of being thus followed in its motion may, I think, be proved. We cannot be said to be able to follow a "bit" of energy in its wanderings unless we are able at all stages to localize it. If in the course of its peregrinations it enter a system of bodies and get so hidden away that we can only say of it that it is in some body or other of the system or is distributed in unknown proportions among them, then we have lost it even more completely than we should have lost our luggage in a railway collision if we knew only that it was distributed somewhere among the *débris*. Now we have seen that the assumption of contact-action alone does not enable us to localize potential energy. While, therefore, the introduction of the axiom of contact-action confers upon energy a certain kind of continuity, telling us that it must pass from one body to another or to others, it does not enable us to follow a bit of energy and to trace its route, because it does not in all cases enable us to localize it. If we wish to be able to trace its route completely, we must introduce a further axiom which, with contact-action and the third law, will make our conception of the transference of energy sufficiently complete. Then we shall be able to localize energy under all circumstances, and the first condition of following its motion will be satisfied.

But more than mere localization is necessary in order to label and follow a "bit" of energy. We must also be able to distinguish it from other bits when several of them at the same time get into the same body; and here the chief difficulty seems to arise. It is easy enough to frame an hypothesis of acting mechanism which will localize energy in all cases, provided we do not mind much whether or not it coordinates for us dynamical phenomena generally; but how we are to distinguish between the portions of energy which are transferred simultaneously, say, to a particle by the various elements of the medium in contact with it, is not so apparent. To my

* Phil. Mag. [5] vol. xix. p. 482.

mind they must get mixed. Yet, before we can be said to follow a bit of energy as we do a labelled portmanteau, we must either have some means of making this distinction, or we must frame our hypothesis of acting mechanism in such a way as to exclude the possibility of two bits of energy getting into the same body at the same time.

Prof. Lodge refers to Prof. Poynting's paper on the "Transfer of Energy in the Electromagnetic Field" * as an illustration of the power which the contact-action hypothesis gives us of labelling and following bits of energy. Prof. Poynting's results, however, were based not only on the assumption of contact-action, but on other hypotheses as well, which made his axiom of acting mechanism, if not complete, at any rate much more complete than contact-action alone would have made it; and, moreover, if I understand him aright, he did not profess to label and follow the bits of energy distributed in the fields which he investigated.

(7) *The complete Transformation of Energy during Transference.*

In the present paper Prof. Lodge gives a formal demonstration, and a discussion of illustrative instances, of his proposition that, according to the contact-action conception, "energy cannot be transferred without being transformed" †. I need not enter into a detailed criticism of the demonstration. It is sufficient for my purpose to draw attention to two points:— (1) The demonstration itself admits the possibility that a body may act as "a mere transmitter, not itself active, only passing on what it receives," and applies to bodies not acting in this way. But a body cannot pass on the energy it receives without the energy being first transferred to it and subsequently transferred by it. The demonstration, therefore, admits that energy may in certain circumstances be transferred without being transformed, excludes such cases from consideration, and restricts itself to other cases ‡. (2) The demonstration is entirely qualitative. It is shown that in these other cases of action between two bodies, if one body lose, or gain, kinetic

* Phil. Trans. 1884, pt. ii. p. 343.

† Phil. Mag. [5] vol. xix. p. 486. The formal statement of the proposition in the present paper is much less precise than in the paper just cited. He says, "My proposition was that the change of form is always from kinetic to potential or *vice versa*," though he certainly would not have set himself to prove anything so obvious. The context, quoted below, shows that it is the complete transformation of energy during transference that the demonstration is held to prove.

‡ It should be noted, however, that on p. 33 Prof. Lodge speaks of the treatment of potential energy as being "conveyed elsewhere as a simple flux without transfer or transformation," as "blindfold treatment" which "does not exhaust the matter."

energy, or potential energy, the other body will gain, or lose, potential, or kinetic, respectively, *i. e.*, that in these cases there will be some transformation. In order to prove complete transformation, it would be necessary to show that the potential or kinetic energy lost or gained by the one body was equal to the kinetic or potential gained or lost respectively by the other. Thus even if we admit the validity of the argument without criticism, all that it proves is that, except in certain specified cases in which transference occurs without transformation, transference always involves some transformation, which is equivalent to the affirmative part of my conclusion that "transference of energy will in general involve partial but not complete transformation."

Besides this demonstration Prof. Lodge gives a discussion of two examples. The first, the loaded air-gun with its muzzle plugged, is an example of the transformation of potential energy during transference; the second, the impact of a couple of equal elastic rods moving end-on, exemplifies the transformation of kinetic energy.

With regard to the former, Prof. Lodge says:—"The compressed air has potential energy; on its release its energy is transferred to the moving wad, which instantaneously hands it on to the air near the muzzle, compressing it, and thus retransforming itself into the potential form." This seems to me a very inadequate account of what occurs. It assumes the wad to be a rigid body. As it is not, however, the first effect of the expansion of the compressed air must be to compress the adjacent end of the wad. But compression involves the relative motion of its parts. Hence during the first small expansion of the compressed air the wad must simultaneously gain both potential and kinetic energy; and therefore the potential energy lost by the compressed air has not been completely transformed in transference. If the wad be "dematerialized" and the example treated from the point of view of the kinetic theory of gases, the energy of the compressed air is practically wholly kinetic; and if, as Prof. Lodge says, the collision of two particles is most conveniently thought of in terms of elasticity, the question which has to be settled is what transformation occurs during the collision of two elastic particles. Treated in this way, the example thus resolves itself into the second example*—the impact of two elastic rods.

* I need not make further reference to Dr. Lodge's discussion of this example from the point of view of the kinetic theory of gases, partly for the reason mentioned and partly because a portion of it is said to be "true in one sense, but not a final or complete statement."

I need not enter into a criticism of the discussion of this example, the conclusion being quite sufficient for my purpose. "By the consideration of instances," Prof. Lodge says, "we have thus been led to the induction that energy can be transmitted without obvious change of form by substances with infinite properties, *e. g.* by an incompressible solid; all molecular processes being either non-existent or being ignored; but that with ordinary matter there is always some percentage of obvious transformation, though we may apparently have all grades of it from complete to very small." This is of course partial, but not complete transformation. "Thinking of these impact cases alone, it might appear as if I had been overhasty in saying that the whole of energy must be transformed when it is transferred*. Yet observe that it has to pass *through* the intermediate condition. A row of ivory balls in contact has another thrown against one end, and from the other end one leaps off. The energy has been transmitted through the row somewhat as it is transmitted through the compressed strata of two impinging rods. Yet if the elastic connexions of every stratum are attended to, and if these be regarded as massless, I think it will be found that all the transmitted kinetic has really passed through a momentary existence as potential." Thus, in order to uphold the complete transformation of kinetic energy during transference, it is found necessary to assume the rods to consist of strata alternately massive and massless. Similarly, in order to make good the complete transformation of potential energy it would be necessary (as in the former example) to assume the rods to consist of strata alternately rigid and elastic. "The fact of necessary transformation," he continues, "is not so obvious when you come to look into some of these special cases; but I would refer once more to the proof given at the beginning of Part IV., which seems to me conclusive as to essential fact." Prof. Lodge therefore finds it difficult to make the accuracy of his thesis obvious in such examples, and falls back upon the general demonstration, which, as shown above, even if it be admitted without criticism, proves only partial transformation. "The difficulty arises because when an elastic body is struck (say a massive molecule with a massless spiral spring connexion) it begins to move a little directly the spring is the least compressed, and is moving half speed when the spring is fully compressed." In my paper (p. 140) I pointed out this "difficulty" as standing in the way of the doctrine

* See footnote † to p. 259.

of complete transformation, in the following words :—" If one body exert on another a certain force through a certain distance, the same work is done on it whether the former body lose kinetic or potential energy in doing the work ; while the effect produced in the latter body will in general be a change both in its motion and its state of strain, *i.e.*, both in its kinetic and its potential energy. Thus, whether the former lose kinetic or potential energy, the latter will in general gain both, or transference of energy will, in general, involve partial but not complete transformation." Prof. Lodge thinks, however, the difficulty may be met. For he observes in conclusion :—" But I venture to say that on any view of the identity of energy the bit of kinetic which it first attains is a bit of energy that has been transmitted through the elastic stress of the spring, and that just as the second half of the energy must admittedly exist in the spring before it can reach the mass, so the first half has already passed through the spring and has reached the mass only after transmutation, although the transformation is disguised while the transference is obvious." The difficulty therefore is overcome only by assuming bodies to consist of massive molecules connected by a massless but elastic medium. Compare with this the following from my paper (p. 141) :—" If we assume the particles [of bodies] to be rigid they can of course have kinetic energy only. If the medium be assumed to have no inertia, its elements can have potential energy only. Hence if both assumptions be made, transference of energy between the particles and the medium must involve complete transformation, while transference from element to element of the medium must occur without transformation. If, however, both the particles and the medium be assumed to have both inertia and elasticity, the transference of energy will, in general, involve only partial transformation, whether it occur between the elements of the medium or between the particles and the medium."

It will thus be obvious that the necessity, which Prof. Lodge here acknowledges, of making definite assumptions as to acting mechanism, when he endeavours to follow his contact-action energy and to make its transformations agree with those prescribed by his thesis, is in entire agreement with what I have pointed out above, *viz.*, that the assumption of contact-action alone is not sufficient for the purpose of completely localizing energy. Without being conscious of the fact, he assumes, not only contact-action, but also that bodies consist of massive and rigid particles, and that the medium through

which they act on one another is massless and elastic*. But even with this axiom of acting mechanism his thesis as to complete transformation during transference holds only for transferences between particles and elements of the medium, and not for transferences from element to element of the medium.

(8) *The Complete Transference of Energy during Transformation.*

Besides the proposition just considered, Prof. Lodge, in the paper referred to above, asserted also that "energy cannot be transformed without being transferred." Although I called this proposition in question also, no reference is made to it in the present paper beyond a reiteration of the assertion (p. 16). In a synopsis of the paper, however, published by Prof. Lodge himself†, the admission is made that the assertion is incapable of proof. For we find it laid down, as the fifth axiom of dynamics, that "energy which is not being actively transferred from one body to another remains unaltered in quantity and form."

Prof. Lodge's right to enunciate this proposition as an axiom may be judged by his own standard. According to him (p. 3 of his paper), in setting forth an axiom, (1) regard must be had to the experience of the human race, (2) hundreds of instances should be adduced in which it holds, (3) a few special cases should be critically examined and in no case found to fail, and (4) "contrary instances" should be called for. Most of these regulations, which are obviously intended to prevent people from carelessly and thoughtlessly enunciating axioms, are admirable. With the exception, perhaps, of the appeal to the experience of the race, such formulators of axioms as Galilei, Newton, and D'Alembert followed them, especially as to the critical examination of special cases. But Prof. Lodge, in the present instance, ignores them all. He does not show how the proposition in question appeals to the race; he gives no instances in which it holds; he examines no special cases critically; and he makes no reference to a contrary instance which I ventured to bring forward in my paper (p. 141). We are forced, therefore, to conclude that according to his own regulations he is not yet in a position to enunciate this proposition as an axiom.

* On p. 21 he speaks of "the potential energy of the particles of a spring," thus assuming its particles to be elastic, but this occurs in a paragraph which is "true in one sense but not a final or complete statement."

† 'Nature,' vol. xlviii. p. 62.

But there is another ground on which this course is seen to be for him entirely illogical. For though his having taken it is an admission that he regards the proposition in question as incapable of deduction, he has been hasty in reaching this conclusion. We have seen that, in order to maintain complete transformation during tranference, he has confessedly to assume that bodies consist of massive particles without elasticity, and that the medium is elastic but without inertia. Now, as pointed out in my paper (p. 141):—"That energy cannot be transformed without being transferred must of course be true if bodies consist of particles with inertia but without elasticity, and if the medium connecting them possess elasticity but not inertia." This is surely quite obvious. Hence with the assumptions already made by Prof. Lodge the proposition under consideration is capable of deduction. For him therefore it cannot be an axiom.

For those of us who do not hold to his theory of the constitution of bodies and media, the proposition is of course not capable of deduction. Whether or not we are to regard it as axiomatic must depend on whether or not it may be shown to be capable of coordinating dynamical phenomena generally.

Edinburgh, July 21st, 1893.

XXIV. *A New Form of Influence-Machine.*

By JAMES WIMSHURST*.

IN April 1891 I had the honour to submit to this Meeting a very useful form of experimental Influence-machine, by means of which I was able to show that almost every combination of glass and metal, and also that plain glass disks, when moved and suitably touched, were capable of producing a flow of electricity.

It is one of those combinations, somewhat modified and extended, which I have now the further pleasure of bringing to your notice.

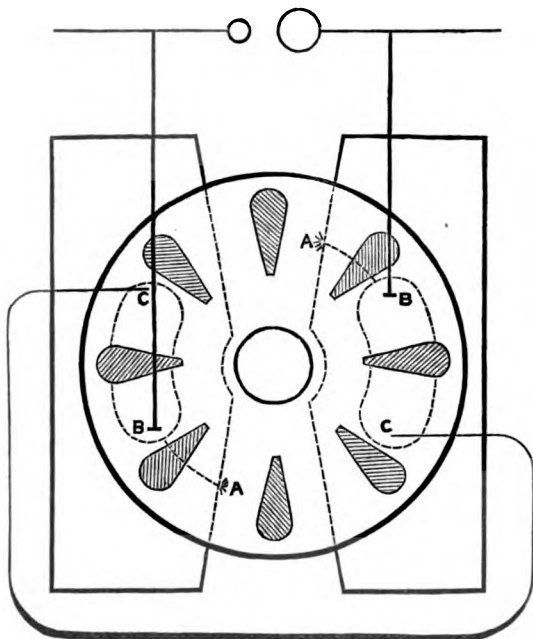
The machine consists of two disks of plate-glass, each of 3 ft. 5 in. diameter and $\frac{1}{4}$ inch thickness, mounted about $\frac{3}{4}$ inch apart on one boss and spindle. This spindle is driven by means of a handle, and the disks rotate in one direction.

In the space between the disks are fitted four vertical slips of glass, two being situated on the right-hand side of the machine and two on the left-hand.

The vertical edges of the slips which come nearest the spindle are cut to an angle, leaving a rather wider opening

* Communicated by the Physical Society: read June 23, 1893.

at the circumference than at the centre of the disk. Upon each slip is a brush, A, and also an inductor, the brush and



A, A. Brushes connected metallically to the inductors.
B, B. Collecting-brushes connected with terminals.
C, C. Brushes connected with the neutralizing circuit.

the inductor being metallically connected ; the brushes are made of fine wire, and touch very lightly on the inner surfaces of the disks. The glass slips slide into place by means of suitable grooves at their top and bottom ends ; they may be removed and replaced readily at pleasure.

The essential parts are fitted together within a glass case, and in all respects the machine is so constructed as to be useful for experimental work. The limited size of the case causes the insulating distances between part and part to be small, hence the length of the sparks is reduced. All the surfaces are coated with shellac, and when the brushes are new and in proper condition the machine is self-exciting.

The charges are not subject to reversal when the terminals are opened beyond the striking distance, for then the whole of the induced charges pass by way of the neutralizing brushes C, C. Another feature is that the neutralizing current may also be broken without reducing the excitement,

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but then the charges alternate from positive to negative with each half revolution of the disks.

An approximate measure of the efficiency of the machine is seen by the following experiments.

The glass throughout was held free from electrical excitement, and the disks were rotated sixty times per minute; the actuating cause was then removed, and the disks came to rest after making forty-seven revolutions. This measures the friction of the machine.

The disks were then similarly turned, but the electrical charges were allowed to collect; it was then found that the disks came to rest after twenty-three revolutions. The friction of the machine, therefore, is about equal to the repulsion of the electrical charges.

Leyden jars having eight square inches of tinfoil in each coating were then connected to the terminals, and the terminals set $3\frac{1}{2}$ in. apart: the disks were turned to the same number of revolutions and then left to come to rest, which they did after producing eighty sparks.

The disks were then turned and the number of sparks counted in relation to each revolution. This gave seven sparks of 1 in. length, five of 2 in., four of 3 in., and three of $4\frac{1}{2}$ in. length.

Eight metal sectors were then added (total 112 square inches on each disk): with them the self-excitement becomes so free that, before any circuit was made, presenting the fingers to the disks caused electrical discharges.

When the circuits are made between the several brushes the disks appear to be seething with electricity, and the charges shoot out for a considerable part of their circumference, but chiefly at the top and the bottom, where they are not covered by the vertical glass slips, for the change of the charges from + to - takes place upon the disks just as they pass the edge of the slip. Improvements in this respect might be made, but the present arrangement has the advantage of giving permanence to the respective charges.

It will be noticed that strips of tinfoil are placed over the receding surfaces of the glass slips. They were intended to afford the means for collecting and carrying to earth any part of the charges from the inductors, but the earth connexion has not been necessary.

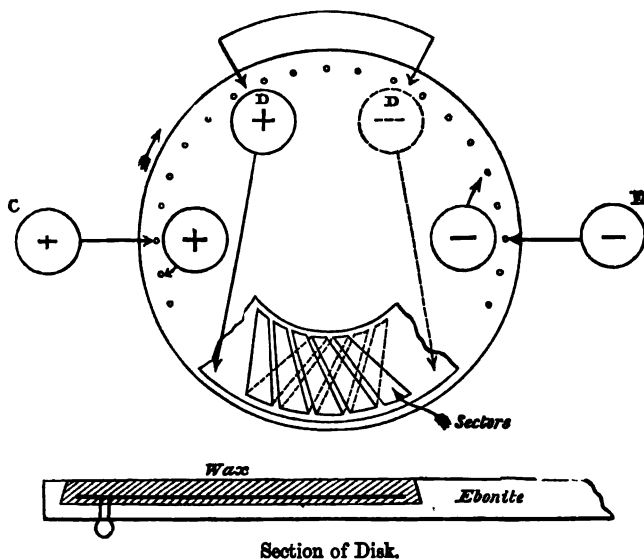
When at work the charges passing from the disks to the brushes may be heard some considerable distance; they resemble the beating of the floats of a paddle-wheel.

The charges are, however, reduced about 25 per cent. by the addition of the sectors.

Further tests have been made by fixing a pulley, 3 in. in diameter, to the overhanging end of the spindle, and suspending therefrom by a cord a weight of 15 lbs. The fall of this weight through three feet produced seventeen revolutions when the disks were not excited and ten revolutions when excited. The same Leyden jars were then connected, and it was found that the fall of the weight through three feet produced twenty-eight sparks of $3\frac{1}{2}$ in. length. Reducing this to the terms of work in relation to sparking length, and omitting friction of the machine, it will be seen that 1 lb. weight falling through rather less than twelve inches produces a spark of $3\frac{1}{2}$ in. length. It must not, however, be forgotten that a considerable amount of electricity is also passing by way of the neutralizing circuit.

XXV. *An Influence Machine.* By W. R. PIDGEON*.

IF we follow the action of any single sector on a disk of one of Mr. Wimshurst's beautiful machines, we find it goes through the following electrical changes:—Suppose it to be just leaving the positive collector C, it comes into a



strong positive field produced by the other disk, and while in this field is earthed by the first neutralizing brush D and

* Communicated by the Physical Society: read June 23, 1893.

becomes charged negatively. Passing on it induces a positive charge on the other disk at the next neutralizing brush D', and ultimately meets a similar negative charge, borne forward by the other disk, at E, where it discharges into the negative collector. I do not mean that this is a full explanation of all that takes place, but I hope by its means to show the lines along which I worked in designing the machine before you. I thought that what had to be done was:—1st, to make the capacity of each sector on the disk as great as possible while being charged at D, and as small as possible while being discharged at E, so that the amount of electricity displaced by each sector should be as large as possible. 2nd. To prevent any leak-back of electricity from sector to sector as they are entering, or leaving, the different fields of induction. 3rd. To make the sectors large and numerous so as to increase the capacity of the machine. And it was with these objects in view that I built the machine which I will now describe. The disks are made of ebonite $\frac{3}{8}$ inch thick and are recessed as shown in the drawing, $\frac{3}{8}$ inch deep \times $5\frac{1}{2}$ inches wide. There are 32 sectors on each disk made of thin sheet-brass, and having short brass wires soldered to them on to which the small brass collecting-knobs are screwed. The sectors were arranged in the recess as shown on the drawing, the wires attached to them were passed through holes in the disk, and the knobs screwed on from the back. The recess was then filled up to slightly above the level of the face of the disk with melted wax composed of equal parts by weight of paraffin and rosin, and when cold the excess wax was turned off in the lathe. Each sector is thus entirely imbedded in an insulating material, the only exposed part, from which the charge might brush back from sector to sector, being the small brass knob. In order to minimize this possible leak the sectors are set at an angle to any radius, as shown on the drawing, so that a sector on one disk does not pass a sector on the opposite one suddenly, but does so with a sort of shearing motion requiring four times the angular movement of the disks for the sectors to clear one another than would be needed were they placed radially. By the time, moreover, that any one sector has entirely entered a field of induction, the next following sector is three parts into the field, and the next behind that again is half in, while the third is one fourth the way in, and the fourth just entering, so that the maximum difference of potential between any two neighbouring knobs is reduced to one fourth of what it would be were the sectors arranged radially. This angular arrangement of the sectors naturally necessitates the collecting and neutralizing brushes

being displaced from the positions they would occupy were the sectors radial so as to touch the latter at the right moment. In order to increase the capacity of each sector while receiving its charge, two stationary inductors are placed opposite each disk, one at each of the points where the sectors on that disk are earthed. Each inductor consists of a sheet of tin-foil imbedded in wax and supported on a disk of ebonite, and is charged from a pin-point connected to it through an ebonite tube; this pin-point stands opposite to the outer knobs on another part of the large disk, where their sign and potential are such as are required to charge the inductor. Each sector at the moment of being earthed is thus placed between two similarly charged inductors,—the sectors on the opposite disk on the one side and the fixed inductor on the other, each of which is large in comparison with itself; its capacity is thereby greatly increased and it is enabled to carry forward a much larger charge of electricity than it can when the stationary inductors are removed.

The effect produced on the output of the machine by using these stationary inductors is remarkable, for though they practically make no difference to the length of the sparks, they greatly increase their apparent thickness; and with other things precisely similar they increase their frequency three-fold. To compare the output of the machine with and without the stationary inductors, I counted the number of sparks which overflowed a Leyden jar, and the revolutions of the disks, for 30 seconds, both when using the inductors and when they were taken off, and I was careful, in every case, to keep the speed of the disks as nearly as possible constant. I thus found that a 25-ounce Leyden jar overflowed 19 times in 30 seconds without inductors and 54 times with them; or, making a slight correction for the revolutions of the disks being less in the second case, the output was increased as 3 to 1 by the use of the inductors. The explanation of this greatly increased output is, I think, to be sought in the fact that connecting the positive and negative terminals of this machine does not stop its action, as it does in the case of the Wimshurst machine, and that it is therefore ready to start sparking, with almost full vigour, the moment they are separated. For when the inductors are removed, and two or three Leyden jars connected to the terminals, it is perfectly easy to note the discharge of the disks with each spark, and the time they take to recover, slowly at first and very rapidly at last, depending on the size of the condensers they are charging; but when the fixed inductors are replaced the recovery is very much more rapid, especially in its early stages, owing I

think to the fact that the inductors apparently do not lose their charge with each spark, and therefore, at once, start up the action of the machine.

With a view to decrease the capacity of each sector at the moment of its being discharged into the collector, I put on another set of inductors, one opposite to each of the main collecting brushes, and so arranged matters that they could be charged either from the neighbouring inductor or from the collector itself. In this way each sector at the moment of discharging itself into the collector is almost surrounded by a field of the same sign as itself, and I hoped by this means to squeeze more of its charge out of it as it passed. I was at first, however, disappointed to find that this second set of inductors made little if any difference to the output of the machine, whether they were connected to the other inductors or to the main collectors. But on arranging them to collect their own charge directly from the small knobs on the revolving disks, at a point just before the main collecting brushes, they became of value and increased the efficiency of the machine nearly $\frac{1}{3}$ th.

By the kindness of Mr. Wimshurst and Dr. Lewis Jones I have been enabled to compare the output of my machine with that of a Wimshurst having eight 15-inch plates and also with one having two 16-inch plates. I find that, area for area, and without using the stationary inductors, the efficiency of my machine is to that of the Wimshurst as 3 to 2; and with the inductors in use it is as 5.64 to 1. That is, from 5 to $5\frac{1}{4}$ times the area of plate is required to pass the collector in the Wimshurst machine to that which must pass it in this machine to produce the same result; or, to give the figures as we took them together:—

| | |
|---|---------|
| Mr. Wimshurst's 8 plate 15-in. diam. machine requires | sq. ft. |
| of area to pass the collector per spark. | 97.07 |
| Mr. Jones's 2 plate 16-in. diam. Wimshurst requires | 87.83 |
| W. R. Pidgeon's 4 plate 24-in. diam. machine, without inductors.. | 63.64 |
| " " " " with one set of inductors on | 21.117 |
| " " " " with both sets of inductors on | 17.2 |

I feel I ought to mention a mistake I fell into, while working on this machine, which nearly made me think that fixed inductors were of no use. When first trying them I used brushes, instead of a single point, to collect their charge, and was disappointed to find the output of the machine reduced to almost *nil*, because, as I ultimately discovered, the brushes formed a bridge between the sector knobs and allowed the charge to flow back from sector to sector, instead of being carried forward to the collector. Another difficulty I have

not been able to get over, and one which greatly decreases the actual output of the machine, is caused by the warping of the ebonite disks, which, although $\frac{3}{8}$ inch thick, will not stand true after being turned up, but move just sufficiently to throw them out of balance and prevent their being driven at anything approaching a high speed. The ebonite, moreover, is not a sufficiently good insulator, and not only prevents my getting a long spark but also reduces the possible efficiency of the machine by becoming an increasingly good conductor as the potential rises.

XXVI. *The Electrical Resistance of Metals and Alloys at Temperatures approaching the Absolute Zero.* By JAMES DEWAR, LL.D., F.R.S., Professor of Chemistry in the Royal Institution, &c., and J. A. FLEMING, M.A., D.Sc., F.R.S., Professor of Electrical Engineering in University College, London, &c.*

[Plate II.]

§ 1. **I**N the autumn of last year we published a short account† of experiments made by us during the previous summer on the electrical resistance of metals, non-metals, and alloys taken at the temperatures produced by the evaporation of liquid oxygen when boiling under normal or under reduced pressures. These experiments, which were merely preliminary, revealed, however, the nature of the difficulties to be overcome in repeating and following out this work. During the past year a much more extended series of investigations have been carried out by us on the same subject, but with more complete appliances for the production of the large quantities of the liquid gases necessary as refrigerating agents, and with greater care in the preparation of the metallic wires used and in the physical measurements to be made.

This inquiry is still far from complete ; but the results are of considerable interest as far as they have gone, and we consider it may be desirable to place on record a portion of the conclusions at which we have arrived. The general object of this research may be stated to be the determination of the Specific Electrical Resistance of Metals and Alloys between the limits of temperature of about 200° C. and the lowest obtainable temperatures approaching the absolute zero. We particularly desired to investigate the variation of resistance

* Communicated by the Authors.

† Philosophical Magazine, October 1892, p. 327.

with temperature below -100°C. , and to determine the form of the temperature-resistance curves as the temperature is lowered down to the lowest points obtainable by the evaporation of liquid oxygen boiling under reduced or normal pressure. The two variables with which we are concerned being, therefore, Specific Electrical Resistance and Temperature, we may point out in the first place how each of these has been defined and measured in tabulating the results.

§ 2. There are, as is well known, two ways in which we may define Specific Electrical Resistance. The first, called the Volume-Specific Resistance, is defined as the resistance of one cubic unit of the material taken between opposed faces of the cube. In this method of defining it the specific electrical resistance is given as the resistance in ohms, or electromagnetic units of one cubic centimetre of the material between opposed faces. The second, called the Mass-Specific Resistance, is the resistance of a wire of the material of a certain length and weight. In this second method of defining it, it is generally stated as the resistance in ohms of a wire of the material one metre in length and weighing one gramme. When it is desired to compare together or state the specific resistance of materials in the form of wires, of which the diameter is not very different from one millimetre or larger, and length, say, of one metre or more, there is no doubt that the most convenient way of stating the results is by means of the mass-specific resistance; and since the mean specific gravity of wires of this size can always be determined with a very fair degree of accuracy, the volume-specific resistance can easily be deduced. If, however, as in the case of our own experiments, the conditions necessitate the employment of very fine wires of about $\cdot 08$ to $\cdot 25$ millim. in not very great lengths, the probable errors on determining the weight per metre, and especially the specific gravity, are very considerable. We therefore preferred to face the difficulty of determining the mean diameter of the wires employed and state our results in terms of the volume-specific resistance. One part of the work consisted, therefore, in the determination of the mean cross section of a series of very fine wires prepared from the metals and alloys under test, taken by means of an optical method to be presently described. From this mean cross section and the length we are able to state, when the resistance is known, the volume-specific resistance of the material. Since, however, the measurements of length and diameter were all taken at temperatures between about 15°C. and 20°C. , it will only be possible to express the true volume-specific resistance at any assigned temperature when

we know the changes in dimensions which the material undergoes when heated or cooled. The true volume-specific resistance of the material at any temperature is the resistance in electromagnetic measure between opposed faces of one cubic centimetre of the material taken at that temperature. Pending, however, the determinations of the temperature-change in dimensions of the metals and alloys employed, we omit the correction (no doubt small) due to the change of dimensions, and state our results in terms of the electrical resistance in electromagnetic measure of one cubic centimetre of the material measured at 15° C., the said electrical resistance being determined at the various temperatures to which the material is raised or lowered. In the next place we have to consider the question of temperature-measurement. As the lowest temperatures reached by us in these experiments were temperatures at which air liquefies under ordinary pressures, the practical employment of the air-thermometer was surrounded with many difficulties. Ultimately it may be necessary to define the temperatures attained in terms of the absolute thermodynamic scale. But even the employment of the constant reduced-pressure hydrogen thermometer-scale, which may be taken as giving us the nearest practicable approximation to the true thermodynamic scale, is a matter in which extreme care will have to be employed in obtaining and interpreting results. We have been led, however, by one part of our results to see that, for our purpose here, by far the most practical method of defining the temperatures employed is to state them in terms of the variation of the specific resistance of one standard metal.

In the practical determination of temperature we select a thermometric substance, it may be air, hydrogen, mercury-in-glass, or some other material, such as a double metallic junction of thermoelectric materials, and we select also a thermometric quality, such as the change in pressure, change in apparent volume, or thermoelectric difference, and define our temperature by the temperature-change of the thermometric quality of this thermometric material. There is, therefore, nothing to prevent us from selecting as a measure of temperature the change in electrical resistance of a wire of a standard material and defining temperature in terms of the change. It will afterwards be possible to translate the temperatures so measured into their equivalents on the absolute thermodynamic or air-thermometer scales.

Our experiments at low temperatures have confirmed us in the view that the most convenient method of determining and stating such temperatures is in terms of the change of specific

resistance of pure platinum. H. L. Callendar* and Callendar and Griffiths have carefully examined this matter for temperatures from about zero Centigrade upwards to about 1000° C. Callendar has indicated the possible causes of the discrepancies in the results obtained by previous observers in the use of the platinum resistance-thermometer, as originally suggested by Siemens; and he has shown that a properly arranged pure platinum wire may be employed to measure temperatures, and may have its fixed points determined. We have in like manner found that a wire of pure soft annealed platinum may be cooled again and again to the lowest attainable temperatures, and heated up to high temperatures, without suffering any permanent change in its specific resistance after the first careful annealing has been made. This property is not, however, confined to pure platinum, but is equally possessed by other properly annealed metals.

There are, of course, good reasons for giving preference to platinum in the construction of resistance-thermometers; but, on the other hand, it is possible that for low temperatures chemically pure nickel, prepared by the process discovered by Mr. Ludwig Mond from nickel carbonyl, will prove to be of great utility on account of its very large mean coefficient of variation of resistance with temperature.

It is, however, clear that a wire of pure platinum which has been carefully annealed possesses a definite electrical resistance at each temperature to which it is exposed, and may be made use of as a thermometric body with great convenience. Callendar has introduced the useful term *platinum temperature* to denote temperatures measured with the platinum resistance-thermometer. On this scale the temperature is defined as follows:—Let R_0 be the electrical resistance of a given wire of pure platinum at zero Centigrade, that is when immersed in melting ice, and let R_{100} be the resistance of the same wire at 100° Centigrade. Then an increment of temperature, which causes a change in the resistance of the platinum equal to $\frac{R_1 - R_0}{100}$, is called one degree of platinum-temperature. If pt denote any temperature measured on this platinum-scale, and R be the resistance of the wire at that temperature, then

$$pt = \frac{R - R_0}{R_1 - R_0} 100.$$

Hence, if we take any straight line as a temperature-axis,

* Phil. Trans. Roy. Soc. vol. clxxiii. (1887) A. pp. 161-230, "On the Practical Measurement of Temperature."

and at any two points erect perpendiculars to it which are proportional to the resistance of the platinum wire at 0° C. and 100° C., and draw through the summits of these ordinates a straight line cutting the axis of temperature, we may define temperature as follows:—Divide the horizontal interval between the ordinates into one hundred equal parts, and continue the division on the scale backwards to the point at which the inclined line cuts the temperature-axis. Measure the resistance of the platinum at any temperature and find the ordinate representing this resistance: the foot of this ordinate marks the temperature on the platinum-scale. Callendar has shown that the difference between temperatures measured on this platinum-scale and the corresponding air-thermometer temperature is very nearly represented by a parabolic function of the air-thermometer temperature. It remains to be seen if all pure platinum wires give the same platinum temperature. We have found slight differences between the specific resistance and temperature-coefficients of platinum wires of different diameters, prepared with the greatest care and supposed to be equally pure, but which differences do no doubt depend upon slightly different degrees of hardness or purity. These differences are sufficient to make small but quite evident differences between the platinum temperatures as determined by these different platinum wires. These differences, however, are not more marked than would be the case with temperatures measured by different mercury-in-glass thermometers. We have accordingly selected one of our platinum wires as a standard thermometer and have referred all our measurements of temperature to it, and subsequently we may determine the equivalent temperatures on the air-thermometer scale. This platinum wire we refer to subsequently as the "thick platinum" wire. In the chart appended to this paper the abscissæ of temperature are therefore platinum-temperatures as measured by our standard platinum wire. The general nature of the measurements made consisted, therefore, first, in the measurement of the length and mean diameter of a fine wire of a metal or alloy of carefully prepared quality; secondly, in the measurement of the resistance of this wire when immersed in a bath giving it the necessary temperature; and thirdly, the determination of this temperature of the bath by the measurement of the resistance of the standard platinum wire before and after the measurement of the given wire. From the results of these observations we could deduce the volume-specific resistance of the material at certain platinum temperatures, and plot a series of curves to represent the variation of this resistance with temperature.

§ 3. Passing on to further details, we proceed to describe briefly the preparation of the metals and alloys in the required state of purity, and the construction of the resistance-coils suitable for the purpose of these experiments and the mode of making the required measurements. Our previous experiments had shown the necessity for the greatest care in the preparation of the metals. The term *pure* is of course a relative term, and absolute purity in a chemical sense is of course a most difficult matter to secure, but every care has been taken to arrive at the greatest possible purity in the majority of the metals employed. In this part of the work we have been greatly aided by several friends. Foremost amongst these we are especially indebted to Mr. George Matthey, who has given us invaluable aid in the preparation of a large series of metals in a state of great purity. Mr. J. W. Swan has furnished us with many samples of electrolytic copper and silver prepared by himself by his own special processes. From Mr. G. Addenbrooke we received samples of aluminium and aluminium alloys which have been of use to us; and Colonel Dyer, of the Elswick Ordnance (Armstrong's) Works, has kindly sent us samples of iron prepared with very great care.

Having these materials in our possession, they were in most cases drawn into wire for us by Messrs. Johnson and Matthey, and in some cases, such as those of lead, tin, thallium, and some others, the metals were pressed into wire in a steel press by the hydraulic 50-ton testing-machine in the Mechanical Laboratory of University College, London.

These different wires had a diameter varying from $\cdot 08$ millim. (3 mils) up to about $0\cdot 25$ millim. (10 mils) and lengths of from 1 to 3 metres.

§ 4. The next step consisted in measuring the mean diameters. For such fine wires no ordinary process of callipering was sufficiently accurate. After many experiments, the following method of obtaining rapidly the mean diameter was perfected.

A compound microscope had the eyepiece removed, and the substage under the object-glass fitted with a large cork, bored out in the centre with a hole, and having two small glass tubes inserted in the sides. This cork was so fixed to the stage that when a wire was drawn through the small tubes, it passed across the field of the objective. The stage had a rack-work motion which enabled it to be moved to or from the objective; but this last remained fixed relatively to the stand of the microscope. The microscope being placed horizontally, an incandescent lamp was placed behind a condenser

lens at the back of the substage, and an image of the wire projected by the objective on to a sheet of fine hot-pressed drawing-paper placed a yard away from the lens. The objective which formed this image always remained fixed relatively to the screen, and the image was focussed by moving the substage which carried the wire.

The magnification of the image was about 300 times linear, so that the image of a wire about $\cdot 003$ inch in diameter could be made to appear one inch in diameter. A 2-inch, 1-inch, or $\frac{1}{2}$ -inch objective could be used as desired. This optical image or shadow could be made exceedingly sharp and well-defined, and could be measured with a pair of dividers to much less than one per cent. In order to infer the real diameter of the wire from the diameter of the image, the following method was employed. A series of five steel-wire gauges was made formed of round parallel steel wire about 10 centimetres in length, rammed into wooden handles. These handles were planed off on one side flat. These gauges varied in diameter from about 3 millim. to $\cdot 04$ of a millimetre. The gauges were sent to the Board of Trade Standardised Laboratory, and the diameters of the steel wires officially measured with their Standard instruments along axes parallel to the flat side of the handle, and taken at the centre of the wire. This being done, we had a series of standard gauges whose diameter in one definite position was known to the one ten-thousandth of an inch. These gauges were marked A, B, C, D, E.

Two more similar gauges were prepared, called F and G, of smaller steel wire, and a number of observations of the diameters of F and G relatively to E were made by means of a micrometer-microscope belonging to the Physical Laboratory of University College. Many observations were also made of the relative diameters of the images of gauges E, F, and G when projected by the projection microscope, the gauges being in the same focal position relatively to the objective and screen. These experiments, which were most carefully made, sufficed to establish the diameters of the steel gauges F and G in the centre and parallel to the flat side of their handles, in terms of the Board of Trade measuring-instrument, and the final mean result expressed in centimetres, is that the central diameters of gauges F and G, parallel to the flat side of the handle, are as follows :—

Central diameter of gauge F = $0\cdot 03966$ of a centimetre.

Central diameter of gauge G = $0\cdot 03959$ of a centimetre,

taken at about the normal temperature 15° C.

The process of measuring the mean diameter of any wire was then as follows:—The appropriate length of the wire being cut off and measured against a standard-metre scale, it was drawn through the field of the microscope, the smallest gauge, F or G, being placed in the same focal plane and parallel with the wire. The gauge was placed with the flat side of the handle parallel with the screen and the centre of the steel gauge in the centre of the objective field. We had then on the screen the images or shadows of two objects, one a wire of steel of known diameter, and the other a wire of unknown diameter; the diametral planes of each wire being in the same focal plane of the lens. The diameters of the images of the steel gauge and the wire were then carefully measured with dividers and expressed in terms of some arbitrary unit. The ratio of these apparent image-diameters was taken as the ratio of the real diameters of the wire and the gauge.

The measurement of the diameter of the wire was taken about every five centimetres in the case of very uniformly drawn wires, and more frequently in other cases. Generally about twenty, and sometimes sixty diametral measurements were taken in the metre length of the wire to be measured, and as the wire was turned round its long axis in passing through the field of the microscope the diametral measurements were taken in numerous directions. The mean of all these measurements gave a close approximation to the mean diameter of the wire. As an instance of the close agreement of the results by this method, and those obtained by the density method, we may give the following comparison of the determination made of the mean diameter of a certain high-conductivity copper wire about $\cdot 01$ inch in diameter. Mr. J. W. Swan sent us this wire, and determined its mean diameter by a very careful measurement of its length and mean density. Our measurement of the mean diameter of this wire was $0\cdot 02609$ centim., and his was $0\cdot 02608$ centim., agreeing thus within 1 part in 2600. By the use of a suitable objective this method was applicable to the smallest wires used as well as to the largest. Each wire having had its mean diameter and length thus ascertained, the mean cross-sectional area was calculated, and a reduction-factor obtained by which the reduced true resistance of the wire in ohms was multiplied to deduce therefrom the volume-specific resistance as above defined.

§ 5. Furnished with these wires, the next step was to prepare suitable resistance-coils by which the resistance of the wires could be taken in a bath of liquid gas. In our former

experiments the wires of which the resistance was to be determined were wound on a rectangle of mica, having serrations or teeth cut upon the edge, and the ends of the wire were then soldered to stout copper connexions. For many reasons this proved to be an undesirable method. Many wires, such as aluminium, were easily broken by the sharp bend in the wire, and other soft wires, such as lead, were deformed at the same point of bending.

In preparing coils for the purpose we had in view it was necessary to keep them small, so that they might be easily contained in a moderate-sized vacuum-jacketed test-tube in which the liquid gas was held. For obvious reasons also any large amount of non-conducting material round the wire was objectionable. After some trials the following method of constructing the resistance-coils to be used was adopted, and answered very well. Stout high-conductivity copper wire of 4 millim. diameter was cut into lengths, and pairs of these wires bent up and bound together at the middle, but insulated from each other with indiarubber tape. The ends of the wires were well tinned and the bottom ends nicked.

A very thin sheet of vulcanized fibre was then bound round the bottom part of the copper rods and sewn to them by silk thread. This formed a thin cylinder on which the wire to be tested was carried. A stout silk thread was then wound spiral fashion round the cylinder. The wire to be tested, generally 1, 2, or 3 metres in length, was then carefully wound on the fibre cylinder in between the silk thread, the several turns of which kept the turns of wire from becoming short-circuited. The dimensions of the cylinder of vulcanized fibre varied according to the length of wire used, but was from two to three centimetres in diameter and four to five centimetres in length. A large number of such bobbins having been prepared, the next step was to anneal the wires on these coils.

The so prepared resistance-coils were immersed in melted paraffin wax and kept at a temperature of 200° C. for some time. These being slowly cooled they were annealed and at the same time the insulating portions of the coils well saturated with paraffin.

§ 6. The resistance measurements were carried out by means of a Wheatstone's Bridge by Messrs. Elliott Bros. The coils of this bridge were of platinum-silver and adjusted to read in standard ohms. The coefficient of variation of resistance of the coils of the bridge with temperature was determined and found to be .031 per cent. per degree Centigrade. The temperature of the bridge-coil box was always taken at the

time of making each set of measurements and the proper correction applied. Another correction of importance was that for resistance of the connecting leads and the copper terminals of each coil. A loop of copper wire was prepared of the same metal and of the same total length as the standard size employed as terminals of each resistance-coil. This blank was always measured before and after each set of experiments on the coils, and so arranged that it was under the same temperature conditions as the terminals of the coils. This together with the resistance of the short thick bridge leads, is always called "resistance of connexions" in the Tables, and is a correction invariably applied in each case. The galvanometer employed with the bridge was a Pitkin-Holden Galvanometer of the suspended coil type, having a resistance of about 10 ohms and nearly perfectly dead-beat. One cell of a Helsen dry battery was used, and the usual battery and galvanometer keys inserted in their respective circuits.

The temperatures above zero Centigrade were obtained by immersing the coils in a beaker of melted paraffin oil standing in a large zinc bath full of water. This water was heated to varying temperatures up to about 98° C. The paraffin was kept well stirred, either by a mechanical stirrer or, better, by passing slowly bubbles of air through it from an elastic bag full of air. The temperature of the paraffin oil was taken by a mercury-in-glass thermometer, the scale-readings of which were corrected for us by Mr. Casella by comparison with those of a standard mercury thermometer which had been checked at Kew. Temperatures close to zero Centigrade were chiefly obtained during the long frost in January 1893, by placing the coils in paraffin oil in beakers which were placed in the zinc bath filled with broken ice. Coils waiting to take their turn to be measured were kept standing in other beakers of paraffin oil also placed in the same large zinc bath. Those who have conducted similar experiments know well that the great difficulty in such resistance measurements is to make sure that the coils have reached the temperature of the surrounding fluid and to avoid changing their temperature by the current employed to measure them. For this reason very weak currents have to be used with the bridge. The temperatures below zero Centigrade were obtained by the use of a bath of carbonic acid snow, and ether, or paraffin oil, which gave temperatures according to desire from 0° C. down to about -78° C., and a series of measurements was thus made at about -40° and -78° . By the employment of liquid ethylene a temperature of -100° C. could be reached. Liquid oxygen was then employed as a refrigerating agent to

lower the temperature of the resistance-coils to about -182° C. The liquid gas was contained in vacuum-jacketed flasks or test-tubes in which the resistance-coil was placed.

Temperatures lower than the above limits were obtained by closing the mouth of the vacuum-jacketed test-tube with a tightly fitting indiarubber cork and producing a partial vacuum above the liquid oxygen. In these experiments the resistance-coils were therefore immersed in liquid oxygen boiling under a very reduced pressure, as low as 14 millimetres of mercury. At all times great care is necessary to preserve the coil entirely immersed in the liquid gas. If the coil is only partially immersed thermoelectric effects are set up, in some cases of such a magnitude as to entirely vitiate the measurements of resistance. Hence the necessity for an abundant supply of the liquid gas. In some of the sets of experiments several litres of liquid oxygen were used up. In the above set of measurements about fifty coils in all were wound, and the measurements of each coil often taken several times at the same temperature. In those instances in which the temperature of the bath was below zero Centigrade the resistance of one of the standard platinum wires was measured in the same bath before and after each measurement of the resistance of the wire. The platinum-thermometer wire was thus placed under identical conditions with the wire under examination. In all the following Tables the temperatures in the columns headed *pt* are platinum temperatures taken with the standard platinum wire.

§ 7. We proceed in the next place to describe some of the results obtained from the comparison of resistances effected as above.

I. *Platinum.*

The samples of platinum wire were prepared for us by Mr. George Matthey with great care. Two wires were chiefly employed, one having a diameter of about 10 mils, called the "thick" wire, and one having a diameter of about 3 mils, called the "thin" wire. The thick wire was the one taken as the standard thermometer.

Thick Platinum wire.

Length = 150 centim. Mean diameter = 0.025945 centim.
Mean cross-sectional area = 0.00052868 sq. centim.

$$\text{Log}_{10} \left[\frac{10^9 \text{ section}}{\text{length}} \right] = 3.5470976 = \log_{10} k.$$

Let R = resistance of wire corrected for connexions and bridge temperature taken at any temperature t° C., and measured in true ohms ;

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and let ρ_t = volume-specific resistance of the metal at temperature $t^\circ \text{C.}$, in C.G.S. units ;

then $\log_{10} \rho_t = \log_{10} R_t + \log_{10} k$ or $\rho_t = R_t k$.

In the following Tables t stands for a Centigrade temperature and pt for the equivalent platinum temperature.

The reduced observations taken with this thick platinum wire were as follows :—

| R_t . Corrected resistance of wire in ohms. | t° . Corrected Centigrade tempera- ture. | ρ_t . Volume- specific resistance. | pt . Platinum tempera- ture. | Remarks on nature of Bath. |
|---|---|--|---|--|
| 5.2171 | 195.2 | 18388 | 192.2 | Taken in melted paraffin wax. |
| 4.6345 | 141.0 | 16334 | 139.8 | |
| 4.1876 | 98.5 | 14759 | 98.55 | |
| 4.1813 | 98.05 | 14737 | 98.10 | |
| 3.9982 | 80.90 | 14092 | 81.20 | Taken in paraffin oil. |
| 3.7695 | 60.0 | 13286 | 60.55 | |
| 3.5440 | 39.60 | 12491 | 40.15 | |
| 3.3108 | 18.45 | 11669 | 18.85 | |
| 3.3043 | 17.90 | 11646 | 18.25 | |
| 3.2991 | 17.20 | 11628 | 17.55 | |
| 3.2739 | 14.90 | 11539 | 15.20 | |
| 3.2487 | 12.80 | 11450 | 13.10 | |
| 3.2450 | 12.60 | 11437 | 12.85 | Taken in melting ice. |
| 3.1136 | 0.60 | 10974 | 0.60 | |
| 2.8034 | ... | 9881 | — 27.8 | Taken in paraffin and solid carbonic acid. |
| 2.6222 | ... | 9242 | — 44.0 | |
| 2.4225 | ... | 8538 | — 62.7 | |
| 2.2085 | ... | 7784 | — 81.9 | Taken in solid carbonic acid and ether. |
| 2.0138 | ... | 7098 | — 99.8 | |
| 1.9446 | ... | 6854 | — 106.1 | Taken in liquid ethylene. |
| 0.9473 | ... | 3339 | — 197 | Taken in liquid oxygen boiling at 760 millim. |
| 0.6951 | ... | 2450 | — 219.7 | Taken in liquid oxygen boiling under reduced pressure. |
| 0.6921 | ... | 2439 | — 219.9 | |

Volume specific-resistance at 100°C. = 14814 C.G.S. units.

Ditto ditto at 0°C. = 10950 " "

Mean temperature-coefficient between

0° and 100°C. = .003529 = α .

Reciprocal of temperature-coefficient = $-\frac{1}{283.4} = -\frac{1}{\alpha}$.

In order to determine the platinum temperatures the first step was to draw a curve from the observations made between $0^\circ.60 \text{C.}$ and $98^\circ.55 \text{C.}$, of which the ordinates were specific resistance and the abscissæ corrected Centigrade temperatures. This curve enabled us by extrapolation to determine the true volume-specific resistance at 0°C. and 100°C. exactly. Through the summits of the ordinates drawn up at 0°C. and

100° C. a straight line was drawn and prolonged both ways. The point where this line cuts the axis of temperature was at a distance of $-283\cdot4$ divisions from the zero Centigrade point. This gave the platinum temperature absolute zero. From the measured value of the platinum resistance in any bath we could then deduce the platinum temperature according to this wire. The numbers in the fourth column are so deduced. Hence when plotted in terms of platinum temperature the curve of platinum resistance is a straight line. The mean temperature-coefficient of this wire between 0° C. and 100° is $\cdot003529$.

A similar series of observations was made with the other platinum wire.

Thin Platinum Wire.

Length = 100 centim. Mean diameter = $0\cdot0078297$ centim.

Mean cross-sectional area = $0\cdot00048148$ sq. centim.

$$\text{Log}_{10} \left[\frac{10^9 \text{ section}}{\text{length}} \right] = 2\cdot6825775 = \log_{10} k.$$

| R _t | t°. | ρ_t | pt. | Remarks on nature of Bath. |
|----------------|-------|----------|---------|--|
| 38-806 | 196-6 | 18684 | 193-5 | Taken in melted paraffin wax. |
| 34-142 | 139-2 | 16439 | 138-00 | |
| 30-850 | 98-35 | 14854 | 98-40 | |
| 30-252 | 90-5 | 14566 | 90-70 | |
| 29-440 | 80-3 | 14175 | 80-65 | Taken in paraffin oil. |
| 27-677 | 59-95 | 13326 | 60-50 | |
| 26-906 | 50-75 | 12954 | 51-35 | |
| 25-997 | 39-60 | 12517 | 40-15 | |
| 24-213 | 18-45 | 11658 | 18-85 | |
| 24-141 | 17-95 | 11623 | 17-70 | |
| 24-038 | 16-30 | 11574 | 16-65 | |
| 24-047 | 16-20 | 11578 | 16-55 | |
| 23-928 | 14-95 | 11521 | 15-25 | |
| 23-726 | 12-70 | 11424 | 12-95 | |
| 23-669 | 11-85 | 11396 | 12-10 | Taken in melting ice. |
| 22-783 | 1-25 | 10970 | 1-30 | |
| 22-717 | 0-55 | 10938 | 0-55 | |
| 19-227 | ... | 9257 | - 41-2 | Taken in solid carbonic acid and paraffin. |
| 15-830 | ... | 7622 | - 81-9 | |
| 14-438 | ... | 6952 | - 99-3 | Taken in solid carbonic acid and ether. |
| 13-848 | ... | 6668 | - 106-1 | |
| 6-326 | ... | 3046 | - 197-1 | Taken in liquid ethylene. |
| | | | | Taken in liquid oxygen. |

Volume-specific resistance at 100° C. = 14923 C.G.S. units.

Ditto ditto at 0° C. = 10917 " "

Mean temperature-coefficient between

0° and 100° C. = $\cdot003669 = \alpha$.

Reciprocal of temperature-coefficient = $-272\cdot5 = -\frac{1}{\alpha}$.

The temperatures in the last column in the above Table are platinum temperatures, as given by the thick platinum wire. If the above specific resistances for the thin platinum wire are plotted out in terms of pt , they give a straight line which cuts the axis of temperature at $-272.5\text{ }pt$ or ten degrees nearer to the zero Centigrade than in the case of the thick wire. The coefficients of the two wires are slightly different, and the platinum temperatures, as determined by the two wires, are slightly different also, but differ by less than half a degree at the boiling-point of oxygen, and by about one tenth of a degree at the boiling-point of ethylene. When plotted in terms of air-thermometer temperature, the platinum resistance-curves are curves which are concave downwards. Hence the coefficient of resistance-variation with temperature is a variable quantity. The first differential coefficient dR/dt has a positive sign, and the second differential coefficient d^2R/dt^2 a negative sign.

§ 8.

II. *Gold.*

This gold was prepared and drawn into wire for us by Messrs. Johnson and Matthey. It was reported by the assayers as of 99.9 degrees of fineness.

Length = 100 centim. Mean diameter = .0078653 centim.

Mean sectional area = .000048586 sq. centim.

$$\text{Log}_{10} \left[\frac{10^9 \text{ section}}{\text{length}} \right] = 2.6865159 = \log_{10} k.$$

| R_t . Corrected resistance in ohms. | t° . Centigrade tempera- ture. | ρ_t . Volume- specific resistance. | pt . Platinum tempera- ture. | Remarks on nature of Bath. |
|--|--|--|---|-------------------------------|
| 7.8048 | 194.5 | 3792.1 | 191.5 | In melted paraffin. |
| 6.7068 | 132.2 | 3258.6 | 131.2 | |
| 6.0538 | 90.4 | 2941.3 | 90.55 | In paraffin oil. |
| 4.7882 | 50.0 | 2606.5 | 50.6 | |
| 4.8319 | 18.7 | 2347.7 | 19.1 | |
| 4.7882 | 16.25 | 2326.4 | 16.6 | |
| 4.7726 | 15.4 | 2318.8 | 15.7 | |
| 4.7636 | 14.3 | 2314.5 | 14.6 | |
| 4.7208 | 11.95 | 2293.7 | 12.2 | |
| 4.5296 | 1.05 | 2200.8 | 1.05 | In melting ice. |
| 3.8056 | ... | 1849.0 | - 44 | |
| 3.1870 | ... | 1548.5 | - 81.9 | In CO_2 and ether. |
| 2.8131 | ... | 1366.8 | - 106.1 | In liquid ethylene. |
| 1.4022 | ... | 681.3 | - 197.1 | In liquid oxygen. |

Volume-specific resistance at 0°C . . . = 2197 C.G.S. units.

Mean temperature-coefficient between

0°C . and 100°C = .00377 = α .

§ 9.

III. Palladium.

This palladium was prepared for us by Mr. George Matthey with the greatest care, and was found to be of a high degree of purity.

Length=100 centim. Mean diameter=0.024478 centim.

Mean sectional area=0.00047061 sq. centim.

$$\text{Log}_{10} \left[\frac{10^9 \text{ section}}{\text{length}} \right] = 3.6726579 = \log_{10} k.$$

| Rt. | t°. | ρ_t . | ρ_t . |
|--------|-------|------------|------------|
| 3.6173 | 194.2 | 17023 | 191.2 |
| 3.2069 | 137.2 | 15092 | 136.1 |
| 2.9304 | 98.5 | 13791 | 98.55 |
| 2.6405 | 60.1 | 12426 | 60.60 |
| 2.3176 | 18.35 | 10907 | 18.75 |
| 2.3115 | 18.05 | 10878 | 18.45 |
| 2.3106 | 17.2 | 10874 | 17.55 |
| 2.1786 | 0.6 | 10253 | 0.6 |
| 1.8259 | ... | 8593 | - 43 |
| 1.5226 | ... | 7166 | - 81.9 |
| 0.5913 | ... | 2783 | - 197.1 |

Volume-specific resistance at 0° C. . . = 10219 C.G.S. units.

Mean temperature-coefficient between

0° and 100° = .00354.

§ 10.

IV. Silver.

Several samples of silver wire were obtained and examined. The purest we were able to obtain was a sample sent to us by Mr. J. W. Swan, prepared by him by the electrolysis of silver nitrate, and drawn into wire directly from the deposit without having been melted. It was annealed in a non-oxidizing atmosphere of CO₂.

Length=150 centim. Mean diameter=0.025550 centim.

Mean sectional area=0.00051272 sq. centim.

$$\text{Log}_{10} \left[\frac{10^9 \text{ section}}{\text{length}} \right] = 3.5337876 = \log_{10} k.$$

| R_t | t° | ρ_t | ρ_t |
|--------|-----------|----------|----------|
| 0.7631 | 192.1 | 2606.4 | 189.2 |
| 0.6652 | 137.2 | 2273.7 | 136.1 |
| 0.6033 | 98.15 | 2062.2 | 98.2 |
| 0.5372 | 60.0 | 1836.2 | 60.55 |
| 0.4646 | 18.30 | 1588.1 | 18.70 |
| 0.4601 | 18.20 | 1572.7 | 18.60 |
| 0.4639 | 17.25 | 1565.7 | 17.60 |
| 0.4355 | 0.65 | 1488.6 | 0.65 |
| 0.3630 | ... | 1240.8 | — 42.3 |
| 0.2988 | ... | 1021.3 | — 81.9 |
| 0.1140 | ... | 389.7 | — 197.1 |

Volume-specific resistance at 0°C . . . = 1468 C.G.S. units*.

Mean temperature-coefficient between.

0° and 100°C = .00400.

§ 11.

V. *Copper.*

A large number of samples of copper have been examined by us at one time or another. The purest copper we have been able to obtain is that sent to us by Mr. J. W. Swan, prepared by him from the electrolysis of pure copper nitrate by his special process. The metal was exceedingly soft and ductile, and was drawn into a very uniform wire without melting or heating, and annealed by heating in hydrogen. We call this particular specimen (May 19th) from the date when it came to us.

Two coils were prepared from this wire—one, a short coil of 300 centim. in length, and one very much longer, of about 2100 centim. The reason for this being that at the very low temperatures the copper loses so much of its resistance and is so good a conductor that unless a considerable length of wire is taken the resistance measurements cannot be made accurately at the very lowest temperatures. For the shorter coil the dimensions were:—

Length = 300 centim. Mean diameter = 0.025789 centim.

Mean sectional area = 0.00052236 sq. centim.

$$\text{Log}_{10} \left[\frac{10^\circ \text{section}}{\text{length}} \right] = 3.2408464 = \log_{10} k.$$

* This is the most probable value deduced from the whole curve.

| Rt. | t°. | pt. | pt. | Remarks. |
|--------|-------|--------|---------|---------------------------|
| 1.6810 | 205.0 | 2926.9 | 201.7 | Taken in melted paraffin. |
| 1.4346 | 141.1 | 2497.7 | 139.9 | |
| 1.2726 | 97.95 | 2215.8 | 98.0 | |
| 1.1262 | 59.95 | 1960.9 | 60.50 | |
| 0.9659 | 18.30 | 1681.8 | 18.70 | Taken in paraffin oil. |
| 0.9658 | 18.25 | 1681.6 | 18.65 | |
| 0.9594 | 16.45 | 1670.5 | 16.80 | |
| 0.8982 | 0.55 | 1563.9 | 0.55 | |
| 0.7452 | ... | 1297.5 | - 39.4 | Taken in melting ice. |
| 0.6863 | ... | 1024.3 | - 81.9 | |
| 0.1658 | ... | 288.7 | - 197.1 | |
| | | | | |

The longer coil was then employed to obtain resistance ratios at lower temperatures reached by the use of liquid oxygen boiling under reduced pressures. The measurements being as follows:—

| Rt. | t°. | pt. | pt. | Remarks. |
|--------|-----|-------|---------|---|
| 1.1687 | ... | 288.7 | - 197.1 | Taken in liquid oxygen boiling under pressures down to 14 millim. of mercury. |
| 0.6391 | ... | 161.3 | - 219.2 | |
| 0.6341 | ... | 160.0 | - 219.3 | |
| 0.5692 | ... | 143.6 | - 223.2 | |

Volume-specific resistance at 0° C. . . = 1561.

Mean temperature-coefficient between

0° and 100° C. = .00428.

It will be noticed that this pure copper has a very large temperature-coefficient, and that its temperature-coefficient is greater between 0° C. and 100° C. than that of silver. This superiority is maintained at lower temperatures, and, as a consequence, the copper resistance line crosses the silver line. Although silver is a better conductor than copper at zero Centigrade and at higher temperatures, yet at a temperature of 200° below zero Centigrade copper is the better conductor, and the cooled pure copper has the highest conductivity of any metal we have obtained. On comparing the specific resistance of the copper at +201.7 pt with that at -223.2 pt, it will be seen that at the lowest temperature the copper has only 4.8 per cent. of the resistance it has at the highest. Hence we have destroyed 95 per cent. of its resistance. At the lowest temperature yet reached the copper has less than one tenth of its specific resistance at zero Centigrade.

§ 12.

VI. *Aluminium.*

We were provided with numerous samples of aluminium by the kindness of Mr. G. Addenbrooke, and also with a solder which enabled us, without difficulty, to attach these wires to the copper terminals. This aluminium was prepared at Neuhausen. One sample was the ordinary Commercial Aluminium which contained 97·5 per cent. of aluminium, and another was a purer kind containing 99 per cent. of aluminium. These we refer to as the Commercial Aluminium and Neuhausen Aluminium. A third sample was obtained from Messrs. Johnson and Matthey. For the first two samples the results of observation were as follows:—

Neuhausen Aluminium, 99 per cent., fine.

Length=200 centim. Mean diameter=0·024446 centim.

Mean sectional area=0·00046936 sq. centim.

$$\text{Log}_{10} \left[\frac{10^9 \text{ section}}{\text{length}} \right] = 3·3704753.$$

Commercial Aluminium, 97·5 per cent., fine.

Length=99·8 centim. Mean diameter=0·024520 centim.

Mean sectional area=0·00047221 sq. centim.

$$\text{Log}_{10} \left[\frac{10^9 \text{ section}}{\text{length}} \right] = 3·6750012.$$

Neuhausen Aluminium, 99 per cent.

| Rt. | °. | pt. | pt. |
|--------|-------|--------|---------|
| 1·9699 | 191·5 | 4623·0 | 188·6 |
| 1·7523 | 145·3 | 4112·3 | 143·9 |
| 1·5217 | 92·20 | 3571·1 | 92·3 |
| 1·3293 | 50·60 | 3119·6 | 51·20 |
| 1·1813 | 18·70 | 2772·3 | 19·10 |
| 1·1536 | 12·80 | 2707·3 | 13·10 |
| 1·1007 | 1·05 | 2583·1 | 1·05 |
| 0·8967 | ... | 2104·4 | — 43·8 |
| 0·7339 | ... | 1704·2 | — 81·9 |
| 0·2461 | ... | 559·7 | — 197·1 |

Volume-specific resistance at 0° C. . . = 2563 C.G.S. units.

Mean temperature-coefficient between

0° C. and 100° C. = ·00423.

Commercial Aluminium, 97·5 per cent., fine.

| <i>R_t</i> | <i>t</i> °. | <i>ρ_t</i> | <i>ρ_t</i> | Remarks. |
|----------------------|-------------|----------------------|----------------------|--|
| 1·0352 | 198·3 | 4898·1 | 190·4 | |
| 0·9134 | 144·4 | 4321·8 | 143·0 | |
| 0·7887 | 91·45 | 3731·8 | 91·6 | |
| 0·6869 | 50·1 | 3250·1 | 50·7 | |
| 0·6064 | 18·85 | 2869·2 | 19·25 | |
| 0·6021 | 15·65 | 2848·9 | 15·05 | |
| 0·5671 | 1·0 | 2683·2 | 1·0 | |
| 0·4577 | ... | 2165·6 | — 44·3 | |
| 0·3672 | ... | 1737·6 | — 81·9 | |
| 0·3127 | ... | 1479·5 | — 106·1 | In liquid ethylene. |
| 0·1070 | ... | 506·3 | — 197·1 | In liquid oxygen. |
| { 0·3744 | ... | 506·3 | — 197·1 | This ratio was obtained from a longer coil of the same wire immersed in oxygen boiling under reduced pressure. |
| { 0·2402 | ... | 324·8 | — 219·2 | |

Volume-specific resistance at 0° C. . = 2665 C.G.S. units.

Mean temperature-coefficient between

0° C. and 100° C. = ·00435.

Contrary to usual experience, this Commercial Aluminium has a larger temperature-coefficient between 0° C. and 100° C. than the purer metal, and larger even than that of the pure copper.

§ 13.

VII. Iron.

It is needless to say that we had great difficulty in obtaining any sample of iron which could properly be called pure. We have not yet succeeded in obtaining iron wire drawn directly from pure electrolytic iron. Colonel Dyer, of the Elswick Ordnance Works, kindly sent us samples of iron very free from carbon, silicon, and phosphorus but in which unfortunately manganese was still present to the extent of nearly 0·25 per cent. and sulphur 0·01 per cent. From Messrs. Hopkins and Williams we procured samples of iron, prepared especially for them, and of a high degree of purity and very soft and well annealed. The electrical behaviour of this last sample shows it to be almost free from admixture of other elements. We call the first iron from Armstrong's works, Iron A, and the other Iron H. W. The last iron has by far the higher conductivity. The Iron A proved to be sufficiently soft to work cold under the hammer and was drawn without heating into a very uniform wire.

Iron A.

Length = 100 centim. Mean diameter = 0.02657 centim.
 Mean sectional area = 0.00055445 sq. centim.

$$\text{Log}_{10} \left[\frac{10^9 \text{ section}}{\text{length}} \right] = 3.7438595.$$

| R_t | t° | ρ_t | ρ_t |
|--------|-----------|----------|----------|
| 4.1985 | 197.3 | 23251 | 194.2 |
| 3.4091 | 138.8 | 18902 | 137.6 |
| 2.8368 | 90.5 | 15729 | 90.7 |
| 2.4167 | 52.10 | 13399 | 52.70 |
| 2.0737 | 18.50 | 11498 | 18.90 |
| 1.9104 | 1.40 | 10592 | 1.45 |
| 1.5086 | ... | 8364 | — 43.6 |
| 1.1909 | ... | 6647 | — 81.9 |
| 0.4223 | ... | 2341 | — 197.1 |

By comparison of resistances of a longer coil of the same wire taken in liquid oxygen boiling under normal and reduced pressures a lower temperature reading was obtained.

| R_t | ρ_t | ρ_t |
|-------|----------|----------|
| 3.834 | | 2341 |
| 2.983 | | 1820 |

Volume-specific resistance at 0° C. . . = 10512

Mean temperature-coefficient between

0° and 100° C. = .00544

Iron H. W.

Length = 100 centim. Mean diameter = 0.023078 centim.
 Mean sectional area = 0.00041830 sq. centim.

$$\text{Log}_{10} \left[\frac{10^9 \text{ section}}{\text{length}} \right] = \log_{10} R = 3.6214907.$$

| R_t | t° | ρ_t | ρ_t | Remarks. |
|--------|-----------|----------|----------|---|
| 5.1395 | 196.1 | 21499 | 193 | Taken in CO ₂ and ether. Taken in liquid oxygen boiling at 760 mm. |
| 4.2536 | 145.4 | 17793 | 144 | |
| 3.4976 | 98.10 | 14631 | 98.15 | |
| 2.9546 | 60.25 | 12359 | 60.80 | |
| 2.3940 | 18.25 | 10014 | 18.65 | |
| 2.1791 | 0.70 | 9115 | 0.70 | |
| 1.7137 | ... | 7168 | — 39.2 | |
| 1.2713 | ... | 5318 | — 81.9 | |
| 0.2918 | ... | 1220 | — 197.1 | |

Two other coils (a) and (b) of the same wire were also prepared, one of about 2600 centim. in length, and the other about 3700 centim., so as to obtain a much greater resistance to measure; and these coils had their resistances taken in liquid oxygen boiling under normal and under reduced pressures. Hence lower temperature readings were obtained as follows:—

| Iron H. W. (a) | | | Iron H. W. (b) | | |
|----------------|----------|--------|----------------|----------|--------|
| Rt. | ρ . | $pt.$ | Rt. | ρ . | $pt.$ |
| 7.081 | 1220 | -197.1 | 9.875 | 1220 | -197.1 |
| 4.154 | 725 | -219 | 5.257 | 649 | -222.4 |
| 3.839 | 660 | -222.2 | 5.222 | 644 | -222.7 |

Volume-specific resistance at $0^{\circ}\text{C}.$. . = 9065 C.G.S. units.

Mean temperature-coefficient between

$0^{\circ}\text{C}.$ and $100^{\circ}\text{C}.$ = .00625.

It will be seen therefore that Iron H. W. has a much greater conductivity (about 15 per cent.) than Iron A and also a much larger temperature-coefficient. There is reason to believe that Iron H. W. is exceedingly pure. Both these iron lines are delineated on the chart. It will be seen that at the lowest temperature reached, viz. -222.7 pt. , the iron has only one thirty-third of its resistance at about $+200^{\circ}\text{ pt.}$; in other words, we have destroyed 97 per cent. of its resistance. The iron resistance-curves are strongly concave upwards; that is, the second differential of resistance with respect to temperature is a positive quantity.

§ 14.

VIII. Nickel.

The only perfectly pure nickel we have been able to obtain is that prepared from nickel carbonyl. Mr. Mond was so good as to prepare for us two pure nickel tubes formed by passing the vapour of nickel carbonyl through a heated glass tube. An attempt was made to draw this nickel down into wire, but it could not be done. We accordingly cut up a portion of a nickel tube into a very fine spiral in the lathe, and employed this spiral of nickel as a resistance-coil.

The dimensions of this strip were not sufficiently regular to allow the specific resistance to be determined. Pending the preparation of other pure nickel in the form of wire, we have taken the ratios of the resistances of this nickel spiral at various temperatures and converted them into specific resistances by the help of Matthiesen's value at 0°C for that metal as given in Everett's 'Physical Units.'

| Rt. | t°. | pt. | pt. |
|--------|-------|-------|--------|
| 1.8475 | 195.3 | 29730 | 192.3 |
| 1.4448 | 133.7 | 23250 | 132.7 |
| 1.2067 | 90.35 | 19419 | 90.55 |
| 1.0058 | 51.7 | 16185 | 52.3 |
| 0.8484 | 18.7 | 14653 | 19.10 |
| 0.7707 | 1.30 | 12402 | 1.35 |
| 0.5876 | ... | 9456 | - 43.6 |
| 0.4500 | ... | 7242 | - 81.9 |
| 0.1185 | ... | 1908 | -197.1 |

Volume-specific resistance at 0° C. . . = 12323

Mean temperature-coefficient between

0° C. and 100° C. = .00622

§ 15.

IX. Tin.

This metal is one of the easiest to obtain in a state of purity. Very pure grain tin was melted in a porcelain crucible under paraffin and then pressed warm in a steel press with a hard steel plunger. The pressure was applied by the hydraulic testing-machine in the University College Engineering Laboratory, a pressure of 25 tons on the square inch was sufficient to press out a very uniform wire of pure tin. The measurements were as follows:—

Length = 300 centim. Mean diameter = 0.067505 centim.

Mean sectional area = 0.0035790 sq. centim.

$$\text{Log}_{10} \left[\frac{10^9 \text{ section}}{\text{length}} \right] = 4.0766454 = \log_{10} R.$$

| Rt. | t°. | pt. | pt. | Remarks. |
|--------|-------|-------|--------|-------------------------------|
| 1.9809 | 176 | 23632 | 173.6 | |
| 1.8233 | 146.1 | 21752 | 144.7 | |
| 1.5340 | 91.45 | 18301 | 91.6 | |
| 1.3398 | 52.10 | 15984 | 52.70 | |
| 1.1849 | 18.75 | 14136 | 19.15 | |
| 1.1512 | 12.70 | 13734 | 13.0 | |
| 1.0981 | 1.0 | 13100 | 1.0 | |
| 0.8941 | ... | 10667 | - 44.2 | |
| 0.7366 | ... | 8788 | - 81.9 | In CO ₂ and ether. |
| 0.2849 | ... | 3399 | -197.1 | In liquid oxygen. |

Volume-specific resistance at 0° C. . . = 13048

Mean temperature-coefficient between

0° C and 100° C. = .00440

§ 16.

X. Magnesium.

This wire was prepared for us by Mr. George Matthey, and was free from any admixture of zinc. As the wire was

rather irregular in section no less than sixty measurements of diameter were made in a length of 300 centimetres.

Length = 282 centim. Mean diameter = 0.061496 centim.

Mean sectional area = 0.0029701 sq. centim.

$$\text{Log}_{10} \left[\frac{10^9 \text{ section}}{\text{length}} \right] = 4.0225326 = \log_{10} k.$$

| Rt. | t°. | pt. | pt. | Remarks. |
|--------|-------|------|---------|-------------------------|
| 0.7285 | 142.2 | 7423 | 140.9 | Taken in liquid oxygen. |
| 0.5859 | 98.5 | 5986 | 98.55 | |
| 0.5261 | 60.0 | 5375 | 60.55 | |
| 0.4598 | 18.40 | 4698 | 18.80 | |
| 0.4549 | 17.70 | 4647 | 17.7 | |
| 0.4378 | 13.8 | 4611 | 14.10 | |
| 0.4268 | 0.55 | 4360 | 0.55 | |
| 0.3603 | ... | 3681 | - 40.1 | |
| 0.3430 | ... | 3613 | - 43.3 | |
| 0.2907 | ... | 2970 | - 81.9 | |
| 0.0080 | ... | 1001 | - 197.1 | |

Volume-specific resistance at 0° C. . . 4355 C.G.S. units.

Mean temperature-coefficient between

0° C. and 100° C. 0.00381

§ 17.

XI. Zinc.

This zinc was carefully prepared for us by Mr. G. Matthey, and analysis showed that it contained no impurity except perhaps the very faintest trace of iron.

Length = 100 centim. Mean diameter = 0.025910 centim.

Mean sectional area = 0.00052725 sq. centim.

$$\text{Log}_{10} \left[\frac{10^9 \text{ section}}{\text{length}} \right] = 3.7220140 = \log_{10} k.$$

| Rt. | t°. | pt. | pt. |
|--------|-------|---------|---------|
| 1.9678 | 191.5 | 10375.2 | 188.6 |
| 1.7663 | 148.8 | 9312.8 | 147.3 |
| 1.4995 | 92.45 | 7906 | 92.60 |
| 1.3157 | 51.65 | 6937 | 52.25 |
| 1.1776 | 18.80 | 6209 | 19.20 |
| 1.1480 | 15.55 | 6052.8 | 15.85 |
| 1.1452 | 12.75 | 6038 | 13.05 |
| 1.0951 | 1.05 | 5774 | 1.05 |
| 0.9088 | ... | 4790.6 | - 44.3 |
| 0.7484 | ... | 3346 | - 81.9 |
| 0.2844 | ... | 1499.5 | - 197.1 |

Volume-specific resistance at 0° C. = 5751 C.G.S. units.

Mean temperature-coefficient between

0° C. and 100° C. = 0.00406.

§ 18.

XII. *Cadmium.*

A wire of pure cadmium was made and drawn for us by Mr. George Matthéy, and with it the following observations were made.

Length = 99·8 centim. Mean diameter = 0·070366 centim.

Mean sectional area = 0·0038888 sq. centim.

$$\text{Log}_{10} \left[\frac{10^9 \text{ section}}{\text{length}} \right] = 4\cdot5906854 = \log_{10} k.$$

| R_t . | t° . | ρ_t . | ρ_t . |
|---------|-------------|------------|------------|
| 0·47136 | 182·2 | 18367 | 179·6 |
| 0·42937 | 148·7 | 16731 | 147·2 |
| 0·35525 | 91·10 | 13843 | 91·25 |
| 0·31144 | 51·95 | 12136 | 52·56 |
| 0·28178 | 18·8 | 10980 | 19·20 |
| 0·27021 | 12·75 | 10529 | 13·05 |
| 0·25827 | 1·00 | 10064 | 1·00 |
| 0·21264 | ... | 8286 | - 46·2 |
| 0·17824 | ... | 6945 | - 81·9 |
| 0·07575 | ... | 2952 | -197·1 |

Volume-specific resistance at 0° C. . . = 10023 C.G.S. units.

Mean temperature-coefficient between

0° C. and 100° = ·00419.

§ 19.

XIII. *Lead.*

This wire was pressed from some very pure lead kindly given to us by Mr. G. Matthéy. The lead was prepared by M. Rommelaere in the laboratory of M. Stas in 1884. It was obtained by precipitating lead sulphate from very pure re-crystallized lead nitrate. The lead sulphate was then converted into lead carbonate and reduced to metallic lead. The pure lead when it came into our possession was pressed cold in a steel press under a pressure of 25 tons on the square inch into a very uniform wire.

Length = 200 centim. Mean diameter = 0·065631 centim.

Mean sectional area = 0·003383 sq. centim.

$$\text{Log}_{10} \left[\frac{10^9 \text{ section}}{\text{length}} \right] = 4\cdot2282751 = \log_{10} k.$$

| Rt. | t°. | pt. | pt. |
|--------|-------|-------|--------|
| 2.2252 | 196.1 | 37640 | 193.0 |
| 1.9384 | 142.7 | 32738 | 141.4 |
| 1.6536 | 90.35 | 27971 | 90.55 |
| 1.4650 | 53.00 | 24781 | 53.60 |
| 1.2982 | 18.65 | 21959 | 19.05 |
| 1.2659 | 12.65 | 21413 | 12.95 |
| 1.2080 | 1.0 | 20433 | 1.0 |
| 0.9972 | ... | 16868 | — 44.6 |
| 0.8310 | ... | 14056 | — 81.9 |
| 0.3564 | ... | 6029 | —197.1 |

Volume-specific resistance at 0° C. = 20380 C.G.S. units.

Mean temperature-coefficient between

0° C. and 100° C. = .00411.

§ 20.

XIV. Thallium.

Prof. Ramsay was so good as to prepare for us some pure thallium by reducing in a porcelain crucible with potassic cyanide some pure re-crystallized thallic iodide. The metal was then pressed cold in a steel press into a wire and kept under paraffin oil.

Length = 150 centim. Mean diameter = 0.066970 centim.

Mean sectional area = 0.0035225 sq. centim.

$$\text{Log}_{10} \left[\frac{10^9 \text{ section}}{\text{length}} \right] = 4.3707588 = \log_{10} k.$$

| Rt. | t°. | pt. | pt. |
|--------|------|-------|--------|
| 1.0663 | 98.5 | 24660 | 98.5 |
| 0.9694 | 60.0 | 22006 | 60.55 |
| 0.8259 | 17.2 | 18749 | 17.55 |
| 0.7798 | 0.7 | 17702 | 0.7 |
| 0.6146 | ... | 14433 | — 44.9 |
| 0.5037 | ... | 11829 | — 81.9 |
| 0.2081 | ... | 4888 | —197.1 |

Volume-specific resistance at 0° C. = 17633.

Mean temperature-coefficient between

0° C. and 100° C. = .00398.

§ 21. The resistance-curves of all the above metals are delineated on the chart (see Plate II.) to a suitable scale. An examination of these lines will show that some of them are concave upwards and some concave downwards; those with the most marked curvature being the magnetic metals nickel and iron. The lines cross one another at low temperatures, and hence the order of conductivity of the

metals at very low temperatures is different to their order at ordinary temperatures. At the lowest temperature reached the best metallic conductor is pure copper. It may be remarked that generally the best conductors amongst the pure metals are those that are most sonorous: silver, aluminium, gold, and copper would make good bells, whilst lead, thallium, tin, and palladium, which are the worst conductors, would be unsuitable for this purpose. The metals platinum, palladium, have resistance-curves which have a marked concavity downwards when plotted in terms of Centigrade temperatures; whilst nickel and iron have a considerable curvature in the opposite direction. An examination of this chart will show that the conclusion reached in our former paper is confirmed by these more careful experiments, viz., that the electrical specific resistance of all *pure* metals will probably vanish at the absolute zero of temperature.

§ 22. An examination has also been made of a large number of alloys of known composition, and as the details are too numerous to tabulate in full, we append two Tables (I. and II.) which will show the volume-specific resistance in C.G.S. units of these various alloys at different temperatures stated in terms of platinum temperatures. At the same time the composition of the alloy is given. Also we add a Table III., in which the volume-specific resistance of each alloy is given at 0° C., and the temperature-coefficient at 15° C. The resistance-curves of these alloys are shown in the chart.

Concerning these curves we may draw attention to the fact that the curve of Hadfield's manganese-steel has a remarkably sudden change of curvature at about -40° C. It will be important to investigate the magnetic qualities of manganese-steel at a temperature of from -30° C. to -80° , and see if possible what other physical changes take place at the time when the temperature-coefficient undergoes a rapid change. It will also be seen that the alloy manganin has a curve which has a maximum at 16° C. Hence manganin has a zero temperature-coefficient at 16° C., but a positive coefficient below that temperature, and a negative one above. It is very interesting to note the effects of the various constituent elements in the alloys. An admixture of 6 per cent. of silver with aluminium has a much greater effect in changing the specific resistance than 6 per cent. of copper, whilst 3 per cent. of aluminium has a greater effect still in changing the character of copper. We have collected together into Table IV. the volume-specific resistances of the pure metals, and also their mean temperature-coefficients between 0° C. and 100° C.

TABLE I.—Volume-Specific Resistances (ρ) of Alloys at various Temperatures (ρt).

| Alloy. | In boiling water. | Ordinary temp. | In melting ice. | In CO_2 and ether. | In liquid ethylene. | In liquid oxygen boiling at 760 mm. | In liquid oxygen boiling in vacuum. |
|---|--------------------------------|----------------|-----------------|-----------------------------|---------------------|-------------------------------------|-------------------------------------|
| Platinum-Silver. $P=33$ p. c. $Ag=66$ p. c. | $\rho=32236$ $\rho t=93.25$ | 31723 16.1 | 31573 1.85 | 30864 -81.9 | 30730 -106.1 | 80173 -197.1 | |
| Platinum-Iridium. $Pt=80$ p. c. $Ir=20$ p. c. | $\rho=38271$ $\rho t=93.3$ | 31240 16.1 | 30833 1.8 | 28836 -81.9 | 28347 -106.1 | 26031 -197.1 | |
| Platinum-Rhodium. $Pt=90$ p. c. $Rd=10$ p. c. | $\rho=23943$ $\rho t=92.25$ | 21635 16.15 | 21186 1.75 | 18648 -81.9 | 18065 -106.1 | 15134 -197.1 | |
| Gold-Silver. $Au=90$ p. c. $Ag=10$ p. c. | $\rho=6897$ $\rho t=91.65$ | 6417 16.4 | 6283 0.9 | 5666 -81.9 | 5510 -106.1 | 4817 -197.1 | |
| Aluminium-Silver. $Al=94$ p. c. $Ag=6$ p. c. | $\rho=5686$ $\rho t=92.5$ | 4824 16.25 | 4654 0.9 | 3723 -81.9 | 3477 -106.1 | 2484 -197.1 | |
| Aluminium-Copper. $Al=94$ p. c. $Cu=6$ p. c. | $\rho=3972$ $\rho t=92.4$ | 3087 16.35 | 2911 0.85 | 1960 -81.9 | 1715 -106.1 | 719 -197.1 | |
| Copper-Aluminium. $Cu=97$ p. c. $Al=3$ p. c. | $\rho=9575$ $\rho t=92.25$ | 8990 16.35 | 8860 0.85 | 8210 -81.9 | 8044 -106.1 | 7328 -197.1 | |
| Hadfield's Manganese-Steel. $Mn=12$ p. c. | $\rho=75294$ $\rho t=89.9$ | 68520 16.15 | 67222 1.0 | 61236 -81.9 | 60042 -106.1 | 55414 -197.1 | |
| Hadfield's Nickel-Steel. $Ni=4.35$ p. c. | $\rho=35185$ $\rho t=91.15$ | 30402 16.15 | 29515 0.95 | 24897 -81.9 | 23750 -106.1 | 19468 -197.1 | |
| Manganin. $Cu=84$ p. c. $Mn=12$ p. c. $Ni=4$ p. c. | $\rho=47628$ $\rho t=91.90$ | 47640 16.25 | 47636 0.9 | 47387 -81.9 | 47225 -106.1 | 46825 -197.1 | 45270 -217 |

TABLE II.
Volume-Specific Resistances (ρ_v) of Alloys at various Temperatures (pt).

| Alloy. | In boiling water. | Ordinary temp. | In melting ice. | In CO_2 and ether. | In liquid ethylene. | In liquid oxygen boiling at 760 mm. |
|--|-------------------|----------------|-----------------|----------------------|---------------------|-------------------------------------|
| German-Silver. | $\rho = 90731$ | 30112 | 29967 | 29297 | 29132 | 28317 |
| | $pt = 92.25$ | 16.2 | 0.9 | -81.9 | -106.1 | -197.1 |
| Platinoid. | $\rho = 42884$ | 41938 | 41745 | 40683 | 40413 | 39189 |
| | $pt = 92.85$ | 16.25 | 0.9 | -81.9 | -106.1 | -197.1 |
| Titanium-Aluminium. | $\rho = 4836$ | 4076 | 3898 | 2943 | 2705 | 1656 |
| | $pt = 90.85$ | 16.4 | 0.85 | -81.9 | -106.1 | -197.1 |
| Silverine. Cu = 77 p. c. Ni = 17 p. c. Fe = 2 p. c. Zn = 2 p. c. Co = 2 p. c. | $\rho = 2614$ | 2166 | 2071 | 1582 | 1452 | 909 |
| | $pt = 90.5$ | 16.25 | 0.95 | -81.9 | -106.1 | -197.1 |
| Copper-Nickel-Aluminium. Cu = 87 p. c. Ni = 6.5 p. c. Al 6.5 p. c. | $\rho = 15785$ | 15066 | 14921 | 14132 | 13939 | 13048 |
| | $pt = 91.45$ | 16.35 | 0.9 | -81.9 | -106.1 | -197.1 |

TABLE III.

Volume-Specific Resistances (ρ_0) in C.G.S. units of Alloys at 0° C., and Temperature-Coefficients (α) at 15° C.

| | ρ_0 . | α_{15} . |
|-------------------------------|------------|-----------------|
| Platinum-Silver | 31582 | ·000243 |
| Platinum-Iridium | 30896 | ·000822 |
| Platinum-Rhodium | 21142 | ·00143 |
| Gold-Silver | 6230 | ·00124 |
| Manganese-Steel | 67148 | ·00127 |
| Nickel-Steel | 29452 | ·00201 |
| German-Silver | 29982 | ·000273 |
| Platinoid | 41731 | ·00031 |
| Manganin | 46678 | ·0000 |
| Silverine | 2064 | ·00285 |
| Aluminium-Silver | 4641 | ·00238 |
| Aluminium-Copper | 2904 | ·00381 |
| Copper-Aluminium | 8847 | ·000897 |
| Copper-Nickel-Aluminium | 14912 | ·000645 |
| Titanium-Aluminium | 3887 | ·00290 |

TABLE IV.

Volume-Specific Resistances in C.G.S. Units of Pure Metals at 0° C., and Mean Temperature-Coefficients between 0° and 100° C. The metals in all cases soft and annealed.

| Metal. | ρ_0 . | α_{0-100} . |
|-----------------|---------------|--------------------|
| | C.G.S. units. | |
| Platinum | 10917 | ·003660 |
| Gold | 2197 | ·00377 |
| Palladium | 10219 | ·00354 |
| Silver | 1468 | ·00400 |
| Copper | 1561 | ·00428 |
| Aluminium | 2665 | ·00435 |
| Iron | 9065 | ·00625 |
| Nickel | 12323 | ·00622 |
| Tin | 13048 | ·00440 |
| Magnesium | 4355 | ·00381 |
| Zinc | 5751 | ·00406 |
| Cadmium | 10023 | ·00419 |
| Lead | 20380 | ·00411 |
| Thallium | 17633 | ·00398 |

In conclusion we desire to express our indebtedness to Messrs. J. and D. Morris for the valuable assistance they have given us in the conduct of this research, and in the reduction and graphic description of the numerous observations. We hope, in a future communication, to be able to state the results of similar observations at still lower temperatures.

XXVII. *Experiments with High Frequency Discharges.**By Mr. A. A. C. SWINTON*.*

EMPLYING the apparatus, described in the Philosophical Magazine for February 1893, pages 142-143, for producing electric discharges of high potential and high frequency, the writer has obtained several curious effects.

A flat tin dish filled to a depth of about half an inch with resin oil was electrically connected to one terminal of the high-frequency coil, and a wire connected to the other terminal of the coil was suspended with its extremity about three or four inches above the surface of the oil in the dish.

On putting the coil in action the oil was immediately thrown into a state of violent agitation, the whole surface bubbling and foaming, while the oil gradually crept up the inclined sides of the dish in a well-defined wave and, finally, overflowed.

The effect appears to be due in great measure to the violent repulsion of the particles of air from the suspended wire into the oil.

A similar result was obtained when alcohol was substituted for oil in the dish, but the alcohol immediately caught fire.

With ordinary paraffin oil the effect was the same and the oil caught fire, but only continued to burn so long as the electric discharge, which supplied the additional heat necessary to keep the oil burning, was maintained.

Distilled water was next tried, but with this no agitation of the surface or creeping up of the liquid ensued.

When, however, the suspended wire was lowered so as to touch the surface of the water, an octopus-like figure of bright sparks, about two to three inches in diameter, was formed on the surface of the water, and even when the wire was further lowered so as to dip three eighths of an inch into the water, so that the point of the wire was within one eighth of an inch of the tin dish, the sparks still spread out, leaving the wire at its intersection with the surface of the water, and not at the point of the wire, which, as already mentioned, was within one eighth of an inch of the tin dish.

In fact, it was not until the point of the wire and the dish were brought very nearly into contact that the discharge took place through the water, which it then did with very white sparks producing small explosions, and the sparks on the surface ceased.

As instancing the strong electrostatic effects produced in

* Communicated by the Author.

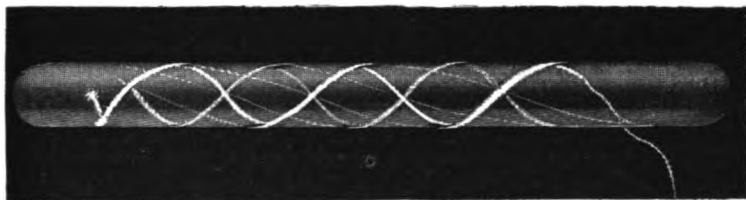
exhausted tubes by high-frequency discharges, the following experiment may be mentioned.

A glass tube, two feet in length and two inches in diameter, exhausted to the extent usual in ordinary incandescent lamps, was supported at its ends on two glass insulating pillars. Outside of the tube were wound three turns of fine copper wire, so as to form a coarse pitch spiral, one end of which was connected to the one pole of the high-frequency coil, the other pole of the coil and the other end of the wire spiral being free.

On starting the coil the wire spiral became luminous, of a dark reddish-purple colour, while there immediately appeared a second bright blue spiral inside the tube, this second spiral keeping exactly half-way between the adjoining turns of the wire. The effect appears to be due to the violent repulsion of the molecules of residual air in the tube, and their bombardment of the tube on the other side.

In the annexed illustration (fig. 1), which is from a photograph of the tube taken when in action in a dark room, the

Fig. 1.



brighter of the two spirals is the wire, which, though to the eye fainter than the bombardment spiral, appears to be the most strongly actinic. The other fine lines are due to reflexion.

The writer has already, in the *Philosophical Magazine* for February (p. 143), shown how it is possible to incandesce the filaments of ordinary electric lamps with high-frequency currents conveyed through the human body, and has given reasons for believing that the quantity of high-frequency current necessary for this purpose must be much smaller than the quantity of continuous current required to produce a similar effect. The following experiment appears to be in further proof of this.

One pole of the coil being connected to one terminal of a 5 c.-p. 100-volt incandescent lamp, two short wires were connected respectively to the other terminal of the lamp and the other pole of the coil and arranged so that their free ends

pointed towards one another, with an intervening space of about a quarter of an inch. In this space was placed a sheet of glass of sufficient size to prevent sparks passing round its edge, the whole arrangement being such as to form a condenser of which the points of the two wires were the conducting plates and the glass the dielectric. On the coil being put in action sparks spread out on each side of the glass so as to cover a circle about three inches in diameter, and the lamp filament immediately became incandescent. The capacity of a condenser of this description must be exceedingly small, even if we consider the acting surface to be represented by the whole area covered by the sparks, consequently, though the frequency is of course enormous, the actual quantity of electricity passing in the circuit must be very minute.

With reference to the heating-effect of very small high-frequency currents, the Hon. Charles A. Parsons has suggested to the writer the following explanation:—

The total heat imparted to a wire is proportional to the average drop in volts between its ends multiplied by the total quantity of electricity passed, *i. e.*, by the number of coulombs. This follows from the usual formulæ

$$E = OR; \text{ Heat} = C^2R = CE.$$

Eliminating time we have

$$\text{Heat} = QE.$$

Now if the volts be increased the quantity required to produce a given number of heat-units is proportionately diminished.

If a 100-volt incandescent lamp taking '6 of an ampere be brought to incandescence by short impulses of current at 10,000 volts average pressure during each impulse, the quantity passed in any considerable time will be only '01 of that which would be required were the 100 volts continuously applied for that time, or will be equal in quantity to '006 ampere continuous current.

This may be expressed in another way. Assuming the resistance constant we have

$$\text{Quantity } Q = \int C dt,$$

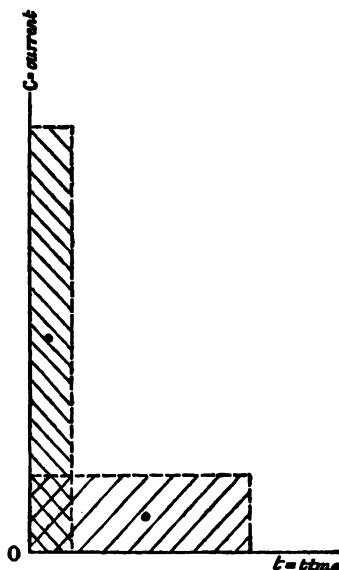
$$\text{Heat varies as } \int C^2 dt.$$

If in fig. 2 the ordinates represent the current, abscissæ time, then the area of the figures $= Q = \int C dt$, the heat $= \int C^2 dt =$ the moment of the figures about the line *Ot*. Figures of peaky

form have much greater moments about the line Ot than figures of the same area of flatter form.

The shaded figures represent equal quantities of electricity. The distances of the centres of gravity from the line Ot repre-

Fig. 2.



sent the heating-powers, which are proportional to the mean volts during each impulse.

The converse, of course, follows, that if the heat be constant the quantity of electricity is inversely proportional to the mean volts during each impulse.

The above is on the assumption that the effects of self-induction are negligible, as is probably the case with small lamp filaments. Where, however, self-induction does exist a similar effect is produced owing to the increased resistance due to this self-induction, as the writer has already suggested.

The same explanation would also apply to the intense heating-effects of sparks, lightning flashes, and other disruptive discharges in which the quantity of electricity is apparently small.

XXVIII. *Experiments on Carbon at High Temperatures and under Great Pressures, and in Contact with other Substances.* By the Hon. CHARLES A. PARSONS*.

THE primary object of these experiments was to obtain a dense form of carbon which should be more durable than the ordinary carbon when used in arc-lamps, and at the same time to obtain a material better suited for the formation of the burners of incandescent lamps.

There were a considerable number of experiments made in which the conditions were somewhat alike, and many were almost repetitions with slightly varying pressures and temperatures. They may, however, be divided into two distinct classes: the first, in which a carbon rod surrounded by a fluid under great pressure is electrically heated by passing a large current through it; the second, in which the liquid is replaced by various substances such as alumina, silica, lime, &c.

The arrangement of the experiment was as follows:—A massive cylindrical steel mould of about 3 inches internal diameter and 6 inches high was placed under an hydraulic press; the bottom of the mould was closed by a spigot and asbestos-rubber packing—similar to the gas-check in guns; the top was closed by a plunger similarly packed; this packing was perfectly tight at all pressures. In the spigot was a centrally bored hole into which the bottom end of the carbon rod to be treated fitted; the top end of the carbon rod was connected electrically to the mould by a copper cap which also helped to support the carbon rod in a central position. The bottom block and spigot were insulated electrically from the mould by asbestos, and the leading wires from the dynamo being connected to the block and mould respectively, the current passed along the carbon rod in the interior of the mould.

The fluid was run in so as to cover the rod completely. The plunger was then free to exert its pressure on the liquid without injuring the carbon. The pressure in the mould was indicated by the gauge on the press.

Experiments. Class I.

Among the liquids tested were benzene, paraffin, treacle, chloride and bisulphide of carbon.

The pressures in the mould during the several experiments were maintained at from 5 to 15 tons per square inch; the

* From the Proceedings of the Royal Society, vol. xlv. Communicated, with an additional note on Diamond Manufacture, by the Author.

initial size of the rod was in all cases $\frac{1}{4}$ inch, and the current from 100 to 300 amperes.

Results.—In some of these experiments a considerable quantity of gas was generated, and the press had to be slightly slackened back during the experiment to accommodate it and maintain the pressure constant.

In all cases there was a soft friable black deposit of considerable thickness on the carbon.

In no case was the specific gravity of the carbon rod increased by this process. There was no change in appearance of the fracture, excepting when chloride of carbon had been the fluid; it was greyer in this case.

The rate of burning of samples placed in arc-lamps was not diminished by the process. Various rates of deposition were tried, but with the same result; and the conclusion seems to be that under very high pressures, such as from 5 to 15 tons per square inch, the deposit of carbon by heat from hydrocarbons, chloride of carbon, bisulphide of carbon, treacle, &c., is of a sooty nature, and unlike the hard steel-grey deposit from the same liquids or their vapours at atmospheric or lower pressures.

Experiments. Class II.

In these experiments the asbestos-rubber packing was omitted, the plunger and spigot being an easy fit in the mould. A layer of coke-powder under the plunger formed the top electrical connexion with the rod.

No. 1. Silver sand or silica was run around the carbon rod, and pressures of from 5 to 30 tons per square inch applied; the rod was usually about $\frac{1}{4}$ inch diameter, and currents up to 300 amperes passed.

Results.—The silica was melted to the form of a small hen's egg around the rod. When the current was increased to about 250 amperes the rod became altered to graphite, the greater the heat apparently the softer the graphite. There was no action between the silica and the carbon, the surface of the carbon remained black, and there were no hard particles in or on the carbon rod.

Other substances, such as an hydrated alumina and mixtures of alumina and silica, gave the same results.

The density of the carbon was considerably increased, in some cases from normal at 1.6 to 2.2 and 2.4; in these cases the carbon appeared very dense, much harder than the original carbon, and about as hard as the densest gas-retort carbon. No crystalline structure was visible.

The specimens were treated with solvents, and there appeared no indication of the surrounding substance having penetrated the rod; the carbon was undoubtedly consolidated by 30 per cent.

In some cases, when the material surrounding the rod was alumina saturated with oil, soft crystals of graphite exuded from specimens that had been kept for some weeks.

No. 2. Pure hydrated alumina, carbonate and oxide of magnesia, and lime all rapidly destroyed the carbon rod, by combining with it, the hydrated alumina forming large volumes of gas of which it appeared to be a constituent. On account of the great diminution of bulk, no analysis was made; the gas issued from the mould explosively at from 10 to 12 tons per square inch. The alumina was found in a crystalline crust, like sugar, around where the rod had been. Hardness that of corundum, almost translucent.

No. 3. The following is the most interesting experiment of the series:—

On the bottom of the mould was a layer of slaked lime about $\frac{1}{2}$ inch thick, over this silver sand 2 inches, then another layer of lime of the same thickness as the former, finally a layer of coke-dust, and then the plunger. With a pressure of from 5 to 30 tons per square inch in the mould, and the carbon of from $\frac{1}{4}$ to $\frac{1}{8}$ inch diameter, currents of from 200 to 300 amperes were passed.

In from 10 to 30 minutes the current was generally interrupted by the breaking or fusing of the rod, or by the action of the lime in dissolving it at the top or bottom. On opening the mould when it had cooled a little, the silica usually appeared to have melted to an egg-shaped mass, and mixed somewhat at the ends with the lime; the surface of the carbon appeared acted on, and sometimes pitted and crystalline in places; silica adhered to the surface, and beneath, when viewed under the microscope, appeared a globular cauliflower-like formation of a yellowish colour, resembling some specimens of "bort"*.

After several days' immersion in concentrated hydrofluoric acid, this formation remained partly adherent to the carbon; on the surface of the carbon was a layer or skin about $\frac{1}{8}$ of an inch thick of great hardness, on the outside grey, the fracture greyer than the carbon, but having a shining coke-like appearance under the microscope.

The powder scraped off the surface of the rod has great hardness, and will cut rock crystal when applied with a piece

* The bort-like powder is not acted on by hydrofluoric and nitric acids mixed.

of metal faster than emery powder. It has, under the microscope, the appearance of bort, the minute particles seem to cling together; they are not transparent as a rule, and though some such particles are found among them, it is not clear that such are hard.

When a piece of the skin has been rubbed against a diamond or other hard body, the projecting or hard portions have a glossy coke-like appearance.

A piece of the skin will continue to scratch rock crystal for some time without losing its edge. It will scratch ruby, and when rubbed for some time against it will wear grooves or facets upon it. When a cut diamond is rubbed on the surface of the skin, it will cut through into the carbon beneath, making a black line or opening about $\frac{1}{4}$ inch long; the facet on the diamond, originally $\frac{1}{32}$ inch diameter, will have its corners evenly rounded, and its polished surface reduced to about one half its original area; the appearance of the edges is as if they had been rubbed down by a nearly equally hard substance.

The subject of the last experiment is scarcely sufficiently investigated to warrant any definite conclusions.

The substance in the several ways it has so far been tested seems to possess a hardness of nearly if not quite the first quality. The minuteness of the particles, which appear more or less cemented together, and are less cohesive after the action of acid, make it very difficult to determine their distinctive features.

The mode of formation is not inconsistent with the conditions of pressure, temperature, and the presence of moisture, lime, silica, and other substances as they appear to have existed in the craters or spouts of the Cape Diamond Mines at some epoch.

From the few experiments that have been made it appears that at pressures below 3 tons per square inch, the deposit does not possess the same hardness, though somewhat similar in appearance.

What part the lime and silica play, whether the former only supplies moisture and oxygen which combine with the carbon, or whether the presence of lime is necessary to the action, is not clear.

We may, however, observe that so far it seems as if the lime and moisture combining with the carbon form a gas or liquid at great pressure, which combining with the silica forms some compound of lime, silica, and carbon, or perhaps pure carbon only, of great hardness.

“Diamond Manufacture.”

With a view of ascertaining the behaviour of carbon at high temperatures and pressures, and in contact with a variety of substances, the above experiments were described in a paper to the Royal Society, June 13th, 1888.

These experiments are of interest from the fact that it was found that under certain conditions of temperature, pressure, and substance in contact with carbon hard particles resembling a diamond were produced, which satisfied all the tests for diamond, so far as they could be applied to particles under $\frac{1}{500}$ inch in length.

At the time of reading the paper a few tests only had been applied to ascertain whether the particles found were veritable diamonds. Shortly after, however, they were examined by Professor Crookes with electrical discharge in high vacua, and appeared to him to behave in a similar manner to diamond powder.

Tests of specific gravity by immersion of the particles in borotungstate of cadmium and iodide of methylene gave a density of 3.3 to 3.5.

The particles appeared to consist of two kinds—one irregular opaque black particles, the other translucent plates resembling flakes of mica, generally of square or irregular shape.

When placed in a cell in iodide of methylene and projected by an electric lantern on the screen they were clearly seen—the plates appeared to be about $\frac{1}{500}$ inch in length and of extreme thinness.

On subjecting the powder to the blowpipe all hard particles disappeared, leaving a yellowish-grey residue, but it should be stated that the powder was not previously levigated to remove the lighter portions, which would account for the residue.

XXIX. *Notices respecting New Books.*

Magnetic Induction in Iron and other Metals. By J. A. EWING, F.R.S., &c. Second issue. ('The Electrician' Series.) 8vo, pp. 346.

PROF. EWING is such a great and well-known authority on Magnetic Induction that it is only necessary to call attention to this second issue of his valuable work to ensure its being in the hands of all who require information upon this important subject.

The book is mostly devoted to a very full and admirable account of the researches of the author and of many other authorities into the behaviour of iron and other metals when subjected to magnetic induction. There is just sufficient theory introduced to enable the

reader to understand the experimental researches, and the book ends with a very interesting account of Prof. Ewing's own modification of Weber's theory of magnetism in magnetic metals which has done so much to advance our insight into the subject. An appendix gives an account of the beautiful curve-tracer which Prof. Ewing has invented and which has already contributed to our knowledge of the effects of rapidly alternating magnetic force on the magnetization of iron, a matter of great interest in connexion with the working of transformers.

In chapter x., when dealing with the magnetic circuit, Prof. Ewing introduces the notion of a magnetic flux and magnetomotive force. It is to be regretted that the idea was not earlier introduced. In the introductory chapter magnetic force and magnetic induction are introduced as more or less similar things, one occurring in a crevasse and the other in a hole. It is to be regretted that Maxwell's notion of induction being analogous to a flux, or displacement, produced by the magnetic force was not the foundation on which the book was built instead of this hole-crevasse definition, which gives little or no insight into the way in which energy is stored in the medium nor how it is that the induced electric force depends on the change of induction and not on the magnetic force, and why on earth induction is continuous and magnetic force is not. Students who are brought up on the hole-crevasse definition require to rearrange all their ideas when they try to develop any sensible theory of what is taking place. This is confessedly the case when our author makes this new departure in introducing the important practical applications of the theory to the dynamo and transformer. That Prof. Ewing so determinedly calls attention to magnetization is a valuable protest against the great temptation to theoretical investigators to simplify their symbols as much as possible. It is, however, most important to call attention continually to the part played by the matter present and to the changes in that matter, all of which are represented by the magnetization thereof.

No practical application has yet been made of the thermodynamic properties of magnetic metals, and this is probably Prof. Ewing's excuse for having given a very interesting and complete account of the effects of temperature without giving an outline even of the accompanying thermodynamic theory. Some part at least of these effects are reversible, for heat-engines can be made to transform heat into work by their means. One of the least worked at departments of both magnetism and thermodynamics is the connexion between them. There is here a large field for the exercise of experimental and analytical skill which has apparently escaped even the searching attention of German seekers after original investigations suitable for doctorate theses.

This subject of thermodynamics and that of the rate at which magnetization takes place are the two departments in which we are at present most obviously ill-informed. They are both seriously complicated by irreversible actions, but this should render their

investigation all the more interesting and keep them for a considerable time in the borderland of theory and experiment from drifting into the clutches of pure theory. It would be very interesting to verify the rough calculation that molecular magnetism ceases to respond to magnetic forces alternating more rapidly than at the rate of about 10^9 per second. In the department of irreversible actions it would be interesting to investigate what is meant by "tapping." What amount and kind of vibration enables the molecules to set themselves? Moving a body gently has no appreciable effect. What is the meaning of a "jar"? There is probably no hard and fast line to be drawn, but these and other borderlands claim investigation by properly qualified experts.

G. F. F.G.

XXX. Intelligence and Miscellaneous Articles.

ON THE ANNUAL AND SEMI-ANNUAL SEISMIC PERIODS. BY CHARLES DAVISON, M.A., MATHEMATICAL MASTER AT KING EDWARD'S HIGH SCHOOL, BIRMINGHAM.

METHOD of Investigation.—The method adopted is similar to that employed by Dr. C. G. Knott in his paper on "Earthquake Frequency."

If $f(\theta)$ be a periodic function of θ , then

$$f(\theta) = a_0 + a_1 \cos(\theta + \alpha_1) + a_2 \cos(2\theta + \alpha_2) + \dots + a_n \cos(n\theta + \alpha_n) + \dots,$$

from which it follows that

$$\begin{aligned} \frac{1}{\pi} \int_{\theta - \pi/2}^{\theta + \pi/2} f(\theta) d\theta &= a_0 + \frac{2a_1}{\pi} \cos(\theta + \alpha_1) - \frac{2a_2}{3\pi} \cos(3\theta + \alpha_2) + \dots \\ &\quad + \frac{2a_n \sin \frac{n\pi}{2}}{n\pi} \cos(n\theta + \alpha_n) + \dots \end{aligned}$$

The latter expression gives the mean value of $f(\theta)$ through an interval $\pi/2$ on either side of θ . From it all terms involving even multiples of θ are eliminated, and the coefficients of all terms after the second are diminished to a greater extent than that of the second.

A definition of the unit earthquake having been adopted, the earthquakes of different districts are classified in half-monthly groups, the first half of February containing fourteen days, and of all the other months fifteen days; and the numbers so obtained are reduced to intervals of equal length (fifteen days). The numbers for the two halves of each month are added together. The mean of the numbers for the six months from November to April gives the six-monthly mean corresponding to the end of January. Six-monthly means are calculated in this way for the end of each month; each mean is divided by the average of all twelve, and the difference between each quotient and unity is multiplied by

the augmenting factor 1.589, in order to obtain the correct value of the ratio $a_1 : a_2$. The curve obtained by plotting these reduced means thus gives special prominence to the annual period, by eliminating the semi-annual period and all those which are fractions of six months, and by diminishing the amplitudes of all other periods with respect to that of the annual period.

In investigating the semi-annual period, the numbers corresponding to the first halves of January and July are added together, and so on; the rest of the method being the same as for the annual period. The result gives special prominence to the semi-annual period by eliminating the annual period, and by eliminating or diminishing the amplitudes of all periods less than six months.

Seismic Periodicity in relation to Intensity.—This discussion is founded on: (1) lists compiled from Mallet's great catalogue, first, of shocks which were so slight as to be just perceptible, and, secondly, of those which were strong enough to damage buildings; (2) Prof. Milne's classification of the Japanese earthquakes of 1885 to 1889 according to the areas disturbed by them; and (3) different catalogues relating to the same district, it being obvious that two such catalogues for the same time can only differ by the omission or inclusion of slight shocks.

The following results are obtained:—(1) In both periods the amplitude is greater for slight than for strong shocks; (2) there appear to be two classes of slight shocks with an annual period, the stronger having their maximum in winter, the weaker in summer; and (3) in the case of the semi-annual period, both strong and slight shocks, as a rule, have nearly the same maximum epochs.

Seismic Periodicity in relation to Geographical Position.—The number of records examined is 62, 45 belonging to the northern hemisphere, 14 to the southern, and 3 to equatorial countries.

1. *Annual Period.*—In every district, and in all but five records (which are obviously incomplete), there is a fairly well-marked annual period. As a rule, different records for the same district agree in giving the same, or nearly the same, maximum epoch. Excluding, however, those which disagree in this respect, we have left 34 records for the northern hemisphere, 9 for the southern, and 2 for equatorial countries. In the northern hemisphere, 4 records give the maximum in November, 16 in December, and 6 in January; in the southern hemisphere, 2 in April, 2 in May, 3 in July, and 2 in August; the end of the month being supposed in each case. As a rule, then, the maximum epoch occurs in winter in both hemispheres. The amplitude of the annual period ranges from 0.05 (New Zealand) to 0.67 (Sicily and Algeria), the average of 57 records being 0.33.

2. *Semi-Annual Period.*—Of the 62 records examined, only 3 fail to show a semi-annual period, the cause of the failure in these cases being no doubt the imperfection of the seismic record. In New Zealand and South-east Australia the maximum epoch generally falls either in February or March and August or September; in North America, as a rule, in March or April and September or

October. But for other regions it does not seem possible as yet to deduce any law. The amplitudes of the semi-annual period range from 0.06 (southern hemisphere) to 0.79 (Mexico), the average value being 0.24.

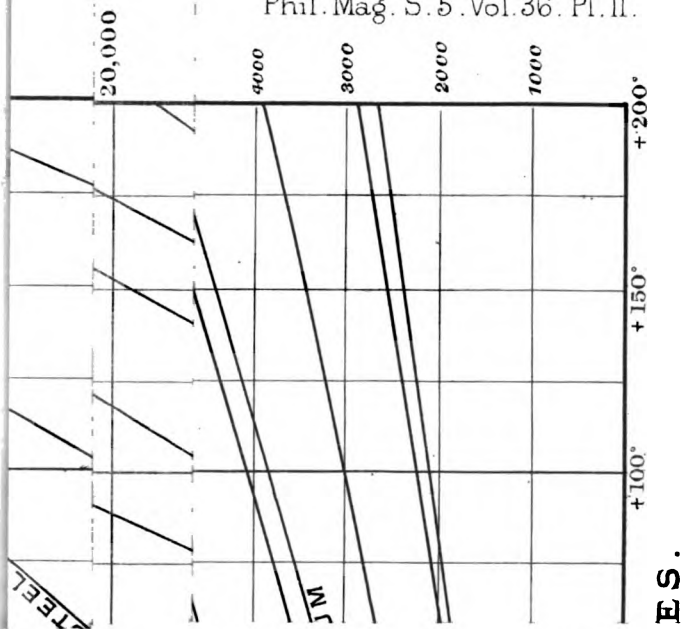
3. In fifteen cases the amplitude of the semi-annual period exceeds that of the annual period. Eleven of these records include the following insular districts, which are among the most well-marked seismic regions in the world :—namely, the Grecian Archipelago, Japan, the Malay Archipelago, New Zealand, and the West Indies. The average amplitude of the annual period in these eleven cases is 0.16, and that of the semi-annual period 0.24; i. e. the average amplitude of the annual period is just half that for all the districts examined, while in the case of the semi-annual period the average amplitudes are the same.

Origin of the Annual Period.—In this, the concluding, section of the paper, an attempt is made to show that the annual change in barometric pressure may be the cause of the annual change in seismic frequency. It would be difficult to prove that such a connexion exists, but reasons are given which seem to render it in some degree probable.

1. The most probable cause of the origin of the majority of non-volcanic earthquakes is the impulsive friction, due to slipping, of the two rock-surfaces of a fault. Now, whatever be the causes of seismic periodicity, it seems probable that they are merely auxiliary, and determine the epoch when an earthquake shall take place, rather than whether there shall be an earthquake at all. Prof. G. H. Darwin has shown that the vertical displacement of the earth's surface by parallel waves of barometric elevation and depression is not inconsiderable, and that it diminishes at first very slowly as the depth increases. Since the fault-slip which produces even a moderately strong shock must be very small, and since the work to be done in such a case is, not the compression of solid rock, but the slight depression of a fractured mass whose support is nearly, but not quite, withdrawn, the annual range of barometric pressure does not seem incompetent to produce the effects observed.

2. Comparisons between the dates of the maximum epochs of the seismic and barometric annual periods are made in §1 of the districts treated in this paper. The seismic maximum approximately coincides with the barometric maximum in 10 districts, and follows it by about one month in 9, and by about two months in 4, districts; the other cases generally admitting of some explanation.

3. In several insular seismic districts, and especially in Japan and New Zealand, the amplitude of the annual period is very small; and, if many of the earthquakes of these districts originate beneath the sea, this should be the case; for, in the course of a year, as the barometric pressure changes, the sea will have time to take up its equilibrium position, and thus the total pressure on the sea-bottom will be unaltered.—*Royal Society*, June 15; *Nature*, xlviii. p. 359.



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Before considering the effect of electrification in increasing the number of water-drops condensed in the jet, it is advisable to consider the effect of the surface-tension of the water-drop, as this is one of the most formidable obstacles in the way of the condensation of the drops.

The pressure of the water-vapour in equilibrium over a spherical drop of water is, as was first shown by Lord Kelvin,

* Communicated by the Author.

† R. v. Helmholtz, Wied. Ann. xxxii. p. 1 (1887).

‡ R. v. Helmholtz & Richarz, Wied. Ann. xl. p. 161 (1890).

§ Bidwell, Phil. Mag. [5] xxix. p. 158 (1890).

|| Aitken, Proc. Roy. Soc. li. p. 408 (1892).

greater than that over a plane surface, the equilibrium vapour-pressure increasing as the curvature of the drop increases: hence, as Maxwell points out in the 'Theory of Heat,' the water will tend to evaporate from a very small drop, which will therefore grow smaller, and the tendency to evaporate will get still greater. Thus the condensation of steam into drops is attended by the difficulty that, even if a small drop happens to get formed, it will, unless the steam around it is excessively supersaturated, begin at once to evaporate. In consequence of the excessive infantile mortality among the drops, the production of fog from water-vapour free from foreign substances is attended by almost insuperable difficulties. This point is illustrated in a very striking way by Aitken's experiments, which show how greatly the deposition of fog is facilitated by the presence of dust. The particles of dust furnish surfaces on which the moisture can be deposited in layers having much smaller curvatures than any layers which could be formed if the drop had no nucleus over which to spread; the dust, in fact, almost annuls the effect of surface-tension by enabling the drop to come into existence without passing through the stages in which surface-tension plays the greatest havoc.

We can apply a more general method of reasoning to the effect of surface-tension, and one which has the merit of being immediately applicable to the consideration of the effect of electrification on the condensation.

The condensation of steam into drops of water is, in consequence of the surface-tension of the water, accompanied by an increase in the potential energy of the system proportional to the area of the water-drop: the ratio of this potential energy to the heat given out by the steam when it condenses to form the drop increases indefinitely as the size of the drop diminishes. Thus the existence of surface-tension causes an increase in the potential energy when the change from steam to water-drop takes place, and will therefore (see J. J. Thomson, 'Application of Dynamics to Physics and Chemistry,' p. 162) tend to retard this change. On the other hand, any circumstance which would cause a diminution in the potential energy when the change from steam to water-drop takes place will facilitate this change. Now an effect of this kind takes place when the water-drops are deposited in an electric field. Water has, as Cohn and Rosa's experiments have shown, a specific inductive capacity of about 76. This value is so large that the diminution due to the water-drop in the potential energy in the electric field is very much the same as if a conductor of the same size were substituted for the water-drop.

In my 'Applications of Dynamics to Physics and Chemistry' I have calculated the change in the vapour-pressure of the water-vapour due to this cause (1) when the electrical field is uniform. If ρ is the equilibrium vapour-pressure when there is no electric field, $\delta\rho$ the increase in ρ due to a uniform electric field of strength H , K the specific inductive capacity of the medium surrounding the drop (that of the drop itself being regarded as infinite), θ the absolute temperature, σ the density of water, and R a quantity defined by the equation

$$p = R\theta\rho,$$

where p is the pressure due to the water-vapour;

$$\frac{\delta\rho}{\rho} = - \frac{3KH^2}{8\pi\sigma R\theta}.$$

The greatest electric field which can exist in air at atmospheric pressure without causing discharge is one where H is about 10^3 in electrostatic measure, for water-vapour at 15°C . $R\theta$ is about 1.3×10^9 ; thus,

$$\frac{\delta\rho}{\rho} = - \frac{1}{10^6} \text{ roughly.}$$

Thus the greatest change is excessively small, and is independent of the size of the drop, so that the uniform field will not be able to counterbalance the effect of surface-tension, since the latter varies inversely as the radius of the drop, and therefore where the drop is very small must be greater than the constant effect due to the electric field.

The case is, however, very different when the electric field, instead of being uniform, is due to a number of charged atoms distributed throughout the volume occupied by the steam. Recent experiments seem to show (see J. J. Thomson, "Electrolysis of Steam," Proc. Roy. Soc. liii. p. 90, 1893) that the charges carried by the atoms of a gas are the same as those associated with them in electrolytic phenomena. To calculate the charge on each atom of hydrogen we require to know the values of some quantities, such as the number of molecules in a gramme of hydrogen, to which we are at present only able to assign approximate values; for the purpose of illustration we may take Richarz's value for the charge on an atom of hydrogen, viz. 12.9×10^{-11} in electrostatic units.

In my 'Applications of Dynamics to Physics and Chemistry,' I give, on page 167, the following expression for the increase $\delta\rho$ in the pressure of the aqueous vapour in equilibrium

with a drop of water of radius a placed with its centre at a distance f from a charge e of electricity:—

$$\frac{\delta\rho}{\rho} = -\frac{1}{R\theta K} \frac{e^2}{\sigma - \rho} \left\{ \frac{3}{2f^2(f^2 - a^2)} + \frac{a^2}{f^2(f^2 - a^2)^2} \right\} \frac{1}{4\pi},$$

where the notation is the same as in the case of the uniform field. In order to see what kind of effect the electrification may produce, let us suppose that the distance between the electrified point and the surface of the drop is very small compared with the radius of the latter. In this case we may put $f - a = x$, where a/x is large. Making this substitution, we have approximately

$$\frac{\delta\rho}{\rho} = -\frac{1}{R\theta K} \frac{e^2}{\sigma - \rho} \frac{1}{16\pi} \frac{1}{a^2 x^2}.$$

The effect due to surface-tension is

$$\frac{\delta\rho}{\rho} = \frac{2}{\sigma - \rho} \frac{T}{a} \frac{1}{R\theta}.$$

Comparing these two expressions, we see that while the effect due to surface-tension varies as $1/a$, the contrary effect due to electrification with a given value of x varies as $1/a^2$: thus, for very small drops, the effect of the electrification to promote condensation will overpower the effect of the surface-tension to prevent it. The electrification thus overpowers the cause which, under ordinary circumstances, puts an end to the existence of the small drops.

To compare the effects of electrification with those of surface-tension, let us consider the case when the charge is as small as it is possible for it to be, *i. e.*, when $e = 12.9 \times 10^{-11}$ approximately, which is the charge on a single atom; let us suppose that this charge is so close to the drop that $x = 10^{-9}$: then, assuming that T for a small drop has the same value as for a large one, $T = 75$. Thus the effect of electrification will overpower that of surface-tension if

$$a < \frac{(12.9)^2 \times 10^{-22}}{16\pi \times 150 \times 10^{-18}},$$

i. e., if $a < 2 \times 10^{-6}$. Thus for drops of less than this size the equilibrium vapour-pressure will be less than that over a flat surface free from electrification, so that the precipitation of the water-vapour into these small drops will be facilitated. The preceding numbers apply to the case when the charge of electricity is as small as possible. If we had a larger

charge of electricity, the formation of larger drops would be facilitated.

I am not aware that any measurements have been made which show directly the influence of electrification on the vapour-pressure; indeed, the preceding expressions for the magnitude of this effect show that such measurements would be hardly realizable. I think, however, that some of the effects of electrification on a steam-jet which were first observed by R. v. Helmholtz, and subsequently by Shelford Bidwell and Aitken, may be explained by these principles. When a jet of steam emerges from a nozzle into dust-free air, there is very little condensation to be observed within half an inch or so of the nozzle. If, however, an electrode from which electricity is escaping is placed close to the origin of the jet, dense condensation occurs right up to the nozzle, the jet appearing coloured, the colour apparently being due to the scattering of light by a great number of very small particles of water, the diameter of the particles being very small compared with the wave-length of light.

An easy method of showing the effect of electrification is to produce the steam by boiling water in a flask, through the cork of which a piece of glass tubing shaped like a T is placed. The steam passes through the vertical portion of the T, then diverges into two horizontal streams, one to the right the other to the left, these emerge into the air through fine nozzles. Two platinum electrodes are fused through the horizontal tube, the one to the right, the other to the left of its junction with the vertical tube, so that one electrode is in the path of the jet to the right, the other in that of the one to the left. These electrodes are connected to the terminals of an induction-coil; when the coil is not working the jets close to the nozzles are almost invisible, but as soon as the coil is turned on copious condensation occurs right up to the nozzles, the jets looking brownish by transmitted light. The condensation in the jet which has swept past the negative electrode is denser than that in the one which has gone past the positive.

The considerations we have previously given of the effect of electricity on the vapour-pressure are in accordance with the behaviour of the jet when under the influence of electricity. The electricity which escapes into the gas is carried by charged atoms of the gas, and since in the region immediately around these atoms there will be a very intense electric field there will be a tendency for the steam to deposit in these regions. Thus around these charged atoms there will be very small drops of water; these drops scatter the blue light

more than the red, so that the jet when seen by transmitted light will appear reddish.

The preceding explanation does not require dust to be present originally in the air, so that it would apply to cases where, if it were not for the electrification, there would be no condensation; when, however, dust is present, it is probable that the effects due to electrification arise from several causes. Thus if the air contained excessively fine dust, so fine that the drops of water deposited on it were too small to be permanent, the electricity, by causing these fine particles to strike together, might produce particles large enough to act as nuclei for the water-drops. Again, as Aitken has pointed out (*Proc. Roy. Soc. li. p. 408, 1892*), the electricity would tend to prevent fine drops from coalescing to form larger ones, it would thus tend to keep the number of individual drops very large, and so promote dense condensation. Even when the drops could be formed without the agency of electricity, the effect of electrification will be to increase the number of the drops, since, as we have seen, it diminishes their tendency to evaporate.

Another very remarkable phenomenon discovered by R. v. Helmholtz, the laws of which are described in two papers, one by himself (*Wied. Ann. xxxii. p. 1*) and another published after his death, describing further results which he had obtained in conjunction with Richarz (*Wied. Ann. xl. p. 161*), is the effect on the steam-jet of chemical action going on in its neighbourhood. They found that chemical action in the neighbourhood of the jet affected it in much the same way as a discharge of electricity, i. e., it produced dense condensation. The chemical actions they investigated were of the most varied character, they included the combination of NO and O, the splitting up of N_2O_4 into NO_2 , the combination of hydrochloric acid and ammonia to form sal-ammoniac,—these all affected jets not only of steam, but also of the vapours of alcohol and of formic and acetic acids.

If we suppose that the forces which hold the atom together in the molecule are electrical in their origin, and that in a diatomic molecule one atom has a positive, the other an equal negative charge, the preceding explanation for the effect of electrification on the jet will also apply in this case. When the molecule of a gas is in its ordinary state, it contains one atom positively electrified, another one negatively electrified. In the region outside the molecule, the equal and opposite charges will produce forces which tend to neutralize each other, so that the electric field round the molecule will be much less intense than that round a single charged atom: hence, though the

field round the latter may be sufficient to cause condensation, that round the molecule may not.

Now, suppose that molecules which enter into chemical combination come together and form a new compound, requiring a rearrangement of the atoms, then while the chemical combination is going on an atom in one of the original molecules must leave its old partner and find a new one; there will therefore be an interval in which it is comparatively free to move: that is, the forces on it must be small compared with what they were previously. In other words (assuming that the forces on it are electrical) this atom is in a very weak electric field: there is thus in the region just round the atom nothing to counterbalance the effect of the charge on the atom, so that in this region we shall get an electric field almost as strong as if the atom were dissociated. In this way the chemical combination may produce very strong local electric fields and thus promote the condensation of the steam.

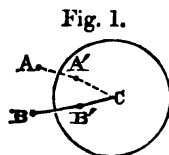
If we apply considerations similar to those previously used for the steam-jet to the case where only a small quantity of aqueous vapour is present, we arrive at results which seem to throw light on the effect of water-vapour in promoting chemical action, the enormous influence of which has been shown in the most striking way by the experiments of Dixon, Pringsheim, and Baker. R. von Helmholtz, in the paper already referred to, found that no white fumes were produced when dry ammonia and hydrochloric acid were mixed together; he attributed this to the sal-ammoniac being unable to condense in the absence of nuclei. Baker, who has recently observed the same phenomenon, attributes the absence of the white fumes to the absence of sal-ammoniac in any form.

In the case of the steam-jet the region in which condensation took place was supersaturated with steam, so that when once the drops were formed they would continue even though the chemical action had ceased to take place. If the region were not supersaturated, then we might have sufficient tendency to produce condensation whilst the chemical combination was proceeding, but the drops would evaporate as soon as the chemical action was over. If, however, drops of water were formed during the chemical action, they would react on this chemical action. For suppose we have two substances A and B in the gaseous state present along with a little vapour, let us suppose that the molecules of A and B act on each other so as to tend to alter the arrangement of the atoms in the molecules (it is not necessary for the success of the explanation that a new compound should be produced by this direct action of the molecules of A and B); then in consequence of this

tendency to rearrangement among the atoms some of them will become comparatively free, when, as before, the electric field in the region around them will become stronger, and consequently the tendency of the steam in that region to condense will increase. Thus this incipient chemical combination may produce throughout the region occupied by the gas minute drops of water. When, however, these are formed, it is not difficult to see that we have the possibilities for very great increase in the chemical action. These drops offer surfaces on which the molecules of A and B may condense; thus a portion of A and B, instead of being in the gaseous state, exists as layers condensed on the drops. Experience shows that combination usually goes on more freely between gases condensed on a surface than between the same gases when free. If, however, the drop acted in this way, it would not seem necessary that the substances condensing into drops should be water, or any other solvent; we might expect this kind of effect to be produced by mercury-vapour, for example. The drop might, however, promote chemical combination in another way, in which the combination, instead of being merely a surface-effect, proceeded through the volume of the drop,—the drop and the gases condensed on its surface behaving like a Grove's gas-battery, the drop itself acting as the electrolyte, and the combination taking place by means of electrolytic process in the drop; the drop itself thus playing an active part in assisting the combination. The view that chemical action is electrolytic in character has been repeatedly urged by Prof. Armstrong. The ability of water to further this kind of action would be much greater if, while the chemical action was going on, the water existed in the liquid than it would if the water were in the gaseous state.

If we take the view that the forces which hold the atoms in the molecule together are electrical in their origin, it is evident that these forces will be very much diminished when the molecule is close to the surface of, or surrounded by, a conductor or a substance like water possessing a very large specific inductive capacity.

Thus let AB represent two atoms in a molecule placed near a conducting sphere, then the effect of the electricity induced on the sphere by A will be represented by an opposite charge placed at A' the image of A in the sphere. If A is very near the surface of the sphere, then the negative charge at A' will be very nearly equal to that at A. Thus the effect of the sphere will be practically to neutralize the



electric effects of A; as one of these effects is to hold the atom B in combination, the affinity between the atoms A and B will be almost annulled by the presence of the sphere. Molecules condensed on the surface of a sphere will thus be practically dissociated. The same effect would be produced if the molecules were surrounded by a substance possessing a very large specific inductive capacity. Since water is such a substance it follows, if we accept the view that the forces between the atoms are electrical in their origin, that when the molecules of a substance are in aqueous solution the forces between them are very much less than they are when the molecule is free and in the gaseous state.

Since water-vapour produces so great an effect on chemical combination, the question suggests itself whether its presence has any considerable influence on the passage of electricity through gases, as there is strong evidence that this phenomenon is closely connected with chemical changes taking place in the gas through which the discharge passes. A very large number of experiments have been made on the effect of the presence of aqueous vapour on the potential-difference required to produce a spark of given length in air. The results of these experiments are very discordant; it is not necessary, however, for our purpose to enter into any detailed discussion of the greater part of them, as they for the most part consisted of determinations of the effect of increasing the amount of aqueous vapour in air already damp, whereas the most striking result produced by aqueous vapour on chemical combination is not so much the difference between the behaviour of gases which contain a moderate amount of aqueous vapour and those which contain still more, as the difference between gases which are damp and those from which as much moisture has been removed as is possible with the means at our control.

The only investigation with which I am acquainted where the gases were comparable in dryness with those used in the chemical experiments previously referred to is one by Warburg* on the cathode fall, *i. e.* the potential-difference between the cathode and the luminous boundary of the dark space in nitrogen and hydrogen, (1) when the gases are very dry, (2) when the gases are damp. Warburg found that the cathode fall in dry nitrogen is greater than that in damp, while in hydrogen the reverse is the case, the cathode fall in the damp gas being greater than that in the dry. The dif-

* Wied. *Ann.* xxxi. p. 545 (1887).

ference between the dry and damp gas is much greater in the case of nitrogen than in that of hydrogen, the cathode fall with platinum electrodes for damp nitrogen being 260 volts, that for the dry 410 volts, while in damp hydrogen the cathode fall was 352, in dry 329. As far as these experiments go, the presence of aqueous vapour seems to retard the passage of the electric discharge through hydrogen; they relate, however, to the special case when a steady discharge is passing through hydrogen at a low pressure. The effect, however, is comparatively small, and it seemed worthy of trial whether this comparatively close agreement between the properties of the damp and dry gas was maintained under other circumstances of the discharge and under higher pressures. For this reason I have compared the potential-differences required to produce a spark of given length through damp and dry hydrogen at different pressures. I prepared the hydrogen in the same way as Warburg, using a Kipp's apparatus with zinc and dilute sulphuric acid (the proportions of acid to water being about 1 to 8 by volume). The gas thus obtained was passed through an alkaline solution of potassium permanganate, which, as well as the acid in the Kipp, had previously been well boiled so as to expel the air. Leduc has shown that this simple process gives very good hydrogen. The hydrogen was allowed to run for some hours through the tubes in which the sparks were to pass so as to expel the air. I was never able, however, to get rid of the last trace of air, as I always found that the gas, if allowed to bubble for some time through an alkaline solution of pyrogallie acid, produced a brown coloration.

In order to compare the spark-potential through the damp and the dry gas two bulbs communicating with each other were filled with hydrogen, each of these bulbs contained a pair of equal electrodes placed at the same distance apart; the distance between the electrodes varied in different experiments, ranging from about $\frac{1}{2}$ to $\frac{1}{10}$ of a millimetre. One of these bulbs, which we shall call A, was furnished with a train of two drying-tubes, one containing stick caustic potash, the other phosphorus pentoxide, the hydrogen passed through these tubes on its way to the bulb A. The phosphorus pentoxide had been previously heated to redness in an earthenware crucible, the crust at the top was taken off, and only the residue, which acquired a granular structure as it cooled down, was used; the floor of the bulb A was also covered with this pentoxide. The hydrogen in the other bulb (B) had passed straight into the bulb after bubbling through the permanganate solution, and no drying materials

were placed in this bulb in order that the hydrogen in it might remain damp. After the bulbs had been filled the communication between them was shut off, and the system left for some time, so that the hydrogen in A might get thoroughly dry. The time required to dry the gas, in order to produce the effects described below, varied from two days to a week; and I am disposed to think that the drying effect of the pentoxide was not exhausted, even after the gas had been in contact with it for these periods.

The following is the arrangement I adopted for measuring the potential-difference required to produce a spark. The difference of potential was produced by a battery of 600 small storage-cells giving a potential-difference of about 1200 volts; the ends of this battery are connected with C and D (fig. 2), which are two terminals sunk into a slate bed; these terminals are connected by a very large resistance formed by drawing on the slate with graphite a semicircle passing through CD with its centre at E; a metal arm turning about E makes movable contact with the graphite semicircle, the contact with the graphite being made by a metal roller. E and D are connected respectively with the terminals of one of Lord Kelvin's vertical electrostatic voltmeters; they are also connected with the spark-gap in one of the hydrogen bulbs, the terminals of the spark-gap are portions of large brass spheres carefully cleaned. By moving the sliding arm EF from D towards C, the difference of potential at the spark-gap was gradually increased until a spark passed, the electrometer indicating the corresponding difference of potential.

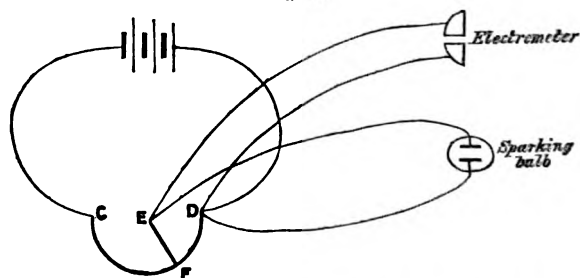
Observations were made both on the dry and the damp hydrogen. As the result of these observations it appears that there are well-marked differences in the appearance and behaviour of the wet and the dry hydrogen. In the first place the colour of the discharge is different, that of the damp hydrogen being much more purplish than that of the dry. The most striking difference however, which I observed was the remarkable disproportion between the potential-difference required to produce the first spark through the dried hydrogen and that which is sufficient to cause one to follow it immediately afterwards. I found that whether the gas was damp or dry the potential-difference required to produce the first spark was always greater than that required to make another follow it after a small interval. In the damp gas, however, the difference was comparatively small, averaging about ten per cent.; *i. e.* after the arm EF had been moved from D until a spark passed through the damp hydrogen, it could not be moved back by more than about $\frac{1}{10}$ of

its distance from B without the spark ceasing. Baillé*, who observed the same effect in air that presumably was not exceptionally dry, gives the following numbers:—

| Sparking-distance in cm. | Pot.-diff. for 1st spark. | Pot.-diff. for spark immediately following. |
|-----------------------------|------------------------------|--|
| ·05 | 14·52 | 12·85 |
| ·10 | 23·98 | 22·64 |
| ·15 | 33·19 | 32·49 |
| ·20 | 40·86 | 39·47 |
| ·25 | 49·34 | 44·53 |
| ·30 | 53·13 | 48·58 |
| ·35 | 59·43 | 50·85 |

Thus the effect in the damp gas, though well marked, is not very large. In the dry gas, however, this effect attains quite abnormal proportions, the potential-difference required to produce the first spark being often more than twice that required to maintain it when once started; indeed, in some cases when the gas had been dried for a very long time the whole electromotive force of the battery was not sufficient to initiate the discharge, and I had to start it by means of an induction-coil: when a spark had been sent through the gas by this means, an electromotive force of about $\frac{1}{3}$ of that which had previously been applied to it without effect was sufficient to send a second spark through the gas, if the interval between the first and second sparks was not more than a minute or two. If a much longer interval than this

Fig. 2.



was allowed to elapse the gas recovered its original strength. The experiments were made as follows:—The arm EF (fig. 2) was slowly moved in the direction of increasing potential until a spark was seen to pass through the dry hydrogen; as

* *Annales de Chimie et de Physique*, [5] xxix. p. 181 (1883).

soon as the spark passed the potential between the electrodes in the dry gas indicated by the voltmeter fell to a fraction of the value it had just before the spark passed; the arm EF could now be moved back in the direction of diminishing potential until it had often got more than halfway back to D before the sparks ceased. The readings of the voltmeter showed that the spark-potential did not vary greatly during this time from the value it had fallen to immediately after the passage of the first spark. Another point to be noticed was that the first spark did not begin as a small faint spark, but, on the contrary, when it did appear it was exceedingly bright, as if the gas under the large electromotive force had been in an unstable condition, and when, by some chance, it did break down it did so with a rush. When, however, after the spark had been started it was made to disappear by moving the arm EF in the direction of diminishing potential, the spark disappeared gradually and was exceedingly faint just before it ceased to be visible. The sudden fall of potential at the spark-gap which took place just after the passage of the first spark was often fatal to the carbon resistance. The reason of this is that the difference of potential between C and D is constant; if the revolving arm is in the position EF when the spark passes and the potential suddenly falls, as it does in these experiments, to less than half its original value, the loss in potential between F and D must be compensated by a gain in potential between C and F. In consequence of this increase in the potential-difference the current along C and F is increased; in the actual experiments this increase in the current was so great that the carbon between C and F continually took fire after the first spark passed, and broke the connexion of the battery with the spark-gap. In the later experiments this inconvenience was avoided by inserting a very large resistance between C and the hydrogen-bulb.

The experiments showed that while the potential at which the sparks stopped when the arm EF was moved in the direction of diminishing potential was nearly constant, and was little influenced by the time the spark had been passing, or by whether the sliding arm had only just been moved far enough to start the sparks or whether it had been carried far past this point; on the other hand, the potential at which the sparks began was very variable, and changed apparently capriciously from time to time. Again, the potential-difference when the sparks stopped was not very different for the damp and dry gases (the voltmeter was not sensitive enough to measure small differences in the electromotive force); on the other hand, the potential-differences when the

sparks began in the dry did not seem to have any relation with the corresponding potential for the wet gas.

These experiments seem to show that hydrogen very carefully dried is able to sustain a much greater potential-difference than when containing a small amount of moisture, but that the gas when under this exceptional potential-difference is apparently in an unstable state, as when a spark is once started the potential difference at once sinks to about the normal value in a gas containing traces of moisture, and this potential-difference is sufficient to produce a second spark, if this follows the first after only a short interval.

It should be observed that the hydrogen has to be very carefully dried in order to show these effects; it is not sufficient, for example, merely to allow the gas to bubble through sulphuric acid, gas so treated seems to differ little in its electrical properties from undried gas.

In order to see whether the effect produced by the presence of water-vapour was due to the behaviour of the vapour itself under electric strain, or to some interaction between the vapour and the hydrogen, a bulb was prepared which contained nothing but water and its vapour. This bulb was made by completely filling a bulb provided with electrodes with distilled water, which was vigorously boiled for about $2\frac{1}{2}$ hours until only a fraction of the water was left; this bulb was sealed off whilst the water was vigorously boiling. On making experiments similar to those described above, the ratio of the difference of the potential required to produce the first to that required to produce the second spark was found to be at least as great as in the case of hydrogen. In the water-bulb the pressure was only that due to the vapour of water at about 18° C. We get the same difference in the behaviour of the first and second sparks if we use a mixture of gases instead of a single gas such as hydrogen. I find that the effect is very marked in air that has been carefully dried and filtered.

These experiments show that the behaviour of a gas with reference to the passage of a spark through it is analogous to that of a vapour condensing to a liquid, to the freezing of a liquid, or to the deposition of crystals from a saturated solution. In all these cases, when no foreign substances are present the temperature can be lowered far below the boiling-point, the freezing-point, or the temperature at which deposition takes place respectively without the corresponding change of state taking place. When, however, foreign substances which can act as nuclei are present, the change of state takes place at a definite temperature. In the case of

the discharge through gases we have seen that when a foreign substance (water-vapour) is present the potential-difference which the gas can support without discharge taking place is approximately steady, but that when the gas is carefully dried it can support an abnormally large potential-difference, though when once the discharge has started the potential-difference falls at once to its normal value. The passage of the spark produces a supply of modified gas which persists for some time after the discharge has stopped; during the existence of this gas the potential-difference required for sparking has only its normal value, whether water-vapour be present or not. If, however, the gas is allowed to rest for a sufficient time for this modified gas to return to its original condition, the gas can again sustain an abnormally great potential-difference before a luminous discharge passes. This result shows, I think, that the decrease in the potential-difference required to produce a luminous discharge through dry hydrogen immediately after a spark has passed through the gas is not due to the formation of water-vapour by the combination of hydrogen with a trace of oxygen that may have been present, for if it were the diminution in electric strength would be permanent instead of temporary.

The most obvious explanation of the great difficulty which the fresh spark experiences in passing through a dry gas is that the passage of a luminous discharge through a gas is preceded by the condensation of some of its molecules into a more complex state of aggregation, and that when these aggregates are formed the potential-difference the gas can support has its normal value; further, that the formation of these aggregates requires or is very much facilitated by the presence of nuclei of a foreign substance, and that when these nuclei are removed or very much diminished in number the gas can sustain an abnormally large potential-difference without its molecules condensing into these aggregates, the gas, however, being in an unstable condition, for as soon as condensation takes place the potential-difference sinks to its normal value. On this view the discharge through a gas does not consist in tearing the atoms of a single molecule apart, but rather in tearing atoms from off a complex aggregate of molecules. This view explains the difficulty which I have alluded to elsewhere ('Notes on Electricity and Magnetism,' p. 193), that on the electrical theory of chemical combination the force holding the atoms together in a single molecule is enormously greater than the force tending to separate them in an electric field strong enough to produce discharge.

XXXII. *On the Refractive Indices of Liquid Nitrogen and Air.* By Professors LIVEING and DEWAR*.

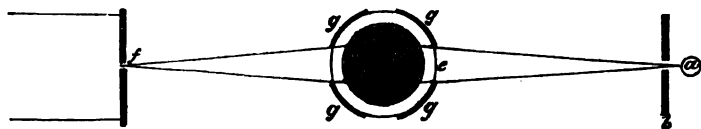
IN describing the spectrum of liquid oxygen (Phil. Mag. August 1892) we gave a determination of the refractive index of that liquid, and of those of some other liquefied gases, for the D ray. The difficulty of such measurements was mainly the mechanical one of making a hollow prism with truly wrought faces which would stand the extreme cold, and not convey heat from outside to the liquid within so fast as to keep it in rapid ebullition. The dispersion of the light by the bubbles passing through the liquid is sufficient to blur the image of the source of light, so much as to render an accurate measurement of the dispersion almost impossible. And though by diminishing the pressure, and thereby causing a rapid evaporation, the liquid oxygen can be reduced to -200° C. and then remains quite tranquil, this was found to be of little avail; for it involved the use of a hollow prism capable of holding rather a large bulk of liquid, and of sustaining variation of pressure as well as of temperature without leaking. We had therefore to turn our attention to other methods of determining refractive indices. Of these the method used by MM. Terquem and Trannin seemed to be most free from difficulty, and had been successfully employed in the determination of the refractive index of liquid oxygen by Olszewski and Witrowski, whose value of the index agreed with ours found with a prism (*Bull. de l'Académie de Cracovie*, 1891). This method consists in suspending in the liquid two plates of glass with a thin layer of air between them, and measuring the angle of incidence at which the chosen ray suffers total reflexion at the surface of the air.

In this method it is not necessary that the vessel containing the liquid should have truly wrought surfaces, and the problem seemed to be simplified by the discovery of Professor Dewar that the amount of heat communicated to the vessel of liquid by radiation is trifling compared with that communicated by convection. He has found that in a double glass vessel of any form, where the outer and inner vessels are separated by even a narrow vacuous space, liquid oxygen can be kept for a great length of time open to the air. Such a liquid, filtered through ordinary filter-paper to remove solid carbonic acid, remains quite tranquil and beautifully transparent of pale blue tint, but of course evaporating

* Communicated by the Authors.

gradually and generally giving off streams of small bubbles. These bubbles do not sensibly mar the distinctness of an object viewed through the liquid with the naked eye, but we found that they did make a difference when a telescope was used. As we had no double vessels with a vacuous interval except such as were either globular or cylindrical, we had to meet the difficulty that such vessels when filled with liquid acted like lenses, and lenses which were irregular and full of striations. In fact we could not by the use of compensating lenses obtain in the field of a small telescope any tolerably definite image of a candle, or other source of light, seen through the vessel. At the same time, when the pair of glass plates above mentioned was suspended in the liquid and a sodium-flame viewed with the unaided eye through them, the extinction of the light, when the plates were turned to the position for total reflexion, appeared quite sudden. The use of a telescope, however, showed that the rays forming the blurred image, even when limited by screens to the central part of the globe, or cylinder, really passed in so many different directions that they were by no means all extinguished at once.

In order to avoid the necessity of observing any image at all through the liquid, we made use of it simply as a lens to concentrate the light observed on the slit of a spectroscope. The arrangement is shown in the annexed figure, where *a* is the source of light, either a sodium-flame or an electric spark, *b* a screen with a slit, *c* the outer glass vessel, *d* the



inner glass vessel with the liquid, *e* the pair of glass plates immersed in the liquid, *f* the slit of a spectroscope, *g g* screens of black paper on the outside of the outer vessel.

The distances of *a* and *f* were arranged so that they should be conjugate foci when the vessel was midway between them. The pair of glass plates were separated by a narrow ring of thin filter-paper, thoroughly wetted with white of egg and allowed to dry. They were held in a small brass clip attached to a rod, which formed the prolongation of the vertical axis of a theodolite, by which the angle through which they were turned was measured. They were adjusted

Phil. Mag. S. 5. Vol. 36. No. 221. Oct. 1893. Z

to the vertical plane by observing with a cathetometer the reflexion at their surface of a flame which had been adjusted to lie in the same horizontal plane as the centre of the plates.

The arrangement was tested by the measurement of the refractive indices for the D ray of water, and of alcohol, contained in one of the same double vessels which were subsequently used for liquefied gases. The results were satisfactory, though, owing to the irregular form of the vessels and the striæ on their surfaces, the extinction of the light on turning the plates was hardly so sudden as we had expected. The angles were measured by first turning the pair of plates in one direction until the ray under observation was extinguished, and reading the position on the graduated circle of the theodolite, and then turning the pair of plates in the opposite direction until the ray was again extinguished, and again reading the circle. The angle between the two positions was the double of the angle required, namely the angle of incidence for total reflexion of the ray observed.

Trying the apparatus with liquid oxygen, we found that the extinction of the ray was less sudden than with either water or alcohol. This was no doubt caused by the small bubbles which scattered the light. Nevertheless it was easy to trace the passage of commencing obscurity from the blue to the red end of the spectrum as the plates approached the positions of total reflexion. Hence approximate values could be found for the indices of refraction for the D ray. In this way liquid oxygen gave $\mu=1.226$, a slightly larger value than that we had found with the prism, which was 1.2236.

We then tried liquid nitrogen at its boiling-point of -190°C . at atmospheric pressure. The mean of six readings gave for the D ray $\mu=1.2053$. The nitrogen was not quite pure, but contained about 5 per cent. of oxygen, notwithstanding that it had been passed before compression through a stack of tubes filled with copper and heated red-hot. We have no reason to think that this small quantity of oxygen had any other effect than to increase the index of refraction by a very small quantity.

Liquid air was next observed. The mean of ten measurements gave for the D ray $\mu=1.2062$. With liquid air the evaporation of the more volatile nitrogen goes on more rapidly than that of the oxygen, so that the liquid gradually gets stronger in oxygen, until at last there is little but oxygen left. Liquid nitrogen is colourless, and the colour of liquid air is merely that of the oxygen it contains.

Further observations with the liquid air when a good deal of nitrogen had evaporated gave $\mu=1.215$; and when still more nitrogen had gone we found $\mu=1.218$.

The value found above for the refractive index of liquid nitrogen at -190° C. when it has, according to Prof. Dewar's observations, a density of .89, gives for the refraction-constant

$$\frac{\mu-1}{d}=0.225, \text{ and for the refraction-equivalent } 3.153.$$

If we take Mascart's value for μ for gaseous nitrogen, namely 1.000298, and the density at .001256, we get for

$$\frac{\mu-1}{d} \text{ the value } 0.237, \text{ which agrees well with that found}$$

above for the liquid.

If we take Lorenz's formula $\left(\frac{\mu^2-1}{\mu^2+2}\right)\frac{P}{d}$ for the constant of refraction, we get the value for liquid nitrogen 0.1474 and the refraction-equivalent 2.063.

Brühl's values of the refraction-equivalent, derived from observations of the compounds, were for free nitrogen 2.21, for nitrogen as in nitrous oxide 2.27 at least, and for nitrogen as in ammonia 2.50. These numbers are somewhat larger than ours, but not a great deal. On the other hand, Gladstone's value for nitrogen in nitriles was 4.1 and in ammonia 5.1, which differ a good deal from our value, using Gladstone's formula, namely 3.153.

We hope in a short time to give the refractive indices for other rays, and the dispersive powers, of liquid oxygen, nitrogen, and air at a temperature as low as -200° C.

August 14, 1893.

XXXIII. *On the Piezo-electric Property of Quartz.*

By LORD KELVIN *.

§ 1. **I**N the present communication we are not concerned with the six-sided pyramid, or planes parallel to the sides of a six-sided pyramid, seen at the ends of a quartz crystal farthest from the matrix. Nor are we concerned with the transverse striæ generally seen on the sides of the prism, which are undoubtedly steps (probably having faces parallel to the faces of the terminal pyramid) by which the prism becomes less in transverse section from the matrix outwards.

* Communicated by the Author, having been read before Section A of the British Association at its recent meeting in Nottingham.

We shall consider only a perfect, and therefore an unstriated, hexagonal prism. The sides of the prism may be, and generally are, unequal in nature but the angles are all exactly 120° . For simplicity of reference to the natural crystalline form, I shall suppose the prism to be equilateral, which it may be in nature, as well as equiangular, which it must be. Thus we have three planes of symmetry, which for brevity I shall call the diagonal planes, being planes through the opposite edges of the prism. We have also three other planes of symmetry, which for brevity I shall call the normal planes, being planes perpendicular to the pairs of parallel faces.

§ 2. In the brothers J. and P. Curie's beautiful instrument for showing their discovery of the piezo-electric property of quartz, a thin plate of the crystal about half a millimetre thick, I believe, is taken from a position with its sides parallel to any of the three normal planes of symmetry; its length perpendicular to the faces of the prisms, and its breadth parallel to the edges. The sides of this plate are, through nearly all their length, silvered by the chemical process to render them conductive *, and are metallicaally connected with two pairs of quadrants of my quadrant electrometer. I find that the effect is also well shown by my portable electrometer; the two sides of the quartz plate being connected respectively to the outer case, and the insulated electrode, of the electrometer. In an instrument which has been made for me under Mr. Curie's direction, the silvered part of the plate is 7 centimetres long and 1·8 broad. A weight of 1 kilogramme hung upon the plate placed with its length vertical causes one side to become positively electrified and the other negatively.

§ 3. A plate parallel to any one of the three normal planes of symmetry will give the same result, of transverse electro-polarization; but a plate cut parallel to any one of the three diagonal planes of symmetry will give no result in the mode of experimenting described in § 2. But with its sides unsilvered it would, if properly tested, show positive electrification at one end and negative at the other when stretched longitudinally, as we see by the hypothesis and theoretical considerations which I now proceed to explain; and by § 11 below without any hypothesis.

§ 4. Electric eolotropy of the molecule, and nothing but electric eolotropy of the molecule, can produce the observed phenomena. The simplest kind of electric eolotropy which

* For a description and drawing of this part of their instrument, given by the brothers Curie, see Appendix to the present paper.

I can imagine is as follows :—For brevity I shall explain it in relation to the chemical constitution which, according to present doctrine, is one atom of silicon to two atoms of oxygen. The chemical molecule may be merely SiO_2 for silica in solution or it may consist of several compound molecules of this type, grouped together : but it seems certain that, in crystallized silica (in order that the crystal may have the hexagonally eolotropic piezo-electric property which we know it has) the crystalline molecule must consist of three SiO_2 molecules clustered together ; or must be *some* configuration three atoms of silica and three double atoms of oxygen combined. As a ready and simple way of attaining the desired result, take a cluster of three atoms of silicon and three double atoms of oxygen placed at equal distances of 60° in alternate order, silicon and oxygen, on the circumference of a circle.

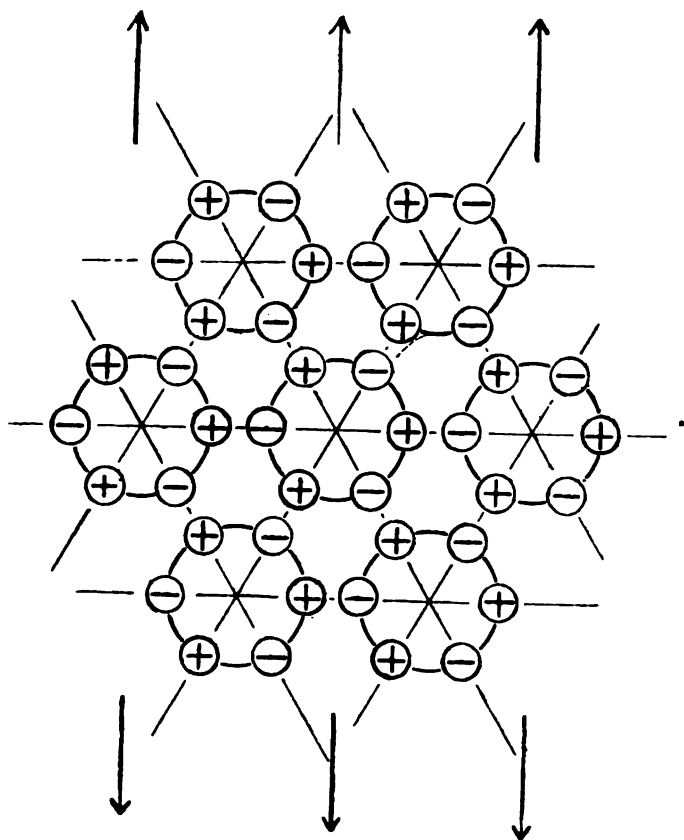
The diagram, fig. 1, shows a crystalline molecule of this kind surrounded by six nearest neighbours in a plane perpendicular to the axis of a quartz crystal. Each silicon atom is represented by + (plus) and each oxygen double atom by — (minus). The constituents of each cluster must be supposed to be held together in stable equilibrium in virtue of their chemical affinities. The different clusters, or crystalline molecules, must be supposed to be relatively mobile before taking positions in the formation of a crystal. But we must suppose, or we may suppose, the mutual forces of attraction (or chemical affinity,) between the silicon of one crystalline molecule and the oxygen of a neighbouring crystalline molecule, to be influential in determining the orientation of each crystalline molecule, and in causing disturbance in the relative positions of the atoms of each molecule, when the crystal is strained by force applied from without.

§ 5. Imagine now each double atom of oxygen to be a small negatively electrified particle, and each atom of silicon to be a particle electrified with an equal quantity of positive electricity. Suppose now such pressures, positive and negative, to be applied to the surface of a portion of crystal as shall produce a simple elongation in the direction perpendicular to one of the three sets of rows. This strain is indicated by the arrow-heads in fig. 1, and is realized to an exaggerated extent in fig. 2.

This second diagram shows all the atoms and the centres of all the crystalline molecules in the positions to which they are brought by the strain. Both diagrams are drawn on the supposition that the stiffness of the relative configuration of atoms of each molecule is slight enough to allow the mutual

attractions between the positive atoms and the negative atoms of neighbouring molecules to keep them in lines through the

Fig. 1.

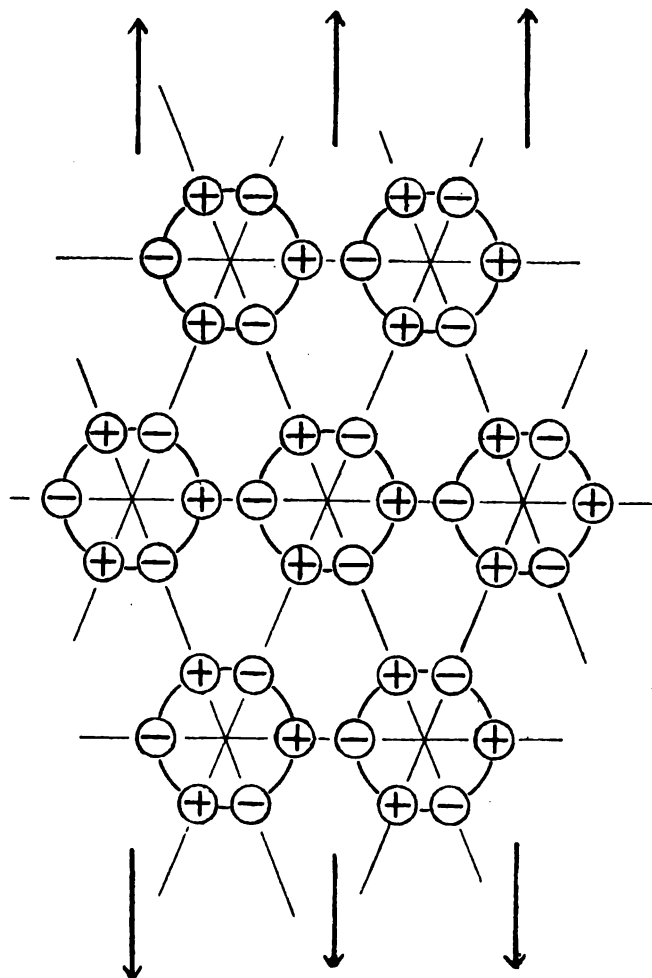


centres of the molecules, as fig. 1 shows for the undisturbed condition of the system, and fig. 2 for the system subjected to the supposed elongation. Hence two of the three diameters through atoms of each crystalline molecule are altered in direction, by the elongation, while the diameter through the third pair of atoms remains unchanged, as is clearly shown in fig. 2 compared with fig. 1.

§ 6. Remark, first, that the rows of atoms, in lines through the centres of the crystalline molecules, perpendicular to the

direction of the strain, are shifted to parallel positions with distances between the atoms in them unchanged. Hence the atoms in these rows contribute nothing to the electrical effect.

Fig. 2.



But, in parallels to these rows, on each side of the centre of each molecule, we find two pairs of atoms whose distances are diminished.

§ 7. This produces an electric effect which, for great distances from the molecule, is calculated by the same formula as the magnetic effect of an infinitesimal bar-magnet whose magnetic moment is numerically equal to the product of the quantity of electricity of a single atom into the sum of the diminutions of the two distances between the atoms of the two pairs under consideration. Hence, denoting by N the number of crystalline molecules per unit bulk of the crystal; by b the radius of the circle of each crystalline molecule; by q the quantity of electricity on each of the six atoms or double-atoms, whether positive or negative; by \S the change of direction of each of the two diameters through atoms which experience change of direction; and by μ the electric moment* developed per unit volume of the crystal, by the strain which we have been considering and which is shown in fig. 2; we have

$$\mu = Nq \cdot 4b \S \cos 30^\circ = N \cdot 2b q \S \sqrt{3} \quad . \quad (1).$$

It is of course understood that \S is a small fraction of a radian.

§ 8. To test the sufficiency of our theory, let us first consider quantities of electricity which probably, we may almost say certainly, are present in the atoms in nature.

Instead of the silicon atoms marked + in the diagram let us substitute globes of polished zinc; and instead of the double-oxygen atoms marked — let us substitute little globes of copper well oxidized (polished copper, heated in air till it becomes of a dark slate-colour). Let us suppose all the six atoms of each compound molecule to be metallically connected, and all the molecules insulated from one another. We are not concerned with conceivable permeation of electricity by conductance through the crystal; and therefore we must suppose the total quantity of electricity on each crystalline molecule to be zero. Let the circle of each compound molecule in the diagram be a real exceedingly thin stiff ring of metal, no matter what kind of metal, and let each of the six atoms be a bead (a perforated spherule), whether of zinc or of copper, moving frictionlessly on it. Thus we have, in idea, a working model of an electrically eolotropic crystalline molecule.

§ 9. I have found by experiment† that the difference of

* I do not know if this designation has hitherto been used. I introduce it with precisely the same significance relatively to electricity, as the well-known "magnetic moment" in reference to magnetism.

† 'Electrostatics and Magnetism,' § 400, and experiments not hitherto published, by another method.

potentials in air, beside a polished surface of zinc and an oxidized surface of copper, is about $\cdot 004$ of a C.G.S. electrostatic unit, provided the zinc and copper are metallically connected. Hence, if α be the radius of each spherule, we have approximately $q = \cdot 002 \times \alpha$; because we shall suppose for simplicity that, except the infinitely thin ring on which it is movable, no spherule has any metal within a distance from it of less than two or three times its diameter. Let now $N = 10^{21}$ per cubic centimetre; and let b be a quarter of $N^{-\frac{1}{3}}$, that is to say, $b = \frac{1}{4} \times 10^{-7}$ of a centimetre. Lastly, to give definiteness to our example, let $\alpha = \cdot 2 \times b$. Equation (1) becomes

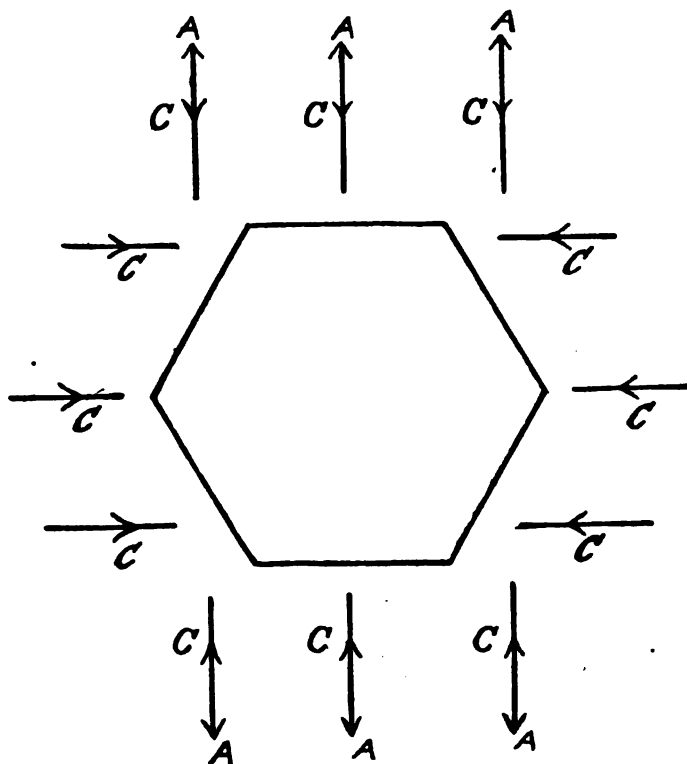
$$\mu = 866 \S \dots \dots \dots (2).$$

§ 10. From the admirable statement of Messrs. Curie of the result of their measurements quoted in the Appendix of the present paper, I find that a stretching force of 1 kilogramme per square centimetre, in their experiment described in § 2 above, produces an electric moment of $\cdot 063$ C.G.S. electrostatic reckoning per cubic centimetre of the crystal. Thus about $\frac{1}{5}$ of a C.G.S. unit of electric moment per cubic centimetre is produced by 5 kilogrammes per square centimetre of stretching force; and this, according to equation (2), requires \S to be $1/2598$, which is an amount of change of direction among atoms quite such as might be expected in pieces of crystal stretched by forces well within the limits of their strength. A rough mechanical illustration of the theory of electric atoms to account for the piezo-electric properties of crystals, is presented in an electrically working model of a piezo-electric pile, submitted to Section A in a separate communication at the present meeting of the British Association.

§ 11. I shall now prove, without any hypothetical assumption, the statement at the end of § 3 above. Consider first a simple elongation perpendicular to one of the three pairs of parallel sides of the hexagon in fig. 3, as indicated by the arrow-heads, A A A A A A, in fig. 3. Superimpose now two equal negative elongations, one of them in the direction of the original elongation, and the other in a direction perpendicular to it. These negative elongations, indicated by the twelve arrow-heads marked C, constitute a condensation equal in all directions; which produces no change on the electrical effect of the first simple elongation. But it leaves us with a simple negative elongation in the direction perpendicular to that of the original positive elongation; which therefore alone produces the same effect as that which was produced by the original one alone. Thus we see that if

elongations perpendicular to the three pairs of parallel sides produce electro-polarizations with electric axis in each case

Fig. 3.

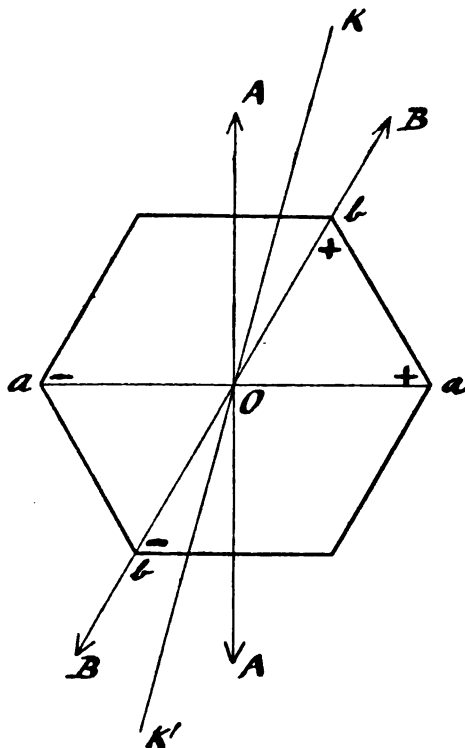


perpendicular to the line of elongation, equal elongations in the directions of the diagonals produce electric polarizations equal to those, but having their axes along the lines of elongation instead of perpendicular to them.

§ 12. Consider now two simple elongations in the direction shown by the arrow-heads *A* in fig. 4. These two elongations produce electro-polarizations with axes and signs indicated by *aa* and *bb* respectively. The resultant of our present two simple elongations is clearly a dilatation equal in all directions in the plane of the diagram, compounded with a single simple elongation in the line *K'OK*, bisecting the angle between them,

and of magnitude equal to $\sqrt{3}$ times the magnitude of each of them, as is easily proved by the elementary geometry of strain. Hence an elongation in the direction $K'OK$ does not produce zero of electric effect. In fact, there are no "Axen fehlender

Fig. 4.



Piëzo-electricität." The three axes so-called by Röntgen* are the lines of elongation in Curie's experiment. Without sufficient consideration it might be imagined that the six lines corresponding to $K'OK$ in fig. 4 are "Axen fehlender Piëzo-electricität." On the contrary, elongation in the line $K'OK$ produces an electro-polarization which is the resultant of the equal polarizations indicated by aa and bb , and which, as it bisects the angle bOa , is in a line inclined at 45° to $O'K$ the line

* Wiedemann's *Annalen*, 1883, xviii. p. 215.

of the elongation. In fact simple elongation in any direction perpendicular to the principal axis of a quartz crystal produces electro-polarization ; and it is only when the lines of two simple elongations are coincident with one another, or are perpendicular to one another, that the resultant of their electro-polarizations can be zero.

§ 13. A most important contribution to our knowledge of the electric properties of crystals has been made by Röntgen*, and by Friedel and J. Curie†, in independent investigations proving that the irregular electrifications of the corners of quartz crystals, which had been observed by many observers as consequences of heatings and of returns to lower temperatures, are wholly due to mechanical stresses developed by inequalities of temperature in different parts of the crystal. Those phenomena are therefore truly *piezo-electric*, and are not at all "pyro-electric" like the electric property of tourmaline which is due to change from one temperature to another, each the same throughout the crystal. The very important and interesting discovery thus made by Röntgen and by Friedel and Curie, is, as they have pointed out, available also to explain the perplexing and seemingly paradoxical statements regarding positive and negative electrifications of corners and hemihedral facets at opposite ends of the four long diagonals of crystals of the cubic class, and of cubes of boracite, which had been given by previous observers and writers, and which have not yet disappeared from elementary treatises on Mineralogy, Electricity, and General Physics.

APPENDIX.

[Extract from a pamphlet published by the "*Société Centrale de Produits Chimiques*," 42, 43 Rue des Écoles, Paris.]

Quartz Piézo-Électrique de MM. J. et P. CURIE.

Cet instrument se compose essentiellement d'une lame de quartz, sur laquelle on exerce des tractions à l'aide de poids placés dans un plateau. Cette action mécanique provoque un dégagement d'électricité sur les faces de la lame.

* "*Ber. der Oberrh. Ges. f. Natur- und Heilkunde*, xxii." [of date, between December 1882, and April 30, 1883].

† "*Bulletin de la Société Minéralogique de France*, t. v. p. 282, decembre 1882."

And *Comptes Rendus* of French Academy of Sciences, April 30, and May 14, 1883.

La lame de quartz *abc* (fig. 5) est montée solidement à ses extrémités dans deux garnitures métalliques H et B. Elle est suspendue, en H, à la partie supérieure ; elle soutient, à son tour, en B, à la partie inférieure, le plateau et les poids, par l'intermédiaire d'une tige munie de crochets.

L'axe optique du quartz est dirigé horizontalement, suivant la largeur *ab* de la lame. Les faces sont normales à un des axes binaires (ou axes électriques) du cristal. On exerce les tractions dans le sens vertical, c'est-à-dire dans une direction à la fois normale à l'axe optique et à l'axe électrique.

Les deux faces de la lame sont argentées.

On a tracé dans l'argenture de chaque face deux traits fins, *mn*, *m'n'*, qui isolent des montures la plus grande partie de la surface. On recueille l'électricité, sur ces portions isolées, à l'aide de deux lames de cuivre faisant ressort (*rr*, *rr*), qui viennent s'appuyer sur les deux faces et communiquent avec les bornes de l'appareil.

Lorsque l'on place des poids dans le plateau, on provoque le dégagement de quantités d'électricité égales et de signes contraires sur les deux faces de la lame.

Lorsque l'on retire les poids, le dégagement se fait encore, mais avec inversion des signes de électricité dégagée sur chaque face.

La quantité d'électricité dégagée sur une face est rigoureusement proportionnelle à la variation de traction *F*.—On a

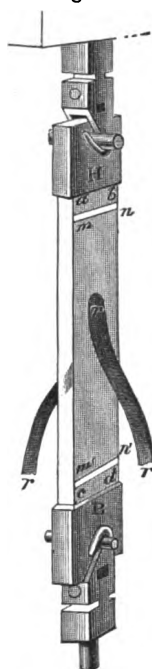
$$q = 0.063 \frac{L}{e} F.$$

L est la longueur *nm'* de la partie argentée utilisée. *e* est l'épaisseur de la lame.

F est exprimé en kilogrammes et *q* est donné en unités C.G.S. électrostatiques.

On a donc avantage, lorsque l'on veut avoir des effets très sensibles, à prendre une lame longue dans le sens de la traction et peu épaisse dans le sens de l'axe électrique. La

Fig. 5.



dimension parallèle de l'axe optique n'a pas d'influence sur la quantité d'électricité dégagée*.

La lame de quartz est placée dans une enceinte métallique desséchée. Cette cage métallique, toutes les pièces métalliques de l'instrument et les montures de la lame de quartz sont mises en communication permanente avec la terre.

Le modèle no. 2 comporte encore un commutateur et un levier qui sert à soulever les plateaux et les poids. Nous reviendrons plus loin sur le rôle de ces organes.

XXXIV. *On a Piezo-electric Pile.* By Lord KELVIN †.

THE application of pressure to a voltaic pile, dry or wet, has been suggested as an illustration of the piezo-electric properties of crystals, but no very satisfactory results have hitherto been obtained, whether by experiment or by theoretical considerations, so far as I know. Whatever effects of pressure have been observed have depended upon complex actions on the moist, or semi-moist, substances between the metals, and electrolytic or semi-electrolytic and semi-metallic conductances of these substances. Clearing away everything but air from between the opposed metallic surfaces of different quality, I have made the piezo-electric pile which accompanies this communication. It consists of twenty-four double plates, each 8 centimetres square, of zinc and copper soldered together, zinc on one side and copper on the other. Half a square centimetre is cut from each corner of each zinc plate, so that the copper square is left uncovered by the zinc at each of its four corners. Thus each plate presents on one side an uninterrupted copper surface, and on the other side a zinc surface, except the four uncovered half square centimetres of copper. A pile of these plates is made, resting one over the other on four small pieces of india-rubber at the four copper corners. The air-space between the opposed zinc and copper surfaces may be of any thickness from half a millimetre to 3 or 4 millimetres. Care must be taken that there are no minute shreds of fibre or dust bridging the air-space. In this respect so small an air-space as half a millimetre gives trouble, but with 3 or 4 millimetres no trouble is found.

The lowest and uppermost plates are connected by fine

* Double breadth, with doubled stretching force, would give double quantity.

† Communicated by the Author, having been read before Section A of the British Association at its recent meeting in Nottingham.

wires to the two pairs of quadrants of my quadrant electrometer, and it is generally convenient to allow the lowest to lie uninsulated on an ordinary table and to connect it metallically with the outer case of the electrometer.

To make an experiment, (1) connect the two fine wires metallically, and let the electrometer-needle settle to its metallic zero.

(2) Break the connexion between the two fine wires, and let a weight of a few hektogrammes or kilogrammes fall from a height of a few millimetres above the upper plate and rest on this plate. A startlingly great deflexion of the electrometer-needle is produced. The insulation of the india-rubber supports and of the quadrants in the electrometer ought to be so good as to allow the needle to come to rest, and the steady deflexion to be observed, before there is any considerable loss.

If, for example, the plates are placed with their zinc faces up, the application of the weight causes positive electricity to come from the lower face of the uppermost plate and deposit itself over the upper surface of plate and weight, and on the electrode and pair of quadrants of the electrometer connected with it.

XXXV. *On the Oscillations of Lightning Discharges and of the Aurora Borealis.* By JOHN TROWBRIDGE*.

[Plate III.]

IT is well known that when air is subjected to a sudden strain at the moment of an electrical discharge, it acts like glass or a similar elastic solid and is cracked in zigzag fissures; indeed the resemblance between the ramifications of lightning and the seams produced in plates of glass by pressure has been commented upon by various observers. Photographs of powerful electric sparks lead one to conclude that a discharge of lightning makes way for its oscillations by first breaking down the resistance of the air by means of a disruptive pilot spark: through the hole thus made in the air the subsequent surgings or oscillations take place.

In examining the early photographs, taken by Fæddersen, of electric sparks, one perceives indications that the electric oscillations tend to follow, for at least some hundred-thousandths of a second, the path made by the pilot spark; and there are observers who believe that by rapidly moving a camera they

* Communicated by the Author.

have obtained evidence that successive discharges of lightning follow the same path. Professor Lodge has protested, with reason, against the conclusions drawn by the method of "waggling" the head or a camera; for the movement of the head or the camera certainly requires the hundredth of a second, while the discharge of lightning is over in less than one hundred-thousandth of a second.

The method of photographing electrical discharges by means of a revolving mirror seems to be the best method of studying the behaviour of air which is suddenly subjected to the electric strain. I have, therefore, examined this behaviour with more powerful means than those employed by previous observers; and it may be well to recall here the fact that in lightning discharges high electromotive force and great quantity are frequently combined in a very short interval of time. The modern alternating machine, therefore, and the device of the transformer enable one to study the character of lightning more successfully than is possible by means of an electrical machine; for both the electromotive force of a discharge and its quantity can be adjusted over a wide range. In my study of this subject I employed an alternating machine which gave three hundred to four hundred alternations per second and a current of from fifteen to twenty amperes; and the photographic apparatus was the same as that which was used in my investigation on the damping of electrical oscillations on iron wires*. By means of a step-up transformer and an oil-condenser, discharges of high electromotive force and great quantity could be readily obtained. The method of the excitation of a Ruhmkorff coil or transformer by means of an alternating dynamo—due originally to Spottiswoode—has placed in the hands of the experimenter, as I have said, powerful means of studying electric discharges; and by the device of an air-blast or other contrivance for obtaining a quick break in the continuity of the electrical discharges, Professor Elihu Thompson has shown how sparks of many feet in length can be obtained. Since my object, however, was to study the photographs of sparks having both great electromotive force and great quantity, I limited myself to discharges of about two centimetres. Figs. 1 and 2 (Pl. III.) are reproductions from untouched negatives—not enlarged; and ten to twelve oscillations can be counted on each photograph. The interval between the oscillations is about one hundred-thousandth of a second: and it will be noticed that the electrical discharge follows exactly the same path in the air for three hundred-thousandths of a second. During

* Phil. Mag. Dec. 1891.

this length of time every sinuosity in the pilot spark is exactly reproduced. I employed terminals of tin; and in fig. 1 it will be noticed that a mass of melted and vaporized tin remained suspended in the air for at least three hundred-thousandths of a second before it was dissipated in a comet-like tail. During the three hundred-thousandths of a second, therefore, the air remained passive while the electrical oscillations took place. During this time it is fair to conclude that the heat produced by the passage of the spark was not sensibly conducted away. If conduction of heat had taken place, the electrical resistance of the air-path would have been sensibly altered and the path of the discharge would have changed in form. Here, I think, we have an interesting limit to the time it takes atmospheric air to respond to the phenomenon of heat-conduction.

I have said that the discharges I employed were powerful both in regard to electromotive force and to quantity. Iron terminals one quarter of an inch in diameter were raised to a white heat by the continuous passage of the sparks, and globules of the melted metal were formed. When the sparks were passed through the secondary of a transformer of about thirty secohms of self-induction, three fifty-volt Edison lamps placed in multiple in the primary of the transformer, which consisted of merely two layers of thick copper wire, were lighted to full incandescence. The spark from two large glass condensers of 5000 electrostatic units each, excited by an electrical machine, and passed through the secondary of the same step-down transformer, barely raised a six-volt lamp in the primary to a red heat. The study of the efficiency of step-down transformers in thus transforming transient currents of high potential to transient currents of low potential and comparatively large current, enables one to obtain an estimate of the high potential of lightning and of the current which accompanies its fall of potential. Thus, if C denote the current in the lightning discharge and E the electromotive force, C' and E' the corresponding quantities in the circuit of the step-down transformer, A the efficiency of the transformer, we shall have

$$C'E' = ACE.$$

The element of time and the mode of transformation must be considered in any estimate of the amount of energy in a lightning discharge. Although a powerful spark of electricity from two Leyden jars, each of 5000 electrostatic units, is incapable of decomposing water directly, yet by its passage through the secondary of a step-down transformer it can

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decompose the water with great evolution of the gases ; and it is probable that an ordinary discharge of lightning of a few hundred feet in length could light for an instant many thousand incandescent lamps if it were properly transformed by means of a step-down transformer. Indeed the ringing of electrical bells and the melting of electrical fuses are of common occurrence during thunderstorms, and manifest the energy of lightning discharges. During a recent visit at a summer hotel which was lighted by incandescent lamps, I was much interested to observe that the lamps blinked at every discharge of lightning, although the interval which elapsed between the blinking and the peals of thunder showed that the storm was somewhat remote. This effect was doubtless due to induction produced by the surgings of the lightning discharges ; for in heavy and in near discharges the lights were completely extinguished, although no fuses were burned. My observation of this effect of lightning upon electric-light circuits also leads me to believe that the system of carrying electric-light wires along gas-fixtures, where both electric-light fixtures and gas fixtures are combined, is fraught with great danger. If there is any leakage of gas at the joints of the gas-pipes or through a sand-hole in the casting of the pipes, electric sparks, arising through resonance effects or from the ordinary passage to earth of an electric charge brought into the building by the electric wires, can ignite the escaping gas and produce a mysterious conflagration. Such a conflagration was averted in the hotel in which I noticed the blinking of the lamps only by the careful scrutiny of an attendant, who noticed a jet of gas from a pin-hole in the gas fixtures impinging on the woodwork. During the storm a minute electric spark had ignited the escaping gas. Electric-light wires and gas-pipes should never be contiguous, for no lightning-guard or protector can ensure that minute sparks, due in some cases to resonance effects, may not arise.

The study of the disruptive or oscillatory discharge of lightning is closely related with that of the brush-discharge and the phenomenon of the *Aurora Borealis* ; for the disruptive discharge ceases to be disruptive after a few hundred-thousandths of a second—as figures 1 and 2 show—and partakes of the nature of a brush-discharge. The zigzag fissure in the air disappears, and only the spark-terminals glow. Recent experimenters have exhibited as a marvel the lighting of a vacuum-tube through the human body by grasping one terminal of a suitable transformer with one hand and by holding the vacuum-tube in the other hand. It must be remembered, however, that the lines of force proceed from

the hand which holds the vacuum-tube through the air and the walls or floor of the room to the other terminal of the transformer. We can change this brush-discharge or luminosity at either terminal of a transformer into a disruptive discharge by lessening the distance between the terminals or by increasing the electromotive force.

I am fully aware that the oscillatory discharge of lightning with its disruptive effects, which I have noted, its permanence of path, and the fading of the disruptive discharge into the brush-discharge or mere luminosity at either of the spark-terminals, is a far simpler phenomenon than the luminosity produced in rarefied tubes; for in the latter phenomenon we have the dissociation and impact of molecules, and we must consider all the problems of atomic motion in addition to those of the oscillatory nature of electrical waves. It is not my purpose to enter into a consideration of the molecular movements involved in oscillatory discharges in vacuum-tubes; but having discussed some of the general features of discharges of electricity in air at the ordinary pressure, I shall endeavour to trace the connexion between such discharges and the phenomenon of the Aurora Borealis. To my mind the luminosity in a vacuum-tube held in one hand while the other hand grasps the terminal of a Ruhmkorff coil closely represents the phenomenon of the Northern Lights; for we have in this case a discharge of electricity from a higher level to a lower through a rarefied medium. Although, in this paper, I restrict myself to a discussion of the general relations between discharges of lightning and the phenomenon of the Aurora Borealis, and do not enter into a study of the molecular movements excited by electrical discharges, I am impelled to devote a few words to the subject of the stratified discharge, and to show that it has no connexion with the oscillatory discharge of electricity such as we are considering. The distances between the stratifications do not seem to be changed by modifying the period of forced oscillation given to the transformer over a wide range. I have produced them by employing an interrupter of a Ruhmkorff coil giving from sixty to one hundred vibrations per second, and by the use of two alternating machines—one giving 300 to 400 alternations per second, and the other 900 to 1000 alternations per second. The distances between the stratifications do not seem commensurate with the rate of alternation of the exciter of the transformer. On the other hand, the distance between the stratifications is not dependent upon the amount of self-induction in the circuit. In one case quadrupling the self-induction reduced the distance between the stratifications

one half. This reduction was due not to the increased self-induction but to the increased resistance ; for the introduction of a water-resistance of some megohms diminished in a similar manner the distance between the stratifications. In short, I could not discover any connexion between the law $t = 2\pi \sqrt{LC}$ and the phenomenon of stratification.

I have said that we can pass by insensible gradations from the condition of the brush-discharge to that of the disruptive discharge. By intercalating a non-inductive water-resistance and a vacuum-tube between the terminals of a suitable transformer, we can exactly imitate the phenomena observed when the vacuum-tube is held in one hand while the other hand grasps one terminal of the transformer. In this case the water-resistance takes the place of the resistance of the air of the room. The intensity of the discharge being thus much diminished, one can readily study various manifestations of stratification which may, perhaps, be termed transitory stratifications in distinction to the stationary wave-like forms observed in narrow tubes. The transitory stratifications can be produced at will by touching suitable points of a vacuum-tube with the finger or by connecting such points with the ground. Such stratifications are stationary as long as the ground connexion is maintained, and are independent of the rate of the alternating machine which excites the transformer. It is evident that the condenser action of the vacuum-tube plays an important part in this phenomenon. In observing the striæ and columnar form of the waving of the light excited in this manner in vessels or tubes filled with rarefied gases, one is led to believe that the stratified form of the Aurora Borealis is produced in a similar manner. Fig. 3 (Pl. III.) is a form of the Aurora noticed by me ; and let us suppose that a discharge of electricity takes place in rarefied air between A and B, and that C is a region of cloud or moisture. C can be regarded as the finger or earth-conductor which is applied to the tube of rarefied air, and which serves to throw the discharge into transitory stratifications and to give the waving form of the Northern Lights.

The pulsation, therefore, of the Aurora is in no way, I believe, connected with any phenomenon of the oscillatory discharge ; yet certain writers have intimated that the glowing of vacuum-tubes which are connected with only one terminal of a transformer and the light of the Aurora are due to millions of electrical oscillations per second. Now it is impossible to study the question of the rate of oscillation of the brush-discharge by means of Feddersen's method, for the light of the discharge is not sufficient to produce a

photograph. A brief consideration, however, of the laws of electrical oscillations shows, I think, that such writers are mistaken; for the rate of decay of the amplitude of such

oscillations is expressed by the well-known factor $e^{-\frac{Rt}{L}}$. In the case of the brush-discharge R is enormously large. A resistance of thirty or forty ohms was sufficient to completely damp the oscillations of the sparks studied by me in the research on the damping produced on iron wires*. In the case of the brush-discharge, although we may be dealing with very small values of self-induction and small values of time, we have, on the other hand, great values of R . I believe, therefore, that the brush-discharge is reduced to the case of one throb, which is analogous to the pilot spark in disruptive discharges. In regard to the Aurora, it may be urged that the resistance of the rarefied air is not enormous. In answer to this it can be said that the phenomenon of the Aurora can be best reproduced by intercalating a tube of rarefied air with some megohms of a water-resistance between the terminals of a suitable transformer. The supposition that the Aurora is produced by the action of extremely rapid electrical oscillation on molecules of rarefied air is not borne out by the theory of transient currents; and experiment shows that the phenomenon of the waving and apparent stratification observed at times in the Aurora is due to the redistribution of the lines of force which is produced by suitable earths or conductors in the shape of regions of cloud or moisture.

The comparatively small resistance of the electric spark in air, noticed by many observers, is due, I believe, to the permanence of path; for this path is intensely heated, and is practically a charred hole in the air. When this path no longer becomes such a hole and the heated air rises and is dissipated, the oscillations of the electric spark become rapidly damped, and we have the phenomenon of the brush-discharge—a glow at each of the spark terminals without a disruptive discharge—the lines of force crowding from one terminal seek the other terminal through the air of the room, and in passing through rarefied air the energy along the lines of force is manifested by molecular actions which are apparently protean in form. I see, therefore, no evidence for believing in the rapid oscillation of the Aurora.

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* Phil. Mag. Dec. 1891.

XXXVI. *Note on the Calculation of Correlation between Organs.* By Professor F. Y. EDGEWORTH, M.A., D.C.L.*

IN a former paper † I have shown how to calculate the coefficients of the quantic which expresses the correlation between a set of organs, say,

$$p_1x_1^2 + p_2x_2^2 + p_3x_3^2 + \&c. + 2q_{12}x_1x_2 + 2q_{13}x_1x_3 + \&c.,$$

where $x_1, x_2, x_3, \&c.$ are the deviations of the organs from their respective means. Form the determinant :—

$$\begin{vmatrix} 1, & \rho_{12}, & \rho_{13} & . & . \\ \rho_{12}, & 1, & \rho_{23} & . & . \\ \rho_{13}, & \rho_{23} & 1, & . & . \\ : & : & : & & \end{vmatrix}$$

where $\rho_{12}, \rho_{13}, \rho_{23}, \&c.$ are the coefficients termed by Mr. Galton r ‡ pertaining to each pair of organs. Call the above-written determinant ${}_1\Delta$; and call the determinant which forms the discriminant of the above-written quantic Δ . The first step of the calculation is to equate each minor of ${}_1\Delta$ to a corresponding coefficient (of the required quantic) $\times \Delta$. To proceed from these *proportionate* values of the coefficients to the absolute values I before employed § the proposition $\Delta = p_1 = p_2 = \&c.$ But it has occurred to me that this second step can be effected more easily by the proposition $\frac{1}{\Delta} = \Delta'$; which may be thus proved. If each of the constituents of ${}_1\Delta$ be multiplied by Δ , the determinant so formed is the reciprocal of Δ ||. But the reciprocal of $\Delta = \Delta^{n-1}$. Therefore $\Delta_1^{*} \times {}_1\Delta = \Delta^{n-1}$; ${}_1\Delta = \frac{1}{\Delta}$. This proposition enables us with great ease to proceed from the proportional to the actual values of the sought coefficients. For example, let there be three variables, and let

$$\rho_{12} = \cdot 8, \quad \rho_{13} = \cdot 9, \quad \rho_{23} = \cdot 8;$$

* Communicated by the Author.

† See "Correlated Averages," Phil. Mag. 1892, xxxiv. p. 190.

‡ Proc. Royal Soc. 1888.

§ Phil. Mag. 1892, xxxiv. p. 197.

|| Ibid. p. 201.

the example worked in the paper referred to*. We have for Δ the determinant

$$\begin{vmatrix} 1 & \cdot 8 & \cdot 9 \\ \cdot 8 & 1 & \cdot 8 \\ \cdot 9 & \cdot 8 & 1 \end{vmatrix};$$

for $\frac{a}{\Delta}$, $\frac{h}{\Delta}$, $\frac{g}{\Delta}$, &c., respectively the values of corresponding minors, viz. $\cdot 36$, $-\cdot 08$, $-\cdot 26$, &c., and, for $\frac{1}{\Delta}$, $1 \times \cdot 36 - \cdot 8 \times \cdot 08 - \cdot 9 \times \cdot 26 = \cdot 062$. Dividing $\cdot 36$, &c., by $\cdot 062$ we obtain the same values for the coefficients as those reached in the paper referred to by a more circuitous route: viz. $p_1 = 5\cdot 806$, &c. The saving of trouble in the case of four variables† is substantial.

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XXXVII. *On Endothermic Reactions effected by Mechanical Force. (First Part.)* By M. CAREY LEA ‡.

IN a previous paper the effects of pressure on the silver haloids were described. These salts were readily blackened and so gave evidence of partial reduction. That investigation was undertaken with the object of bringing into complete harmony the effects upon these haloids of the different forms of energy. It had been previously shown with respect to all the other forms of energy that a slight impression made upon the haloids caused an effect not visible to the eye but capable of indefinite increase by the application of a reducing agent. Also it had been shown in the case of mechanical force that a slight application would cause an invisible effect which could be rendered evident by the application of a reducing agent. It seemed to follow almost necessarily that a powerful application of the same agent would bring about an effect visible to the eye. Experiment proved this to be the case.

It next appeared worth while to examine whether the same agent, mechanical force, would not be capable of bringing about analogous chemical changes in other compounds. For the nature of these changes was something quite different from anything that had been previously described. In Prof. Spring's well-known investigation, combination was brought about

* Phil. Mag. 1892, xxxiv. p. 196.

† Ibid. p. 202.

‡ Communicated by the Author.

between substances whose tendency to combine was restrained by their being in the solid form. This obstacle was removed by subjecting them to great pressure, and the same remark applies to some of the interesting experiments of Dr. Hallock. But the reduction of the silver haloids and other reactions presently to be described involve a quite different principle. The reactions produced are all endothermic; energy is consumed in accomplishing them, and this energy is supplied by mechanical force.

The combination of screw and lever affords the best means of applying pressure. A careful study as to the most suitable method of using these powers led to the selection of the vice form. It was found, however, that the manufacturers of heavy vices were unwilling to undertake to furnish vices with jaws that would sustain the force intended to be exerted on them, namely, that of a steel lever three feet long acting on a screw with six turns to the inch. I was therefore obliged to have them made under my own supervision. From a bar of tough rolled iron 4 inches wide by $1\frac{1}{2}$ inch thick, pieces about 18 inches long were cut and were forged into shape by a blacksmith; where the jaws met they were faced with steel welded on. Suitable screws were easily obtained, but the nuts furnished with them having commonly a length of only an inch would subject the thread to the danger of stripping. They were replaced with nuts 4 inches in length, thus distributing the strain on 24 turns of the thread. Two vices made in this way over a year ago have endured severe use without the least sign of strain.

With a lever three feet in length between the centre of the screw-head and the end at which the force is applied acting on a screw with six turns to the inch, the multiplication of force is 1357 times. As it is easy to apply a pull of a hundred pounds or even much more, a pressure of 135,000 lb. is easily obtained. As it was intended to keep the substances which were to be subjected to pressure from any contact that might affect them, they were folded up in platinum-foil, and this was set in a V-shaped piece of soft sheet copper. The portion of material which received the pressure was about $\frac{1}{2}$ inch long by $\frac{1}{4}$ wide; it consequently had an area of about $\frac{1}{8}$ of a square inch. This limited surface received a pressure in the proportion of over a million pounds to the square inch, or about seventy thousand atmospheres. These, of course, are calculated pressures subject to deduction for friction. The amount lost in this way cannot be determined, but is known to be considerable.

By the aid of these means the following results were

obtained. In all cases the material was wrapped in either platinum- or silver-, usually platinum-, foil. There was no action in any case on the metal, which preserved its full brightness in the parts in contact with the material, so that the effects observed were due to pressure only.

Silver sulphite in platinum-foil was moderately darkened by two days' pressure.

Silver salicylate was rendered very dark by two days' pressure.

Silver carbonate was moderately darkened by a somewhat longer pressure.

Silver tartrate was not affected.

Silver oxide was thoroughly dried at 150°. A piece of platinum-foil was heated to redness and rapidly cooled, a portion of oxide was folded up in it and weighed. Weight found .7639. It was then subjected to very great pressure for four days. Weight found to be .7639; no change.

Ferric oxide recently precipitated and dried. No effect produced by pressure; no formation of ferrous oxide.

Potassium platinobromide.—Where the pressure was greatest the brilliant red colour of this substance was blackened, not superficially only, but all through.

Ammonium platinochloride.—Moderate but well-marked darkening.

Potassium chlorate.—When this substance was subjected to pressure by itself, no effect whatever was produced, and not a trace of chloride was formed. But when it was mixed with silver nitrate, both in fine powder, and subjected to pressure there was an evident formation of silver chloride. The material was no longer completely soluble in water, but left an abundance of white flakes which darkened when exposed to light.

Mercuric oxide requires a very high pressure to produce an effect upon it. It then darkens slightly but very distinctly, and this change seems to be accompanied by a slight loss of weight, requiring, however, very careful weighing to detect it. The darkened part, as well as the rest, dissolves without difficulty in acetic acid, and consisted therefore probably of traces of mercurous oxide and not metallic mercury.

Mercurous chloride showed no change.

Mercuric chloride.—Corrosive sublimate perfectly free from calomel, which commercial sublimate is very apt to contain, was subjected to great pressure and then treated with ammonia. As no darkening took place, there had evidently been no reduction.

Mercuric iodide.—Red mercuric iodide, when subjected to

very great pressure, darkened considerably, and at points where the pressure was greatest it became absolutely black. It did not appear, however, that any iodine was set free; none could be extracted with alcohol.

Mercuric oxychloride, 2HgO , HgCl_2 . — Heavy pressure caused much darkening.

Sodium thiosulphate with a moderate pressure compresses to a hard translucent cake, but does not undergo any decomposition.

To the foregoing cases are to be added those of the three silver haloids described in a previous paper. These blackened with a quite moderate pressure, even in the case of the iodide.

Although in all these instances the darkening is well marked, still the actual proportion of material affected is small; so that in many cases it is difficult to apply tests to decide as to the precise nature of the substances formed. In some cases, however, this can be done, and we are justified in concluding that many of the salts of easily reducible metals, especially of silver, mercury, and platinum, undergo reduction by pressure. Such reactions are endothermic; and *it therefore follows that mechanical force can bring about reactions which require expenditure of energy, which energy is supplied by mechanical force precisely in the same way that light, heat, and electricity supply energy in the endothermic changes which they bring about.*

In the second part of this paper additional support will be adduced for these conclusions.

XXXVIII. *On the Flow of Viscous Liquids, especially in Two Dimensions.* By LORD RAYLEIGH, Sec. R.S.*

THE problems in fluid motion of which solutions have hitherto been given relate for the most part to two extreme conditions. In the first class the viscosity is supposed to be sensible, but the motion is assumed to be so slow that the terms involving the squares of the velocities may be omitted; in the second class the motion is not limited, but viscosity is supposed to be absent or negligible.

Special problems of the first class have been solved by Stokes and other mathematicians; and general theorems of importance have been established by v. Helmholtz† and by Korteweg‡, relating to the laws of steady motion. Thus in

* Communicated by the Author.

† Collected Works, i. p. 223.

‡ Phil. Mag. xvi. p. 112 (1883).

the steady motion (M_0) of an incompressible fluid moving with velocities given at the boundary, less energy is dissipated than in the case of any other motion (M) consistent with the same conditions. And if the motion M be in progress, the rate of dissipation will constantly decrease until it reaches the minimum corresponding to M_0 . It follows that the motion M_0 is always stable.

It is not necessary for our purpose to repeat the investigation of Korteweg; but it may be well to call attention to the fact that problems in viscous motion *in which the squares of the velocities are neglected*, fall under the general method of Lagrange, at least when this is extended by the introduction of a dissipation function*. In the present application there is no potential energy to be considered, and everything depends upon the expressions for the kinetic energy T and the dissipation function F . The conditions to be satisfied may be expressed by ascribing given constant values to some of the generalized velocities; but it is unnecessary to introduce more than one into the argument, inasmuch as any others may be eliminated beforehand by means of the given relations. Suppose, then, that $\dot{\psi}_r$ is given. The other coordinates ψ_1, ψ_2, \dots may be so chosen that no product of their velocities enters into the expressions for T and F , although products with $\dot{\psi}_r$, such as $\dot{\psi}_1 \dot{\psi}_r$, will enter. These coordinates are, in fact, the *normal* coordinates of the system when $\dot{\psi}_r$ is constrained to vanish. Thus simplified F becomes

$$F = \frac{1}{2} b_1 \dot{\psi}_1^2 + \dots + \frac{1}{2} b_s \dot{\psi}_s^2 + \dots + b_{rs} \dot{\psi}_s \dot{\psi}_r + \dots \quad (1)$$

and a similar expression applies to T with a written for b . Lagrange's equation is now

$$a_s \ddot{\psi}_s + a_{rs} \ddot{\psi}_r + b_s \dot{\psi}_s + b_{rs} \dot{\psi}_r = 0,$$

ψ_s being any one of the coordinates ψ_1, ψ_2, \dots . In this equation $\ddot{\psi}_r = 0$, and $\dot{\psi}_r$ has a prescribed value; so that

$$a_s \ddot{\psi}_s + b_s \dot{\psi}_s = -b_{rs} \dot{\psi}_r \quad \dots \quad (2)$$

is the equation giving $\ddot{\psi}_s$. The solution of (2) is well known, and it appears that ψ_s settles gradually down to the value given by

$$b_s \dot{\psi}_s = -b_{rs} \dot{\psi}_r, \quad \dots \quad (3)$$

since a_s, b_s are intrinsically positive. Further,

$$\frac{dF}{dt} = \Sigma \{ b_s \dot{\psi}_s \ddot{\psi}_s + b_{rs} (\ddot{\psi}_s \dot{\psi}_r + \dot{\psi}_s \ddot{\psi}_r) \},$$

* Theory of Sound, § 81.

in which the summation extends to all values of s other than r . In this $\ddot{\psi}_r = 0$, so that

$$\frac{dF}{dt} = \sum \ddot{\psi}_s \{b_s \dot{\psi}_s + b_{rs} \dot{\psi}_r\} = -\sum a_s \dot{\psi}_s^2, \quad \dots \quad (4)$$

by (2). The last expression is intrinsically negative, proving that until the steady motion is reached F continually decreases. Korteweg's theorem is thus shown to be of general application to systems devoid of potential energy for which T and F can be expressed as quadratic functions of the velocities with constant coefficients.

It may be mentioned in passing that a similar theorem holds for systems devoid of *kinetic* energy, for which, however, F and V (the potential energy) are sensible, and may be proved in the same way. If such a system be subjected to given displacements, it settles down into the configuration of minimum V ; and during the progress of the motion V continually decreases.

The theorem of Korteweg places in a clear light the general question of the slow motion of a viscous liquid under given boundary conditions, and the only remaining difficulty lies in finding the analytical expressions suitable for special problems. It is proposed to consider a few simple cases relating to motion in two dimensions.

Under the above restriction, as is well known, the motion may be expressed by means of Earnshaw's current function (ψ), which satisfies

$$\nabla^4 \psi = 0, \quad \dots \quad (5)$$

the same equation as governs the transverse displacement of an elastic plate, when in equilibrium. Of this analogy we shall avail ourselves in the sequel. At a fixed wall ψ retains a constant value, and, further, in consequence of the friction $d\psi/dn$, representing the tangential velocity, is evanescent. The boundary conditions for a fixed wall in the fluid problem are therefore analogous to those of a clamped edge in the statical problem.

The motion within a simply connected area is determined by (5) and by the values of the component velocities over the boundary. If we suppose that two such motions are possible, their difference constitutes a motion also satisfying (5), and making ψ and $d\psi/dn$ zero over the boundary. Considerations respecting energy in this or in the analogous problem of the elastic plate are then sufficient to show that ψ must vanish throughout; and an analytical proof may

readily be given by means of Green's theorem. For if ψ and χ are any two functions of x and y ,

$$\int \left\{ \chi \frac{d\psi}{dn} - \psi \frac{d\chi}{dn} \right\} ds = \iint \{ \chi \nabla^2 \psi - \psi \nabla^2 \chi \} dx dy, \quad (6)$$

the integrations being taken round and over the area in question. If we suppose that ψ and $d\psi/dn$ are zero over the boundary, the left-hand member vanishes. If, further, $\chi = \nabla^2 \psi$, we have

$$\iint (\nabla^2 \psi)^2 dx dy = \iint \psi \nabla^4 \psi dx dy, \quad (7)$$

of which the right-hand member vanishes by (5). Hence $\nabla^2 \psi$ vanishes all over the area, and by a known theorem, as ψ vanishes on the contour, this requires that ψ vanish throughout.

We will now investigate in detail the slow motion of viscous fluid within a circular boundary. In virtue of (5) $\nabla^2 \psi$, which represents the vorticity, satisfies Laplace's equation, and may therefore be expanded in positive and negative integral powers of r , each term such as r^n , or r^{-n} , being accompanied by the factor $\cos(n\theta + \alpha)$. But if, as we shall suppose, the vorticity be finite at the centre of the circle, where $r=0$, the negative powers are excluded, and we have to consider only such terms as

$$\nabla^2 \psi = \left(\frac{d^2}{dr^2} + \frac{1}{r} \frac{d}{dr} + \frac{1}{r^2} \frac{d^2}{d\theta^2} \right) \psi = r^n \cos(n\theta + \alpha). \quad (8)$$

The solution of this is readily obtained. If we assume

$$\psi = r^m \cos(n\theta + \alpha), \quad (9)$$

we find $m=n+2$. To this may be added, as satisfying $\nabla^2 \psi = 0$, a term corresponding to $m=n$; so that the type of solution for $n\theta$ is

$$\psi = A_n r^{n+2} \cos(n\theta + \alpha) + B_n r^n \cos(n\theta + \beta). \quad (10)$$

By differentiation,

$$\frac{d\psi}{dn} = (n+2) A_n r^{n+1} \cos(n\theta + \alpha) + n B_n r^{n-1} \cos(n\theta + \beta). \quad (11)$$

The first problem to which we will apply these equations is that of motion within the circle $r=1$ under the condition that the tangential motion vanishes at every part of the

circumference. By (11) $\beta = \alpha$, and

$$(n+2)A_n + nB_n = 0. \quad \dots \quad (12)$$

The normal velocity at the boundary is represented by $d\psi/d\theta$, and we might be tempted, in our search after simplicity, to suppose that this is sensible in the neighbourhood of one point only, for example $\theta=0$. But in that case the condition of incompressibility would require that the total flow of fluid at the place in question should be zero. If the total quantity of fluid entering the enclosure at $\theta=0$ is to be finite, provision must be made for its escape elsewhere. This might take the form of a *sink* at the centre of the circle; but it will come to much the same thing, and be more in harmony with our equations as already laid down to suppose that the escape takes place uniformly over the entire circumference. This state of things will be represented analytically by ascribing to ψ a sudden change of value from -1 to $+1$ at $\theta=0$, with a gradual passage from the one value to the other as θ increases from 0 to 2π , or, as it may be more conveniently expressed for our present purpose, ψ is to be regarded as an *odd* function of θ such that from $\theta=0$ to $\theta=\pi$ its value is

$$\theta = 1 - \frac{\theta}{\pi}. \quad \dots \quad (13)$$

The symmetry with respect to $\theta=0$ shows that we are concerned in (10) only with the sines of multiples of θ , so that having regard to (12) we may take as the form of ψ applicable in the present problem,

$$\psi = \Sigma C_n \sin n\theta \{ (n+2)r^n - nr^{n+2} \}, \quad \dots \quad (14)$$

in which n is any integer and C_n an arbitrary constant. It remains to determine the coefficients C in accordance with (13). When $r=1$,

$$\psi = 2\Sigma C_n \sin n\theta = 1 - \frac{\theta}{\pi};$$

and this must hold good for all values of θ from 0 to π . Multiplying by $\sin m\theta$ and integrating as usual, we find

$$C_n = \frac{1}{n\pi}; \quad \dots \quad (15)$$

so that

$$\pi \cdot \psi = \Sigma \sin n\theta \left\{ \left(1 + \frac{2}{n}\right)r^n - r^{n+2} \right\} \quad \dots \quad (16)$$

is the value of ψ expressed in series.

These series may be summed. In the first place, $\Sigma r^n \sin n\theta$ is the real part of $-i\Sigma (re^{i\theta})^n$, or of

$$\frac{-ir e^{i\theta}}{1 - r e^{i\theta}}.$$

Thus

$$\Sigma r^n \sin n\theta = \frac{r \sin \theta}{1 - 2r \cos \theta + r^2}. \quad (17)$$

Again, $\Sigma n^{-1} r^n \sin n\theta$ is the real part of $-i\Sigma n^{-1} (re^{i\theta})^n$, or of $i \log (1 - re^{i\theta})$; so that

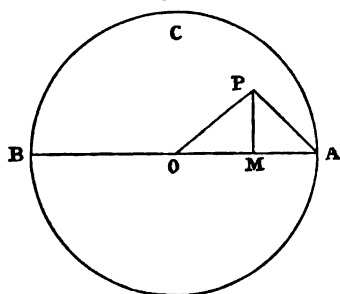
$$\Sigma n^{-1} r^n \sin n\theta = \tan^{-1} \frac{r \sin \theta}{1 - r \cos \theta}. \quad (18)$$

Thus, as the expression for ψ in finite terms, we have

$$\pi \cdot \psi = \frac{(1 - r^2) r \sin \theta}{1 - 2r \cos \theta + r^2} + 2 \tan^{-1} \frac{r \sin \theta}{1 - r \cos \theta}. \quad (19)$$

In (19) the separate parts admit of simple geometrical interpretation. The second represents simply twice the angle

Fig. 1.



PAO, fig. 1, which is known to constitute a solution of $\nabla^2 \psi = 0$. In the first term,

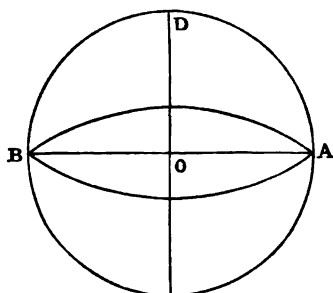
$$\frac{r \sin \theta}{1 - 2r \cos \theta + r^2} = \frac{PM}{AP^2} = \frac{\sin PAO}{AP},$$

which is also obviously a solution of $\nabla^2 \psi = 0$. The remaining part of (19) is not a solution of $\nabla^2 \psi = 0$; but it satisfies $\nabla^4 \psi = 0$, as being derived from a solution of $\nabla^2 \psi = 0$ by multiplication with r^2 .

On the foundation of (19) we may build up by simple integration the general expression for ψ subject to the conditions that $d\psi/dr$ vanishes over the whole circumference, and that $d\psi/d\theta$ has any prescribed values consistent with the recurrence of ψ .

A simple example is afforded by the case of a source at A and an equal sink at B, where $\theta = \pi$ (fig. 2). The fluid enters

Fig. 2.



and leaves the enclosure by two perforations situated at opposite ends of a diameter, the walls being elsewhere impenetrable. The solution may be found independently, or from (19), by changing the sign of $\cos \theta$, and adding the equations together. Thus

$$\frac{1}{2}\pi \cdot \psi = \frac{(1-r^4)r \sin \theta}{1-2r^2 \cos 2\theta + r^4} + \tan^{-1} \frac{2r \sin \theta}{1-r^2}. \quad (20)$$

In this case the walls of the enclosure are of necessity stream-lines, the value of ψ being $+1$ from 0 to π , and -1 from 0 to $-\pi$.

When $\theta = \frac{1}{2}\pi$, that is along OD (fig. 2),

$$\frac{1}{2}\pi \cdot \psi = \frac{r-r^3}{1+r^2} + 2 \tan^{-1} r, \quad \dots \dots (21)$$

$$\frac{1}{2}\pi \frac{d\psi}{dr} = \frac{(3+r^2)(1-r^2)}{(1+r^2)^2}. \quad \dots \dots (22)$$

From (21) we obtain by interpolation the following corresponding values:—

| | | | | | | |
|--------|--|-----|-------|-------|-------|--------|
| ψ | | ·00 | ·25 | ·50 | ·75 | 1·00 |
| r | | ·00 | ·1330 | ·2800 | ·4698 | 1·0000 |

In the neighbourhood of A or B, fig. 1, (20) assumes a special form. Thus in the former case,

$$1-2r^2 \cos 2\theta + r^4 = (1-r^2)^2 + 4r^2 \sin^2 \theta = 4\{AM^2 + PM^2\},$$

$$(1-r^4)r \sin \theta = 4 PM \cdot AM,$$

$$\tan^{-1} \frac{2r \sin \theta}{1-r^2} = \text{angle PAO}.$$

Thus if PAO be denoted by ϕ , the value of ψ in the neighbourhood of A is given by

$$\pi.\psi = \sin 2\phi + 2\phi. \quad (22')$$

That the functions of ϕ which occur in (22') satisfy the fundamental equation may be readily seen.

By calculation from (22') we get the following values for ϕ expressed as fractions of degrees:—

| | | | | | |
|--------|----|---------|---------|---------|--------|
| ψ | 0, | ·25, | ·50, | ·75, | 1·00 |
| ϕ | 0, | 11°·40, | 23°·83, | 39°·40, | 90°·00 |

This example is of interest, from its bearing upon the laws of flow at a place where a channel is enlarged. In actual fluids there would be a tendency to shoot directly across from A to B, the region about C being occupied by an eddy or backwater such that the motion of the fluid near the wall was reversed. Nothing of the kind is indicated by the present solution. In (22) $d\psi/dr$ represents the velocity across the line $\theta = \frac{1}{2}\pi$, and we see that there is no change of sign. In fact the velocity decreases, as r increases, all the way from $r=0$ to $r=1$. The formation of a backwater may thus be connected with the terms involving the squares of the velocities, which are neglected in the present solution. And we may infer that if the motion were slow enough, or if the fluid were viscous enough, the backwater, usually observed in practice, would disappear.

Another particular case of some interest, included in the general solution already indicated, would be obtained by supposing similar sources to be situated at $\theta=0$, $\theta=\pi$, and equal sinks at $\theta=\frac{1}{2}\pi$, $\theta=\frac{3}{2}\pi$.

We will now suppose that it is the radial velocity which vanishes at every point of the circumference $r=1$, and that the tangential velocity also vanishes except in the neighbourhood of $\theta=0$. In this case, by the symmetry, ψ in (10) reduces to a series of cosines. And

$$-\frac{d\psi}{d\theta} = \sum n \sin n\theta (A_n r^{n+2} + B_n r^n),$$

which is to vanish when $r=1$ for all values of θ . Hence

$$A_n + B_n = 0; \quad (23)$$

so that

$$\psi = (1-r^2) \sum B_n r^n \cos n\theta, \quad (24)$$

$$\frac{d\psi}{dr} = B \sum_n \cos n\theta \{n r^{n-1} - (n+2) r^{n+1}\}. \quad (25)$$

When $r=1$,

$$\frac{d\psi}{dr} = -2\sum B_n \cos n\theta, \quad (26)$$

and is to be made to vanish for all values of θ except in the neighbourhood of $\theta=0$. If we suppose that the integral of $d\psi/dr$ with respect to θ over the whole region where $d\psi/dr$ is sensible, is 2, we find

$$B_0 = -\frac{1}{2\pi}, \quad B_n = -\frac{1}{\pi}, \quad (27)$$

the second equation applying to all values of n other than 0. Hence,

$$-\pi \cdot \psi = -\frac{1}{2}(1-r^2) + (1-r^2)\sum_0^\infty r^n \cos n\theta, \quad . . (28)$$

or in finite terms,

$$-\pi \cdot \psi = -\frac{1}{2}(1-r^2) + (1-r^2) \frac{1-r \cos \theta}{1-2r \cos \theta + r^2}. \quad . . (29)$$

The equation may also be written

$$-2\pi \cdot \psi = \frac{(1-r^2)^2}{1-2r \cos \theta + r^2}. \quad . . . (30)$$

In (29),

$$\frac{1-r \cos \theta}{1-2r \cos \theta + r^2} = \frac{AM}{AP^2} = \frac{\cos PAO}{AP},$$

which is a solution of $\nabla^2\psi=0$. When multiplied by r^2 , or by $(1-r^2)$, it remains a solution of $\nabla^4\psi=0$.

In (30) we may write x for $r \cos \theta$, and if the point under consideration lie upon the axis, $x^2=r^2$. Hence on the axis,

$$-2\pi \cdot \psi = (1+x)^2, \quad (31)$$

$$-\pi \frac{d\psi}{dx} = (1+x), \quad (32)$$

equations which may be applied at all points except near $x=1$. It appears from (32) that the velocity transverse to the axis increases continuously from $x=-1$ to the neighbourhood of $x=+1$.

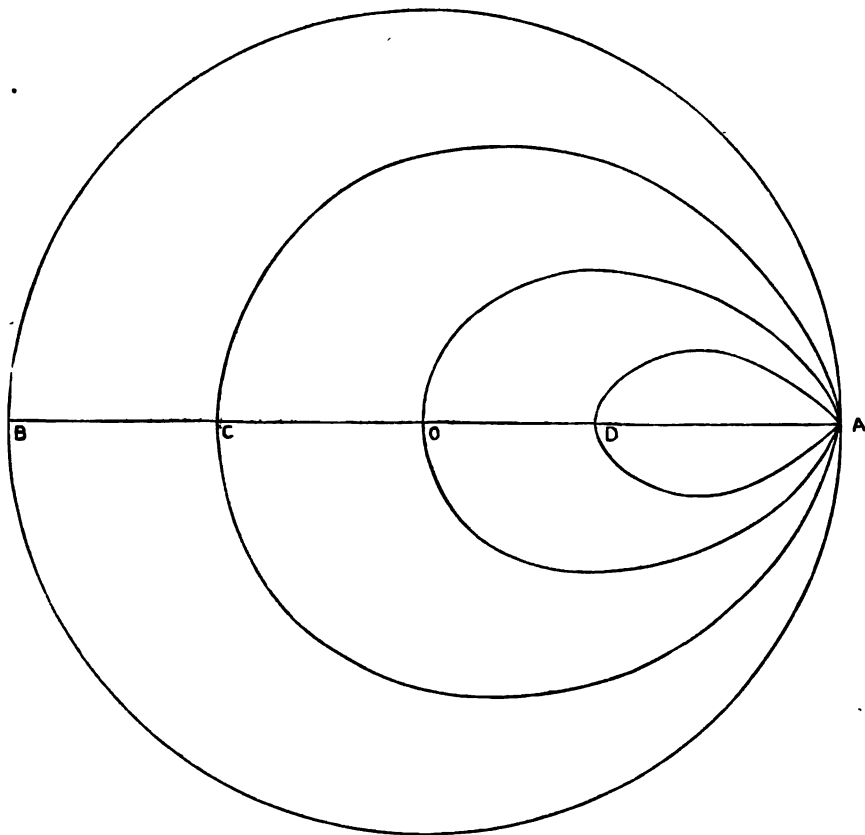
The lines of flow are readily constructed from (30), which we may write in the form

$$AP = \frac{1-OP^2}{\sqrt{(-2\pi\psi)}}, \quad (33)$$

showing how P may be determined by the intersection of circles struck from O and A. A few of the lines of flow are

shown in fig. 3. The external circle AB corresponds to $\psi=0$; AC, AO, AD correspond respectively to $-2\pi\psi=\frac{1}{2}, 1, 2$. As appears from (31), the highest value of $-2\pi\psi$ is 4, and gives a curve at A of infinitely small area.

Fig. 3.



In the neighbourhood of A (fig. 1), (30) reduces to a simpler form. Thus

$$-\pi \cdot \psi = \frac{(1 - OP^2)^2}{2 AP^2} = 1 + \cos 2\phi, \quad \dots \quad (33')$$

where $\phi = PAO$. The second term here satisfies the fundamental equation as being derived by multiplication with AP^2 from a solution, $AP^{-2} \cos 2\phi$, of $\nabla^2 \psi = 0$.

Equations (19), (30) give the means of expressing the

stream-function subject to the conditions that both ψ and $d\psi/dr$ shall have values arbitrarily given at all points of the circumference of the circle. It is not necessary actually to write down the formulæ; but it may be well to notice that the same solution applies to the question of determining the transverse displacement w of a thin circular plate when w and dw/dr have arbitrarily prescribed values on the boundary.

As a preliminary to further questions it will be desirable to consider for a moment the form of the general equations of viscous motion. In the usual notation,

$$\frac{du}{dt} + u \frac{du}{dx} + v \frac{du}{dy} + w \frac{du}{dz} = X - \frac{1}{\rho} \frac{dp}{dx} + \nu \nabla^2 u, \quad (34)$$

with two similar equations. Further, if q^2 denote the resultant velocity, and ξ, η, ζ be the component rotations,

$$u \frac{du}{dx} + v \frac{du}{dy} + w \frac{du}{dz} = \frac{1}{2} \frac{dq^2}{dx} - 2v\zeta + 2w\eta. \quad (35)$$

In steady motion $du/dt=0$; and if the terms of the second order in velocity (35) be omitted and there be no impressed forces except such as have a potential, the equations reduce to the form already considered. A solution thus obtained for small velocities will fail to satisfy the conditions when the velocities are increased; but the equations lead readily to an instructive expression for the forces X, Y, Z , which must be introduced in order that the solution applicable without impressed forces to small velocities may still continue to hold good. From (35) we see that the necessary forces are

$$X = \frac{1}{2} \frac{dq^2}{dx} - 2v\zeta + 2w\eta, \quad (36)$$

with two similar equations. In this the term $\frac{1}{2} dq^2/dx$ need not be regarded, as it tells only upon the pressure and does not influence the motion. We may therefore write

$$X = 2w\eta - 2v\zeta, \quad Y = 2u\zeta - 2w\xi, \quad Z = 2v\xi - 2u\eta. \quad (37)$$

These equations show that

$$\left. \begin{aligned} uX + vY + wZ &= 0 \\ \xi X + \eta Y + \zeta Z &= 0 \end{aligned} \right\}, \quad (38)$$

signifying that the force whose components are X, Y, Z , acts at every point in a direction perpendicular both to the velocity and to the axis of rotation. As regards its magnitude,

$$\frac{1}{4}(X^2 + Y^2 + Z^2) = (u^2 + v^2 + w^2)(\xi^2 + \eta^2 + \zeta^2) - (u\xi - v\eta - w\zeta)^2. \quad (39)$$

If the motion take place in two dimensions, $w=0$, $\xi=\eta=0$, and

$$\frac{1}{4}(X^2 + Y^2) = (u^2 + v^2)\xi^2. \quad (40)$$

In the case of symmetry round an axis,

$$u\xi + v\eta + w\zeta = 0,$$

and (39) reduces to

$$\frac{1}{4}(X^2 + Y^2 + Z^2) = (u^2 + v^2 + w^2)(\xi^2 + \eta^2 + \zeta^2). \quad (41)$$

These expressions for the forces necessary to the maintenance of a motion similar to the infinitely small motion give us in simple cases an idea of the direction in which the law is first departed from as the motion increases.

There are very few cases in which the problem of the rapid motion of a viscous fluid has been dealt with. When the motion is in one dimension, the troublesome terms do not present themselves, and the same solution holds good mathematically for the steady motion at all velocities. When the motion is so small that the laws appropriate to infinitely small motion hold good as a first approximation, a correction may be calculated. This has been effected by Whitehead*, and in an unpublished paper by Rowland, for the problem, first investigated by Stokes, of a sphere moving with velocity V through viscous liquid. For infinitely small motion the velocity of the fluid in the neighbourhood of the sphere is of order V . It follows from the solution referred to, or may be proved independently by considerations of dimensions, that in the second approximation involving V^2 , the terms are of the order $V^2 a/\nu$, a being the radius of the sphere, and ν , equal to μ/ρ , the kinematic coefficient of viscosity. This method of approximation is thus only legitimate when Va/ν is small, a condition of a very restricting character. In the case of water $\nu = .01$ C.G.S., and if $Va/\nu = .1$, it is required that $Va = .001$.

Thus even if a were as small as one millimetre ($\cdot 1$), V should not exceed $\cdot 01$ centimetre per second. With such diameters and velocities as often occur in practice, Va/ν would be a large, instead of a small, quantity; and a solution founded upon the type of infinitely slow motion is wholly inapplicable.

We will now recur to the suppositions that the motion is steady, is in two dimensions, and that its square may be

* Quart. Journ. of Math. vol. xxiii. p. 153 (1889).

neglected. Thus, writing as usual

$$u = d\psi/dy, \quad v = -d\psi/dx,$$

we get from (34)

$$\nu \nabla^2 \psi = \frac{dY}{dx} - \frac{dX}{dy} \dots \dots \dots (42)$$

Forces derivable from a potential do not disturb the equation $\nabla^2 \psi = 0$. In the analogy with a thin elastic plate, already referred to, a place where $dY/dx - dX/dy$ assumes a finite value in the fluid problem corresponds to a place where transverse force acts upon the plate.

The simplest example of the finiteness of the second member of (42) occurs when it is sensible at one point only. This is the case of forces derivable from a potential θ , where θ denotes the angle measured round the point in question. It is to be observed that in the fluid problem the forces themselves are not limited to the one point, but they have no "circulation" except round that point. In the elastic problem, on the other hand, the transverse force is limited to the one point.

The circumstance last mentioned renders the elastic problem the easier of the two to deal with in thought and expression, and we will accordingly avail ourselves of the analogy in the investigation which follows. It is proposed to examine the infinitely slow motion of fluid within an enclosure, which is maintained by forces having circulation at one point only, with the view of determining whether a contrary flow, or backwater, is possible. In the analogous elastic problem we have to consider a plate, subject at the boundary to the conditions that w (the transverse displacement) and dw/dn shall everywhere vanish, and disturbed from its original plane condition by a force acting transversely at a single point P. For distinctness we may suppose that the plate is horizontal and that the force at P acts downwards, in which direction the displacements are reckoned positive. At the point P itself the principle of energy shews that the displacement is positive, and it might appear probable that the displacement would be also positive at all other points of the plate. A similar conclusion is readily proved to be true in the case of a stretched membrane of any shape subjected to transverse force at any point, and also in one dimension for a bar resisting flexure by its stiffness. But a consideration of particular cases suffices to show that the theorem cannot be generally true in the present case.

For suppose that the plate fig. (4) is almost divided into

two independent parts by a straight partition CD extending across, but perforated by an aperture AB; and that the force is applied at a distance from CD on the left. If the partition were complete, w and dw/dn would be zero over the whole, and the displacement in the neighbourhood on the left would be simple one-dimensional bending, with w positive throughout. On the right w would vanish throughout. In order to maintain this condition of things a certain couple acts upon the plate in virtue of the supposed constraints along CD.

Along the perforated portion AB the couple required to produce the one-dimensional bending fails. The actual deformation accordingly differs from the one-dimensional bending by the deformation that would be produced by a couple over AB acting upon the plate as clamped along CA, BD, but otherwise free from force. This deformation is evidently symmetrical with change of sign upon the two sides of CD, w being positive on the left, *negative* on the right, and vanishing on AB itself. Thus upon the whole a downward force acting on the left gives rise to an upward motion on the right, in opposition to the general law proposed for examination.

In the application to the hydrodynamical problem we see that the fluid moving on the left from D to B passes on in a straight course to A, and thence along AC, and that on the right an eddy, or backwater, is formed. At distances from the aperture large in comparison with AB the supplementary motion is of the character expressed in (33').

A similar argument may be applied to the case (fig. 5) where fluid moves along a wall DC into which a channel AF opens, and it leads to the conclusion that the fluid on arrival at B will refuse to follow the wall BF, but will rather shoot across towards A.

These examples are of some interest as establishing that the formation of eddies observed in practice is not wholly due to

Fig. 4.

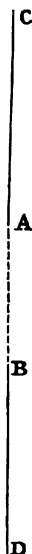
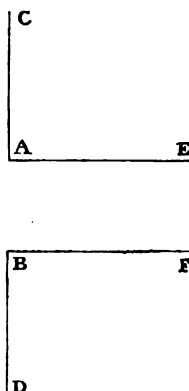


Fig. 5.



the influence of the terms involving the squares of the velocities, but would persist in certain cases even though the motion were made infinitely slow.

We will now investigate the motion in two dimensions of

Fig. 6.



a viscous incompressible fluid past a corrugated wall AB (fig. 6), whose equation may be taken to be

$$y = \beta \cos kx. \quad (43)$$

In this $k\beta$ will be supposed to be a small quantity; in other words, the depth of the corrugations small in comparison with their wave-length ($2\pi/k$). Further we shall suppose, in the first instance, that the motion is slow enough to allow the terms involving squares of the velocities to be neglected; in which case the equation for the stream-function may be written

$$\nabla^4 \psi = 0. \quad (44)$$

At a distance from the wall we suppose the motion to take place in plane strata, as defined by

$$\psi = Ly^2. \quad (45)$$

In the absence of corrugations this value of ψ might hold good throughout, up to the wall at $y=0$. The effect of the corrugations will be to introduce terms periodic with respect to x ; but the influence of these will be confined to the neighbourhood of the wall. For any term in ψ , proportional to $\cos mx$, (44) gives

$$\left(\frac{d^2}{dy^2} - m^2\right)^2 \psi = 0, \quad (46)$$

or

$$\psi = Ae^{-my} + Bye^{-my} + Ce^{my} + Dye^{my};$$

but the condition last named requires that of the four arbitrary constants C and D vanish. Also for our present purpose m is limited to be a multiple of k .

The form of ψ applicable to our present purpose is accordingly

$$\begin{aligned} \psi = A_0 + B_0 y + Ly^2 + \cos kx (A_1 e^{-ky} + B_1 y e^{-ky}) \\ + \cos 2kx (A_2 e^{-2ky} + B_2 y e^{-2ky}) + \dots, \end{aligned} \quad (47)$$

in which the constants A_0, B_0, A_1, \dots are to be determined from the conditions that ψ and $d\psi/dy$ vanish when $y = \beta \cos kx$. It may be observed that the problem is mathematically identical with that of an elastic plate clamped at a sinuous edge, and deformed in such a manner that if there were no sinuosity the bending would be one-dimensional.

The boundary conditions are—

$$\begin{aligned} A_0 + B_0\beta \cos kx + L\beta^2 \cos^2 kx \\ + \cos kx (A_1 + B_1\beta \cos kx) e^{-k\beta \cos kx} \\ + \cos 2kx (A_2 + B_2\beta \cos kx) e^{-2k\beta \cos kx} \\ + \dots = 0 \end{aligned} \quad (48)$$

and

$$\begin{aligned} B_0 + 2L\beta \cos kx \\ + \cos kx (B_1 - kA_1 - B_1k\beta \cos kx) e^{-k\beta \cos kx} \\ + \cos 2kx (B_2 - 2kA_2 - 2B_2k\beta \cos kx) e^{-2k\beta \cos kx} \\ + \dots = 0; \end{aligned} \quad (49)$$

or, with use of (48),

$$\begin{aligned} kA_0 + B_0 + (B_0k\beta + 2L\beta) \cos kx + Lk\beta^2 \cos^2 kx \\ + B_1 \cos kx e^{-k\beta \cos kx} \\ + (B_2 - kA_2 - B_2k\beta \cos kx) e^{-2k\beta \cos kx} \\ + \dots = 0. \end{aligned} \quad (50)$$

The exponentials in (48), (50) could be expanded in Fourier's series by means of Bessel's functions of an imaginary argument, and the complete equations formed which express the evanescence of the various Fourier terms. But the results are too complicated to be useful in the general case; and, if we regard $k\beta$ as small, it is hardly worth while to introduce the Bessel's functions at all. The first approximation, in which β^2 is neglected in (48), (50), gives

$$\left. \begin{aligned} A_0 = 0, \quad A_1 = 0, \quad A_2 = 0, \dots \\ B_0 = 0, \quad B_1 = -2L\beta, \quad B_2 = 0, \dots \end{aligned} \right\}; \quad (51)$$

and the second approximation, in which β^2 is retained, gives

$$\left. \begin{aligned} A_0 = \frac{1}{2}\beta^2 L, \quad A_1 = 0, \quad A_2 = \frac{1}{2}\beta^2 L, \dots \\ B_0 = -2k\beta^2 L, \quad B_1 = -2\beta L, \quad B_2 = -k\beta^2 L, \dots \end{aligned} \right\}, \quad (52)$$

the coefficients with higher suffixes than 2 vanishing to this order of approximation. Thus

$$\begin{aligned} \psi/L = \beta^2 \left(\frac{1}{2} - 2ky \right) + y^2 - 2\beta y e^{-ky} \cos kx \\ + \beta^2 \left(\frac{1}{2} - ky \right) e^{-2ky} \cos 2kx, \end{aligned} \quad (53)$$

$$\frac{1}{L} \frac{d\psi}{dy} = -2k\beta^2 + 2y - 2\beta(1-ky)e^{-ky} \cos kx \\ - 2k\beta^2(1-ky)e^{-2ky} \cos 2kx, \quad . \quad . \quad . \quad (54)$$

solutions applicable also to the problem of the elastic plate, if ψ be understood to mean the transverse displacement.

In the above investigation, so far as it applies to the hydrodynamical question, L^2 has been supposed to be negligible. We will now retain the square of L , but simplify the problem in another direction by neglecting the square of β , so that the first approximation is

$$\psi = Ly^2 - 2L\beta y e^{-ky} \cos kx. \quad . \quad . \quad . \quad (55)$$

The exact equation (derivable from (34)) for the motion of a viscous fluid in two dimensions is

$$\nabla^4 \psi = \frac{u}{\nu} \frac{d\nabla^2 \psi}{dx} + \frac{v}{\nu} \frac{d\nabla^2 \psi}{dy}. \quad . \quad . \quad . \quad (56)$$

From (55),

$$\nabla^2 \psi = 2L + 4Lk\beta e^{-ky} \cos kx, \\ u \frac{d\nabla^2 \psi}{dx} + v \frac{d\nabla^2 \psi}{dy} = -8L^2 k^2 \beta y e^{-ky} \sin kx. \quad . \quad . \quad (57)$$

Using this in (56) we have

$$\nabla^4 \psi = -\frac{8k^2 \beta L^2}{\nu} y e^{-ky} \sin kx. \quad . \quad . \quad . \quad (58)$$

The solution of

$$\left(\frac{d^2}{dy^2} - k^2 \right)^2 \psi = y e^{-ky} \quad . \quad . \quad . \quad (59)$$

is

$$\psi = \frac{y^2 e^{-ky}}{8k^3} + \frac{y^3 e^{-ky}}{24k^3}; \quad . \quad . \quad . \quad (60)$$

so that the required solution of (58), correct as far as the term involving L^2 , is

$$\psi = Ly^2 - 2L\beta y e^{-ky} \cos kx - \frac{\beta L^2}{k\nu} (y^3 + \frac{1}{3}ky^3) e^{-ky} \sin kx. \quad (61)$$

It may be well to repeat that, though L^2 is retained, β^2 is neglected in (61); that is, the depth of the corrugations is supposed to be infinitely small.

The part of the motion proportional to L^2 is, of course, independent of the direction of the principal motion of the fluid, and is thus in a manner applicable even when the principal motion is alternating. With regard to the relative

importance of the third and second terms in (61), we have to consider the value of

$$\frac{L}{2k\nu} (y + \frac{1}{2}ky^2),$$

and the conclusion will depend upon the value of y . If we suppose that $ky=1$, the ratio is $2L : 3k^2\nu$; or, if we denote by V the undisturbed velocity of the fluid when $ky=1$, $V/3k\nu$, or $V\lambda/6\pi\nu$, λ being the wave-length of the corrugation. With ordinary liquids and moderate values of λ , V would have to be very small in order to permit the success of the method of approximation.

The character of the motion proportional to L^2 is easily seen from the value of v . We have

$$v = -\frac{d\psi}{dx} = \frac{\beta L^2}{\nu} (y^2 + \frac{1}{2}ky^2)e^{-ky} \cos kx, \quad . \quad . \quad (62)$$

indicating a motion directed outwards from the wall over the places where the sinuosities encroach upon the fluid, and an inward motion where the sinuosities recede.

The application of the results towards the explanation of such phenomena as ripple-mark and wave-formation requires a calculation of the forces operative upon the boundary. We will confine ourselves to the first term in β and L , as expressed in (55).

The normal stress, parallel to y , is given by

$$Q = -p + 2\mu \frac{dv}{dy} = -p - 2\mu \frac{d^2\psi}{dx dy}; \quad . \quad . \quad (63)$$

and the tangential stress, parallel to x , is

$$U = \mu \left(\frac{dv}{dx} + \frac{du}{dy} \right) = \mu \left(\frac{d^2\psi}{dy^2} - \frac{d^2\psi}{dx^2} \right). \quad . \quad . \quad (64)$$

From (34), (55) we find

$$p = -4\mu k\beta e^{-ky} \sin kx,$$

or when $y=0$,

$$p = -4k\beta \sin kx, \text{ simply.}$$

Also, when $y=0$,

$$2\mu \frac{d^2\psi}{dx dy} = -4k\beta \sin kx;$$

so that

$$Q = 0. \quad . \quad . \quad . \quad . \quad . \quad (65)$$

In like manner, when $y=0$,

$$U = 2\mu \{1 + 2k\beta \cos kx\}. \quad . \quad . \quad . \quad . \quad . \quad (66)$$

So far as the first power of β the action upon the boundary is thus purely tangential, and of magnitude given by (66). The periodic part has the same sign as the constant part at the places where the boundary encroaches upon the fluid.

This result finds immediate application to the question of wave-formation under the action of wind, especially if we suppose that the waves move very slowly, as they would do if gravity (and cohesion) were small. The maintenance or augmentation of the waves requires that the forces operative at the surface be of suitable phase. Thus pressures acting upon the *retreating* shoulders are favourable, as are also tangential forces acting forwards at the *crests* of the waves, where the internal motion is itself in the forward direction. Equation (65) shows that the pressures produce no effect, and that we have only to consider the action of the tangential stress. We see from (66) that when the waves move in the same direction as the wind, the effect of the latter is to favour the development of the former. Whether the waves will actually increase depends upon whether the supply of energy, proportional to β^2 , is greater or less than the loss from internal dissipation, itself proportional to the same quantity. If the waves are moving against the wind, the tendency is to a more rapid subsidence than would occur in a calm.

Terling Place, Witham.

XXXIX. *An Example in "Correlation of Averages" for Four Variables.* By SOPHIE BRYANT, D.Sc.*

IN Professor Edgeworth's papers† on "Correlated Averages" he has shown how to obtain for any number of variables the coefficients of the quantic of the second degree which, taken negatively, is the exponent of e in the equation expressing frequency of correlation. Thus, w denoting frequency, and $x_1, x_2 \dots x_n$ the correlated variables, such as lengths of limb in an n -limbed animal, the locus of $w, x_1, x_2 \dots x_n$ is given by the equation

$$w = J e^{-R},$$

where

$$R = p_1 x_1^2 + p_2 x_2^2 + \dots + p_n x_n^2 + 2q_{12} x_1 x_2 + \dots + 2q_{n-1n} x_{n-1} x_n.$$

And all the n -dimensional quartics with equations of the form

$$R = \text{constant}$$

* Communicated by the Author.

† See Phil. Mag., Aug., Nov., Dec., 1892, and Jan. 1893.

are loci of equal frequency, analogous to Mr. Galton's ellipses and Professor Edgeworth's ellipsoids; the former of which can easily be observed as loci of equal height on a probability-surface, the vertical being taken as the dimension of frequency.

Professor Weldon's measurements of the organs of shrimps supply a real biological example to which can be applied for more than three variables the principles of correlated averages. The theoretic, no less than the practical, interest of this example is much enhanced by the fact that specimens from the Plymouth and from the Naples coast were measured, the number of measurements being 1000 in each case. Thus excellent material exists for the computation of the quantic pertaining to two distinct groups of the same species, and the two sets of coefficients thus calculated may be compared.

Selecting from Professor Weldon's ρ -coefficients the six, correlating four organs, that appear to be most suitable, we have for our data the following systems :—

| | ρ_{12} | ρ_{13} | ρ_{14} | ρ_{23} | ρ_{24} | ρ_{34} |
|--------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Naples | ·29 | —·23 | ·27 | ·71 | ·76 | ·63 |
| Plymouth ... | ·24 | —·18 | ·22 | ·78 | ·78 | ·67 |

It is proposed in the following pages to calculate the two quantics to which these systems of coefficients respectively give rise, as examples of correlation between the averages of four variables.

Since ρ_{12} and ρ_{21} have the same meaning, and a similar remark applies to all the coefficients, it is allowable to change the order of the numerals for the sake of symmetry whenever it is found convenient to do so, there being in each case an order which is best for securing the immediate detection of a mistake. Also it is often of assistance to write ρ_{11} , ρ_{22} , &c. for unity, as this makes the order of the numerals more apparent.

Let Δ , as usual, be the discriminant of R, *i. e.*

$$\Delta = \begin{vmatrix} p_1 & q_{12} & q_{13} & q_{14} \\ q_{21} & p_2 & q_{23} & q_{24} \\ q_{31} & q_{32} & p_3 & q_{34} \\ q_{41} & q_{42} & q_{43} & p_4 \end{vmatrix} *$$

* The p 's here might, for symmetry, be called q_{11} , q_{22} , q_{33} , q_{44} .

Then Δ' , its reciprocal, is given* thus:—

$$\Delta' = \begin{vmatrix} \Delta\rho_{11} & \Delta\rho_{12} & \Delta\rho_{13} & \Delta\rho_{14} \\ \Delta\rho_{21} & \Delta\rho_{22} & \Delta\rho_{23} & \Delta\rho_{24} \\ \Delta\rho_{31} & \Delta\rho_{32} & \Delta\rho_{33} & \Delta\rho_{34} \\ \Delta\rho_{41} & \Delta\rho_{42} & \Delta\rho_{43} & \Delta\rho_{44} \end{vmatrix}$$

Hence, since each first minor of Δ' is equal to Δ^2 multiplied by the corresponding constituent of Δ †, we have the series of equations required for the proportionate values of the coefficients

$$\frac{p_1}{\Delta}, \frac{p_2}{\Delta} \dots \frac{q_{12}}{\Delta}, \frac{q_{13}}{\Delta} \dots$$

Consider, first, the Naples case. We have

$$\Delta^2 p_1 = \Delta^2 \begin{vmatrix} \rho_{22} & \rho_{23} & \rho_{24} \\ \rho_{32} & \rho_{33} & \rho_{34} \\ \rho_{42} & \rho_{43} & \rho_{44} \end{vmatrix} = \Delta^2 \begin{vmatrix} 1 & \cdot 71 & \cdot 76 \\ \cdot 71 & 1 & \cdot 63 \\ \cdot 76 & \cdot 63 & 1 \end{vmatrix} = \Delta^2 \times \cdot 2013,$$

$$\therefore p_1 = \Delta \times \cdot 2013.$$

$$\frac{p_2}{\Delta} = + \begin{vmatrix} \rho_{33} & \rho_{34} & \rho_{31} \\ \rho_{43} & \rho_{44} & \rho_{41} \\ \rho_{13} & \rho_{14} & \rho_{11} \end{vmatrix} = + \begin{vmatrix} 1 & \cdot 63 & -\cdot 23 \\ \cdot 63 & 1 & \cdot 27 \\ \cdot 71 & \cdot 27 & 1 \end{vmatrix} = \cdot 3991.$$

Similarly, for $\frac{p_3}{\Delta}$ and $\frac{p_4}{\Delta}$ we have the values of the other two principal minors of the original determinant, i. e. $(\rho_{33}, \rho_{44}, \rho_{11})$ and $(\rho_{11}, \rho_{22}, \rho_{33})$, each taken with its proper—that is with the positive—sign ‡. For the signs of the remaining minors which have to be equated to $\frac{q_{12}}{\Delta}$, &c., the following is a convenient rule. The minors of the constituents in the first row are alternately positive and negative, beginning with ρ_{11} , whose minor is positive. The minors of the constituents in the second row observe the same rule, beginning with ρ_{22} and proceeding in cyclic order $\rho_{23}, \rho_{34}, \rho_{31}$. Similarly for the third and fourth rows beginning with ρ_{33} and ρ_{44} . Thus:—

$$\frac{q_{12}}{\Delta} = -(\rho_{23} \rho_{34} \rho_{41}) = - \begin{vmatrix} \rho_{23} & \rho_{34} & \rho_{41} \\ \rho_{33} & \rho_{34} & \rho_{31} \\ \rho_{43} & \rho_{44} & \rho_{41} \end{vmatrix} = - \begin{vmatrix} \cdot 71 & \cdot 76 & \cdot 29 \\ 1 & \cdot 63 & -\cdot 23 \\ \cdot 63 & 1 & \cdot 27 \end{vmatrix} = -\cdot 1436.$$

* See Prof. Edgeworth, on Correlated Averages, in Phil. Mag. August 1892, pp. 200, 201 especially.

† Ibid.

‡ See Salmon's 'Higher Algebra.'

$$\frac{q_{12}}{\Delta} = +(\rho_{24} \rho_{41} \rho_{13}) = \cdot 1886.$$

$$\frac{q_{14}}{\Delta} = -(\rho_{21} \rho_{32} \rho_{43}) = -\cdot 0640.$$

$$\frac{q_{23}}{\Delta} = -(\rho_{24} \rho_{41} \rho_{12}) = -\cdot 2483.$$

$$\frac{q_{24}}{\Delta} = +(\rho_{21} \rho_{42} \rho_{13}) = -(-\cdot 1081) = +\cdot 1081.$$

$$\frac{q_{34}}{\Delta} = -(\rho_{41} \rho_{12} \rho_{23}) = -\cdot 1045.$$

Treating the Plymouth values of the ρ 's in the same way, we obtain the second set of proportionate coefficients. The following Table exhibits all the results :—

| | $\frac{p_1}{\Delta}$ | $\frac{p_2}{\Delta}$ | $\frac{p_3}{\Delta}$ | $\frac{p_4}{\Delta}$ | $\frac{q_{12}}{\Delta}$ | $\frac{q_{13}}{\Delta}$ | $\frac{q_{14}}{\Delta}$ | $\frac{q_{23}}{\Delta}$ | $\frac{q_{24}}{\Delta}$ | $\frac{q_{34}}{\Delta}$ |
|------------|----------------------|----------------------|----------------------|----------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| Naples ... | $\cdot 2013$ | $\cdot 3991$ | $\cdot 3844$ | $\cdot 2642$ | $-\cdot 1436$ | $\cdot 1886$ | $-\cdot 0640$ | $-\cdot 2483$ | $-\cdot 1081$ | $-\cdot 1045$ |
| Plymouth | $\cdot 1486$ | $\cdot 4172$ | $\cdot 3680$ | $\cdot 2342$ | $-\cdot 1220$ | $\cdot 1458$ | $-\cdot 0355$ | $-\cdot 2373$ | $-\cdot 1195$ | $-\cdot 0701$ |

Next to find $\frac{1}{\Delta}$ we may use the method of Professor Edgeworth's last paper*, which is less laborious than the other method. Accordingly

$$\begin{aligned} \frac{1}{\Delta} &= \begin{vmatrix} \rho_{11} & \rho_{12} & \rho_{13} & \rho_{14} \\ \rho_{21} & \rho_{22} & \rho_{23} & \rho_{24} \\ \rho_{31} & \rho_{32} & \rho_{33} & \rho_{34} \\ \rho_{41} & \rho_{42} & \rho_{43} & \rho_{44} \end{vmatrix} \\ &= 1 \cdot \frac{p_1}{\Delta} + \rho_{12} \frac{q_{12}}{\Delta} + \rho_{13} \frac{q_{13}}{\Delta} + \rho_{14} \frac{q_{14}}{\Delta} \\ &= \cdot 2013 \\ &\quad - \cdot 1023 \\ &= \cdot 099 = \cdot 10 \text{ correct to two places of decimals } \dagger. \end{aligned}$$

* *Ante*, p. 350.

† It should be noticed that these results, like all the others, can be relied on to two places of decimals only, since this is the number given in the original data, i. e. the values of the ρ 's.

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Similarly for the Plymouth group it is found to be .086.

The results may be verified by equating $\frac{1}{\Delta}$ to any of its other values, as

$$\frac{1}{\Delta} = 1 \cdot \frac{p_2}{\Delta} + \rho_{23} \frac{q_{23}}{\Delta} + \rho_{24} \frac{q_{24}}{\Delta} + \rho_{21} \frac{q_{21}}{\Delta},$$

or

$$\frac{1}{\Delta} = 1 \cdot \frac{p_3}{\Delta} + \rho_{34} \frac{q_{34}}{\Delta} + \rho_{31} \frac{q_{31}}{\Delta} + \rho_{32} \frac{q_{32}}{\Delta}.$$

I have used the first of these equations, and with the same result as before, i. e. .099 and .086.

Verification may also be obtained by means of the equation originally used *, i. e.

$$\frac{1}{\Delta^2} = \begin{vmatrix} p_2 & q_{23} & q_{24} \\ q_{32} & p_3 & q_{34} \\ q_{42} & q_{43} & p_4 \end{vmatrix} = \text{either of the other principal minors.}$$

By this method I find $\frac{1}{\Delta}$ for Naples to be .103, and for Plymouth .087, which coincides to two places of decimals with the results already determined. This tests very satisfactorily the consistency of the arithmetical work.

It now remains to find the values of p_1, p_2 , &c., which may readily be done by dividing each of the proportionate coefficients by $\frac{1}{\Delta}$. Performing this operation for each of the twenty coefficients their values are determined to be as follows :—

| | p_1 | p_2 | p_3 | p_4 | q_{12} | q_{13} | q_{14} | q_{23} | q_{24} | q_{34} | $\frac{1}{\Delta}$ |
|--------------|-------|-------|-------|-------|----------|----------|----------|----------|----------|----------|--------------------|
| Naples | 2.03 | 4.03 | 3.88 | 2.67 | -1.45 | 1.91 | -.65 | -2.51 | -1.09 | -1.06 | .099 |
| Plymouth ... | 1.73 | 4.85 | 4.28 | 2.73 | -1.42 | 1.70 | -.41 | -3.11 | -1.39 | -.82 | .086 |

The quantities therefore are :—

For Naples,

$$2.03x^2 + 4.03y^2 + 3.88z^2 + 2.67w^2 \\ - 2(1.45xy - 1.91xz + .65xw + 2.51yz + 1.09yw + 1.06zw).$$

* See Phil. Mag. Aug. 1892, p. 196.

For Plymouth,

$$1.73x^2 + 4.85y^2 + 4.28z^2 + 2.73w^2 \\ - 2(1.42xy - 1.70xz + .41xw + 3.11yz + 1.39yw - .82zw).$$

The comparison between the two sets of results, with a view to ascertaining whether the discrepancy can be accounted for by accident or is indicative of a real difference in species, presents a problem in the theory of errors the consideration of which may be deferred to another occasion.

XL. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 280.]

June 21st, 1893.—Dr. H. Woodward, F.R.S., Vice-President, in the Chair.

THE following communications were read:—

1. "On Composite Dykes in Arran." By Prof. J. W. Judd, F.R.S., V.P.G.S.

It is proposed to apply the term 'composite dyke' to any fissure which contains two or more distinct varieties of igneous rock, differing from one another in chemical composition or mineralogical constitution. Such dykes, it is shown, fall into two classes:—

(A) Dykes in which differentiation has evidently taken place in the materials after their injection, as in the examples described by Dr. Lawson in Canada and by Prof. Vogt in Norway.

(B) Dykes in which we have evidence of the reopening of the fissure after its first injection and the introduction of materials of totally different composition. It is this class of dykes of which we find such interesting illustrations in Arran.

These Arran dykes belong to the latest volcanic eruptions of the British Islands; their analogues are found alike in the South of Scotland, and in the North of England and of Ireland. They are the infilled fissures along which sporadic volcanic outbursts took place after the extinction of the great volcanoes of the Inner Hebrides. The subaerial products of these later, and, for the most part, insignificant volcanic eruptions, have been all swept away by denudation, except at Beinn Hiant and the Sgùr of Eigg.

The materials filling these dykes belong to two totally different classes,—one distinctly basic, with about 55 per cent. of silica; and the other markedly acid in composition, with from 65 to 75 per cent. of silica. The basic rock is an augite-andesite, which passes sometimes into an intersertal and occasionally into an ophitic dolerite (tholeiite and diabase); the glass of this rock shows a great tendency to separate from the phenocrysts. The acid rock is often a highly

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vitreous material ('pitchstone' or 'pitchstone-porphyry') which by devitrification passes into various forms of felsite and quartz-felsite. These rocks, if we class them according to the nature of the porphyritic minerals they contain, fall into the several groups of vitrophyric and trachytoid lavas, to which the terms pantellerite, quartz-pantellerite, rhyolite, andesite, and dacite have been applied. The glassy groundmass in the whole of these rocks, however, is always abundant, and its characters are remarkably uniform however much the phenocrysts may vary.

An admirable type of the Arran composite dykes is found at Cir Mhor; this dyke traverses the granite, and has been excellently described by Ramsay and Bryce. The sides of the dyke are composed of augite-andesite, having a specific gravity of 2.71 and a silica percentage of 56; the centre of the dyke consists of a quartz-pantellerite with glassy base ('pitchstone-porphyry') passing into various stony varieties: this acid rock has a specific gravity of 2.36, and contains from 72 to 75 per cent. of silica, it is rich in soda as well as potash, and yields much water. The acid and basic rocks are strikingly contrasted with one another, alike in the characters of all their porphyritic crystals and of their vitreous bases. The acid rocks, however, contain a few crystals which have evidently been derived from the basic rock.

There is one fact with respect to the acid rock of the Cir Mhor dyke, to which attention is now called for the first time. Hyalite, the clear form of opal, occurs in it as a rock-constituent, and forms globules made up of several concentric layers which envelop the grains of quartz, are moulded on the angles of the felspar-crystals, and sometimes form independent segregations, with nuclei of tridymite-crystals. The identity of this interesting mineral has been established, not only by its optical properties, but by various micro-chemical tests.

On the shore and in the cliffs at Tormore, on the west coast of Arran, there occurs a remarkable plexus of dykes, many of which supply striking illustrations of our second class of 'composite dykes.' The locality was first described by Jameson, and some of the dykes have since been noticed by Allport, Zirkel, and other authors. In these composite dykes both the basic and the acid rocks are present; but while in some cases the acid rock was clearly introduced after the basic, in others the order of ejection of the two materials was reversed. In some instances, the plane of weakness along which the opening and re-injection of the dyke took place follows its central line; at other times it is at the side of the dyke; and occasionally it traverses the dyke-mass in a sinuous manner. The younger rock often contains numerous crystals derived from the older one, and these often show much alteration from the action of the magma in which they have been caught up. It is evident that the interval between the first and second injection of these dykes was sufficiently long to allow of the complete consolidation of the older rock.

In conclusion, it is pointed out that, while the peculiarities of the first class of composite dykes can be accounted for by selective

crystallization and liquation going on within the magma which has been injected into the dyke, no such explanation is sufficient in the case of the composite dykes of the second class, to which the examples cited from Arran belong.

That the association of two totally different rocks in the same dyke is not accidental, the numerous and varied examples at Tormore sufficiently prove. Where, as in these cases, we find that there is the greatest dissimilarity between both the crystals and the glassy groundmass of the two rocks, it is clear that the differentiation has taken place in the magma prior to its injection into the dykes, and before the work of crystallization had commenced. The physical causes which have been suggested to account for such differentiation in a fluid mixture of silicates are discussed.

2. "Notes on an Intrusive Sheet of Diabase and Associated Rocks at Robin Hood, near Bassenthwaite." By J. Postlethwaite, Esq., F.G.S.

The positions of the outcrops of the igneous rock are described, and a grit-band is recorded as running parallel to the diabase. The diabase, and vein-stuff associated with it, have furnished antimony, lead, copper, and arsenic; and the same ores, with the exception of the last two, are also found in minute grains in the grit. Analyses of the grit and diabase, made by Messrs. Hellon and Brockbank, are given. The igneous rock has produced slight metamorphism in the surrounding rocks of the Skiddaw Slates.

3. "On Two Dinosaurian Teeth from Aylesbury." By R. Lydekker, Esq., B.A., F.G.S.

4. "On a new Plesiosaur from the Waipara River, New Zealand." By Capt. F. W. Hutton, F.R.S., F.G.S.

5. "Observations on the Affinities of the Genus *Astroccenia*." By Robert F. Tomes, Esq., F.G.S.

6. "Description of a new Genus of *Madreporaria* from the Sutton Stone of South Wales." By Robert F. Tomes, Esq., F.G.S.

7. "Study of the Dykes of Hope, Idaho." By Herbert R. Wood, Esq.

In this paper a description of the geographical distribution and characters of acid and basic dykes traversing slates and quartzites along the northern shore of Lake Pend Oreille, Idaho, is accompanied by notes on the glaciation of the area. A brief description of the microscopic features of the igneous rocks is appended.

8. "The Rise and Fall of Lake Tanganyika." By Dr. Robert Sieger.

The author refers to Mr. Carson's paper on the same subject in the Society's Journal for 1892. He himself believes the oscillation of level to be analogous to variations reported as occurring in other

African lakes, and to be due to climatic change. He brings forward evidence in favour of the coincidence of change of level and climatic change, but does not believe that his views are by any means contradictory to those of Mr. Carson, for the phenomena may be explained by a combination of the influences of climate with those of mechanical agencies.

9. "On Cheilostomatous Bryozoa from the Middle Lias." By Edwin A. Walford, Esq., F.G.S.

XLI. Intelligence and Miscellaneous Articles.

ON A PHOTOMETRIC METHOD WHICH IS INDEPENDENT OF COLOUR.

BY OGDEN N. ROOD.

THE principle underlying most of the photometric methods now in use depends on a comparison of the illumination of two adjacent fields; in some instances, as where a spot or a ring is made to disappear, this idea is thinly disguised, but instantly becomes apparent when the lights are differently coloured.

The object of the present paper is to present a mode of procedure in which the coloration of the two surfaces, even though at a maximum of vividness, is a matter of entire indifference, since the process depends not on a comparison of these surfaces, but on the shock which the retina experiences when one surface is quickly withdrawn and replaced by another. If we take a uniform circular disk of any colour, illuminate it evenly, and then set it in rotation slowly or rapidly, the retina will receive no shock, since the parts replacing each other in the retinal image are in all respects identical; in other words, no flickering will be perceived. If, however, one half of the disk reflects less light than the other by $\frac{1}{10}$ of the total amount, with appropriate rates of rotation a faint flickering will be noticed, which will increase in intensity as the difference of the luminosities of the two halves of the disk is made greater.

Accordingly I prepared a set of about a hundred disks of drawing-paper, their depth of tint ranging from the whitest paper down to the blackest, the gradation being as even as practicable. For the determination, then, of the reflecting-power, for example of a vermilion disk, it was only necessary to select from the series a grey disk which, when combined with it in equal parts, gave no perceptible flicker, and afterwards to determine the reflecting-power of this grey disk in terms of the standard white cardboard. Results were thus obtained for the principal colours—red and blue-green, yellow and blue, green and purple. The difficulty in measuring the reflecting-power of these coloured disks was in all cases the same, and was due to the fact that it is hard to obtain grey disks with absolutely uniform surfaces. This trouble, or a lack of uniformity in the coloured disks themselves, was to a considerable extent obviated by reversing the halves of the composite

disk so as to employ the previously unused surfaces. Small irregularities of texture or a sandy appearance do not interfere with the use of the disks to a noticeable extent, but when the depth of the tint changes slowly over an extended surface it gives more trouble. Of course the case frequently arose where in the entire hundred disks not one could be found with which the flickering entirely disappeared at quite low rates of rotation, and here it was necessary to determine with which grey disk the flicker was at a minimum. This was accomplished by combining the same coloured disk with *two* grey disks, a larger and a smaller, on the same axis, when it would become evident which was the more favourable combination, and the observer would notice that the luminosity of the coloured disk must be nearer to one grey disk than to its mate, or about equally distant from both.

As before stated, results were obtained for six disks, but these were selected so as to be complementary to each other in pairs, and in order to test the process they were now combined pair-wise and the resultant luminosities of their grey mixtures were determined by the old method, and afterwards *calculated* on the basis of the figures furnished by the flickering process :—

| | Grey mixture. | Difference. |
|---------------------------|------------------|-------------|
| Purple and green | 27.5 observed. | 0 |
| | 27.5 calculated. | |
| Red and blue-green .. | 20.2 observed. | 1.0 |
| | 21.1 calculated. | |
| Yellow and blue | 27.85 observed. | 1.25 |
| | 29.1 calculated. | |

These experiments were not at all elaborate, and as their greatest difference barely exceeds one per cent. of the reflecting-power of white cardboard, they may be taken as furnishing a proof of the correctness of the process employed.

Thus far we have dealt with the combination of white (grey) disks with those that are strongly coloured, and it remains to give an example of the process as applied to two differently coloured but not complementary disks. To test this matter it was necessary to find two coloured disks having the same or nearly the same reflecting-power. In my collection I finally found two such disks, a cyan-blue with a reflecting-power of 23.9 and a purple for which the figure 23.3 had been obtained: these disks, when combined, gave a scarcely perceptible flicker. Since then graded series of yellow disks have been made, but it has been impossible to find time to hunt up their equivalents in luminosity and make the necessary determinations.

This flickering process having answered so well, the procedure was reversed and used with great advantage to facilitate the determinations of the values of the grey disks executed in the ordinary way; in other words, the series of grey disks as made by myself is not pure grey but has a slightly yellowish tint that makes estimation of equality of luminosity a little more difficult than it ought to be.

Accordingly, in measuring the reflecting-power of the grey disks by the old method, the standard white and black disks were combined with a *small* amount of an orange-yellow disk, which made their mixture match the tint of the grey disk under experiment. The luminosity of the orange-yellow disk in terms of standard white cardboard being known, the final result was calculated with equal facility and the annoyance removed. It is hardly necessary to add that in all cases the amount of white light reflected from the standard black disk was taken into account.

An experiment was now made to test the flicker process by using it to determine the reflecting-power of two grey disks which were afterwards measured in the ordinary way, and the following result was obtained :—

| | | | |
|----------------------|-------|-------|-------|
| Direct determination | | 34.1 | 29.1 |
| Flicker | „ | 33.7 | 28.6 |
| | | <hr/> | <hr/> |
| Difference | | .4 | .5 |

These determinations were not elaborate but may suffice for the purpose.

Afterwards a more careful set of observations was made to ascertain with what minimum difference in luminosity the flicker became insensible ; a series of five light-grey disks was made with gradations so small that these would have required elaborate work for their individual determination, which was not attempted directly, the method of measuring the least and the most luminous disk being employed, and the difference between the figures divided by four. When these disks were tested flicker fashion in pairs, it was found that the intervals between them were not at all identical, one being larger and its neighbour smaller than the average interval, but each pair nevertheless furnished a faint but distinct flicker. If the intervals had been regular, as was intended, the experiments would have proved that with a difference of $\frac{1}{10}$ part of the total light a flicker could be perceived ; as it was it showed that a considerably smaller difference suffices, probably about $\frac{1}{100}$.

It is evident that for the purpose of measuring the reflecting-power of coloured disks it will not in every case be necessary to undergo the labour of making an elaborate set of grey disks : if the experimenter is furnished with six or eight brilliantly-coloured disks, the reflecting-power of which has been carefully determined, then, with these and black and white disks, he will be able to match new disks and measure their luminosity in the old way.

There does not seem to be any reason why this process with the aid of well-known optical devices should not be applied to ordinary photometric work, or to such as is carried on in the interior of the observing-telescope of a spectroscope. In simple work with disks like that here presented, the flicker photometer is necessarily on the model of a staircase, and the transitions, though small, are always abrupt ; but when there are other modes of regulating the illumination this would not be the case, and the advantage of mul-

tipling observations would be more fully experienced. Some experiments for dividing up even the interval between two disks have been begun, with promising results, but are not yet finished.

It is well known that gazing steadily at a flickering surface is trying to the eyes, but in the operations above described no inconvenience whatever from this source was experienced, since if the flicker was strong a glance revealed the fact and another disk was substituted; the faint flickering which demands more prolonged attention seems to be no more trying to the eyes than ordinary optical work.

It may be a matter of some interest in physiological optics to know that the sensation called "flickering" is independent of wavelength and connected with change in luminosity. When two differently-coloured surfaces of the same luminosity are successively presented to the eye as above described, no shock is experienced, and the colours are seen to mingle in a soft streaky way; if observation is prolonged for some time, subjective effects begin to manifest themselves, especially with quite low rates of rotation; it is of course best not to study these with undue curiosity.—*American Journal of Science*, September 1893.

EXPERIMENTAL INVESTIGATIONS ON DIELECTRICS.

BY DR. G. BENISCHKE.

In the first part of the research the author determines the dielectric constants of a few solid bodies by Gordon's method, as modified by Lester, but in which, instead of the Ruhmkorff's coil, the alternating current of the Innsbruck installation was used for charging the condenser. This charges the condenser alternately positively and negatively, so that the formation of residues of either kind is thereby avoided. In order to attain greater sensitiveness the alternating current was transformed into one of higher tension by means of an induction-coil. In this way it was possible to use various tensions. It was found that the dielectric constant is independent of the strength of the electric field in the condenser; this also proves that there is no appreciable conductivity in the dielectric, for if there had been its capacity must also have been increased with increase of tension. The dielectric constant of paraffin was found to be 1.89, ebonite 2.03, sulphur 2.42, ordinary glass 4.17-4.52, plate glass 3.85.

In the second part of the research the influence of the alternating current on the dielectric constant was investigated, by exposing the dielectric for various periods to tensions of 8 to 1600 volts, and then investigating them. No such influence could be ascertained. The capacity of the condenser was, it is true, 2 to 3 per cent. less, but after a long time it reverted to the original amount. This change may be ascribed to a transitory condition of strain, or to a kind of hysteresis.—*Wiener Berichte*, April 13, 1893.

ON THE USE OF CUPRIC NITRATE IN THE VOLTAMETER, AND THE ELECTRO-CHEMICAL EQUIVALENT OF COPPER. BY F. E. BEACH.

According to the author the advantages possessed by the nitrate may be enumerated as follows:—

1st. The weight of copper deposited does not appear to depend on the current-density.

2nd. It permits the use of a high current-density.

The limit is not easily stated. When 0.25 ampere per square centimetre is reached the cathode needs watching, for it will fringe at the edge but does not become powdery.

No way was found to prevent the branching with a high current-density.

A greater amount of NH_4Cl should be present when the current-density is increased.

3rd. The weight of copper is practically independent of the temperature between 10° and 35°C .

The tendency to oxidation is increased by lowering the temperature, but this may be easily counteracted by the addition of more NH_4Cl .

4th. The solution may be used a number of times.

5th. The equivalent agrees to four figures with that calculated from the best chemical determinations, viz.:—

$$\text{Richards} \quad \text{Eq.} = (3294.4 \pm 0.1) \times 10^{-7}.$$

$$\text{First Series} \quad \text{Eq.} = (3294.8 \pm 0.43) \times 10^{-7}.$$

$$\text{Second Series} \quad \text{Eq.} = (3293.9 \pm 0.39) \times 10^{-7}.$$

The purity of the nitrate as a condition of success is to be emphasized. One specimen tried, which contained nitrite, was absolutely worthless with the foregoing treatment.—*American Journal of Science*, August 1893.

NOTE BY LORD KELVIN ON ELECTRIC MOLECULES FOR THE EXPLANATION OF THE PIEZO-ELECTRIC AND PYRO-ELECTRIC PROPERTIES OF CRYSTALS.

Since my communication of a short article "On a Piezo-electric Pile" to the Philosophical Magazine (*suprà*, p. 342), I have found a very important article* by Messrs. J. and P. Curie, in which precisely the same combination is described, and the application of the principle illustrated by it to explain all the piezo-electric and pyro-electric properties of crystals is pointed out.

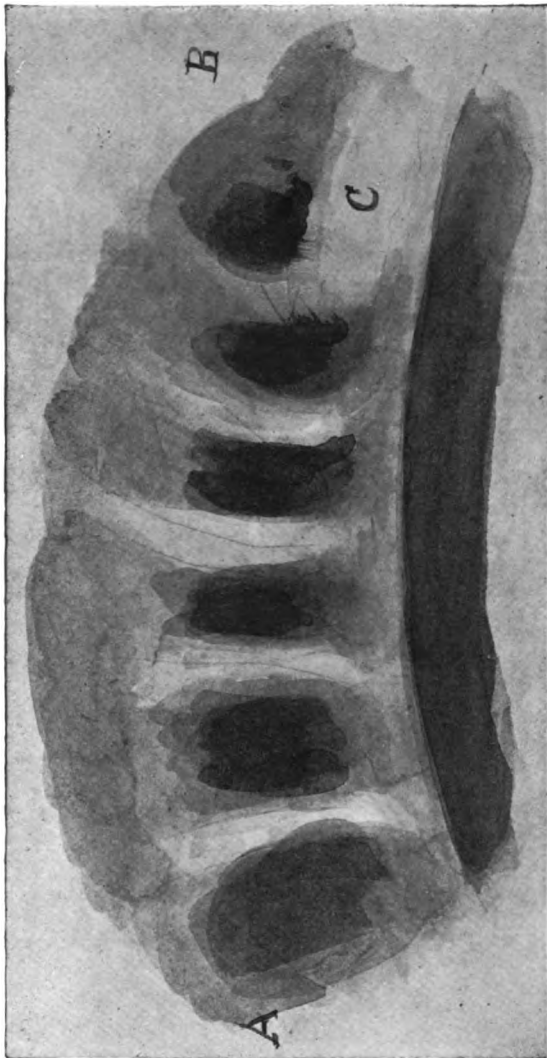
The discovery of the piezo-electric property in crystalline matter has been made known to the world by the experimental researches of the brothers Curie; and it now interests me exceedingly to find that they have also given what seems to me undoubtedly the true electro-molecular theory of the constitution of crystals, explaining not only piezo-electricity, but the old known pyro-electricity; and bringing these properties into relation with the electro-chemical constitution of the crystalline molecule.

KELVIN.

Aix-les-Bains, Sept. 21, 1893.

* *Comptes Rendus* of the French Academy of Sciences for Feb. 14, 1881.

Fig. 3.



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[FIFTH SERIES.]

NOVEMBER 1893.

XLII. *New Methods of Measuring the Surface-Tension of Liquids.* By T. PROCTOR HALL*.

I. HISTORICAL.

THE common way of measuring the surface-tension of liquids by finding the height to which they will rise in capillary tubes is simple and convenient, and is applicable to nearly all liquids. The degree of accuracy attainable is limited by (a) the narrowness of the tube, or else the shortness of the elevated liquid column, which limits the accuracy of measurement; by (b) irregularities in the bore of the tube; by (c) the difficulty in securing a clean surface, particularly in very small tubes; and by (d) impurities, such as dissolved air, in the body of the liquid. It is to the last two causes that most of the differences seen in the following table are probably due. The table gives the values of the surface-tension of water as found by various observers by means of capillary tubes. All values are given in dynes per centimetre, and the numbers in the second column are, where necessary, deduced by Brunner's formula for the relation of surface-tension to temperature.

* Communicated by the Author.

Phil. Mag. S. 5. Vol. 36. No. 222. Nov. 1893. 2 D

Surface-Tension of Water, by capillary tubes.

| T. | T at 0° C. | Observer. | Reference. |
|-----------------------|---------------|-----------------------------|--|
| 74.4 at 0° C. | 74.4 | Artur. | <i>Théorie élémentaire de la capillarité</i> |
| 75.2 - 1405 t. | 75.2 | Brunner. | <i>Pogg. Ann.</i> lxx. p. 481 (1847). |
| 74.0 at 8° 5. | 75.2 | Desain. | <i>Ann. Chim. Phys.</i> li. p. 383 (1857). |
| 75.0 at 0°. | 75.0 | Frankenheim. | <i>Pogg. Ann.</i> xxxvii. p. 409 (1836). |
| 75.4 - 141 t. | 75.4 | Frankenheim. | <i>Pogg. Ann.</i> lxxii. p. 177 (1847). |
| 75.6 - 146 t. | 75.6 | Frankenheim & Sondhausa. | <i>Journ. Pr. Chem.</i> xxiii. p. 401 (1841). |
| 74.2 at 8° 5. | 75.4 | } Gay-Lussac. | { <i>Poisson, Nouvelle Théorie etc.</i> pp. 112, 181 (1831). |
| 73.7 at 11°. | 75.2 | | |
| 73.1 at 10°. | 74.5 | Hagen. | <i>Pogg. Ann.</i> lxxvii. pp. 1, 152 (1846). |
| 77.1 - 179 t. | 77.1 | Jäger. | <i>Beibl.</i> xvi. p. 345 (1892); <i>Wiemer Ber.</i> pp. 99 & 100 (1891). |
| 71.0 at 19° 25. | 73.7 | Magie. | <i>Wied. Ann.</i> xxv. p. 432 (1885). |
| 71.0 at 16° 2. | 73.3 | Quincke. | <i>Pogg. Ann.</i> cxxxix. p. 1 (1870); <i>Phil. Mag.</i> April 1871, p. 252. |
| 72.1 betw. 15° & 20°. | ? | Quincke. | <i>Pogg. Ann.</i> clx. p. 371 (1877). |
| 71.8 at 17° 5. | 74.3 | Rodenback. | <i>Beibl.</i> iv. p. 105 (1880). |
| 79.7 - 204 t. | 79.7 | Simon. | <i>Ann. Chim. Phys.</i> xxxii. p. 5 (1851). |
| 75.4 - 144 t. | 75.4 | Sondhausa. | <i>Pogg. Ann.</i> Erg. viii. 1878, p. 266. |
| 71.3 at 16° 2. | 73.6 | Volkmann. | <i>Wied. Ann.</i> xi. p. 177 (1880). |
| 75.8 - 143 t. | 75.8 | Volkmann. | <i>Wied. Ann.</i> xvii. p. 361 (1882). |
| 76.5 - 144 t. | 76.5 | Wolf. | <i>Pogg. Ann.</i> cii. p. 571 (1857). |
| 77.3 - 1406 t. | 77.3 | Wolf. | <i>Ann. Chim. Phys.</i> xlix. p. 269 (1857). |
| 54.9. | ? | Wertheim. | <i>Pogg. Ann.</i> cii. p. 598 (1857). |
| Mean | 75.4 | | |

Capillary plates have been used by a few investigators in place of capillary tubes, with no apparent advantage. Volkmann* found for water at 16° C., $T = 71.8$ dynes (7.4 at zero), while Wertheim† and Hagen‡ obtained values approaching 50 dynes.

Wertheim§ and Hagen|| obtained equally low values by measuring the capillary elevation of water at a single vertical plane wall. Quincke¶, neglecting the curvature in glass bottles 50 millim. in diameter, deduced from the capillary elevation of water in them $T = 86.2$ dynes at zero. This method is obviously of no practical value.

In all of these three methods it is assumed that when the solid wall is wet by the liquid the angle of contact is zero. The validity of this assumption has been questioned by Quincke, who maintains** the actual existence of a finite

* *Wied. Ann.* xi. p. 177 (1880).

† *Pogg. Ann.* cii. p. 595 (1857).

§ *Ibid.* cii. p. 595 (1857).

¶ *Ibid.* cxxxv. p. 641 (1868), and *Phil. Mag.* August 1869, p. 95.

** Quincke, *Wied. Ann.* xxvii. p. 219 (1886).

‡ *Ibid.* lxxvii. p. 453 (1849).

|| *Ibid.* lxxvii. pp. 1, 153 (1846).

contact-angle in some cases in which the wall is wet by the liquid. In support of this assertion he gives the result of a large number of measurements of bubbles and drops, from which the surface-tension is found to be considerably greater than the values found from the measurement of elevations in capillary tubes. For water at 25° C. the mean of a small number of measurements, which differ from each other by ten per cent. in some cases, gives $T = 81$ dynes (84·5 at zero). Worthington† points out that Quincke's formula is only roughly approximate under the conditions of his measurements, and recalculates some of his results. The number 81 is thus reduced to 72·1 (75·6 at zero). Magie‡ prefers the value 77·6 (81·1 at zero), calculating from the same data. From his own measurements of drops and air-bubbles Magie§ found for water $T = 71·9$ dynes at 22°·5 C. (75·1 at zero). Timberg|| from similar measurements found $T = 80·5 - 182t$ for water. Bravais¶ and others have used the same method for other liquids. The discussion regarding these results has put a premium on methods which are independent of a contact-angle and whose mathematical relations are undisputed.

Buyss-Ballot**, who made a large number of determinations of the surface-tension of water between 10° and 97°·8 C. by adhesion-disks, calls attention to the rapid decrease in the adhesion of the disk as the boiling-point is approached. This is no doubt due to disengagement of vapour near the surface of the disk, and may perhaps be an indication that the water was not completely deprived of air. Buyss-Ballot gives $T = 75·1 - 236t$ dynes. Merian†† objects both to the calculation and to the formula used, and calculates from the same data $T = 78·5 - 253t$. Hagen‡‡ finds by this method a result much too low for the tension of pure water. Weinberg§§ finds $T = 80·1 - 177t$ dynes. Miss Poekels||| obtained some interesting qualitative results with very simple apparatus.

The surface-tension has been calculated from the weight of drops falling from a small disk or tube of known perimeter by Hagen¶¶, Timberg***, and others. Quincke††† found in a

* Quincke, Pogg. *Ann.* cxxxix. p. 1 (1870); *Phil. Mag.* April 1871, p. 253.

† Wied. *Ann.* xxv. p. 437 (1885).

‡ Wied. *Ann.* xxx. p. 545 (1887).

** Pogg. *Ann.* lxxi. p. 191 (1847).

†† Ibid. lxxvii. p. 464 (1849).

§§ *Beibl.* xvi. p. 496 (1892); *Journ. de Physique*, Sept. 1892, p. 378.

||| 'Nature,' xliii. p. 437 (March 1891).

¶¶ Pogg. *Ann.* lxxvii. pp. 449, 456 (1849).

*** Wied. *Ann.* xxx. p. 545 (1887).

††† Pogg. *Ann.* cxxxv. p. 621 (1868).

similar way the tension of metallic wires at or near their melting-points.

From measurements of pendent drops of water Worthington* found $T = 75$ dynes at 16° C. (77 at zero).

Henry† and Voille‡ measured the contractile force of soap-bubbles formed on U-tubes.

Dupré§ suggested that the existence of a distinct tension in a soap-film might be shown by its effect upon a straight wire laid across the legs of another U-shaped wire when a film is formed between.

Van der Mensbrugghe|| had already measured the tension of such a film in a wire frame by finding the weight supported by the free end of a string which was fastened to the frame and looped within it, so that the film was bounded by the greater part of the wire frame together with the outer edge of the circular loop.

Van der Mensbrugghe¶ also added weights to the lower of two equal horizontal circular wire rings until the barrel-shaped bubble formed between them became cylindrical. Sondhauss**, who employed the same method, dispensed with the lower ring and suspended the upper from the arm of a balance above the liquid. In this way he obtained as an approximation $T = 76 - \cdot 186 t$ dynes for water between $1^{\circ}6$ and $16^{\circ}6$ C. Timberg†† found $T = 80\cdot8 - \cdot 221 t$ dynes, using for calculation the maximum increase of weight as the ring is raised from the water-surface. Cantor‡‡ calculated the ratio of the maximum weight to the surface-tension, and found for water $T = 72\cdot3$ dynes at a temperature not stated.

Terquem§§ connected the ends of a horizontal wire by two equal strings to the ends of another wire of the same length above it. He then hung a small weight to the lower wire and measured the curvature of the strings when a film was formed between them.

Magie||| measured the curvature of the lower part of the meniscus in a capillary tube, and concluded that if any contact-angle exists at all when the liquid wets the tube it is very small. He found for water at $19^{\circ}25$ C., $T = 70\cdot9$ dynes ($73\cdot6$ at

* Proc. Roy. Soc. xxxii. p. 362 (1881); Phil. Mag. Jan. 1885, p. 46.

† Phil. Mag. June 1845, p. 363.

‡ Journ. de Physique, iv. p. 313.

§ Théorie mécanique de la Chaleur, 1869.

|| Phil. Mag. April 1867, p. 270.

¶ Ibid.

** Pogg. Ann. Erg. viii. (1878) p. 266.

†† Wied. Ann. xxx. p. 545 (1887).

‡‡ Ibid. xlvii. p. 399 (1892).

§§ Journ. de Physique, vii. p. 406 (1878).

||| Wied. Ann. xxv. p. 432 (1885).

zero) as compared with 71.0 by the common method at the same temperature.

Wilhelmy* weighed a rectangular plate of known dimensions and specific gravity when dipped a determinate distance into the liquid. He made a large number of determinations which agreed closely for any one plate, but varied greatly for plates of different materials in the same liquid. Using a glass plate in water at 0° C. he found $T=77.9$ dynes, assuming that the angle of contact is zero.

Waterston† and Worthington‡ modified Wilhelmy's method, touching only the lower edge of the plate to the liquid surface.

Sentis§ measured with a spherometer the height of a weighed and measured rectangular iron plate floating on mercury, eliminated the irregularity due to the corners by means of a second plate of the same thickness and density, and deduced the value of the surface-tension of the mercury.

Lenard|| arranged a regular succession of falling drops so as to be seen by intermittent light; measured the extent and time of their oscillations; and from these data calculated the surface-tension. For water he found $T=70.3$ dynes at 16° C. (72.6 at zero), the mean of a considerable number of determinations. With reasonable care in this method a clean surface is ensured, and no question of contact-angle interferes with confidence in the results.

Rayleigh¶ measured the wave-length of the transverse vibrations of water-jets issuing under constant pressure from elliptical orifices. The results, which are not closely concordant, are in harmony with the supposition that the surface-tension is about 76 dynes.

Rayleigh** also measured the wave-length of ripples and calculated the surface-tension by Thomson's formula. Particular attention was given to the purity of the water-surface, and the results appear to be free from constant errors. Individual determinations differ by 2 dynes in a few cases. The mean of all, for both distilled water and tap water, is $T=73.9$ dynes at 18° C., corresponding to 75.4 at zero, which happens to be exactly the mean of all the results quoted for capillary tubes.

The correctness of the assumption formerly made, that when a liquid wets a solid the angle between the two surfaces may be considered zero, is now pretty well established.

* Pogg. *Ann.* cxix. p. 186 (1863).

† Phil. Mag. Jan. 1858, p. 4.

‡ Ibid. Jan. 1885, p. 43.

§ *Journ. de Phys.* ix. p. 384 (1890); or Phil. Mag. Dec. 1891, p. 564.

|| Wied. *Ann.* xxx. p. 200 (1887).

¶ Proc. Roy. Soc. xxix. p. 71 (1879).

** Phil. Mag. Oct. 1890, p. 386.

None of the methods in use seem to exceed in general accuracy or convenience the ordinary plan with capillary tubes, the limitations of which have been already referred to. The direct dependence of surface-tension upon molecular cohesion, and its consequent importance as a reliable indication of changes of condition in liquids, makes it very desirable that some more accurate plan of measurement should be devised.

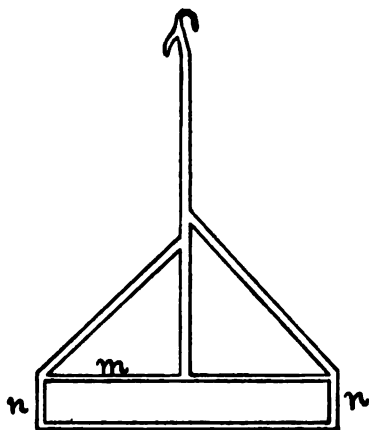
II. NEW METHODS.

A.

Two years ago, at the suggestion of Professor Michelson and under his direction, I undertook the investigation of a direct method which, from some preliminary experiments, he expected to give results ten times as accurate as those found by any method now in general use.

This method consists in finding the weight of a thin horizontal bar, suspended a few millimetres above the liquid surface, whose extremities are bent at a right angle so as to dip into the liquid. The weight is taken first when a film of the liquid is extended between the bar and the level surface, and, secondly, in exactly the same position after the film is broken. The difference between the two weights divided by twice the width of the film gives the surface-tension in grams per centimetre, which is reduced to dynes per centimetre when

Fig. 1.



multiplied by the constant g , whose value at Clark University is 980.3.

For nearly all ordinary liquids a glass rod is suitable, but

a rod of almost any material sufficiently rigid which is wet by the liquid will serve as well. For mercury a steel needle plated with copper and well amalgamated has been suggested. In my investigations the rod was of glass, and formed part of a glass frame (fig. 1) whose form was varied to suit the circumstances. The essentials of a good frame are the following:—

- (a) It must not yield sensibly under the tension of the film.
- (b) The bar m must be thin, and all parts of m and n must lie evenly in the vertical plane.
- (c) The frame must be balanced so that m hangs horizontally both with and without the film.
- (d) The two short sides, nn , must be of uniform and nearly equal diameter, must be as nearly as possible parallel, perfectly straight, and make sharp right angles with m .

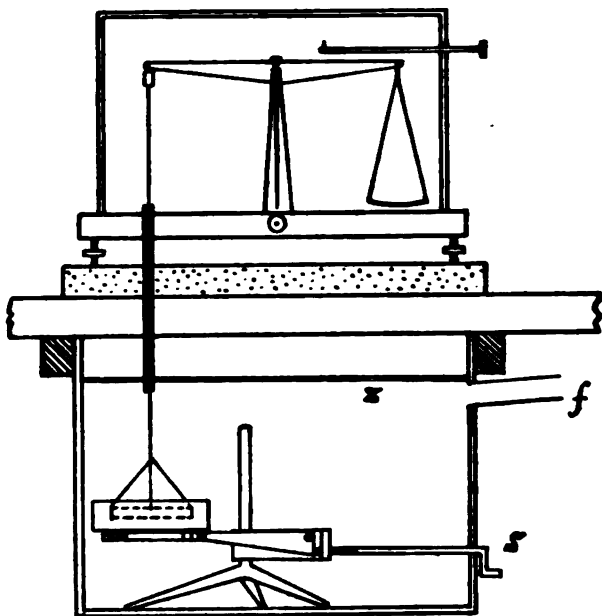
With a little practice and more patience good frames were readily made in the following way. Taking ten centimetres of a small hard-glass tube, I bent it at a right angle near one end, then fused that end until only a minute hole with a very thick margin was left. This was connected by a thin rubber tube to a gas-pipe, and the small jet lighted. It burned with a clear blue flame 10 to 15 millim. long, and quite hot enough to melt glass rods a millimetre in diameter. If the orifice is too large the flame has a white tip and is not so hot. An improved jeweller's blowpipe connected by slender rubber tubes to the gas-supply and to the mouthpiece will do nearly as well. This blowpipe is held in the hand. Glass threads of suitable size are laid upon an asbestos mat, which has a number of pencil lines drawn upon it exactly at right angles, and are there fused together in the required form. For general use a frame like the one shown in the figure may be made of rods $\frac{1}{8}$ to 1 millim. thick (the handle thicker); having the bar m 10 centim., n 2 centim., and the handle 15 to 20 centim. long. In some cases the lower horizontal bar may be omitted with advantage.

The frames were measured along lines parallel to m , between the inner edges of nn , at measured distances from m . If nn were not nearly parallel they were reset with the hand blowpipe. The measurements were made by comparison with a standard metre bar on the bed of a dividing-engine, where it was easy to get a degree of accuracy in excess of what was required for this investigation.

Figure 2 is a diagram of the general arrangement for weighing the tension. The balance stood upon a marble slab on a high shelf projecting from a brick partition-wall of the

laboratory. Under the shelf was a wooden closet having a door in front, a zinc top, *z*, and a pipe, *f*, leading to a ventilating-flue. The liquid to be examined was placed in a deep

Fig. 2.



glass evaporating-dish, which sometimes was fitted with a ground-glass cover, and rested upon the specially constructed arm of a heavy retort-stand, so arranged that it could be raised or lowered several centimetres by turning the screw-handle, *s*, outside the closet. Arrangements were also made for stirring the liquid by twirling in the fingers the end of a long-handled glass stirrer (fig. 3), and also for changing the glass frames, without opening the closet-door.

The liquid was placed so that its surface was 10 or 15 millim. below the bar *m* (fig. 1) of the frame. The latter was lowered into the liquid by tipping the balance-beam.

For work in which an error due to a change of half a degree in temperature may be neglected, such an arrangement is very satisfactory. But if it is desired to find the surface-tension at high or low temperatures, and especially

Fig. 3.



if the greatest attainable accuracy is desired, I should advise a different arrangement. A deep, thin-walled glass dish with a close-fitting cover in which are three holes—one in the centre for the arm of the frame, one for the thermometer, and one for the stirrer—should fit loosely into a double-walled box, also partly covered over the top, within which are air- or water-pipes, resistance-coils, or other arrangement for controlling the temperature. The large wooden closet of figure 2 may then be replaced by a simple subshelf for the box. For volatile liquids it is necessary to keep a slow current of air passing down the tube from the balance, to prevent condensation of the liquid on the rod that carries the frame.

A small correction is required for the capillarity of the sides nn of each frame. When the film is broken after the first weighing, a capillary elevation remains completely surrounding each side, n (fig. 1). But our calculation of the tension is based on the assumption that during the second weighing no tension is exerted at all between the sides nn . In effect, the difference between the two weighings gives the tension of a film a little narrower than the frame. The amount of this correction was found by taking the tension of the same liquid with two or more frames of the same thickness but of different widths. An example will explain the method.

The surface-tension of distilled water at $19^{\circ}.5$ C. was measured with three frames, whose widths a , b , c , and whose tension-weights m , n , r , were respectively

$$\begin{array}{ll} a = 5.2321 \text{ centim.} & m = .7742 \text{ gram.} \\ b = 2.0325 \text{ ,,} & n = .3001 \text{ ,,} \\ c = 0.2037 \text{ ,,} & r = .0291 \text{ ,,} \end{array}$$

Disregarding the capillary correction, the resulting values for the surface-tension in grams per centim. are :—

$$\frac{m}{2a} = .073985,$$

$$\frac{n}{2b} = .073825,$$

$$\frac{r}{2c} = .0714.$$

The true value of the tension, however, is

$$T = \frac{m}{2(a-x)} = \frac{n}{2(b-x)} = \frac{r}{2(c-x)}.$$

Eliminating x by the principle of proportion,

$$T = \frac{m-n}{2(a-b)} = \frac{m-r}{2(a-c)} = \frac{n-r}{2(b-c)};$$

also

$$x = a - \frac{m}{2T} = b - \frac{n}{2T} = c - \frac{r}{2T};$$

from which the following values are obtained :—

| T (gram). | x (centim.). |
|------------------|----------------|
| ·074089 | ·0074 |
| ·074088 | ·0073 |
| ·074092 | ·0073 |
| Mean ... ·074090 | ·0073 |

The value of x , for rigid frames, depends almost wholly upon the thickness of the vertical sides nn . If the frame be so slender as to allow these sides to approach each other sensibly under the tension of the film, the value of x will be increased. The following results were obtained in the course of my work :—

| Widths of frames, in centim. | Thickness of sides (centim.). | Liquid. | T (dynes). | x (centim.). | Notes. |
|------------------------------|-------------------------------|-----------------------|------------|----------------|----------------------|
| 5·23 2·03 0·20 | ·025 to ·029 | Water. | 72·6 | ·0073 | Frames nearly rigid. |
| 11·76 0·92 | ·038 to ·040 | " | 72·8 | ·0073 | Rigid. |
| 11·22 1·06 | ·076 to ·080 | " | 73·4 | ·0191 | " |
| " | " | 50 per cent. alcohol. | 30·3 | ·0186 | " |
| 11·88 0·96 | ·028 to ·033 | Water. | 72·9 | ·0136 | Slender. |
| " | " | " | " | ·0139 | " |

The capillary correction for a rigid frame 10 centim. wide, whose vertical sides are half a millimetre thick, does not exceed 1 part in 1000.

The weight required to balance a film of soap solution increased slightly for some time after its formation. The apparent tension of films of glycerine and of strong sulphuric acid decreased, at first rapidly, then more and more slowly for several minutes, finally becoming sensibly constant. The whole amount of increase or decrease after the first few seconds was generally about .02 per cent. of the tension.

The apparent tension of a film of water was in all cases sensibly constant as long as the film lasted. This seems remarkable when it is remembered that the water-film must have been growing thinner by evaporation, and also that the water under the bar *m* and along the sides *nn* was gradually flowing down into the liquid. The first process tended to decrease the weight very little and to increase the surface-tension by lowering the temperature; the second to decrease the weight. A change of one part in ten thousand could be readily detected.

The second weight—the weight of the frame *plus* adherent water after the film is broken—is variable. If the film is broken two or three seconds after its formation, the weight of the frame may be two or three milligrams greater than it is when the film lasts ten seconds. But the differences when the film has lasted more than five or six seconds are very small, amounting to only one or two tenths of a milligram for a frame 10 centim. wide.

This variability in the second weighing marks the limit of accuracy of the method as about one part in 5000, or .02 per cent., though a change in the tension amounting to less than .01 per cent. may be readily measured.

It will be shown later that the bar *m* must be raised from five to ten millimetres above the liquid surface before a true film is formed, and that the tension is not correctly found at a less height. It follows that the tension of alcohol, ether, chloroform, and similar liquids, in which the film breaks almost instantly at such a height, cannot be found by this method.

B.

In order to find the surface-tension of such liquids I adopted a modification of Wilhelmy's method. When the edge of a thin vertical plate is touched to a liquid surface, the liquid usually rises along the line of contact, and the weight of the plate is increased by

$$w = 2(a+b)T \cos \theta,$$

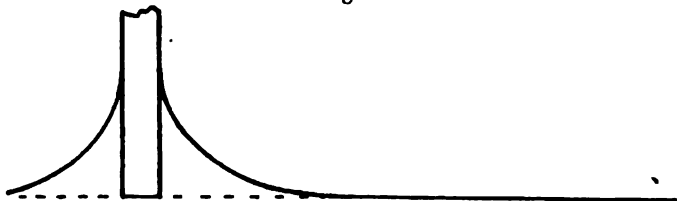
where *a* is the length and *b* the thickness of the plate in centimetres, *T* the surface-tension in grams per centimetre,

and θ the contact-angle. When the plate is wet by the liquid,

$$\theta = 0 \quad \text{and} \quad w = 2(a+b)T.$$

When the lower edge of the plate is kept at the general level of the surface, as in fig. 4, the thickness of the plate

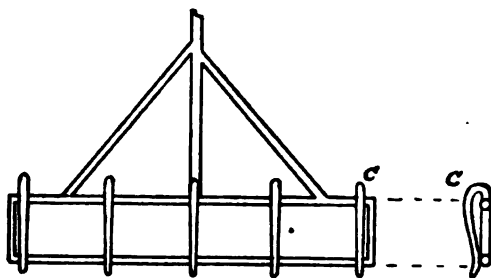
Fig. 4.



is of no consequence; but if it be placed h centimetre too high or too low there will be an error introduced equal to the weight of the liquid supported under the plate or displaced by it. That is to say, if ρ be the density of the liquid and h positive when the plate is too high, an error of $ab h \rho$ gram is introduced. This error becomes very small without material alteration in w when the plate is made very thin. In practice I found that for a plate 10 centim. long h rarely exceeded ± 0.01 centim., and that the amount of this error of setting for a plate 0.005 millim. thick was not more than $\frac{1}{20}$ milligram; or, for alcohol, about 0.1 per cent. of the surface-tension.

Thin plates were placed in a holder (fig. 5) made of glass

Fig. 5.



rods 1 millim. thick. Before inserting a plate the holder was balanced so that the stem hung vertically. The spring clips c (also of glass) were then wedged with little bits of wood, the plate inserted under them, two of the clips released, and the plate adjusted by trial over a liquid until the whole

edge seemed to enter the liquid at once when lowered, and when raised slowly parted from the liquid first at the two ends and lastly in the middle of the lower edge. After adjustment the holder and plate were washed, dried over a Bunsen flame, attached to the balance in the same way as the frame (fig. 2), left hanging over the liquid to be examined until the temperatures were nearly the same, then weighed. The index of the balance was next set exactly at zero, taking care that the beam was not lifted, and the liquid slowly raised by turning the screw-handle *s* until it touched the plate. The weight was again adjusted to bring the index exactly to zero. For a second determination the plate was lifted out of the liquid by tipping the balance-beam, the liquid lowered a little, and after all visible disturbance of the surface had ceased the operation of setting was repeated. The surface-area of the liquid must be so great that the measurement is not sensibly increased by the lowering of level due to the capillary elevation; or else this must be taken account of in the calculation.

It was necessary to ascertain, in the first place, whether the contact-angle can be considered zero to the limit of accuracy attainable by this method, and if so under what conditions. I proceeded to try plates of various materials in some liquids whose tension could be found by Michelson's method.

(1) *Glass Plate in glycerine.*

A microscope cover-glass, 5.044 centim. long and .026 centim. thick, was cleaned, dried, and touched to the glycerine surface without being allowed to sink even momentarily deeper. The first three weighings were made rapidly; the last three after an hour's contact.

| | <i>w</i> (gram). | $T \cos \theta$ (dynes). | Temp. C. |
|----|------------------|-----------------------------|----------|
| 1. | .6405 | 61.92 | 16°6 |
| 2. | .6391 | 61.79 | " |
| 3. | .6420 | 62.06 | " |
| 4. | .6550 | 63.32 | 16.9 |
| 5. | .6536 | 63.07 | " |
| 6. | .6534 | 63.12 | " |

The tension, as found by Michelson's method immediately afterwards, was

63.14 dynes at 17° C.

The error of setting calculated for this plate is ± 13 dyne. The angle of contact may therefore be considered zero for glycerine and glass, if time is allowed for attaining equilibrium.

(2) *Platinum in glycerine.*

In the same liquid a platinum plate, 6.375 centim. long, .0045 centim. thick, was touched to the surface and let stand a few minutes.

| <i>w.</i> | $T \cos \theta.$ | Temp. C. |
|-----------|------------------|----------|
| .8234 | 63.26 | 16.0 |

The error of setting is $\pm .02$ dyne.

(3) *Glass Plate in tap-water.*

The same plate as in (1).

| <i>w.</i> | $T \cos \theta.$ | Temp. C. |
|-----------|------------------|----------|
| .7585 | 73.33 | 14.52 |
| .7581 | 73.29 | 14.55 |
| .7583 | 73.31 | 14.58 |

T , by frame, = 73.32 at 14.41.

(4) *Platinum in tap-water.*

The plate used in (2) in the liquid of (3).

| <i>w.</i> | $T \cos \theta.$ | Temp. C. |
|-----------|------------------|----------|
| .8618 | | |
| .9541 | 73.30 | 14.8 |
| .9535 | 73.26 | " |
| .9538 | 73.28 | " |

The first weight was taken with the same precautions as before to prevent dipping below the water-level. In the other three cases the plate was dipped 1 millim. into the water, to wet it. The correction for -0.4 is $+0.6$ dyne, which makes the mean of the last three results 73.34 dynes at 14.4.

(5) *Platinum in distilled water.*

Plate the same as in (2), dipped 1 millim.

| w. | $T \cos \theta$. | Temp. C. |
|-------|-------------------|---------------------|
| ·9536 | 73·26 | 15 ^o ·28 |
| ·9544 | 73·32 | 15·10 |

The mean of these corresponds to 73·31 dynes at 15°·04, at which the tension was found by a frame to be 73·36 dynes.

Another trial with water freshly boiled gave with the plate

$$T \cos \theta = 72·10,$$

and with a frame

$$T = 72·76,$$

both at 19°·9 C.

In all these cases the platinum plate was washed with a caustic soda solution, well rinsed either in distilled water or at the tap, and made red-hot in a Bunsen flame before touching the liquid. I found that if the plate touched the liquid surface before it had time to cool after leaving the flame, the contact-angle would remain (sensibly) zero for a few minutes, without dipping the plate at all. It seems probable that condensation of air upon the plate may be one cause of the failure to get a zero angle. When the plate was washed without alkali, with or without acids, I failed to make the contact-angle even approximate to zero.

(6) *Platinum in a dilute solution of caustic soda.*

Plate the same as in (2).

| w. | $T \cos \theta$. | Temp. C. |
|-------|-------------------|---------------------|
| ·9023 | 69·32 | 16 ^o ·24 |
| ·9019 | 69·29 | 16·24 |
| ·9019 | 69·29 | 16·22 |
| ·9019 | 69·29 | 16·20 |

By a frame, $T = 69·36$ dynes at 16°·17.

(7) *Silver plate in distilled water.*

This plate was 7·625 centim. long, ·0025 centim. thick. It was washed in caustic soda solution, then in water, and dipped 1 millim. into the liquid before each weighing.

| | $w.$ | $T \cos \theta.$ | Temp. C. |
|----|--------|------------------|----------|
| 1. | 1.0000 | 64.27 | 17.70 |
| 2. | 1.0030 | 64.46 | " |
| 3. | 1.0035 | 64.49 | " |
| 4. | 1.0950 | 70.37 | 18.00 |
| 5. | 1.0855 | 69.76 | 17.70 |
| 6. | 1.0850 | 69.73 | " |

By a frame, $T = 72.84$ dynes at $18^{\circ}37$.

Before the fourth weighing the plate was warmed over a Bunsen flame, touched immediately to the water surface, and allowed to remain in contact ten minutes. 5 and 6 were taken after two hours of contact.

(8) These results, along with some others of the same kind, show that the contact-angle can be considered zero for

Glass and water, sulphuric acid, glycerine,
Mica and water,
Zinc and water,

when the surfaces are clean, and, in the case of zinc, freshly shaved; and that the angle for

Platinum and water,
Silver and water,

can be made zero, or nearly zero, with certain precautions.

In every case it is easy to see by a glance along the line of contact in a good light whether the angle of contact is zero or not.

(9) Though there could be no reasonable doubt that the angle of contact for alcohol and similar liquids would be zero in nearly all cases, as some observers have supposed otherwise I thought it worth while to measure the surface-tension of alcohol by several different plates. If there is a finite contact-angle for each plate, the values found for $T \cos \theta$ will be different. If these values are all alike, it is reasonably certain that the contact-angle is zero. The following table gives the results. In no case was any difference found in the weight after dipping the plate one or two millimetres into the alcohol, provided the plate was then allowed to stand two or three minutes in the normal position. During the operations the surface-tension probably increased a little by absorption of water-vapour from the air.

Common Alcohol.

| Plate. | Length (centim.) | Thick- ness (centim.) | $T \cos \theta$ (dynes). | Temp. C. | $T \cos \theta$ at 16° C. | Variation from mean of (1) and (2). | Error of setting, calcu- lated. |
|--------------|---------------------|-----------------------------|-----------------------------|----------------|------------------------------|---|--|
| Platinum (1) | 6.375 | .0045 | 23.38 23.38 | 15.80 " | 23.36 23.36 | -.02 -.02 | .02 dyne. |
| Zinc | 12.3065 | .0105 | 23.52 23.53 | 15.90 15.92 | 23.51 23.52 | +.13 +.14 | .05 " |
| Silver | 7.625 | .0025 | 23.56 23.57 | 16.00 " | 23.56 23.57 | +.18 +.19 | .01 " |
| Tin | 11.480 | .004 | 23.34 23.34 | 16.20 16.24 | 23.36 23.36 | -.02 -.02 | .02 " |
| Glass | 5.044 | .026 | 23.40 23.41 | 16.30 " | 23.43 23.44 | +.05 +.06 | .10 " |
| Platinum (2) | 13.481 | .002 | 23.37 23.37 | 16.43 " | 23.40 23.40 | +.02 +.02 | .01 " |

The zinc plate was slightly wedge-shaped and not very regular on the edge. There was no such irregularity in the silver plate; but on watching closely I could see that the alcohol crept rapidly up the plate, wetting it to a height of several millimetres above the normal line of contact. Several other trials with a silver plate showed the same peculiarity. There may have been something similar happening on the zinc plate, but if so I failed to detect it. Mica plates give the same result as plates of platinum and glass.

A platinum plate, if it can be obtained of the right thickness, is most satisfactory for liquids like alcohol. But mica makes a very good substitute. Mica can be split into sheets 10 or 15 centim. square and less than one hundredth of a millimetre thick by a thin paper-knife under water. The thin sheets may be floated upon sheets of paper, taken out and left to dry. They are easily cut with the point of a sharp knife when lying under a sharp-edged rule upon a glass plate; but they require rather delicate handling at every stage.

One of the difficulties of this method is caused by the tendency of minute specks, if there be any on the liquid surface, to gradually collect upon the plate and affect the measurement more than they affect the tension of the whole surface. A platinum plate should therefore be occasionally heated in the Bunsen flame, and for this reason it is convenient to have the plate in a metal holder. On a mica plate the effects of

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dust &c. are more easily seen, but it requires careful washing with a soft brush.

Under favourable conditions—a fresh clean surface, constant temperature, no dust, no disturbing vapours—a high degree of accuracy is attainable by this method. The following are selected from my results when these conditions were most nearly fulfilled.

1. Platinum plate, 13·495 centim. long, ·0045 centim. thick, in 99·8 per cent. alcohol. Error of setting, calculated, ·02 dyne.

| w. | T (dynes). | Temp. |
|--------|------------|-------|
| ·6210 | 22·548 | 18·22 |
| ·62095 | 22·543 | 18·25 |
| ·6209 | 22·537 | 18·29 |
| ·6209 | 22·537 | 18·31 |

The temperature-correction for 0°·1 is —·008 dyne.

2. Mica plate, 11·3180 centim. long, ·0007 centim. thick, in common alcohol at 17°·20 C. Calculated error of setting, ·003 dyne.

| w. | T (dynes). |
|--------|------------|
| ·55304 | 23·949 |
| ·55307 | 23·950 |
| ·55306 | 23·950 |

3. Mica plate, 11·42285 centim. long, ·0004 centim. thick, in common alcohol. Calculated error of setting, ·002 dyne.

| w. | T (dynes). | Temp. |
|--------|------------|-------|
| ·56360 | 24·183 | 16·20 |
| ·56363 | 24·184 | 16·24 |
| ·56363 | 24·184 | 16·26 |

C.

It has been already stated that, in order to form a true film between the liquid and the bar *m* of the frame (fig. 1), this bar must be from five to ten millimetres above the level surface. Even when the bar is excessively thin a distinct

maximum of weight is noticeable as the frame is raised, just before the true double-film is formed. This maximum can be found very exactly, and is made the basis of a third method of measuring surface-tension.

An equation to the capillary curve is found in the expression of the fact, that the vertical component of the surface-tension at any point is equal to the weight of liquid raised above the level surface, by the curved surface, from the level up to a perpendicular through that point. That is to say, taking a section of the capillary elevation of unit thickness (fig. 6),

$$T \sin \alpha = g\rho \int_{-\infty}^x y \, dx, \quad . \quad . \quad . \quad (1)$$

where

α = the angle made by the tangent with axis of x (the level surface);

T = the surface-tension, in dynes per centim.;

ρ = the liquid density;

g = the constant of gravitation.

If $c^2 = 4T/g\rho$, then

$$\frac{dx}{d\alpha} = \frac{c^2}{4y} \cos \alpha.$$

And since $\tan \alpha = dy/dx$,

$$\therefore \frac{dy}{d\alpha} = \frac{c^2}{4y} \sin \alpha.$$

Integrating,

$$\cos \alpha = \frac{c^2 - 2y^2}{c^2}; \quad . \quad . \quad . \quad (2)$$

$$\therefore \frac{dy}{dx} = \tan \alpha = \frac{\pm \sqrt{1 - \cos^2 \alpha}}{\cos \alpha} = \frac{\pm 2y \sqrt{c^2 - y^2}}{c^2 - 2y^2}.$$

Integrating again,

$$\pm x = \frac{c}{2} \log \frac{c + \sqrt{c^2 - y^2}}{y} - \sqrt{c^2 - y^2} + C.$$

Taking the origin so that the axis of y is tangent to the curve, when $x=0$, $y^2 = c^2/2$, from (2), and therefore

$$\pm x = \frac{c}{2} \log \frac{c + \sqrt{c^2 - y^2}}{y} - \sqrt{c^2 - y^2} + \frac{c}{2} \{ \sqrt{2} - \log (\sqrt{2} + 1) \}. \quad (3)$$

Suppose a horizontal circular cylinder of density ρ , whose diameter may be neglected in comparison with its length, to be suspended from one arm of a balance and to be in equilibrium just below the surface of a liquid, of density ρ , which wets it. When the cylinder is raised through a distance h ,

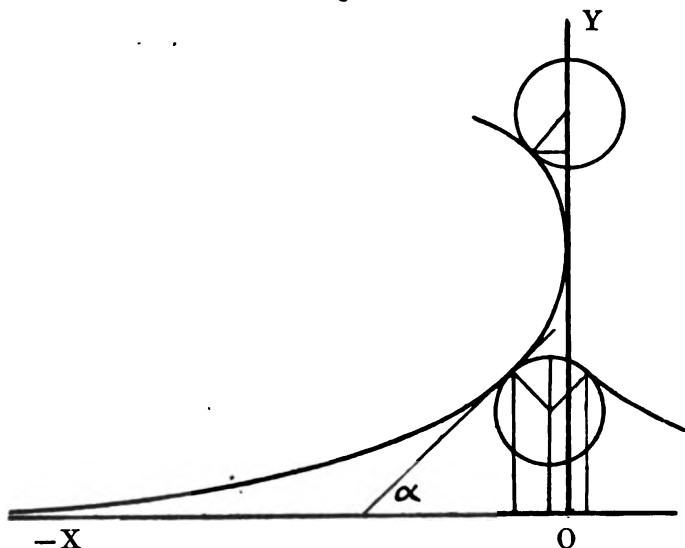
the increase of weight is ρ times the volume of cylinder and of liquid raised above the level surface. If r be the radius of the cylinder and w the increase of its weight, in grams, then (fig. 6) for unit length of the cylinder,

$$wg = 2T \sin \alpha + 2r\rho y g \sin \alpha + r^2 \rho g \alpha - r^2 \rho g \sin \alpha \cos \alpha,$$

$$\text{or } w = \rho \left\{ \frac{c^2}{2} \sin \alpha + 2ry \sin \alpha + r^2 \alpha - r^2 \sin \alpha \cos \alpha \right\}, \dots (4)$$

where αy is a point of contact of the cylinder and the surface film.

Fig. 6.



We have also (fig. 6)

$$h = y + r - r \cos \alpha, \dots (5)$$

$$\therefore h = y + \frac{2r}{c^2} y^2 \dots \text{from (2),}$$

$$\therefore y = \frac{c}{4r} (\sqrt{c^2 + 8rh} - c) \dots (6)$$

Equations (4), (5), and (6) are sufficient to determine w when h , r , ρ , and T are given.

The condition that w shall be a maximum is that $dw/dh = 0$.

Now

$$\begin{aligned} \frac{dw}{dh} &= \frac{dw}{d\alpha} \cdot \frac{d\alpha}{dh} \\ &= \frac{d\alpha}{dh} \rho \left\{ \frac{c^2}{2} \cos \alpha + 2ry \cos \alpha + 2r \sin \alpha \frac{c^2 \sin \alpha}{4y} + 2r^2 \sin^2 \alpha \right\}, \end{aligned}$$

and putting for $\cos \alpha$ and $\sin \alpha$ their values from (2), the condition that w shall be a maximum is

$$16r^2y^4 + 12c^2ry^3 + 2c^2(c^2 - 8r^2)y - 8c^4ry - c^6 = 0. \quad (7)$$

The numerical value of y may be found in any particular case by assuming that when w is a maximum $\alpha = \frac{\pi}{2}$, and finding for c^2 from (4) an approximate value to use in (7).

h is a maximum when $dh/dw = 0$, in which case $\alpha = \pi$ and $w = \pi r^2 \rho$. But before this condition is attained the liquid surfaces meet below the cylinder and form (in some cases) a film. This occurs when (fig. 6)

$$\mp x = \pm r \sin \alpha,$$

$$= \pm \frac{2yr}{c^2} \sqrt{c^2 - y^2}, \text{ from (2),}$$

$$= \frac{c}{2} \log \frac{c \pm \sqrt{c^2 - y^2}}{y} - \sqrt{c^2 - y^2} + .51572 c, \text{ from (3),}$$

or

$$\log \frac{c - \sqrt{c^2 - y^2}}{y} = \left(\frac{4ry}{c^3} + \frac{2}{c} \right) \sqrt{c^2 - y^2} - 1.03144, \quad (8)$$

from which y may be found approximately in terms of c and r by trial. The required value of y is greater than $c/\sqrt{2}$ and less than c , hence the selection of signs in (8).

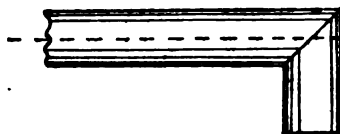
As soon as a true film is formed having plane surfaces, the quantity $2ry \sin \alpha$ in (4) is reduced to $2r \sin \alpha (y - c/\sqrt{2})$, because the column of liquid below the film no longer acts directly to produce a (negative) pressure upon the bottom of the cylinder; and w is reduced to $2T$ plus the weight of the cylinder and of the small quantity of liquid suspended under the cylinder and above the film.

Up to this point the ends of the cylinder, which in practice must be turned down, have been disregarded. Their effect may be eliminated by the use of a long and a short cylinder having the same thickness and their ends alike; but if the bend is like an elbow, or is made by a rectangular prism abutting squarely on the end of the cylinder, the effect of the ends may be calculated.

Taking the former case, let l (fig. 7) be the whole length of the cylinder along the dotted line, r its radius, h as before the height of the top of the horizontal cylinder above the general level of the liquid, and k the length of each vertical end-piece, measured from the top. Equation (4) may be applied over the length $l - 2r - \pi r/2$. And if we subtract

the weight of liquid displaced by the cylinder, the increase in

Fig. 7.



weight over the weight of the frame in air is, for this central part,

$$(l - 2r - \pi r/2) \rho \left\{ \left(\frac{c^2}{2} + 2ry \right) \sin \alpha + r^2(\alpha - \pi) - r^2 \sin \alpha \cos \alpha \right\}.$$

To this is to be added the surface-tension around the vertical ends, and also the weight of liquid supported under them above the level of the surface; making as a very close approximation the whole increase of weight to be W , where

$$W/\rho = (l - 2r - \pi r/2) \{ (c^2/2 + 2ry) \sin \alpha + r^2(\alpha - \pi) - r^2 \sin \alpha \cos \alpha \} + \pi r c^2 + 2\pi r^2(h - k). \quad (9)$$

In the following table are given the observed weights with a somewhat irregular glass frame, along with the calculated values of the four terms on the right of equation (4) for the same height h , in grams per centim. The liquid was water, whose density is assumed as unity.

$r = .0375$ (mean); $l = 9.76$; $T = .07395$ gram per centim.

| $h(\text{mm.})$ | w , obs. | α | $2T \sin \alpha$ | $2ry \sin \alpha$ | $r^2 \alpha$ | $-r^2 \sin \alpha \cos \alpha$ | w , calc. |
|-----------------|------------|----------------|------------------|---|--------------|--------------------------------|-------------|
| $\frac{1}{2}$ | .0109 | $13^\circ 47'$ | .0352 | .0019 | .0003 | -.0003 | .0364 |
| 2 | .1042 | $41^\circ 4'$ | .0972 | .0149 | .0010 | -.0007 | .1124 |
| $3\frac{1}{2}$ | .1547 | $69^\circ 16'$ | .1383 | .0217 | .0017 | -.0005 | .1612 |
| 4 | .1724 | $84^\circ 29'$ | .1472 | .0273 | .0021 | -.0001 | .1765 |
| $4\frac{1}{2}$ | .1755 | $92^\circ 49'$ | .1477 | .0298 | .0023 | +.0001 | .1799 |
| $4\frac{3}{4}$ | .1763 | $97^\circ 9'$ | .1468 | .0304 | .0024 | +.0002 | .1798 |
| † | —* | $99^\circ 42'$ | .1458 | .0307 | .0025 | +.0003 | .1793 |
| $4\frac{1}{2}$ | .1755 | | | | | | |
| $4\frac{1}{4}$ | .1739 | | | | | | |
| 5 | .1722 | | | | | | |
| $5\frac{1}{4}$ | .1579 | | | | | | |
| $5\frac{1}{2}$ | .1547 | | | | | | |
| $5\frac{3}{4}$ | .1520 | | | | | | |
| 6 | .1520 | ... | .1458 | $2r \sin \alpha(y - c/\sqrt{2})$.0023 ‡ | .0025 | +.0003 | .1509 |

* During the next five weighings the balance was in unstable equilibrium.

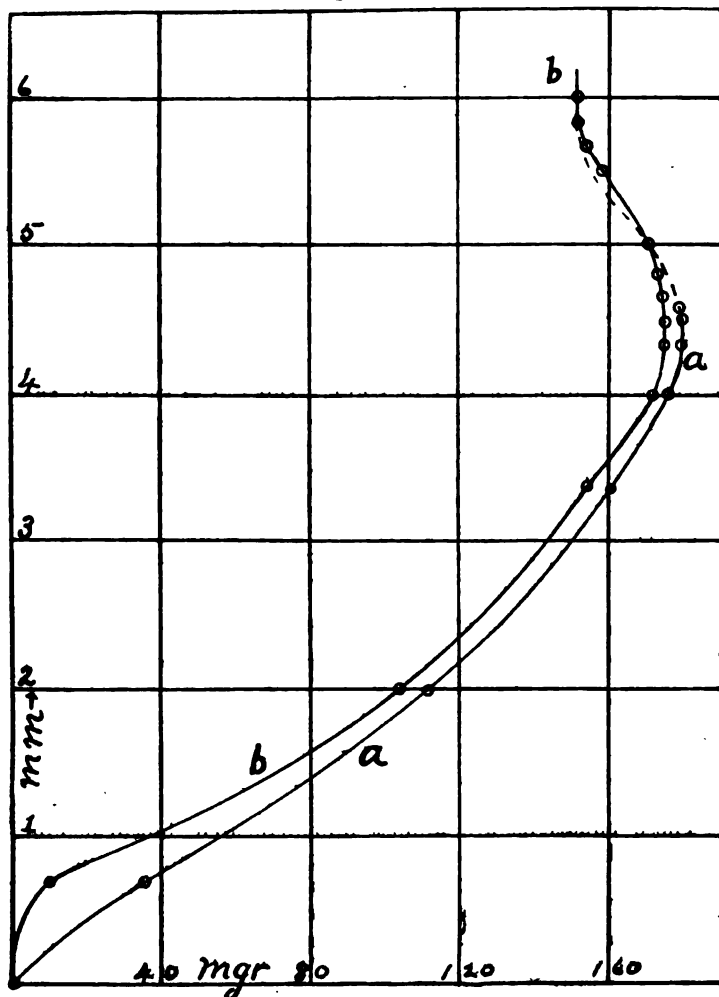
† The numbers in this row are calculated from the value of y found from equation (8), and are for the point at which the two liquid surfaces meet below the bar.

‡ See the paragraph following equation (8).

To the last calculated value of w is to be added .0005 for the displacement of the two end-pieces of the frame, leaving +.0006 per centim. to account for the surface-tension about the (irregular) ends.

In fig. 8 the curves a and b represent the calculated and observed values of w given in the table. The calculated

Fig. 8.



curve, a , is left incomplete because some of the factors needed for the calculation of the rest of it are uncertain. It probably should go somewhere near the dotted line.

This method is capable of showing a change of surface-tension with almost incredible delicacy when the frame is rigid. A single example is given below. The liquid was common alcohol, at 20°-20 C., and each weight was found with a fresh film. The increase of weight (W) due to the tension is given in grams. The corresponding values of T were not calculated.

| | W. |
|----------|--------|
| 1..... | ·72422 |
| 2..... | ·72420 |
| 3..... | ·72424 |
| 4..... | ·72422 |
| Mean ... | ·72422 |

Frames of this sort cannot be made with such exactness as to give practical results agreeing with those calculated to 1 part in 70,000, nor to 1 in 7000. But if the values of the surface-tension are found by either of the methods before described, and compared with W/ρ in each case, the values of r and k may be corrected for any particular frame, so that reliable results may be obtained with it for other liquids with much greater ease than by the former methods.

For this purpose put $n=l-2r-\pi r/2$, and $\beta=\alpha/2$. Then equation (9) becomes

$$2\pi r^2 \sin \beta (c + 2r \sin \beta) + n \sin \beta \cos \beta \{c^2 - 2r^2 + 4cr \sin \beta + 4r^2 \sin^2 \beta\} + r^2 n (\alpha - \pi) + \pi r c^2 - 2\pi r^2 k - W/\rho = 0. \quad (10)$$

When W is a maximum,

$$16r^2 n \sin^4 \beta + 12rcn \sin^3 \beta + (2c^2 - 16r^2)n \sin^2 \beta - 8rnc \sin \beta - 8\pi r^3 \sin \beta \cos \beta - 2\pi r^2 c \cos \beta - c^2 n = 0. \quad (11)$$

These equations are almost unmanageable, however, and time will be saved in most cases by disregarding them and plotting a curve of experimental values to show the relation between T and W/ρ for a given frame.

The convenience of this method in practice will repay the trouble of finding such a relation. While Michelson's method has the merit of directness and simplicity, its use is limited to such liquids as form a fairly stable film in air. The method of thin plates is constantly open to suspicion as to the

existence of a finite contact-angle. The maximum-weight method is free from both these objections, and can be used for almost any liquid. If the specific gravity of the liquid is not accurately known, a thin frame should be used, so that an error in the specific gravity will have small influence on the final result. For accurate results great care must be taken to prevent any oscillation of the balance as the weight approaches the maximum. Zero weighings are also essential.

III. SURFACE-TENSION OF WATER.

In spite of the labours of a large number of investigators, the surface-tension of water is still more or less uncertain. Apart from experimental errors, which are seldom less than one half of one per cent., there is very great difficulty in retaining a pure water surface throughout the measurement. Using the methods of measurement described in Part II. of this paper, it became evident at once that the problem of finding the surface-tension of water accurately, to one tenth of one per cent. or less, was practically reduced to that of securing a clean surface and a constant temperature for pure water.

The weights used were found consistent with each other, and therefore presumably correct, to one tenth of a milligram, with two or three exceptions which were taken note of. The arms of the balance were sensibly equal, and the riders accurate. One of the mercury thermometers was graduated in half degrees, Centigrade, from -10° to $+100^{\circ}$; the other in fifths of a degree, from -4° to $+30^{\circ}$. The latter could be easily read to fiftieths. The zeros of both were correct.

Some water that had been distilled repeatedly by Dr. Loeb in such a manner as to remove carbon dioxide and organic matter and ammonia, was kindly furnished by him for measurement of the surface-tension. I preserved it in a large well-washed glass bottle whose stopper and neck were covered by an inverted beaker to keep off dust.

The deep evaporating-dish already mentioned, its cover, the thermometer, and the glass frames (fig. 1) were well washed in a dilute solution of caustic soda and thoroughly rinsed, first in ordinary distilled water and secondly in some of the water that was to be examined. The ground-glass cover remained on the dish except while frames were being put in or taken out; and before each measurement the temperature of the whole was kept nearly constant for half an hour or more.

The observations extended over two days, partly because of the difficulty there was in getting a film to last long enough to be weighed. On the third day the surface-tension was so

much reduced that it was evident that the surface had become contaminated. I have reason to believe that only the first two, if any, of the observations were made with a clean surface, and have therefore in the fourth column given the values calculated by the formula

$$T = 75.48 - .140t \text{ dynes}$$

obtained by taking the first two observations only.

| Weight (in grams.). | Temp. C. | T found. | T calc. | Difference. |
|---------------------|----------|----------|---------|-------------|
| .8044 | 0.1 | 75.468 | 75.466 | |
| .7859 | 12.5 | 73.733 | 73.730 | |
| .7836 | 13.8 | 73.52 | 73.55 | .03 |
| .7795 | 16.2 | 73.13 | 73.21 | .08 |
| .7742 | 19.5 | 72.63 | 72.75 | .12 |

The width of the frame was 5.2321 centim., and its capillarity correction .0075 centim. The same frame was used for the following observations, which were made at different times for the purpose of finding the effect of dissolved air upon the surface-tension. The first seven of the following measurements were made with fresh portions of the same water as the foregoing. In the last column they are reduced to 18° C., at which the surface-tension according to the formula given above is 72.96 dynes.

| | Weight (in grams.). | Temperature. | T found. | T at 18°. |
|-----|---------------------|--------------|----------|-----------|
| 1. | .7762 | 18.37 | 72.82 | 72.87 |
| 2. | .7753 | 19.90 | 72.74 | 73.00 |
| 3. | .7748 | 20.60 | 72.69 | 73.06 |
| 4. | .7752 | 18.64 | 72.73 | 72.82 |
| 5. | .7750 | 19.32 | 72.71 | 72.89 |
| 6. | .7768 | 17.85 | 72.86 | 72.84 |
| 7. | .7772 | 18.35 | 72.92 | 72.87 |
| 8. | .7813 | 15.97 | 73.30 | 73.02 |
| 9. | .7780 | 17.76 | 72.99 | 72.96 |
| 10. | .7697 | 19.60 | 72.21 | 72.44 |

On several occasions water that was left in the glass dish in the closed closet over night was found next morning to have a surface-tension considerably lower than it had the night before. If left two or three days the difference was greater, even when the cover was on the dish during the whole time. But after a vigorous stirring the surface-tension was in each case a little greater than it had been at first. The substance, whatever it was, that made the change, being present in small quantity in the surface-layers of the water, reduced the tension. The same amount of the substance scattered throughout the whole volume of the water, and hence present in very minute quantity in the surface-layers, increased the surface-tension.

Some of the purified water mentioned above was boiled briskly half an hour in a covered glass beaker to expel the air. A smaller bottle was completely filled with the boiled water and left to cool. Half of it was then poured into the dish and its surface-tension measured without delay. The remaining half was shaken up with the air in the bottle, and its surface-tension measured. In the table above (2) is water freed from air, (3) the portion shaken up with air. The tension when air is present is greater by .06 dyne. (4) and (5) are similarly related, and the difference is .07 dyne. (6) was simply poured into the dish from the large bottle; and (7) was stirred vigorously in the open dish with a glass rod. (8) and (9) are two specimens of clean snow melted and not boiled. (10) is a portion of (9), well stirred, after remaining two weeks in a covered dish.

The mean of these values is one dyne less than the mean of Lord Rayleigh's results* from measurements of the wavelength of ripples. The difference is not accounted for by the presence or absence of dissolved air, though it is probable that carbon dioxide in moderate amount would make more difference than the more perfect gases; and it seems very improbable that the difference is owing to constant errors in either of the methods. Two possible explanations remain: (1) unnoticed contaminations of the surface, and (2) real differences in the surface-tension of the different specimens of water.

In order to secure a fresh clean surface I arranged a long glass siphon to reach from a glass vessel on the shelf near the balance into the glass dish in the closet below. Its lower end was drawn out small and turned upward from the bottom of the dish so that the incoming stream continually swept the whole surface of the dish, which was tilted up at one side to

* Rayleigh, *Phil. Mag.* October 1890, p. 386.

secure a more steady overflow. The flow was at the rate of two or three litres per hour. The reservoir above was well washed, filled with ordinary distilled water, covered, and left till next day to acquire the temperature of the room. Then the siphon was inserted, and after the flow had continued half an hour the measurements were begun. The flow continued and the temperature of the air in the closet remained constant at 22°·2 C. throughout.

| W (grams). | Temperature. | T found. | T at 18° C. |
|------------|--------------|----------|-------------|
| 2·5612 | 22·20 | 73·138 | 73·726 |
| 2·5613 | 22·20 | 73·141 | 73·729 |
| 2·5615 | 22·15 | 73·146 | 73·727 |

These measurements were made with a glass frame by the maximum-weight method, and the corresponding values of T found by the formula

$$T = 4·8926 + 14·027w + 7·6891w^2 - 1·0786w^3,$$

which was calculated from a series of measurements of the surface-tension of mixtures of water and alcohol, by two methods, as follows :—

| W found (grams). | T by Method A or B (dynes). |
|------------------|-----------------------------|
| 1·1033 | 28·280 |
| 1·9180 | 52·472 |
| 2·1220 | 58·975 |
| 2·3261 | 65·549 |

A few days later tap-water was allowed to run more slowly through the siphon for four hours, the surface-tension measured in the same way ; then a fresh portion allowed to run more rapidly for half an hour, then again for forty-five minutes. The temperature of the air was in each case 22°·0 C. The three measurements gave :—

| W (grams). | Temperature. | T (dynes). | T at 18° C. |
|------------|--------------|------------|-------------|
| 2·5650 | 20·6 | 73·280 | 73·644 |
| 2·5631 | 20·5 | 73·190 | 73·540 |
| 2·5613 | 20·5 | 73·141 | 73·491 |

In these cases there can be no doubt that the surface was as pure as the interior of the water. Small bits of cork and dust were sprinkled on the surface after the last measurement, as a test, and the surface was swept clean in a few seconds, all visible particles (except the largest) being carried off in the overflow. In finding the maximum weight, in no case was an observation accepted as final when there was the least visible oscillation of the balance or variation of the pointer from zero just before the final overturn.

With the same arrangements for overflow, except that the glass reservoir was replaced by a large galvanized iron tank and that the connecting-tube was in two pieces united by a new perforated cork, a large number of measurements were made by thin plates at various times on tap-water. The highest value in each set of observations is given below. In each case very great care was taken to secure a zero contact-angle.

| Plate. | Weight (grm.). | Temperature. | T (dynes). | T at 18° C. |
|----------------|----------------|--------------|------------|-------------|
| Platinum | 1.9735 | 18.96 | 72.19 | 72.33 |
| Silver..... | 1.1383 | 19.01 | 73.22 | 73.36 |
| Zinc | 1.8421 | 19.85 | 73.29 | 73.55 |
| Silver..... | 1.1358 | 20.08 | 73.06 | 73.35 |
| Platinum | 1.9904 | 20.16 | 72.81 | 73.12 |
| Glass | 0.744 | 20.50 | 71.91 | 72.26 |

These results in connexion with the foregoing point to very distinct differences in the surface-tension of different specimens of water. The very great differences in the values of the temperature-coefficient found by different investigators are probably also due to real differences in the specimens examined. Water free from gases has a temperature-coefficient not far from 0.14 dyne for each degree C. But if care be not taken to free the water from dissolved gases, the coefficient may be as high as 0.20 dyne, or even higher. The great differences in determinations of the critical temperature of water and of alcohol by different observers may be due to the same cause.

My thanks are due to the authorities of Clark University for the facilities afforded me, and to Professor Michelson and Assistant-Professor Webster for valuable suggestions during the progress of this work.

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XLIII. *On the Elasticity of a Crystal according to*
*Boscovich. By Lord KELVIN, P.R.S.**

§ 1. A CRYSTAL in nature is essentially a homogeneous assemblage of equal and similar molecules, which for brevity I shall call crystalline molecules. The crystalline molecule may be the smallest portion which can be taken from the substance without chemical decomposition—that is to say, it may be the group of atoms kept together by chemical affinity, which constitutes what for brevity I shall call the chemical molecule; or it may be a group of two, three, or more of these chemical molecules kept together by cohesive force. In a crystal of tartaric acid the crystalline molecule may be, and it seems to me probably is, the chemical molecule, because if a crystal of tartaric acid is dissolved and recrystallized it always remains dextro-chiral. In a crystal of chlorate of soda, as has been pointed out to me by Sir George Stokes, the crystalline molecule probably consists of a group of two or more of the chemical molecules constituting chlorate of soda, because, as found by Marbach†, crystals of the substance are some of them dextro-chiral and some of them levo-chiral; and if a crystal of either chirality is dissolved the solution shows no chirality in its action on polarized light; but if it is recrystallized the crystals are found to be some of them dextro-chiral and some of them levo-chiral, as shown both by their crystalline forms and by their action on polarized light. It is possible, however, that even in chlorate of soda the crystalline molecule may be the chemical molecule, because it may be that the chemical molecule in solution has its atoms relatively mobile enough not to remain persistently in any dextro-chiral or levo-chiral grouping, and that each individual chemical molecule settles into either a dextro-chiral or levo-chiral configuration in the act of forming a crystal.

§ 2. Certain it is that the crystalline molecule has a chiral configuration in every crystal which shows chirality in its crystalline form or which produces right- or left-handed rotation of the plane of polarization of light passing through it. The magnetic rotation has neither right-handed nor left-handed quality (that is to say, no chirality). This was perfectly understood by Faraday and made clear in his writings; yet even to the present day we frequently find the chiral rotation and the magnetic rotation of the plane of polarized light classed together in a manner against which Faraday's

* Communicated by the Author; having been read before the Royal Society, June 15, 1893.

† Pogg. *Ann.* vol. xci. pp. 482–487 (1854); or *Ann. de Chimie*, vol. xliii. (1v.) pp. 252–255.

original description of his discovery of the magnetic polarization contains ample warning.

§ 3. These questions, however, of chirality and magnetic rotation do not belong to my present subject, which is merely the forcive* required to keep a crystal homogeneously strained to any infinitesimal extent from the condition in which it rests when no force acts upon it from without. In the elements of the mathematical theory of elasticity† we find that this forcive constitutes what is called a homogeneous stress, and is specified completely by six generalized force-components, $p_1, p_2, p_3, \dots, p_6$, which are related to six corresponding generalized components of strain, $s_1, s_2, s_3, \dots, s_6$, by the following formulas:—

$$w = \frac{1}{2}(p_1 s_1 + p_2 s_2 + \dots + p_6 s_6) \quad \dots \quad (1),$$

where w denotes the work required per unit volume to alter any portion of the crystal from its natural unstressed and unstrained condition to any condition of infinitesimal homogeneous stress or strain:

$$p_1 = \frac{dw}{ds_1}, \dots, p_6 = \frac{dw}{ds_6} \quad \dots \quad (2),$$

where $\frac{d}{ds_1}, \dots, \frac{d}{ds_6}$ denote differential coefficients on the supposition that w is expressed as a homogeneous quadratic function of s_1, \dots, s_6 :

$$s_1 = \frac{\partial w}{\partial p_1}, \dots, s_6 = \frac{\partial w}{\partial p_6} \quad \dots \quad (3),$$

where $\frac{\partial}{\partial p_1}, \dots, \frac{\partial}{\partial p_6}$ denote differential coefficients on the supposition that w is expressed as a homogeneous quadratic function of p_1, \dots, p_6 .

§ 4. Each crystalline molecule in reality certainly experiences forcive from some of its nearest neighbours on two sides, and probably also from next nearest neighbours and others. Whatever the mutual forcive between two mutually acting crystalline molecules is in reality, and however it is produced, whether by continuous pressure in some medium, or by action at a distance, we may ideally reduce it, according to elementary statical principles, to two forces, or to one single force and a couple in a plane perpendicular to that force. Boscovich's theory, a purely mathematical idealism, makes each crystalline molecule a single point, or a group of points, and assumes that there is a mutual force between each point of one crystalline molecule and each point of neighbouring

* This is a word introduced by my brother, the late Professor James Thomson, to designate any system of forces.

† Phil. Trans. April 24, 1856; reprinted in vol. iii. 'Math. and Phys. Papers, Sir W. Thomson,' pp. 84-112.

crystalline molecules, in the line joining the two points. The very simplest Boscovichian idea of a crystal is a homogeneous group of single points. The next simplest idea is a homogeneous group of double points.

§ 5. In the present communication I demonstrate that, if we take the very simplest Boscovichian idea of a crystal, a homogeneous group of single points, we find essentially six relations between the twenty-one coefficients in the quadratic function expressing w , whether in terms of s_1, \dots, s_6 or of p_1, \dots, p_6 . These six relations are such that infinite resistance to change of bulk involves infinite rigidity. In the particular case of an equilateral* homogeneous assemblage with such a law of force as to give equal rigidities for all directions of shearing, these six relations give $3k=5n$, which is the relation found by Navier and Poisson in their Boscovichian theory for isotropic elasticity in a solid. This relation was shown by Stokes to be violated by many real homogeneous isotropic substances, such, for example, as jelly and india-rubber, which oppose so great resistance to compression and so small resistance to change of shape that we may, with but little practical error, consider them as incompressible elastic solids.

§ 6. I next demonstrate that if we take the next simplest Boscovichian idea for a crystal, a homogeneous group of double points, we can assign very simple laws of variation of the forces between the points which shall give any arbitrarily assigned value to each of the twenty-one coefficients in either of the quadratic expressions for w .

§ 7. I consider particularly the problem of assigning such values to the twenty-one coefficients of either of the quadratic formulas as shall render the solid incompressible. This is most easily done by taking w as a quadratic function of p_1, \dots, p_6 , and by taking one of these generalized stress-components, say p_6 , as uniform positive or negative pressure in all directions. This makes s_6 uniform compression or extension in all directions, and makes s_1, \dots, s_6 five distortional components with no change of bulk. The condition that the solid shall be incompressible is then simply that the coefficients of the six terms involving p_6 are each of them zero. Thus, the expression for w becomes merely a quadratic function of the five distortional stress-components, p_1, \dots, p_6 , with fifteen independent coefficients; and equations (3) of § 3 above

* That is to say, an assemblage in which the lines from any point to three neighbours nearest to it and to one another are inclined at 60° to one another; and these neighbours are at equal distances from it. This implies that each point has twelve equidistant nearest neighbours around it, and that any tetrahedron of four nearest neighbours has for its four faces four equal equilateral triangles.

express the five distortional components as linear functions of the five stress-components with these fifteen independent coefficients.

§ 8. To demonstrate the propositions of § 5, let O X, O Y, O Z be three mutually perpendicular lines through any point O of a homogeneous assemblage, and let x, y, z be the co-ordinates of any other point P of the assemblage, in its unstrained condition. As it is a homogeneous assemblage of single points that we are now considering, there must be another point P', whose coordinates are $-x, -y, -z$. Let $(x + \delta x, y + \delta y, z + \delta z)$ be the coordinates of the altered position of P in any condition of infinitesimal strain, specified by the six symbols e, f, g, a, b, c , according to the notation of Thomson and Tait's 'Natural Philosophy,' vol. i. pt. 2, § 669. In this notation, e, f, g denote simple infinitesimal elongations parallel to OX, OY, OZ respectively; and a, b, c infinitesimal changes from the right angles between three pairs of planes of the substance, which, in the unstrained condition, are parallel to (X O Y, X O Z), (Y O Z, Y O X), (Z O X, Z O Y) respectively (all angles being measured in terms of the radian). The definition of a, b, c may be given, in other words, as follows, with a taken as example: a denotes the difference of component motions parallel to OY of two planes of the substance at unit distance asunder, kept parallel to Y O X during the displacement; or, which is the same thing, the difference of component motions parallel to OZ of two planes at unit distance asunder kept parallel to Z O X during the displacement. To avoid the unnecessary consideration of rotational displacement, we shall suppose the displacement corresponding to the strain-component a to consist of elongation perpendicular to OX in the plane through OX bisecting Y O Z, and shrinkage perpendicular to OX in the plane through OX perpendicular to that bisecting plane. This displacement gives no contribution to δx , and contributes to δy and δz respectively $\frac{1}{2}az$ and $\frac{1}{2}ay$. Hence, and dealing similarly with b and c , and taking into account the contributions of e, f, g , we find

$$\left. \begin{aligned} \delta x &= ex + \frac{1}{2}(bz + cy) \\ \delta y &= fy + \frac{1}{2}(cx + az) \\ \delta z &= gz + \frac{1}{2}(ay + bx) \end{aligned} \right\} \dots \dots (4).$$

§ 9. In our dynamical treatment below, the following formulas, in which powers higher than squares or products of the infinitesimal ratios $\delta x/r, \delta y/r, \delta z/r$ (r denoting OP) are neglected, will be found useful:—

$$\frac{\delta r}{r} = \frac{x\delta x + y\delta y + z\delta z}{r^2} + \frac{1}{2} \frac{\delta x^2 + \delta y^2 + \delta z^2}{r^2} - \frac{1}{2} \left(\frac{x\delta x + y\delta y + z\delta z}{r^2} \right)^2. (5).$$

Now by (4) we have

$$x\delta x + y\delta y + z\delta z = ex^2 + fy^2 + gz^2 + ayz + bzx + cxy \quad (6),$$

and

$$\begin{aligned} \delta x^2 + \delta y^2 + \delta z^2 &= e^2 x^2 + f^2 y^2 + g^2 z^2 \\ &\quad + \frac{1}{2} [a^2 (y^2 + z^2) + b^2 (z^2 + x^2) + c^2 (x^2 + y^2)] \\ &\quad + [\frac{1}{2} bc + (f+g)a] yz + [\frac{1}{2} ca + (g+e)b] zx \\ &\quad + [\frac{1}{2} ab + (e+f)c] xy \quad \dots \quad (7). \end{aligned}$$

Using (6) and (7) in (5), we find

$$\frac{\delta r}{r} = r^{-2} (ex^2 + fy^2 + gz^2 + ayz + bzx + cxy) + Q(e, f, g, a, b, c) \quad (8),$$

where Q denotes a quadratic function of e, f , &c., with coefficients as follows :—

$$\left. \begin{array}{ll} \text{Coefficient of } \frac{1}{2}e^2 \text{ is } & \frac{x^2}{r^2} - \frac{x^4}{r^4} \\ \text{,, } \text{,, } \frac{1}{2}a^2 \text{,,} & \frac{1}{2} \frac{y^2 + z^2}{r^2} - \frac{y^2 z^2}{r^4} \\ \text{,, } \text{,, } fg \text{,,} & - \frac{y^2 z^2}{r^4} \\ \text{,, } \text{,, } bc \text{,,} & \frac{1}{2} \frac{yz}{r^2} - \frac{x^2 yz}{r^4} \\ \text{,, } \text{,, } ea \text{,,} & - \frac{x^2 yz}{r^4} \\ \text{,, } \text{,, } eb \text{,,} & \frac{1}{2} \frac{zx}{r^2} - \frac{x^2 z^2}{r^4} \end{array} \right\} \dots \quad (9),$$

and corresponding symmetrical expressions for the other fifteen coefficients.

§ 10. Going back now to § 3, let us find w , the work per unit volume, required to alter our homogeneous assemblage from its unstrained condition to the infinitesimally strained condition specified by e, f, g, a, b, c . Let $\phi(r)$ be the work required to bring two points of the system from an infinitely great distance asunder to distance r . This is what I shall call the mutual potential energy of two points at distance r . What I shall now call the potential energy of the whole system, and denote by W , is the total work which must be done to bring all the points of it from infinite mutual distances to their actual positions in the system ; so that we have

$$W = \frac{1}{2} \Sigma \Sigma \phi(r) \quad \dots \quad (10),$$

where $\Sigma\phi(r)$ denotes the sum of the values of $\phi(r)$ for the distances between any one point O, and all the others, and $\Sigma\Sigma\phi(r)$ denotes the sum of these sums with the point O taken successively at every point of the system. In this double summation $\phi(r)$ is taken twice over, whence the factor $\frac{1}{2}$ in the formula (10).

§ 11. Suppose now the law of force to be such that $\phi(r)$ vanishes for every value of r greater than $\nu\lambda$, where λ denotes the distance between any one point and its nearest neighbour, and ν any small or large numeric exceeding unity, and limited only by the condition that $\nu\lambda$ is very small in comparison with the linear dimensions of the whole assemblage. This, and the homogeneousness of our assemblage, imply that, except through a very thin surface-layer of thickness $\nu\lambda$, exceedingly small in comparison with diameters of the assemblage, every point experiences the same set of balancing forces from neighbours as every other point, whether the system be in what we have called its unstrained condition or in any condition whatever of homogeneous strain. This strain is not of necessity an infinitely small strain, so far as concerns the proposition just stated, although in our mathematical work we limit ourselves to strains which are infinitely small.

§ 12. Remark also that if the whole system be given as a homogeneous assemblage of any specified description, and if all points in the surface-layer be held by externally applied forces in their positions as constituents of a finite homogeneous assemblage, the whole assemblage will be in equilibrium under the influence of mutual forces between the points; because the force exerted on any point O by any point P is balanced by the equal and opposite force exerted by the point P' at equal distance on the opposite side of O.

§ 13. Neglecting now all points in the thin surface-layer, let N denote the whole number of points in the homogeneous assemblage within it. We have, in § 10, by reason of the homogeneousness of the assemblage,

$$\Sigma\Sigma\phi(r) = N\Sigma\phi(r) \quad . \quad . \quad . \quad . \quad . \quad (11),$$

and equation (10) becomes

$$W = \frac{1}{2}N\Sigma\phi(r) \quad . \quad . \quad . \quad . \quad . \quad (12).$$

Hence, by Taylor's theorem,

$$\delta W = \frac{1}{2}N\Sigma \{ \phi'(r)\delta r + \frac{1}{2}\phi''(r)\delta r^2 \} \quad . \quad . \quad . \quad (13);$$

and using (8) in this, and remarking that if (as in § 14 below) we take the volume of our assemblage as unity, so that

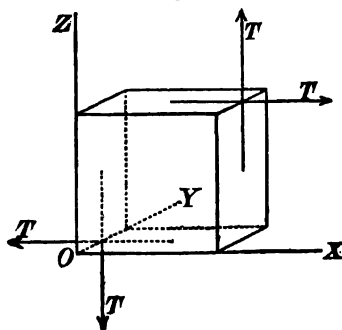
$$2 F 2$$

N is the number of points per unit volume, δW becomes the w of § 3, we find

$$w = \frac{1}{2} N \Sigma \left\{ \frac{\phi'(r)}{r} (ex^2 + fy^2 + gz^2 + ayz + bzx + cxy) \right. \\ \left. + r\phi'(r)Q(e, f, g, a, b, c) \right. \\ \left. + \frac{1}{2} \frac{\phi''(r)}{r^2} (ex^2 + fy^2 + gz^2 + ayz + bzx + cxy)^2 \right\} \quad (14).$$

§ 14. Let us now suppose, for simplicity, the whole assemblage, in its unstrained condition, to be a cube of unit edge, and let P be the sum of the normal components of the extraneous forces applied to the points of the surface-layer in one of the faces of the cube. The equilibrium of the cube, as a whole, requires an equal and opposite normal component P in the opposite face of the cube. Similarly, let Q and R denote the sums of the normal components of extraneous force on the two other pairs of faces of the cube. Let T be the sum of tangential components, parallel to OZ , of the extraneous forces on either of the YZ faces. The equilibrium of the cube as a whole requires four such forces on the four faces parallel to OY , constituting two balancing couples, as shown in the accompanying diagram. Similarly, we must

Fig. 1.



have four balancing tangential forces S on the four faces parallel to OX , and four tangential forces U on the four faces parallel to OZ .

§ 15. Considering now an infinitely small change of strain in the cube from (e, f, g, a, b, c) to $(e+de, f+df, g+dg, a+da, b+db, c+dc)$; the work required to produce it, as we see by considering the definitions of the displacements e, f, g, a, b, c , explained above in § 8, is as follows:—

$$dw = Pde + Qdf + Rdg + Sda + Tdb + Udc \quad (15).$$

Hence we have

$$\left. \begin{aligned} P &= dw/de; & Q &= dw/df; & R &= dw/dg; \\ S &= dw/da; & T &= dw/db; & U &= dw/dc; \end{aligned} \right\} \quad (16).$$

Hence, by (14), and taking L, L to denote linear functions, we find

$$\left. \begin{aligned} P &= \frac{1}{2} N \Sigma \left\{ \frac{\phi'(r)}{r} x^2 + L(e, f, g, a, b, c) \right\} \\ S &= \frac{1}{2} N \Sigma \left\{ \frac{\phi'(r)}{r} yz + L(e, f, g, a, b, c) \right\} \end{aligned} \right\} \quad (17).$$

and symmetrical expressions for Q, R, T, U .

§ 16. Let now our condition of zero strain be one* in which no extraneous force is required to prevent the assemblage from leaving it. We must have $P=0, Q=0, R=0, S=0, T=0, U=0$, when $e=0, f=0, g=0, a=0, b=0, c=0$. Hence, by (17), and the other four symmetrical formulæ, we see that

$$\left. \begin{aligned} \Sigma \frac{\phi'(r)}{r} x^2 &= 0, & \Sigma \frac{\phi'(r)}{r} y^2 &= 0, & \Sigma \frac{\phi'(r)}{r} z^2 &= 0, \\ \Sigma \frac{\phi'(r)}{r} yz &= 0, & \Sigma \frac{\phi'(r)}{r} zx &= 0, & \Sigma \frac{\phi'(r)}{r} xy &= 0, \end{aligned} \right\} \quad (18).$$

Hence, in the summation for all the points x, y, z , between which and the point O there is force, we see that the first term of the summed coefficients in Q , given by (9) above, vanishes in every case, except those of fg and ea , in each of which there is only a single term; and thus from (9) and (14) we find

$$w = \frac{1}{2} N \left\{ \frac{1}{2} e^2 \Sigma \varpi \frac{x^4}{r^4} + (fg + \frac{1}{2} a^2) \Sigma \varpi \frac{y^2 z^2}{r^4} + (bc + ea) \Sigma \varpi \frac{x^2 yz}{r^4} + eb \Sigma \varpi \frac{x^3 z}{r^4} + \&c. \right\} \quad (19),$$

where

$$-r\phi'(r) + r^2\phi''(r) = \varpi \quad . \quad . \quad . \quad . \quad (20).$$

The terms given explicitly in (19) suffice to show by symmetry all the remaining terms represented by the “&c.”

§ 17. Thus we see that with no limitation whatever to the number of neighbours acting with sensible force on any one

* The consideration of the equilibrium of the thin surface-layer, in these circumstances, under the influence of merely their proper mutual forces, is exceedingly interesting, both in its relation to Laplace's theory of capillary attraction, and to the physical condition of the faces of a crystal, and of surfaces of irregular fracture. But it must be deferred.

point O, and with no simplifying assumption as to the law of force, we have in the quadratic for w equal values for the coefficients of fg and $\frac{1}{2}a^2$; ge and $\frac{1}{2}b^2$; ef and $\frac{1}{2}c^2$; bc and ea ; ca and eb ; and ab and ec . These equalities constitute the six relations promised for demonstration in § 5.

§ 18. In the particular case of an equilateral assemblage, with axes O X, O Y, O Z parallel to the three pairs of opposite edges of a tetrahedron of four nearest neighbours, the coefficients which we have found for all the products except fg , ge , ef clearly vanish; because in the complete sum for a single homogeneous equilateral assemblage we have $\pm x$, $\pm y$, $\pm z$ in the symmetrical terms. Hence, and because for this case

$$\Sigma \varpi \frac{x^4}{r^4} = \Sigma \varpi \frac{y^4}{r^4} = \Sigma \varpi \frac{z^4}{r^4}, \text{ and } \Sigma \varpi \frac{y^2 z^2}{r^4} = \Sigma \varpi \frac{z^2 x^2}{r^4} = \Sigma \varpi \frac{x^2 y^2}{r^4} \quad (21),$$

(19) becomes

$$w = \frac{1}{2} A (e^2 + f^2 + g^2) + B (fg + ge + ef) + \frac{1}{2} n (a^2 + b^2 + c^2) \quad (22),$$

where

$$A = \frac{1}{2} N \Sigma \varpi \frac{x^4}{r^4}, \text{ and } B = n = \frac{1}{2} N \Sigma \varpi \frac{y^2 z^2}{r^4} \quad \dots (23).$$

§ 19. Looking to Thomson and Tait's 'Natural Philosophy,' § 695 (7)*, we see that n in our present formula (22) denotes the rigidity-modulus relative to shearings parallel to the planes Y O Z, Z O X, X O Y; and that if we denote by n_1 the rigidity-modulus relative to shearings parallel to planes through O X, O Y, O Z, and cutting (O Y, O Z), (O Z, O X), (O X, O Y) at angles of 45° , and if k denote the compressibility-modulus, we have

$$\left. \begin{aligned} A &= k + \frac{4}{3} n_1; & B &= k - \frac{2}{3} n_1; \\ n_1 &= \frac{1}{2} (A - B); & k &= \frac{1}{3} (A + 2B) \end{aligned} \right\} \dots (24);$$

and our expression (22), for the elastic energy of the strained solid, becomes

$$2w = (k + \frac{4}{3} n_1) (e^2 + f^2 + g^2) + 2(k - \frac{2}{3} n_1) (fg + ge + ef) + n (a^2 + b^2 + c^2) \dots (25).$$

§ 20. Using in (24) the equality $B = n$ shown in (23), we find

$$3k = 2n_1 + 3n \dots (26).$$

This remarkable relation between the two rigidities and the

* This formula is given for the case of a body which is wholly isotropic in respect to elasticity moduluses; but from the investigation in §§ 681, 682 we see that our present formula, (22) or (25), expresses the elastic energy for the case of an elastic solid possessing cubic isotropy with unequal rigidities in respect to these two sets of shearings.

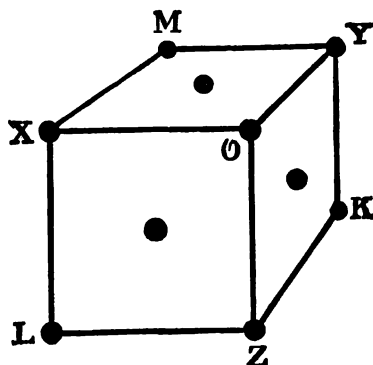
compressibility of an equilateral homogeneous assemblage of Boscovich atoms was announced without proof in § 27 of my paper on the "Molecular Constitution of Matter"*. In it n denotes what I called the facial rigidity, being rigidity relative to shearings parallel to the faces of the principal cube†: and n_1 the diagonal rigidity, being rigidity relative to shearings parallel to any of the six diagonal planes through pairs of mutually remotest parallel edges of the same cube. By (24) and (23) we see that if the law of force be such that

$$\Sigma \sigma \frac{x^4}{r^4} = 3 \Sigma \sigma \frac{y^2 z^2}{r^4} \quad . \quad . \quad . \quad (27),$$

we have $n=n_1$, and the body constituted by the assemblage is wholly isotropic in its elastic quality. In this case (26) becomes $3k=5n$, as found by Navier and Poisson; and thus we complete the demonstration of the statements of § 5 above.

§ 21. A case which is not uninteresting in respect to Boscovichian theory, and which is very interesting indeed in respect to mechanical engineering (of which the relationship with Boscovich's theory has been pointed out and beautifully illustrated by M. Brillouin‡), is the case of an equilateral homogeneous assemblage with forces only between each point and its twelve equidistant nearest neighbours. The annexed diagram (fig. 2) represents the point O and three of its twelve

Fig. 2.



nearest neighbours (their distances λ), being in the middles

* R. S. E. Proc. July 1889; Art. xcvi. of my 'Math. and Phys. Papers,' vol. iii.

† That is to say, a cube whose edges are parallel to the three pairs of opposite edges of a tetrahedron of four nearest neighbours.

‡ *Conférences Scientifiques et Allocutions* (Lord Kelvin), *traduites et annotées*, P. Lugol et M. Brillouin: Paris, 1893, pp. 320-325.

of the near faces of the principal cube shown in the diagram; and three of its six next-nearest neighbours (their distances $\lambda\sqrt{2}$), being at X, Y, Z, the corners of the cube nearest to it; and, at other corners of the cube, three other neighbours, K, L, M, which are next-next-nearest (their distances 2λ). The points in the middles of the three remote sides of the cube, not seen in the diagram, are next-next-nearest neighbours of O (their distances $\lambda\sqrt{3}$).

§ 22. Confining our attention now to O's nearest neighbours, we see that the nine not shown in the diagram are in the middles of squares obtained by producing the lines YO, ZO, XO to equal distances beyond O and completing the squares on all the pairs of lines so obtained. To see this more clearly, imagine eight equal cubes placed together, with faces in contact and each with one corner at O. The pairs of faces in contact are four squares in each of the three planes cutting one another at right angles through O; and the centres of these twelve squares are the twelve nearest neighbours of O. If we denote by λ the distance of each of them from O, we have for the coordinates x, y, z of these twelve points as follows:—

$$\left. \begin{aligned} & \left(0, \frac{\lambda}{\sqrt{2}}, \frac{\lambda}{\sqrt{2}}\right), \left(0, -\frac{\lambda}{\sqrt{2}}, \frac{\lambda}{\sqrt{2}}\right), \left(0, \frac{\lambda}{\sqrt{2}}, -\frac{\lambda}{\sqrt{2}}\right), \left(0, -\frac{\lambda}{\sqrt{2}}, -\frac{\lambda}{\sqrt{2}}\right), \\ & \left(\frac{\lambda}{\sqrt{2}}, 0, \frac{\lambda}{\sqrt{2}}\right), \left(-\frac{\lambda}{\sqrt{2}}, 0, \frac{\lambda}{\sqrt{2}}\right), \left(\frac{\lambda}{\sqrt{2}}, 0, -\frac{\lambda}{\sqrt{2}}\right), \left(-\frac{\lambda}{\sqrt{2}}, 0, -\frac{\lambda}{\sqrt{2}}\right), \\ & \left(\frac{\lambda}{\sqrt{2}}, \frac{\lambda}{\sqrt{2}}, 0\right), \left(-\frac{\lambda}{\sqrt{2}}, \frac{\lambda}{\sqrt{2}}, 0\right), \left(\frac{\lambda}{\sqrt{2}}, -\frac{\lambda}{\sqrt{2}}, 0\right), \left(-\frac{\lambda}{\sqrt{2}}, -\frac{\lambda}{\sqrt{2}}, 0\right), \end{aligned} \right\} \quad (28).$$

§ 23. Suppose now O to experience force only from its twelve nearest neighbours; the summations Σ of § 18 (23) will include just these twelve points with equal values of ϖ for all. These yield eight terms to $\Sigma(x^4/r^4)$, and four to $\Sigma(y^2z^2/r^4)$; and the value of each term in these sums is $\frac{1}{4}$. Thus we find that

$$A = N\varpi, \text{ and } B = n = \frac{1}{2}N\varpi \quad \dots \dots (29).$$

Hence and by (24), we see that

$$n_1 = \frac{1}{2}n \quad \dots \dots (30).$$

Thus we have the remarkable result that, relatively to the principal cube, the diagonal rigidity is half the facial rigidity when each point experiences force only from its twelve nearest neighbours. This proposition was announced without proof in § (28) of "Molecular Constitution of Matter"*.

* 'Math. and Phys. Papers,' vol. iii. p. 403.

§ 24. Suppose now the points in the middles of the faces of the cubes which in the equilateral assemblage are O's twelve equidistant nearest neighbours to be removed, and the assemblage to consist of points in simplest cubic order; that is to say, of Boscovichian points at the points of intersection of three sets of equidistant parallel planes dividing space into cubes. Fig. 2 shows O; and at X, Y, Z, three of the six equidistant nearest neighbours which it has in the simple cubic arrangement. Keeping λ with the same signification in respect to fig. 2 as before, we have now for the coordinates of O's six nearest neighbours:—

$$(\lambda\sqrt{2}, 0, 0), (0, \lambda\sqrt{2}, 0), (0, 0, \lambda\sqrt{2}), \\ (-\lambda\sqrt{2}, 0, 0), (0, -\lambda\sqrt{2}, 0), (0, 0, -\lambda\sqrt{2}).$$

Hence, and denoting by ϖ_1 the value of ϖ for this case, we find, by § 18 (23),

$$A = N\varpi_1 \quad \text{and} \quad B = n = 0. \quad . \quad . \quad . \quad (31)$$

The explanation of $n=0$ (facial rigidity zero) is obvious when we consider that a cube having for its edges twelve equal straight bars, with their ends jointed by threes at the eight corners, affords no resistance to change of the right angles of its faces to acute and obtuse angles.

§ 25. Replacing now the Boscovich points in the middles of the faces of the cubes, from which we supposed them temporarily annulled in § 24, and putting the results of § 23 and § 24 together, we find for our equilateral homogeneous assemblage its elasticity moduluses as follows:—

$$\left. \begin{aligned} A &= N(\varpi_0 + \varpi_1), \\ B &= n = \frac{1}{2}N\varpi_0, \end{aligned} \right\} . \quad . \quad . \quad . \quad (32)$$

where, as we see by § 16 (20) above,

$$\left. \begin{aligned} \varpi_0 &= \lambda F(\lambda) - \lambda^2 F'(\lambda), \\ \varpi_1 &= \lambda\sqrt{2} F(\lambda\sqrt{2}) - 2\lambda^2 F'(\lambda\sqrt{2}), \end{aligned} \right\} . \quad . \quad (33),$$

$F(r)$ being now taken to denote repulsion between any two of the points at any distance r , which, with $\phi(r)$ defined as in § 10, is the meaning of $-\phi'(r)$. To render the solid, constituted of our homogeneous assemblage, elastically isotropic, we must, by § 19 (24), have $A - B = 2n$, and therefore, by (32),

$$\varpi_0 = 2\varpi_1. \quad . \quad . \quad . \quad . \quad . \quad (34)$$

§ 26. The last three of the six equilibrium equations § 16

(18) are fulfilled in virtue of symmetry in the case of an equilateral assemblage of single points whatever be the law of force between them, and whatever be the distance between any point and its nearest neighbours. The first three of them require in the case of § 23 that $F(\lambda)=0$; and in the case of (24) that $F(\lambda\sqrt{2})=0$, results of which the interpretation is obvious and important.

§ 27. The first three of the six equilibrium equations, § 16 (18), applied to the case of § 25, yield the following equation :

$$\sqrt{\frac{1}{2}}F(\lambda\sqrt{2}) = -F(\lambda) \quad . \quad . \quad . \quad (35);$$

that is to say, if there is repulsion or attraction between each point and its twelve nearest neighbours, there is attraction or repulsion of $\sqrt{2}$ of its amount between each point and its six next-nearest neighbours, unless there are also forces between more distant points. This result is easily verified by simple synthetical and geometrical considerations of the equilibrium between a point and its twelve nearest and six next-nearest neighbours in an equilateral homogeneous assemblage. The consideration of it is exceedingly interesting and important in respect to, and in illustration of, the engineering of jointed structures with redundant links or tie-struts.

§ 28. Leaving, now, the case of an equilateral homogeneous assemblage, let us consider what we may call a scalene assemblage; that is to say, an assemblage in which there are three sets of parallel rows of points, determinately fixed as follows, according to the system first taught by Bravais* :—

- I. Just one set of rows of points at consecutively shortest distances λ_1 .
- II. Just one set of rows of points at consecutively next-shortest distances λ_2 .
- III. Just one set of rows of points at consecutive distances shorter than those of all other rows not in the plane of I. and II.

To the condition $\lambda_3 > \lambda_2 > \lambda_1$ we may add the condition that none of the angles between the three sets of rows is a right angle, in order that our assemblage may be what we may call wholly scalene.

§ 29. Let A'OA, B'OB, C'OC be the primary rows thus determinately found having any chosen point, O, in common; we have

* *Journal de l'École Polytechnique*, tome xix. cahier xxxiii. pp. 1-128 : Paris, 1850.

$$\left. \begin{aligned} A'O &= OA = \lambda_1 \\ B'O &= OB = \lambda_2 \\ C'O &= OC = \lambda_3 \end{aligned} \right\} \dots \dots \dots (36).$$

Thus A' and A are O's nearest neighbours; and B' and B, O's next-nearest neighbours; and C' and C, O's nearest neighbours not in the plane AOB. (It should be understood that there may be in the plane AOB points which, though at greater distances from O than B and B', are nearer to O than are C and C'.)

§ 30. Supposing, now, BOC, B'OC', &c., to be the acute angles between the three lines meeting in O; we have two equal and dichirally similar* tetrahedrons of which each of the four faces is a scalene acute-angled triangle. That every angle in and between the faces is acute we readily see, by remembering that OC and OC' are shorter than the distances of O from any other of the points on the two sides of the plane AOB†.

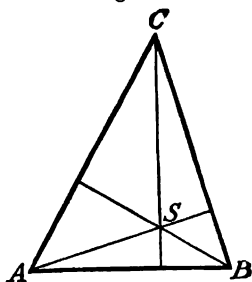
§ 31. As a preliminary to the engineering of an incompressible elastic solid according to Boscovich, it is convenient now to consider a special case of scalene tetrahedron, in which perpendiculars from the four corners to the four opposite faces intersect in one point. I do not know if the species of tetrahedron which fulfils this condition has found a place in geometrical treatises, but I am informed by Dr. Forsyth that it has appeared in Cambridge examination papers. For my present purpose it occurred to me thus:—Let QO, QA, QB, QC be four lines of given lengths drawn from one point, Q. It is required to draw them in such relative directions that the volume of the tetrahedron OABC is a maximum. Whatever be the four given lengths, this problem clearly has one real solution and one only: and it is such that the four planes BOC, COA, AOB, ABC are cut perpendicularly by the lines AQ, BQ, CQ, OQ, respectively, each produced through Q. Thus we see that the special tetrahedron is defined by four lengths, and conclude that two equations among the six edges of the tetrahedron in general are required to make it our special tetrahedron.

* Either of these may be turned round so as to coincide with the image of the other in any plane mirror. Either may be called a *pervert* of the other; as, according to the usage of some writers, an object is called a *pervert* of another if one of them can be brought to coincide with the image of the other in a plane mirror (as, for example, a right hand and a left hand).

† See "Molecular Constitution of Matter," § (45), (*h*), (*i*), 'Math. and Phys. Papers,' vol. iii. pp. 412–413.

§ 32. Hence we see the following simple way of drawing a special tetrahedron. Choose as data three sides of one face and the length perpendicular to it from the opposite angle. The planes through this perpendicular, and the angles of the triangle, contain the perpendiculars from these angles to the opposite sides of the tetrahedron, and therefore cut the opposite sides of the triangle perpendicularly. (Thus, parenthetically, we have a proof of the known theorem of elementary geometry that the perpendiculars from the three angles of a triangle to the opposite sides intersect in one point.) Let ABC be the chosen triangle and S the point in which it

Fig. 3.



is cut by the perpendicular from O , the opposite corner of the tetrahedron. AS , BS , CS , produced through S , cut the opposite sides perpendicularly, and therefore we find the point S by drawing two of these perpendiculars and taking their point of intersection. The tetrahedron is then found by drawing through S a line SO of the given length perpendicular to the plane of ABC . (We have, again parenthetically, an interesting geometrical theorem. The perpendiculars from A , B , C to the planes of OBC , OCA , OAB cut OS in the same point; SO being of any arbitrarily chosen length.)

§ 33. I wish now to show how an incompressible homogeneous solid of wholly oblique crystalline configuration can be constructed without going beyond Boscovich for material. Consider, in any scalene assemblage, the plane of the line $A'OA$ through any point O and its nearest neighbours, and the line $B'OB$ through the same point and its next-nearest neighbours. To fix the ideas, and avoid circumlocutions, we shall suppose this plane to be horizontal. Consider the two parallel planes of points nearest to the plane above it and below it. The corner C of the acute-angled tetrahedron $OABC$, which we have been considering, is one of the points in one of the two nearest parallel planes, that above AOB we

shall suppose. And the corner C' of the equal and dichirally similar tetrahedron $OA'B'C'$ is one of the points in the nearest parallel plane below. All the points in the plane through C are corners of equal tetrahedrons chirally similar to $OABC$, and standing on the horizontal triangles oriented as BOA . All the points C' in the nearest plane below are corners of tetrahedrons chirally similar to $OA'B'C'$ placed downwards on the triangles oriented as $B'OA'$. The volume of the tetrahedron $OABC$ is $\frac{1}{6}$ of the volume of the parallelepiped, of which OA, OB, OC are conterminous edges. Hence the sum of the volumes of all the upward tetrahedrons having their bases in one plane is $\frac{1}{6}$ of the volume of the space between large areas of these planes: and, therefore, the sum of all the chirally similar tetrahedrons, such as $OABC$, is $\frac{1}{6}$ of the whole volume of the assemblage through any larger space. Hence any homogeneous strain of the assemblage which does not alter the volume of the tetrahedrons does not alter the volume of the solid. Let tie-struts OQ, AQ, BQ, CQ be placed between any point Q within the tetrahedron and its four corners, and let these tie-struts be mechanically jointed together at Q , so that they may either push or pull at this point. This is merely a mechanical way of stating the Boscovichian idea of a second homogeneous assemblage, equal and similarly oriented to the first assemblage and placed with one of its points at Q , and the others in the other corresponding positions relatively to the primary assemblage. When it is done for all the tetrahedrons chirally similar to $OABC$, we find four tie-strut ends at every point O , or A , or B , or C , for example, of the primary assemblage. Let each set of these four ends be mechanically jointed together, so as to allow either push or pull. A model of the curious structure thus formed was shown at the conversazione of the Royal Society of June 7, 1893. It is for three dimensions of space what ordinary hexagonal netting is in a plane.

§ 34. Having thus constructed our model, alter its shape until we find its volume a maximum. This brings the tetrahedron, $OABC$, to be of the special kind defined in § 30. Suppose for the present the tie-struts to be absolutely resistant against push and pull; that is to say, to be each of constant length. This secures that the volume of the whole assemblage is unaltered by any infinitesimal change of shape possible to it; so that we have, in fact, the skeleton of an incompressible and inextensible solid*. Let now any forces whatever, sub-

* This result was given for an equilateral tetrahedral assemblage in § 67 of "Molecular Constitution of Matter," 'Math. and Phys. Papers,' vol. iii. pp. 425-426.

ject to the law of uniformity in the assemblage, act between the points of our primary assemblage : and, if we please, also between all the points of our second assemblage ; and between all the points of the two assemblages. Let these forces fulfil the conditions of equilibrium ; of which the principle is described in § 16 and applied to find the equations of equilibrium for the simpler case of a single homogeneous assemblage there considered. Thus we have an incompressible elastic solid ; and, as in § 17 above, we see that there are fifteen independent coefficients in the quadratic function of the strain-components expressing the work required to produce an infinitesimal strain. Thus we realize the result described in § 7 above.

§ 35. Suppose now each of the four tie-struts to be not infinitely resistant against change of length, and to have a given modulus of longitudinal rigidity, which, for brevity, we shall call its stiffness. By assigning proper values to these four stiffnesses, and by supposing the tetrahedron to be freed from the two conditions making it our special tetrahedron, we have six quantities arbitrarily assignable, by which, adding these six to the former fifteen, we may give arbitrary values to each of the twenty-one coefficients in the quadratic function of the six strain-components with which we have to deal when change of bulk is allowed. Thus, in strictest Boscovichian doctrine, we provide for twenty-one independent coefficients in Green's energy-function. The dynamical details of the consideration of the equilibrium of two homogeneous assemblages with mutual attraction between them, and of the extension of §§ 9-17 to the larger problem now before us, are full of purely scientific and engineering interest, but must be reserved for what I hope is a future communication.

XLIV. *The Highest Waves in Water.* By J. H. MICHELL,
M.A., Fellow of Trinity College, Cambridge*.

THE waves contemplated are those in which the motion is parallel to one plane and which advance without change of form. Most of the work already done on irrotational waves applies only to those of small height and unbroken outline. Stokes† has, however, long since expressed the opinion that the height of the wave could be increased until the summit became pointed, and showed that the angle at the summit would be 120° . The object of this communication is to make known a method of investigating such maximum waves.

* Communicated by the Author.

† Collected Papers, vol. i. p. 227.

The work of Prof. Stokes fills the gap between these and the infinitesimal waves.

Waves in Deep Water.

Suppose at first the water so deep that it may be considered infinitely so. Make the motion steady by moving the water forward bodily with the backward velocity V of the wave. Take rectangular axes, x horizontal, y vertically downwards, in a plane of motion, with the origin at a wave-summit. Let ϕ , ψ be the velocity and stream functions, the surface of the water being $\psi=0$ and the bottom $\psi=\infty$.

Call the velocity q , the inclination of the wave-line to the horizontal at ϕ , θ , the curvature at the same point K .

At the summit the curvature and the velocity are zero, and the ratio of the two is finite and not far from constant along the whole wave-line, as appears from the investigation following.

Accordingly we assume, taking $\phi=0$, $\phi=\pi$ as consecutive summits,

$$K = q(a_0 + a_1 \cos 2\phi + a_2 \cos 4\phi + \dots),$$

where $a_1, a_2 \dots$ are small compared with a_0 .

$$\text{Since } K = q \frac{d\theta}{d\phi},$$

$$\frac{d\theta}{d\phi} = a_0 + a_1 \cos 2\phi + a_2 \cos 4\phi + \dots$$

In order to find the connexion between $\phi + i\psi \equiv w$ and $x + iy \equiv z$ throughout the liquid, we proceed in the manner of Riemann and Schwarz, that is, we find by means of the assumed surface-condition a function of z which is real over the surface and possesses only simple *poles* in the liquid. This function can then be extended continuously in its range, throughout the plane w , its value at $(\phi, -\psi)$ being the conjugate of that at (ϕ, ψ) . We then have a function throughout the plane w whose singularities are confined to simple poles, and whose form can be written down according to the principles of Cauchy.

Put

$$\log \frac{dz}{dw} \equiv U.$$

Along the surface, or $\psi=0$,

$$U = \log e^{i\theta}/q = -\log q + i\theta,$$

and therefore, along the surface,

$$\frac{dU}{dw} = \frac{dU}{d\phi} = -\frac{d \log q}{d\phi} + i \frac{d\theta}{d\phi};$$

or, from the assumed form of $\frac{d\theta}{d\phi}$,

$$\frac{dU}{dw} - i(a_0 + a_1 e^{2iw} + a_2 e^{4iw} + \dots) = -\frac{d \log q}{d\phi} + a_1 \sin 2\phi + \dots$$

The function on the left is therefore real over the surface.

At $\psi = \infty$,

$$\frac{dz}{dw} = 1/V,$$

and the function will be finite there and equal to $-ia_0$.

The only singular points to be considered are, then, the summits of the waves.

Suppose near the summit $w=0$,

$$\frac{dz}{dw} = Aw^n,$$

and therefore

$$\frac{dw}{dz} = A^{-\frac{1}{n+1}} (n+1)^{-\frac{n}{n+1}} z^{-\frac{n}{n+1}},$$

and

$$q^2 = A^{-\frac{2}{n+1}} (n+1)^{-\frac{2n}{n+1}} r^{-\frac{2n}{n+1}},$$

where r is the distance from the summit. Now, since the pressure is constant over the surface we have $q^2 = 2gy$; and, comparing, we see that $n = -\frac{1}{3}$; so that

$$\frac{dz}{dw} = Aw^{-\frac{1}{3}}$$

near $w=0$. From this it follows that the angle at the summit is 120° , as was first shown by Stokes*.

Hence, also,

$$\frac{dU}{dw} = -\frac{1}{3w}$$

near the summit $w=0$; and the summits are simple infinities of the function considered.

According, then, to the principles of Cauchy, the function can only differ from the sum of the polar elements by a constant, and we have

$$\begin{aligned} \frac{dU}{dw} - i(a_1 e^{2iw} + a_2 e^{4iw} + \dots) &= -\frac{1}{3} \sum \frac{1}{w - n\pi} - \frac{i}{3} \\ &= -\frac{1}{3} \cot w - \frac{i}{3}, \end{aligned}$$

* Collected Papers, vol. i. p. 227.

the constant being so chosen as to make things right at infinity.

Integrating, we have

$$U = \log(-i \sin w)^{-\frac{1}{2}} e^{-\frac{1}{2} i w} + a_0' + \frac{1}{2} a_1 e^{2i w} + \dots,$$

where a_0' is real, since U is real at $\psi = \infty$; or, writing the series in the form

$$\log A(1 + c_1 e^{2i w} + c_2 e^{4i w} + \dots),$$

we have

$$\frac{dz}{dw} = A(-i \sin w)^{-\frac{1}{2}} e^{-\frac{1}{2} i w} (1 + c_1 e^{2i w} + c_2 e^{4i w} + \dots),$$

the velocity at $\psi = \infty$, or the wave-velocity, being $2^{-\frac{1}{2}}/A$, and the real root of $(-i \sin w)^{-\frac{1}{2}}$ being taken along $\phi = 0$.

Suppose the units so chosen that $A = 1$, and hence $V = 1/2^{\frac{1}{2}}$, and the length of wave $L = \pi/V = \pi \times 2^{\frac{1}{2}}$.

It will be more convenient, at first, to invert $\frac{dz}{dw}$ and write

$$\frac{dw}{dz} = (-i \sin w)^{\frac{1}{2}} e^{\frac{1}{2} i w} (1 + b_1 e^{2i w} + b_2 e^{4i w} + \dots).$$

On the surface between $\phi = 0$ and $\phi = \pi$,

$$\frac{dw}{dz} = \sin^{\frac{1}{2}} \phi e^{\frac{1}{2} i (\phi - \frac{\pi}{2})} (1 + b_1 e^{2i \phi} + b_2 e^{4i \phi} + \dots),$$

the real root of $\sin^{\frac{1}{2}} \phi$ being taken. The surface-condition

$$q^2 = 2gy$$

may be written

$$\frac{dq^2}{d\phi} = 2g \frac{dy}{d\phi} = 2g \frac{1}{q^3} \frac{d\phi}{dy},$$

or

$$\frac{dq^4}{d\phi} = 4g \frac{d\phi}{dy}.$$

Taking

$$\left(\frac{dw}{dz}\right)^2 = \sin^2 \phi e^{i(\phi - \frac{\pi}{2})} \{ 1 + 2b_1 e^{2i \phi} + (2b_2 + b_1^2) e^{4i \phi} + (2b_3 + 2b_1 b_2) e^{6i \phi} + \dots \},$$

and multiplying by its conjugate, we get, omitting terms of order 4 in the b 's,

$$q^4 = \sin^2 \phi \{ 1 + 4b_1^2 + (4b_1 + 8b_1 b_2 + 4b_1^3) \cos 2\phi + (4b_2 + 2b_1^2) \cos 4\phi + (4b_3 + 4b_1 b_2) \cos 6\phi \},$$

Phil. Mag. S. 5. Vol. 36. No. 222. Nov. 1893. 2 G

and therefore

$$\begin{aligned}\frac{dg^4}{d\phi} = & \frac{4}{3} \sin^3 \phi \{ (1 - b_1 + 4b_1^2 - b_1^3 - 2b_1b_2) \cos \phi \\ & + (5b_1 - 2b_1^2 - 4b_2 + 10b_1b_2 + 5b_1^3) \cos 3\phi \\ & + (4b_1^2 + 8b_2 - 7b_1b_2 - 7b_3) \cos 5\phi \\ & + (11b_1b_2 + 11b_3) \cos 7\phi \}.\end{aligned}$$

To put $\frac{d\phi}{dy}$ into a similar form we use the Fourier expansion

$$\sin\left(2r + \frac{1}{3}\phi - \frac{\pi}{6}\right) = \Sigma A_{2n+1} \cos(2n+1)\phi,$$

where

$$A_{2n+1} = -\frac{6\sqrt{3}}{\pi} \frac{6r+1}{3^2(2n+1)^2 - (6r+1)^2}.$$

Since

$$\frac{d\phi}{dy} = -\sin^3 \phi \left(\sin \frac{1}{3}\phi - \frac{\pi}{6} + b_1 \sin 2\phi + \frac{1}{3}\phi - \frac{\pi}{6} + \dots \right),$$

we get

$$\begin{aligned}\frac{d\phi}{dy} = & \frac{6\sqrt{3}}{\pi} \sin^3 \phi \left[\frac{1}{8} \cos \phi + \frac{1}{80} \cos 3\phi + \frac{1}{224} \cos 5\phi + \frac{1}{440} \cos 7\phi + \dots \right. \\ & + b_1 \left(-\frac{7}{40} \cos \phi + \frac{7}{32} \cos 3\phi + \frac{1}{176} \cos 5\phi + \frac{1}{352} \cos 7\phi + \dots \right) \\ & + b_2 \left(-\frac{1}{160} \cos \phi - \frac{1}{88} \cos 3\phi + \frac{1}{56} \cos 5\phi + \frac{1}{272} \cos 7\phi + \dots \right) \\ & + b_3 \left(-\frac{1}{352} \cos \phi - \frac{1}{80} \cos 3\phi - \frac{1}{384} \cos 5\phi + \frac{1}{80} \cos 7\phi + \dots \right) \\ & \left. + \dots \right].\end{aligned}$$

Equating the coefficients of corresponding cosines and writing $18\sqrt{3}g/\pi = k$, the following equations are obtained for k and the b 's :—

$$\begin{aligned}1 - b_1 + 4b_1^2 - b_1^3 - 2b_1b_2 \\ = k(\cdot125 - \cdot175b_1 - \cdot08125b_2 - \cdot05398b_3),\end{aligned}$$

$$\begin{aligned}5b_1 - 2b_1^2 - 4b_2 + 10b_1b_2 + 5b_1^3 \\ = k(\cdot0125 + \cdot21875b_1 - \cdot14772b_2 - \cdot06786b_3),\end{aligned}$$

$$\begin{aligned}4b_1^2 + 8b_2 - 7b_1b_2 - 7b_3 \\ = k(\cdot00446 + \cdot039773b_1 + \cdot232143b_2 - \cdot13970b_3),\end{aligned}$$

$$\begin{aligned}11b_1b_2 + 11b_3 \\ = k(\cdot00227 + \cdot01785b_1 + \cdot04779b_2 + \cdot2375b_3).\end{aligned}$$

Solving, we find as sufficiently close values :

$$\begin{aligned}k &= 8.25, \\b_1 &= .0397, \\b_2 &= .0094, \\b_3 &= .002 ;\end{aligned}$$

and thus, as a close approximation to the value of $\frac{dw}{dz}$,

$$\frac{dw}{dz} = (-i \sin w)^{\frac{1}{2}} e^{\frac{1}{2} i w} (1 + .0397 e^{2 i w} + .0094 e^{4 i w} + .002 e^{6 i w}).$$

The Depth of the Wave.

Since

$$\begin{aligned}18 \sqrt{3} g / \pi = k = 8.25, \\2g = 1.66.\end{aligned}$$

Now at $\phi = \frac{\pi}{2}$,

$$\begin{aligned}q^2 &= (1 - b_1 + b_2 - b_3 + \dots)^2 \\&= (.9677)^2.\end{aligned}$$

The depth of the wave is $q^2/2g$, and therefore the ratio of depth to length is

$$\frac{h}{L} = \frac{(.9677)^2}{1.66 \times 3.96} = .142 ;$$

so that the height of the wave is very nearly one seventh of its length.

As was to be expected, actual record of high waves does not come within some distance of this: Abercromby, for example, measured waves 46 feet high and 765 long (Phil. Mag. xxv. 1888).

At the Summit.

Near the summit $\phi = 0$ we have

$$\frac{dw}{dz} = \phi^{\frac{1}{2}} \left(\cos \frac{\pi}{6} - i \sin \frac{\pi}{6} \right) (1 + b_1 + b_2 + \dots),$$

and therefore

$$q^2 = \phi^2 (1 + b_1 + b_2 + \dots)^2$$

and,

$$z = \frac{2}{3} \phi^{\frac{1}{2}} \left(\cos \frac{\pi}{6} + i \sin \frac{\pi}{6} \right) / (1 + b_1 + b_2 + \dots),$$

so that, since $q^2 = 2gy$, we have

$$(1 + b_1 + b_2 + \dots)^2 = \frac{3}{2}g \\ = 1.245,$$

and

$$1 + b_1 + b_2 + \dots = 1.0758,$$

while

$$b_1 + b_2 + b_3 = .0511.$$

Near the summit, the series for q^2 , every term having the same sign, will not be well represented by the first three terms. This is of little consequence since the sum of the terms is known at the summit. Elsewhere the first three terms give a good approximation, as appears below.

Form of the Wave.

The coordinates of any point ϕ on the surface are got from the two equations:—

$$\frac{dx}{d\phi} = \sin^{-\frac{1}{3}} \phi \left[\cos \left(\frac{1}{3} \phi - \frac{\pi}{6} \right) - .04 \cos \left(2\phi - \frac{1}{3} \phi + \frac{\pi}{6} \right) \right. \\ \left. - .008 \cos \left(4\phi - \frac{1}{3} \phi + \frac{\pi}{6} \right) - .001 \cos \left(6\phi - \frac{1}{3} \phi + \frac{\pi}{6} \right) \right],$$

$$\frac{dy}{d\phi} = \sin^{-\frac{1}{3}} \phi \left[\sin \left(\frac{\pi}{6} - \frac{1}{3} \phi \right) - .04 \sin \left(2\phi - \frac{1}{3} \phi + \frac{\pi}{6} \right) \right. \\ \left. - .008 \sin \left(4\phi - \frac{1}{3} \phi + \frac{\pi}{6} \right) - .001 \sin \left(6\phi - \frac{1}{3} \phi + \frac{\pi}{6} \right) \right].$$

The first terms do not integrate in convenient form and are best calculated by means of the expansions

$$\sin^{-\frac{1}{3}} \phi \cos \frac{1}{3} \phi = \phi^{-\frac{1}{3}} (1 + .0008 \phi^4 + \dots)$$

$$\sin^{-\frac{1}{3}} \phi \sin \frac{1}{3} \phi = \frac{1}{3} \phi^{\frac{2}{3}} (1 + .037 \phi^2 + .0023 \phi^4 + \dots).$$

The other terms integrate simply.

The following table gives the values of x , y , and q^2 for the specified values of ϕ :—

| ϕ . | x . | y . | q^2 . | q^2/y . |
|-------------------|-------|-------|---------|-----------|
| $\frac{\pi}{50}$ | .196 | .110 | .174 | 1.58 |
| $\frac{\pi}{20}$ | .366 | .197 | .318 | 1.61 |
| $\frac{\pi}{10}$ | .501 | .298 | .489 | 1.64 |
| $\frac{\pi}{5}$ | .974 | .428 | .707 | 1.65 |
| $\frac{3\pi}{10}$ | 1.321 | .507 | .837 | 1.65 |
| $\frac{2\pi}{5}$ | 1.654 | .552 | .912 | 1.65 |
| $\frac{\pi}{2}$ | 1.979 | .567 | .936 | 1.65 |

The form of the wave is shown in the diagram. The error in q^2/y near the summit means an error of about 1·5 per cent.



in x, y , and q , due, as before stated, to the slower convergency of the series for dw/dz at that point. This does not affect the determination of the height of the wave.

Velocity of the Wave.

The length of the wave is 3·96 and $2g=1·66$, so that, in general units, if L is the length of the wave and V its velocity,

$$V^2 = \cdot 191 gL.$$

For the infinitesimal wave,

$$V^2 = gL/2\pi.$$

The ratio of the velocities of the highest wave and the infinitesimal wave is therefore 1·2. The wave observed by Abercromby (*loc. cit.*) of length 765 feet and height 46 feet had a velocity of 47 miles per hour; the highest wave of the same length would be nearly 100 feet high and would have a velocity of 47 miles an hour very nearly.

Water of Finite Depth.

Here the poles of the function dU/dw have to be indefinitely reflected in $\psi = K'$, the bottom of the water, and $\psi = 0$, the surface, in order to make U real or θ constant at the bottom. The singular points in the whole field are therefore at

$$w = 2nK + 2n'iK',$$

$w = 2nK$ being the wave summits.

We are thus led to the form

$$\frac{dw}{dz} = H^{\frac{1}{2}}(w) e^{\frac{\pi i}{2K}(w-K)} \left\{ 1 + a_1 \cos \frac{\pi}{K}(w - iK') + \dots \right\},$$

where H is Jacobi's function so denoted. This equation is susceptible of the same treatment as the simpler case.

University, Melbourne,
August 7.

XLV. *Note on some Thermal Properties of a Mixture of Carbonic Acid and Nitrogen.* By K. TSURUTA, *Rigakushi, Tokio, Japan* *.

LITERATURE.

IN his classical researches on thermal properties of carbonic acid, Andrews found the isothermals for $13^{\circ}\cdot 1$ and $21^{\circ}\cdot 5$ a little rounded-off at the points of complete liquefaction and of complete evaporation, and pointed out that this was due to a very small unavoidable admixture of air in the gas. Maxwell was much interested in this "question, of an exceedingly interesting nature," as appears from his letters to Andrews †. Andrews then made a further investigation on the subject, the results of which were given in an abstract ‡. A further account was published as a posthumous paper in the 'Philosophical Transactions' for 1886 §.

The subject did not remain unattacked by other physicists working in this part of the field of investigation. Caillaet † made some experiments as early as 1880 on mixtures of carbonic acid and other gases, on which Jamin wrote a note **. In England, Ansdell was occupied with various mixtures of hydrochloric acid and carbonic acid ††.

Caillaet studied especially the very curious fact of the appearance and disappearance of the condensed state at certain temperatures and pressures; Ansdell confined his attention to the determinations of the critical temperatures of the mixtures; while Dewar described many interesting facts relating to the behaviour of carbonic acid in presence of other substances †‡. Andrews's paper contains a series of measurements on changes of volumes, pressures, and temperatures of the mixture of carbonic acid and nitrogen in the proportion of 3 to 4. Thus, although the paper was published, according to Prof. Tait, twelve years after the date of experiment, yet it has remained, and still remains, so far as I am aware, a very complete investigation and perhaps the only one.

* Communicated by the Author.

† The Memoir on the Life of T. Andrews, by Tait and Brown, pp. 14-15.

‡ 'The Scientific Papers of T. Andrews,' pp. 383-392.

§ Ibid. pp. 457-471.

†† *Journ. de Phys.* tom. ix. (1880).

** *Comptes Rendus*, xvi. (1883).

‡‡ Proc. Roy. Soc. vol. xxxiv. (1882).

†† Ibid. vol. xxx. (1880).

Soon after the publication of the posthumous paper, Herr Margules* calculated some thermodynamical magnitudes based on the data supplied. Herr Galitzene† developed the incomplete result of comparison made by Andrews himself between the experimental data and Dalton's law of gaseous mixtures.

CHARACTERISTIC EQUATION.

We are not at present in possession of a rational form of characteristic equation applicable to all substances. Some of those which have been proposed as such hold good only for one class of substances, nor do they continue to hold strictly through the whole range of physical changes within the reach of experiment even in the case of the very substances for which they were particularly given. They are therefore to be looked upon as empirical and tentative, and we have to make use of them as such for the time being, or to regard them as interpolation formulæ whose mathematical forms are much like those of a rational one. In choosing the Clausius' form of characteristic equation, I was guided by no other consideration than the above. It is

$$P = \frac{RT}{v - \alpha} - \frac{\Theta}{(v + \beta)^2},$$

in which Θ is a certain undetermined function of T , the simplest form being

$$\Theta = \frac{K \text{ (a constant)}}{T}.$$

In the first place I have to determine the four constants R , K , α , and β for the mixture under consideration.

As Andrews used a hydrogen-manometer, and hydrogen presents a decided deviation from the gaseous laws, corrections for the given manometric values of pressure are to be applied. It is certain, although not explicitly mentioned, that Andrews calculated pressures by the equation‡

$$p = \frac{V_0(1 + \alpha t)}{V_1} \mp \frac{q}{760},$$

in which V_0 is the volume of the mixture at 0° and under the normal pressure, V_1 that at the temperature t and under the

* Wiener *Sitzungsbericht*, Bd. xcvii. (1888).

† Wied. *Ann.* Bd. xci. (1890).

‡ 'The Scientific Papers,' p. 422.

pressure p , and q denotes the difference of mercury-levels in the manometer and the tube containing the mixture. V_1 was not given by Andrews, so that I must proceed in the inverse manner to deduce V_1 from p according to the above formula. $q/760$ is an unknown factor; but inasmuch as Andrews mentions in his first Bakerian Lecture that the difference rarely exceeded 200 mm., a correction arising from this is so small that it can be safely neglected. For example, since

$$\frac{V_1}{V_0} = \frac{1}{p} + \frac{\alpha t}{p} + \frac{q}{760 \times p^2},$$

taking the greatest possible value, 200 mm., for q , and the least possible value, 40 atmospheres, for p , we have

$$\frac{q}{760 \times p^2} = 0.000164.$$

Thus I get the values of V_1 , which will not perhaps much differ from the directly observed ones.

We are now able to calculate the corrections for the manometric readings by applying the Clausius' form of characteristic equation for hydrogen with the values of the constants determined by Sarrau* based on the data supplied by Amagat's classical research—

$$R=0.003665, \quad K=0.0551, \quad \alpha=0.000889,$$

$$\beta = -0.00043.$$

I have myself found that these values are very good, not only in the few instances given by Sarrau, but also throughout.

Although I was satisfied so far, yet I was anxious to extend the verification to the temperatures of our manometer, 7°·2, 7°·4, 12°·0, 12°·8, the temperature-range in Amagat's investigation being from 30° to 100°. Wroblewski's posthumous paper† on the compressibility of hydrogen was the only one available for me. I give below so much as is thought sufficient of my results of comparison:—

* *Comptes Rendus*, xciv. (1882).

† *Wiener Sitzungsbericht*, Bd. xcvii. (1888).

| <i>t.</i> | Wroblewski's measurements. | Clausius, Amagat, and Sarrau. | Diff. |
|-----------|-------------------------------|----------------------------------|--------|
| 0 | atm. 29·635 | atm. 29·488 | -0·147 |
| " | 39·355 | 38·654 | -0·701 |
| " | 49·097 | 48·050 | -1·047 |
| " | 68·791 | 67·641 | -1·150 |
| 98·14 | 1·000 | 1·006 | +0·006 |
| " | 19·552 | 19·516 | -0·036 |
| " | 49·223 | 48·565 | -0·658 |
| " | 68·582 | 67·702 | -0·880 |

The method of Wroblewski was quite different from that of Amagat, yet their results agree sufficiently well with one another.

I then proceeded to the calculation of pressures by equation (1). The results are contained in the following Tables; the corrected values in I., II., III. agree very well with those given by Margules and Galitzene, but those in IV. show some, though small differences.

TABLE I.

| <i>t.</i> | V_1 . | P, given. | P, corrected. |
|-----------|----------|--------------|------------------|
| 7·30 | 0·024416 | 42·05 | 43·30 |
| 7·30 | 0·021091 | 48·68 | 50·36 |
| 7·22 | 0·019877 | 51·64 | 53·54 |
| 7·26 | 0·018755 | 54·73 | 56·87 |
| 7·21 | 0·017566 | 58·43 | 60·88 |
| 7·21 | 0·016388 | 62·63 | 65·45 |
| 7·20 | 0·015272 | 67·20 | 70·47 |
| 7·18 | 0·013247 | 79·47 | 81·66 |
| 7·17 | 0·011698 | 87·73 | 93·40 |
| 7·17 | 0·010557 | 97·21 | 104·23 |
| 7·17 | 0·009450 | 108·60 | 117·46 |
| 7·17 | 0·008316 | 123·40 | 135·01 |

TABLE II.

| t . | V_1 . | P, given. | P, corrected. |
|-------|----------|--------------|------------------|
| 7.47 | 0.025890 | 39.68 | 40.79 |
| 7.48 | 0.024714 | 41.56 | 42.79 |
| 7.42 | 0.023526 | 43.66 | 44.14 |
| 7.46 | 0.022332 | 46.00 | 47.61 |
| 7.48 | 0.019957 | 51.48 | 53.36 |
| 7.42 | 0.018761 | 54.75 | 56.89 |
| 7.54 | 0.017644 | 58.24 | 60.67 |
| 7.50 | 0.016450 | 62.46 | 65.27 |
| 7.48 | 0.015320 | 67.07 | 70.31 |
| 7.59 | 0.014079 | 73.00 | 76.87 |
| 7.65 | 0.012976 | 79.22 | 83.80 |
| 7.55 | 0.011785 | 87.20 | 92.80 |
| 7.80 | 0.010660 | 96.50 | 103.43 |
| 7.54 | 0.009454 | 108.70 | 117.54 |
| 7.58 | 0.007134 | 144.00 | 160.20 |
| 7.79 | 0.006181 | 166.40 | 188.42 |
| 7.63 | 0.005928 | 173.40 | 197.50 |
| 7.67 | 0.004766 | 215.70 | 254.73 |
| 7.58 | 0.003620 | 283.90 | 357.17 |

TABLE III.

| t . | V_1 . | P, given. | P, corrected. |
|-------|----------|--------------|------------------|
| 11.61 | 0.024668 | 42.26 | 43.51 |
| 11.97 | 0.021115 | 49.43 | 51.15 |
| 11.86 | 0.018692 | 55.82 | 58.03 |
| 12.38 | 0.016366 | 63.87 | 66.78 |
| 12.38 | 0.014450 | 72.34 | 76.12 |
| 12.38 | 0.011711 | 89.26 | 95.08 |
| 11.96 | 0.009489 | 110.00 | 119.02 |
| 11.63 | 0.007160 | 145.60 | 161.76 |
| 11.70 | 0.004704 | 221.70 | 262.78 |

TABLE IV.

| t . | V_1 . | P, given. | P, corrected. |
|-------|----------|--------------|------------------|
| 8.39 | 0.024600 | 41.90 | 43.14 |
| 8.42 | 0.021123 | 48.80 | 50.49 |
| 12.06 | 0.018692 | 55.86 | 58.07 |
| 12.08 | 0.016270 | 64.18 | 67.13 |
| 12.18 | 0.014400 | 72.54 | 76.33 |
| 12.36 | 0.009459 | 110.50 | 119.60 |
| 12.36 | 0.007105 | 147.10 | 163.81 |
| 12.40 | 0.004675 | 223.60 | 265.41 |

The constants R , K , α , β were calculated by the method of least squares, taking into account all the measurements given by Andrews, altogether 48 in number. Their values actually found by me were a little different from those given by Margules, which latter are :—

$$\begin{aligned} R &= 0.003674, & K &= 0.953, \\ \alpha &= 0.0014, & \beta &= 0.00015. \end{aligned}$$

But when I compared the values of pressure calculated with my values of the constants with the above corrected values, I found that Margules' values are on the whole rather preferable to mine, so that, to avoid useless diversities, I determined to adopt Margules' values throughout the following pages.

The following Table contains, besides the corrected results of Andrews's measurements, the calculated values of pressure according to equation (1) with the above values of the constants; it contains all data that are wanted to get isothermals, isomerics, and isopiestic of the mixture. It will be seen how well equation (1) represents the results of measurements, and so all that is possibly contained in it may as reasonably be accepted as the measurements themselves.

TABLE I.

| t . | v . | p (obs.). | p (calc.). | Diff. |
|-------|---------|-------------|--------------|-------|
| | | atm. | atm. | |
| 2.32 | 0.02138 | 43.30 | 43.16 | -0.14 |
| 2.34 | 0.01805 | 50.36 | 50.31 | -0.05 |
| 2.08 | 0.01681 | 53.54 | 53.54 | 0.00 |
| 2.28 | 0.01575 | 56.87 | 56.82 | -0.05 |
| 2.06 | 0.01455 | 60.88 | 60.83 | -0.05 |
| 2.10 | 0.01338 | 65.45 | 65.44 | -0.01 |
| 2.16 | 0.01229 | 70.47 | 70.45 | -0.02 |
| 2.21 | 0.00908 | 84.08 | 84.10 | +0.02 |
| 2.21 | 0.00881 | 93.40 | 93.32 | -0.08 |
| 2.17 | 0.00772 | 104.23 | 104.05 | -0.18 |
| 2.21 | 0.00668 | 117.46 | 117.27 | -0.19 |
| 2.25 | 0.00568 | 135.01 | 134.41 | -0.60 |

TABLE II.

| <i>t.</i> | <i>v.</i> | <i>p</i> (obs.). | <i>p</i> (calc.). | Diff. |
|-----------|-----------|------------------|-------------------|--------|
| | | atm. | atm. | |
| 7.50 | 0.02350 | 40.79 | 40.56 | -0.23 |
| 7.50 | 0.02231 | 42.79 | 42.55 | -0.24 |
| 7.50 | 0.02109 | 45.01 | 44.81 | -0.20 |
| 7.53 | 0.01987 | 47.61 | 47.34 | -0.27 |
| 7.51 | 0.01744 | 53.36 | 53.27 | -0.09 |
| 7.59 | 0.01625 | 56.89 | 56.78 | -0.11 |
| 7.50 | 0.01512 | 60.67 | 60.54 | -0.13 |
| 7.50 | 0.01391 | 65.27 | 65.19 | -0.08 |
| 7.50 | 0.01274 | 70.31 | 70.43 | +0.12 |
| 7.50 | 0.01149 | 76.87 | 77.06 | +0.19 |
| 7.51 | 0.01054 | 83.80 | 83.03 | -0.77 |
| 7.50 | 0.00926 | 92.80 | 92.75 | -0.05 |
| 7.08 | 0.00808 | 103.43 | 103.81 | +0.38 |
| 7.48 | 0.00691 | 117.54 | 118.15 | +0.61 |
| 7.54 | 0.00496 | 160.20 | 159.74 | -0.46 |
| 7.50 | 0.00422 | 188.42 | 187.54 | -0.88 |
| 7.49 | 0.00404 | 197.50 | 196.82 | -0.68 |
| 7.50 | 0.00332 | 254.73 | 254.58 | -0.15 |
| 7.49 | 0.00272 | 357.17 | 368.21 | +11.04 |

TABLE III.

| <i>t.</i> | <i>v.</i> | <i>p</i> (obs.). | <i>p</i> (calc.). | Diff. |
|-----------|-----------|------------------|-------------------|-------|
| | | atm. | atm. | |
| 31.35 | 0.02445 | 43.51 | 43.34 | -0.17 |
| 31.31 | 0.02055 | 51.15 | 51.07 | -0.08 |
| 31.21 | 0.01795 | 58.03 | 57.97 | -0.06 |
| 31.40 | 0.01542 | 66.78 | 66.85 | +0.07 |
| 31.14 | 0.01337 | 76.12 | 76.21 | +0.09 |
| 31.06 | 0.01045 | 95.08 | 95.57 | +0.49 |
| 31.36 | 0.00816 | 119.02 | 120.07 | +1.05 |
| 31.35 | 0.00586 | 161.76 | 164.03 | +2.27 |
| 31.30 | 0.00377 | 262.78 | 267.92 | +5.14 |

TABLE IV.

| <i>t.</i> | <i>v.</i> | <i>p</i> (obs.). | <i>p</i> (calc.). | Diff. |
|-----------|-----------|------------------|-------------------|-------|
| | | atm. | atm. | |
| 48.22 | 0.02635 | 43.14 | 43.09 | -0.05 |
| 48.11 | 0.02239 | 50.49 | 50.36 | -0.13 |
| 48.48 | 0.01929 | 58.07 | 58.18 | +0.11 |
| 48.43 | 0.01662 | 67.13 | 67.05 | -0.08 |
| 48.66 | 0.01448 | 76.33 | 76.51 | +0.18 |
| 48.38 | 0.00896 | 119.60 | 120.45 | +0.85 |
| 48.49 | 0.00646 | 163.81 | 165.58 | +1.77 |
| 48.47 | 0.00430 | 265.41 | 257.57 | -7.84 |

ISOTHERMALS, ISOMETRICS, AND ISOPIESTICS OF THE MIXTURE.

Having obtained the characteristic equation of the mixture, I proceeded to construct a series of isothermals, the parametric values ($2^{\circ}2$, $7^{\circ}5$, $31^{\circ}3$, $48^{\circ}4$) of four of which were chosen according to Andrews.

TABLE I. $2^{\circ}2$.

| <i>p.</i> | <i>v.</i> | <i>pv.</i> | <i>p.</i> | <i>v.</i> | <i>pv.</i> |
|-----------|-----------|------------|-----------|-----------|------------|
| 43.13 | 0.02138 | 0.92212 | 70.30 | 0.01229 | 0.86399 |
| 50.27 | 0.01805 | 0.90737 | 83.82 | 0.00998 | 0.83652 |
| 53.57 | 0.01681 | 0.90101 | 93.31 | 0.00881 | 0.82206 |
| 56.63 | 0.01575 | 0.89192 | 104.07 | 0.00772 | 0.80342 |
| 60.86 | 0.01455 | 0.88551 | 117.26 | 0.00668 | 0.78330 |
| 65.48 | 0.01338 | 0.87612 | 134.35 | 0.00568 | 0.76311 |

TABLE II. $7^{\circ}5$.

| <i>p.</i> | <i>v.</i> | <i>pv.</i> | <i>p.</i> | <i>v.</i> | <i>pv.</i> |
|-----------|-----------|------------|-----------|-----------|------------|
| 40.56 | 0.02350 | 0.95316 | 118.87 | 0.00691 | 0.82139 |
| 42.55 | 0.02231 | 0.94929 | 127.61 | 0.00636 | 0.81160* |
| 44.81 | 0.02109 | 0.94504 | 143.52 | 0.00556 | 0.79797* |
| 47.32 | 0.01987 | 0.94025 | 152.23 | 0.00521 | 0.79312* |
| 53.27 | 0.01744 | 0.92903 | 159.67 | 0.00495 | 0.79037 |
| 56.77 | 0.01625 | 0.92251 | 176.92 | 0.00446 | 0.78906* |
| 60.54 | 0.01512 | 0.91536 | 187.54 | 0.00422 | 0.79142 |
| 65.19 | 0.01391 | 0.90679 | 196.84 | 0.00404 | 0.79523 |
| 70.43 | 0.01274 | 0.89728 | 220.39 | 0.00368 | 0.81103* |
| 77.06 | 0.01149 | 0.88542 | 254.58 | 0.00332 | 0.84520 |
| 83.02 | 0.01054 | 0.87503 | 281.43 | 0.00312 | 0.87806* |
| 92.74 | 0.00926 | 0.85877 | 324.02 | 0.00289 | 0.93642* |
| 104.11 | 0.00808 | 0.84121 | 368.25 | 0.00272 | 0.00164 |

TABLE III. $31^{\circ}3$.

| <i>p.</i> | <i>v.</i> | <i>pv.</i> |
|-----------|-----------|------------|
| 43.33 | 0.02445 | 1.05942 |
| 51.07 | 0.02055 | 1.04949 |
| 57.99 | 0.01795 | 1.04092 |
| 66.82 | 0.01542 | 1.03036 |
| 76.27 | 0.01337 | 1.01973 |
| 95.66 | 0.01045 | 0.99965 |
| 120.03 | 0.00816 | 0.97944 |
| 138.20 | 0.00701 | 0.96878* |
| 163.97 | 0.00586 | 0.96086 |
| 179.17 | 0.00536 | 0.96035* |
| 205.17 | 0.00471 | 0.96635* |
| 223.73 | 0.00436 | 0.97546* |
| 244.34 | 0.00405 | 0.98958* |
| 267.92 | 0.00377 | 1.01006 |

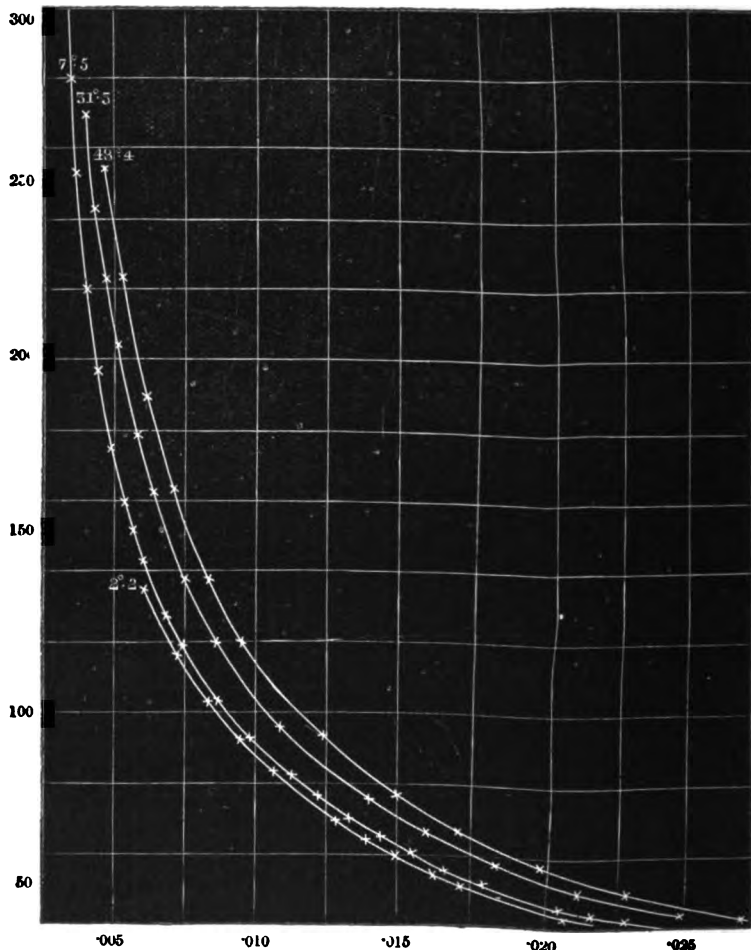
TABLE IV. $48^{\circ}4$.

| <i>p.</i> | <i>v.</i> | <i>pv.</i> |
|-----------|-----------|------------|
| 43.10 | 0.02635 | 1.13568 |
| 50.42 | 0.02239 | 1.12890 |
| 58.16 | 0.01929 | 1.12190 |
| 67.04 | 0.01662 | 1.11420 |
| 76.42 | 0.01448 | 1.10656 |
| 92.93 | 0.01178 | 1.09471* |
| 120.46 | 0.00896 | 1.07932 |
| 138.28 | 0.00776 | 1.07305* |
| 165.50 | 0.00646 | 1.06913 |
| 169.71 | 0.00630 | 1.06917* |
| 178.30 | 0.00600 | 1.06930* |
| 189.70 | 0.00565 | 1.07180 |
| 228.29 | 0.00480 | 1.08619* |
| 257.44 | 0.00436 | 1.10699 |

The isothermals in fig. 1 are plotted from these numbers, of which those distinguished by stars are simply supplied from the characteristic equation. They are considerably removed from the critical temperature of the mixture, which was

Fig. 1.

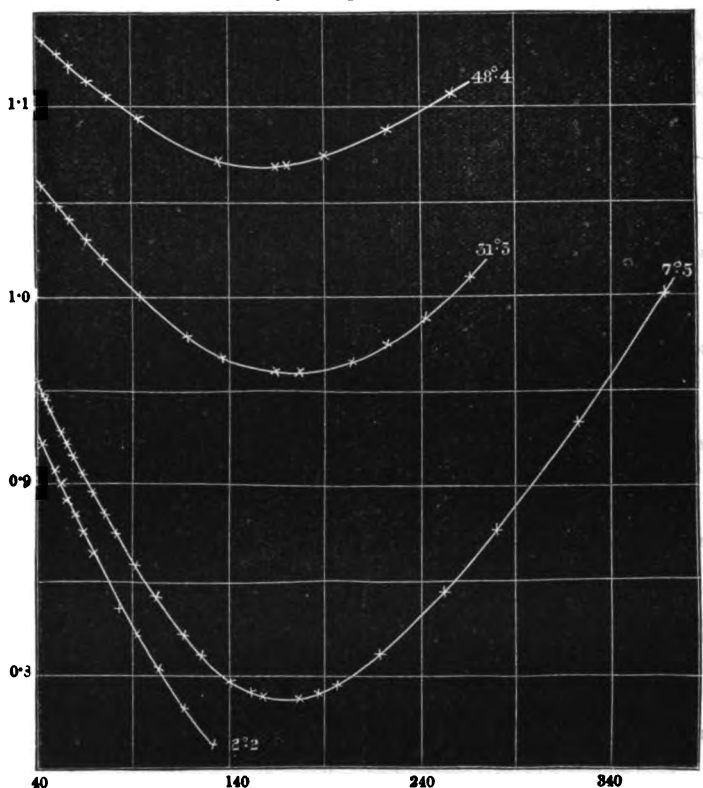
The Isothermals.



found by Andrews to be below -20° . Inasmuch as they are so regular over a wide range of temperature, we shall not go far wrong in extending our results of measurements within a few degrees of temperature above and below that range.

M. Amagat makes use of isothermals of another type, of which the product pv is taken for ordinate, and the pressure p for abscissa. For the sake of comparison they are drawn in fig. 2. The product pv has a minimum value for each

Fig. 2.
 p and pv lines.

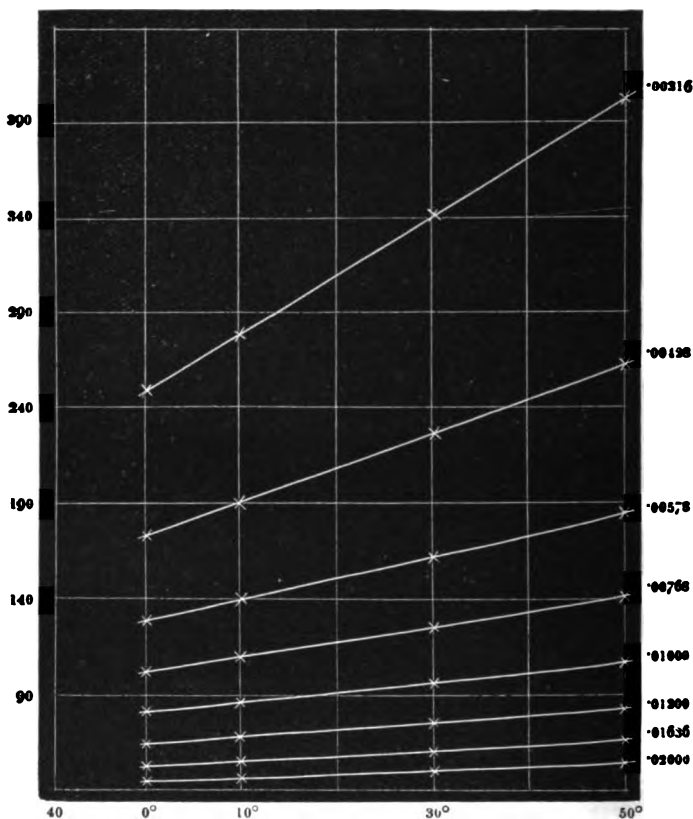


temperature. The parts of the isothermals which are on the left-hand side of that value are appreciably convex towards the origin, while those which are on the right-hand side seem to converge asymptotically, their curvatures tending to become zero. These features belong to isothermals of this type for pure carbonic acid at much higher temperatures; thus an admixture of a more permanent gas like nitrogen seems to have the same effect as a rise of temperature, as *a priori* would be probable. The locus of these minima can be found from the characteristic equation, but its equation is almost uselessly complex. The following values were found by trials:—

| $t.$ | $p.$ | $v.$ | $pv.$ |
|------|--------|----------|---------|
| 7.5 | 171.65 | 0.004595 | 0.78873 |
| 31.3 | 174.07 | 0.005516 | 0.96017 |
| 48.4 | 166.40 | 0.006425 | 1.06912 |

Thus the locus is convex towards the axis of pv , and there is a mini-max point; in fact the existence of such a point was already pointed out by M. Amagat, for the case of pure carbonic acid.

Fig. 3.
Isometrics.



The parametric values of volumes and pressures for isometrics and isopiestic respectively are so chosen that we can easily compare the results with those for pure carbonic acid, as given by the most recent experiments of M. Amagat* (see fig. 3).

* *Comptes Rendus*, 1891.

| 0°. | | 10°. | | 30°. | | 50°. | | v. |
|----------|-----------|----------|-----------|----------|-----------|----------|-----------|---------|
| Mixture. | Pure Gas. | Mixture. | Pure Gas. | Mixture. | Pure Gas. | Mixture. | Pure Gas. | |
| atm. | atm. | atm. | atm. | atm. | atm. | atm. | atm. | |
| 45·33 | | 47·60 | | 52·10 | | 56·53 | | 0·02000 |
| 54·24 | 34·4 | 57·15 | 41·8 | 62·87 | 48·3 | 68·50 | 54·5 | 0·01636 |
| 66·28 | 34·4 | 70·16 | 44·4 | 77·78 | 55·5 | 85·24 | 63·8 | 0·01300 |
| 82·74 | 34·4 | 88·21 | 44·4 | 98·91 | 62·8 | 109·35 | 74·5 | 0·01000 |
| 102·78 | 34·4 | 110·66 | 44·4 | 125·96 | 68·3 | 140·84 | 84·8 | 0·00768 |
| 129·73 | 34·4 | 141·62 | 44·4 | 164·72 | 70·7 | 187·03 | 94·7 | 0·00578 |
| 170·39 | 34·4 | 189·43 | 44·4 | 226·27 | 70·7 | 261·71 | 104·8 | 0·00428 |
| 251·27 | 34·4 | 280·40 | 44·4 | 345·44 | 71·5 | 404·96 | 125·3 | 0·00316 |

It will be seen that these isometrics have much of their general features in common with those of pure carbonic acid and ether* under conditions far apart from their critical points. Several obvious remarks which arise from such a comparison are left to the reader.

The following table, which contains the average values of $(\partial p / \partial t)_v$, was constructed from the preceding :—

$$\left(\frac{\partial p}{\partial t}\right)_v.$$

| v. | 0°-10°. | 10°-30°. | 30°-50°. |
|---------|---------|----------|----------|
| 0·02000 | 0·228 | 0·225 | 0·222 |
| 0·01636 | 0·291 | 0·286 | 0·281 |
| 0·01300 | 0·388 | 0·381 | 0·373 |
| 0·01000 | 0·547 | 0·535 | 0·522 |
| 0·00768 | 0·789 | 0·765 | 0·744 |
| 0·00578 | 1·190 | 1·155 | 1·116 |
| 0·00428 | 1·904 | 1·842 | 1·772 |
| 0·00316 | 3·213 | 3·102 | 2·976 |

In the abstract already referred to, Andrews gives a few measurements relating to a mixture of about 11 volumes of carbonic acid and 1 volume of air, and remarks that “the

* W. Ramsay and S. Young, *Phil. Mag.* 1887, vol. xxiii.

Phil. Mag. S. 5. Vol. 36. No. 222. Nov. 1893. 2 H

values of $\alpha \left(\equiv \left(\frac{\partial p}{\partial t} \right)_v \right)$, deduced for the same range of temperature from the elastic forces at different pressures, are directly proportional to one another." This remark applies also to the present case. Graphically it means that the isometrics are very nearly straight, and also from equation (1) we have

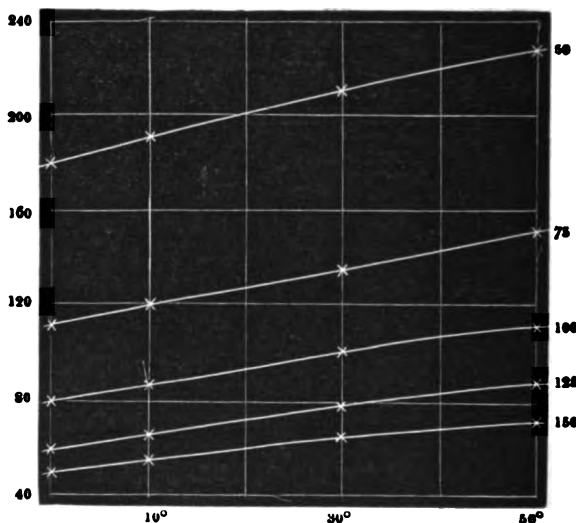
$$\left(\frac{\partial p}{\partial t} \right)_v = \frac{R}{v - \alpha} + \frac{K}{T^2(v + \beta)^2},$$

so that when T is sufficiently great the first term on the right-hand side supersedes the second, and consequently

$$\frac{\left(\frac{\partial p}{\partial t} \right)_v}{\left(\frac{\partial p}{\partial t} \right)_{v'}} = \frac{v' - \alpha}{v - \alpha} = \text{const.}$$

Thus the above relation appears less remarkable than at first sight.

Fig. 4.
Isopiistics.



The following Tables give a few numbers relating to isopiistics (see fig. 4).

| 0°. | | 10°. | | 30°. | | 50°. | | p. |
|----------|-----------|----------|-----------|----------|-----------|----------|-----------|------------|
| Mixture. | Pure Gas. | Mixture. | Pure Gas. | Mixture. | Pure Gas. | Mixture. | Pure Gas. | |
| 0-01793 | 0-02100 | 0-01896 | 0-02290 | 0-02090 | 0-01550 | 0-02273 | 0-01840 | atm. 50 |
| 0-01125 | 0-02047 | 0-01205 | 0-02173 | 0-01352 | 0-00292 | 0-01487 | 0-00996 | 75 |
| 0-00793 | 0-02020 | 0-00864 | 0-02130 | 0-00388 | 0-00255 | 0-01099 | 0-00491 | 100 |
| 0-00604 | 0-01992 | 0-00666 | 0-02096 | 0-00775 | 0-00240 | 0-00869 | 0-00316 | 125 |
| 0-00480 | 0-01966 | 0-00542 | 0-02060 | 0-00637 | 0-00230 | 0-00720 | 0-00279 | 150 |

$$\left(\frac{\partial v}{\partial t}\right)_p.$$

| p. | 0°-10°. | 10°-30°. | 30°-50°. |
|------------|----------|----------|----------|
| atm. 50 | 0-000103 | 0-000097 | 0-000091 |
| 75 | 0-000080 | 0-000074 | 0-000067 |
| 100 | 0-000071 | 0-000062 | 0-000055 |
| 125 | 0-000062 | 0-000056 | 0-000047 |
| 150 | 0-000052 | 0-000047 | 0-000041 |

SUNDRY REMARKS.

Could we, as is often done, make use of equation (1) far beyond the region of direct measurements, the critical point would be given by the following equation:—

$$T^2 = \frac{8}{27} \cdot \frac{K}{(\alpha + \beta) \cdot R}$$

which gives in the present case $T = 222^{\circ} \cdot 55$; accordingly the critical point of the mixture under consideration would be $-50^{\circ} \cdot 45$. As already mentioned, Andrews found it to be below -20° .

One effect of an admixture of carbonic acid with a gas like nitrogen is that isothermals of the former are somewhat deformed*. It seems to me likely, but requires to be decided

* One sees this very clearly even from a few measurements of Janssen on nitrous oxide at $25^{\circ} \cdot 15$ and $32^{\circ} \cdot 2$, as well as from Andrews's on carbonic acid at $13^{\circ} \cdot 1$ and $21^{\circ} \cdot 5$.

experimentally, that as the admixture becomes greater in proportion, the slope of isothermals between the gas- and liquid-lines against the line of constant pressure will become greater.

Graphically speaking, those intermediate portions of isothermals in case of an absolutely pure gas shift parallel to themselves as the temperature becomes higher, and, preserving their straight form till the critical point is neared, at last vanish there, to make up the continuity of curvature of those portions which lie on both sides of them. For a mixture, the slope of those intermediate portions seems to become greater as the temperature becomes higher, and thus that continuity to be smoothly made up. In such a discussion one will get much help from experiments already referred to as made by Cailletet and, if any, others.

The curious phenomenon that a gaseous mixture presents an optically homogeneous appearance once for a while within the region bounded by the gas- and liquid-lines, attracted much attention from physicists. Jamin ascribes it to the mutual approach to equality of densities of the mixed gases due to high pressures; while Duhem* tries to deduce the existence of, and to explain graphically, that homogeneous appearance from his mathematical equations of thermodynamic potentials. Jamin's explanation is physical to a certain extent, yet seems to be somewhat deficient, while Duhem's may not be deficient, yet seems to be not quite physical. At the same time, Andrews was undoubtedly the first to observe the phenomenon, and his descriptions and experiments seem to contain the right means towards understanding the true physical processes by which the phenomenon under consideration is occasioned. Dewar's experiments on the critical points of mixed vapours seem to direct us for an explanation towards the same point as Andrews's; so also do the experiments of Cailletet.

The course of isothermals of a gaseous mixture much below the critical point may probably not be much different from the usual course. Andrews observed near the point of complete condensation how a little mass of nitrogen diffuses into the condensed liquid. A little increase of volume due to that diffusion must be of the same nature, as was pointed out by Ångström†. In the meantime, evaporation, a special type of diffusion, of the condensed liquid into the little atmosphere of nitrogen must have been going on under the special conditions of temperature and pressure.

These interdiffusions of one part into another of the hetero-

* *Journ. de Phys.* vii. 1888.

† *Wied. Ann.* Bd. xvii. 1882.

geneous mass must have presented themselves in a very striking manner at higher temperatures and under stronger pressures, and at a certain stage resulted in the production of the above optically homogeneous appearance.

It is therefore very likely, as Jamin remarked, that we have under those circumstances of temperature and pressure nothing that is different in kind from what we see under ordinary circumstances.

Dewar's experiments, especially those on liquefaction of carbonic acid in presence of other liquids, are interesting from our point of view, and we cannot but think of some such process as interdiffusion being in action through all cases, not excepting the case of pure gases.

XLVI. *On the Theory of Pyro-electricity and Piezo-electricity of Crystals.* By Lord KELVIN*.

§ 1. **T**HE doctrine of bodily electro-polarization masked by an induced superficial electrification, which I gave thirty years ago in Nichol's *Cyclopædia*†, wanted a physical explanation of the assumed molecular polarization to render it a satisfying physical theory of pyro-electricity; and it was essentially defective, as has been remarked by Röntgen‡ and by Voigt§, in that it contained no suggestion towards explaining the multiple electric polarities irregularly produced by irregular changes of temperature in boracite, in quartz, and in tourmaline itself; which had perplexed many naturalists and experimenters. A short but very important paper by MM. Jacques and Pierre Curie in the *Comptes Rendus* for Feb. 14, 1881, supplies that want in a manner which suggests what seems to me the true matter-of-fact electro-chemical theory of a crystalline molecule, and at the same time makes easy the extension of my slight primitive doctrine, to remedy its defect in respect to multipolarity, and to render it available for explaining not only the old-known pyro-electricity of crystals, but also the piezo-electricity discovered by the brothers Curie || themselves. The element of zinc and copper soldered together and surrounded only by air, which they suggest, represents perfectly a true electro-

* Communicated by the Author.

† Reprinted in 'Collected Mathematical and Physical Papers' (Sir W. Thomson), vol. i. p. 315.

‡ Wiedemann's *Annalen*, 1883, xviii. p. 213.

§ "Allgemeine Theorie der Piëzo- und Pyro-electrischen Erscheinungen an Krystallen," p. 6; separate publication from vol. xxxvi. of *Abhand. Königl. Ges. Wiss. Göttingen*, 1880.

|| *Comptes Rendus*, Aug. 2 and Aug. 16, 1880.

chemical compound molecule such as H_2O or SiO_2 , in a realizable model, which indeed I actually made three weeks ago and described in a communication to the *Philosophical Magazine* * without knowing that I had been anticipated.

§ 2. To represent pyro-electric and piezo-electric qualities in a crystal, take as crystalline molecule a rigid body of any shape, bounded by a surface made up of pieces of different metals, soldered together so as to constitute one metallic conductor. Arrange a large number of such molecules in order, as a Bravais homogeneous assemblage, not touching one another. Connect every molecule with neighbours by springs of non-conducting material (india-rubber may be taken if we wish to make a practically working model). We may, for example, suppose each molecule to be connected with only twelve neighbours; its two nearest, its two next-nearests, its two next-next-nearests in the plane of those four, and the three pairs of nearests, next-nearests, and next-next-nearests on the two sides of that plane. Thus we have a perfect mechanical model for the elasticity and the piezo-electricity of a crystal; and for pyro-electricity also, if we suppose change of temperature to produce either change of the contact-electricities of the metals, or change of configuration of the assemblage, whether by changing the shape of each molecule or by changing the forces of the springs.

§ 3. The mathematical problem which this combination presents is as follows :—

Given a homogeneous assemblage of a large number of equal and similar closed surfaces, S , each composed of two or more different kinds of metal soldered together, all insulated in a large closed chamber, of which the bounding surface C is everywhere at a practically infinite distance from the assemblage, and is of the same metal as one of the metals of S , copper we shall suppose, to fix the ideas.

It is required to find :—

(1) The potential in the copper of every molecule when the total quantity of electricity on each is zero.

(2) The quantity of electricity on each molecule when all are metallically connected by infinitely fine wire.

§ 4. The mathematical expression of the conditions and requirements of the problem is as follows :—

Let $f(P)$ denote a given function of the position of a point P on the surface S of any one of the molecules; expressing the difference of the potential in the air infinitely near to P , from the potential in the air infinitely near to the copper

* For October 1893, "On a Piezo-electric Pile."

parts of the surface S . This function is the same for corresponding points of all the molecules.

Let V_n be the potential at the copper of the molecule numbered n .

Let $D(P_i, P_n)$ be the distance between a point P_i on the molecule numbered i , and a point P_n on the molecule numbered n .

Let $\iint ds_i$ denote integration over the surface of molecule i , and ρ_i a function of the position of P_i on the surface of this molecule; (the electric density at P_i).

Let Σ_i denote summation for all the molecules, including the case $i=n$.

Let q_n be the total quantity of electricity on molecule n .

The equation of electric equilibrium is

$$\Sigma_i \iint \frac{\rho_i ds_i}{D(P_i, P_n)} = f(P_n) + V_n \quad \dots (a),$$

and we have

$$\iint \rho_n ds_n = q_n \quad \dots (b).$$

It is required to find

(1) V_n , when $q_n=0$, for every value of n ;

and (2) q_n , when $V_n=0$, " "

§ 5. The problem thus proposed is of a highly transcendental character, unless the surface S is spherical. In this case it can be solved for any finite number of molecules by mere expenditure of labour; perhaps the work of the natural working-life of a competent mathematician, if the assemblage is a Bravais parallelepiped of 125 globes in 5 "réseaux" of 25 globes each, would suffice to give the solution for each item within one per cent. of accuracy; and not much more labour would be needed to solve the problem to the same degree of accuracy for each of 125×10^{21} spherical molecules in a similar Bravais parallelepiped of 5×10^7 "réseaux," if the distance (h we shall call it) between the planes of corresponding points of two consecutive "réseaux" of nearest and next-nearest molecules is not greater than about twice the diameter of each molecule.

§ 6. When this last condition is fulfilled, we can see, from general knowledge of the doctrine of electric screening, without solving the problem as proposed for every individual molecule, that the solution of the second part (2) of the requirements is $q_n \doteq 0$, very approximately for every molecule at any distance exceeding two or three times h from every

part of the boundary of the assemblage ; and this whether the molecules are spherical, or of any other shape not too wildly different. We see also that for all molecules not nearer than $3h$, or perhaps $4h$, or $5h$, from any part of the boundary of the assemblage, the distribution of electricity is similar. That is to say, the whole assemblage within a thin surface-layer (of some such thickness as $3h$ or $4h$) is homogeneous, not only geometrically and mechanically, but also electrically. The problem of finding, with moderate accuracy, the distribution of electricity on each molecule of the homogeneous assemblage thus constituted, is comparatively un-laborious if the shape of each molecule is spherical.

§ 7. We also see, by the known elements of electrostatics, without solving the problem of finding the quantity of electricity on each molecule of the surface-layer in the circumstances described in § 6, that the sum of the quantities on all the molecules of this layer, per unit of the surface, is equal to the component, in the direction normal to the surface, of the electric moment per unit-volume of the homogeneous assemblage within the surface-layer.

§ 8. The condition of the whole assemblage, surface-layer and homogeneous assemblage within it, at which we have arrived in §§ 6 and 7, may be regarded as representing the natural undisturbed condition of a crystal. Let now any homogeneous change of configuration of our assemblage be produced either by proper application of force to the molecules of the surface-layer, or by uniform change of temperature throughout the interior, or by both these causes acting simultaneously. We need not exclude the case of no change of shape or bulk of the boundary ; that is to say, the case of no change of the relative positions of corresponding points of the molecules ; and our "change of configuration" only an infinitesimal rotation of each molecule. The inclusion of this case is important to guard against a tendency which I find in the writings both of MM. Curie and of Voigt :—a tendency to a hypothetical assumption unduly limiting the pyro-electric property to identity with the piezo-electric effect produced by force causing the same change of shape or bulk as that which is produced by the change of temperature. In nature, we may expect as a general possibility, and as a probable result in some cases, a bodily electro-polarization produced by change of temperature, even though change of bulk and shape are prevented by force applied to the surface. And, in our model, changes of forces of the springs would certainly cause rotation of the molecules, and so produce electro-polarization, even when the molecules of the boundary are held fixed, unless the

springs are specially designed and constructed to annul this effect.

§ 9. Solve now the electrical problem of finding the change of electric moment of each molecule of the homogeneous assemblage, produced by the change of configuration described in § 8, when the potential is zero throughout the surface-layer. To avoid tampering with the separate insulation of all or any of the molecules, and to conform our ideas to the realities of experiments on the electric properties of crystals, I suppose this equality of potential to be produced not by temporary metallic connexion between the molecules as in § 3 (2), but by a metal coat enclosing our model, and having its inner surface everywhere very near to the boundary of the assemblage; for example, everywhere within a distance of less than $2h$ or $3h$ in our model, or of less than $10^6 \times h$ if we are dealing with a real crystal in a real experiment.

§ 10. To find experimentally the solution of the mathematical problem of § 9, divide the metal coat into two parts; one of them (corresponding to Coulomb's "proof-plane") we shall call for brevity E . It may be either so small that it is sensibly plane, or it may be a portion of the coat covering a finite plane part of the boundary of the assemblage. Commence now with the crystal in its natural undisturbed state, and having the metal coat on it with E insulated from the rest of the coat. Produce a change of configuration as in § 8; and then measure how much electricity would need to pass from E to the rest of the coat to equalize the potential between them. This is wholly and exactly what MM. Curie do in their admirably designed measurement with their "quartz piézo-électrique," avoiding all need for consideration of the essentially transcendent problem of the distribution of electric potential at the surface of an uncoated crystal when there is either pyro-electric or piezo-electric disturbance of its interior.

The quantity of electricity thus measured, divided by the area of E , is equal to the component perpendicular to E of the interior electro-polarization when E and the rest of the coat are metallically connected.

§ 11. In conclusion, following Voigt in his *Allgemeine Theorie*, already referred to, we see that there are essentially 18 independent coefficients for the piezo-electricity of a crystal in general; in three formulas expressing the three components of the electric moment per unit of its volume each as a linear function of the six components of the geometrical strain of the substance. To each of these expressions I add a term for the component of the electric moment due

to change of temperature when force acting on the surface prevents change of volume or shape. Thus we have in all 21 independent coefficients for piezo-electricity and pyro-electricity; to be determined for a real crystal by observation. It is interesting to see how our model can be constructed to realize the piezo-electric and pyro-electric phenomena in accordance with any given values of these 21 coefficients, by experimental solution of as much of the mathematical problem of § 4 as is necessary for the purpose.

§ 12. Choose any convenient shape, spherical or not wildly different from spherical, for each molecule. Divide the whole surface into 22 parts (not wildly unequal nor extravagantly different from squares or equilateral equi-angular hexagons), and number them 0, 1, 2, 21. Construct a trial molecule with part 0 always of copper; and with, for first trial, part 1 of zinc, and parts 2, 3, 21 of copper. Take a large number of such molecules and make of them a Bravais homogeneous assemblage with any arbitrarily chosen values for the six edges of the fundamental acute-angled tetrahedrons. Connect the molecules homogeneously by springs of non-conducting material in the manner described in § 2 above. To provide fully for pyro-electricity, without hypothesis, we must now take care that these springs are such, that when the temperature is changed, and the border molecules are held fixed, all the interior molecules shall be caused to rotate round parallel axes through equal angles proportional to the difference of temperature. For this purpose the springs must be of two or more different materials; and when set in their proper positions between the molecules they must be under stress, some of them pushing and some pulling, in the undisturbed condition of the assemblage.

§ 13. Subject now the assemblage successively to six different geometrical strain-components, e, f, g, a, b, c ; and to one change of temperature, t , with the boundary molecules held fixed. With each of these seven configurations, measure, by three separate measurements conducted according to the method described in § 10, the three components of the sum of the electric moments of the molecules in unit volume.

§ 14. Repeat the same 21 measurements with part 2 of the surface of each molecule zinc, and all the rest copper: next with part 3 zinc, and all the rest copper: and so on. Thus we have 21^2 distinct measurements, each giving independently one of the 21^2 multipliers $[x, e, 1]$, $[x, e, 2]$, &c., which appear in the following 21 equations:—

$$\begin{aligned}
 [x, e, 1]v_1 + [x, e, 2]v_2 + \dots [x, e, 21]v_{21} &= (x, e), \\
 [x, f, 1]v_1 + [x, f, 2]v_2 + \dots [x, f, 21]v_{21} &= (x, f), \\
 [x, g, 1]v_1 + [x, g, 2]v_2 + \dots [x, g, 21]v_{21} &= (x, g), \\
 [x, a, 1]v_1 + [x, a, 2]v_2 + \dots [x, a, 21]v_{21} &= (x, a), \\
 [x, b, 1]v_1 + [x, b, 2]v_2 + \dots [x, b, 21]v_{21} &= (x, b), \\
 [x, c, 1]v_1 + [x, c, 2]v_2 + \dots [x, c, 21]v_{21} &= (x, c), \\
 [x, t, 1]v_1 + [x, t, 2]v_2 + \dots [x, t, 21]v_{21} &= (x, t),
 \end{aligned}$$

&c., &c., &c., with y and z instead of x .

In these equations $v_1, v_2, \dots v_{21}$ denote the volta-electric differences from copper which must be given to part 1, part 2, ... part 21 of the surface of the molecule in order that the 21 piezo-electric and pyro-electric coefficients may have their given values $(x, e), (x, f) \dots (z, t)$; the meaning of these coefficients being explained by the following three equations:—

$$\begin{aligned}
 X &= (x, e)e + (x, f)f + (x, g)g + (x, a)a + (x, b)b + (x, c)c + (x, t)t, \\
 Y &= (y, e)e + \dots + (y, t)t, \\
 Z &= (z, e)e + \dots + (z, t)t,
 \end{aligned}$$

where X, Y, Z denote the components of the electric moment per unit of volume, produced in the crystal by geometrical change, and change of temperature (e, f, g, a, b, c, t) . Thus, the volta-electric difference of zinc from copper being taken as unity, the 21 volta-differences from copper, of parts 1 to 21 of the surface of each molecule, are determined by 21 linear equations.

§ 15. Thus we have, in idea, constructed a model for the piezo-electric and pyro-electric quality of a crystal in which each one of the 21 piezo-electric and pyro-electric coefficients has an arbitrarily given value.

XLVII. A Modified Form of Bunsen and Roscoe's Pendulum Actinometer. By Dr. A. RICHARDSON and Mr. J. QUICK*.

IN Bunsen and Roscoe's pendulum actinometer (Proc. Royal Soc. 1862, p. 139), the time is measured in which a given intensity of light will produce a degree of darkening on sensitized paper equal in shade to a standard tint.

Without going into details, the apparatus may be briefly described as follows:—The oscillations of a pendulum cause an attached sliding shutter to pass backwards and forwards over a slit, in the direction of its longer axis, beneath which

* Communicated by the Authors.

is placed specially prepared sensitized paper. Before the pendulum is set vibrating, the shutter is in such a position that it completely covers the slit, one complete vibration causing the shutter to be withdrawn and to be again returned to its original position. The edge of the slit is graduated into millims., and the time during which each division is opened is calculated. The different parts of the paper are thus exposed for known and varying times, a graduated tint of darkening being produced. The shaded paper is then compared with the standard tint, and the point where the two shades are equal is determined. From this the time of exposure can be found, since the degree of darkening is directly proportional to the time of exposure within wide limits. The unit of actinic intensity taken is that intensity of light which will produce, on such sensitized paper, a degree of darkening equal to a standard tint in one second of time. The reciprocal of the above time of exposure thus gives the intensity of light at the time of the experiment.

The present modification was devised in order that the process of opening and shutting the slit might be brought about by a motion applied to the shutter in one direction only.

Fig. 1.

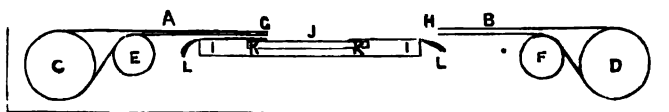
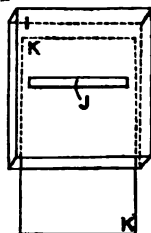


Fig. 1 shows the arrangement by which this is attained.

The shutter AB consists of a wide strip of thin, black, waterproof, fabric in the form of an endless band, running over two wooden rollers CD; its upper and lower surfaces being brought just into contact by means of two additional smaller rollers EF, so that the two layers move freely past each other in opposite directions when set in motion.

An aperture GH, 20 centim. long and 1 centim. wide, is cut in each surface, in such a position that the two openings exactly coincide when midway between the rollers. The sensitized paper is contained in the slide I, the top of which is made of very thin sheet ebonite, over which the shutter runs, the edges LL of the ebonite being bent down to prevent any possibility of the edges of the shutter catching as they come round. A slit J (fig. 2), 10 centim. long and 1 centim. wide, is cut in the ebonite, beneath which the paper is exposed; the latter is fastened to the board KK, by means of which

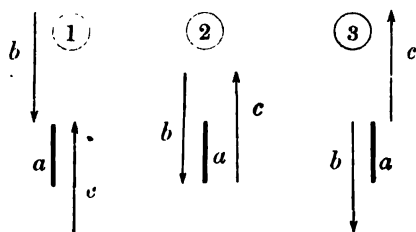
Fig. 2.



fresh portions can be brought beneath the slit, against which the paper is pressed, thus preventing any possibility of shadows.

It will be seen that the band represents two shutters moving in opposite directions. Fig. 3 shows the relative positions of the apertures in the upper and lower surface, with regard to the sensitized paper. The three slits are shown side by side, although of course superimposed in reality.

Fig. 3.



(1) represents the state of affairs just before an exposure, the arrow *b* showing the position and direction of the aperture in the upper portion of the band, *c* that of the aperture in the lower portion, and *a* the slit beneath which the sensitized paper is exposed. At this instant the top edge of *c* and the bottom edge of *b* are just beginning to overlap—that is, *a* is just about to be uncovered. (2) represents the conditions under which the entire length of *a* is exposed, *c* having ascended and *b* having descended a length equal to that of *a*: the bottom edge of *c* will now begin to close *a* from below. In (3) *a* is completely covered by the upward motion of *c*.

It will be thus seen that the opening process is entirely brought about by the downward movement of *b*, the closing process being solely due to the upward movement of *c*.

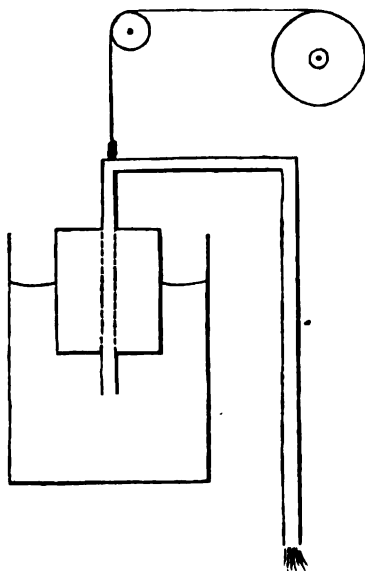
If sufficient darkening of the paper has not been attained by one exposure, two or more are allowed to take place, otherwise the movement is stopped after the first revolution.

In order to rotate the shutter a motor giving a uniform and comparatively high rate of speed is required. That first employed consisted of a tin drum to which a syphon was attached, and this was floated on water, as shown in fig. 4, and was connected, by means of a cord passing over a pulley, to a wheel working on the spindle of one of the rollers, so that on syphoning off the water the drum sank at a uniform rate, causing the wheel to rotate.

Although this arrangement answered the purpose, yet it was cumbersome and troublesome to work, and has therefore

been abandoned in favour of clockwork, which, after many trials, has been adapted so as to give and maintain the required

Fig. 4.



speed at a uniform rate, for periods well within the limits required for our purpose.

The spindle of one of the rollers is attached to an 8-day English clock from which the escapement has been removed, the change of speed ordinarily occurring when a clock is running down under such circumstances being compensated for by means of a fusee adjustment.

The following measurements were made to determine to what extent the clock, thus modified, could be relied upon to give a constant speed to the shutter at different stages of the unwinding of the spring.

Four sets of ten consecutive readings were taken of the time of opening of the shutter. Two series of measurements were made.

These numbers show that during forty revolutions of the shutter the variation in the time of exposure is exceedingly small, and it is obvious that by using the same portion of the spring in each case 10 or 15 exposures may be made where the time is practically constant*.

* The fact that it takes a slightly shorter time to open the shutter when the spring has partly run down, as is seen from the above readings, must be due, we think, to the fusee not being turned quite accurately.

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Both the clock and shutter are fastened to a tilting base, so that the paper can be exposed in a position at right angles to the sun's rays at any time during the day.

In conclusion, it may be pointed out that the present modification has the advantage of portability, and measurements can be taken when it is placed in any position. Further, since the shutter moves at a constant rate, the time during which any portion of the slit is open is directly proportional to that occupied in opening the entire slit, whereas in the pendulum apparatus a series of calculations is necessary to determine the length of time during which each millim. of the total length of the slit is open.

University College, Bristol.

XLVIII. Notices respecting New Books.

Murby's "Science and Art Department" Series of Text-Books.

PRACTICAL SOLID GEOMETRY: *or, Orthographic and Isometric Projection.* By J. PAYNE, late of the School of Science, Charterhouse. To which is added GRAPHIC ARITHMETIC AND STATICS, by J. J. PRINCE: In accordance with the recent requirements of the Science and Art Department. (London: Murby.)

SINCE this is at least the fourth edition of Mr. Payne's portion (pp. 1-206) of the volume, it may be presumed to have met the requirements of the examinees of the Science and Art Department, as also of many "Draughtsmen, Engineers and persons engaged in machine and building construction," satisfactorily. Indeed a glance through it shows that this elementary treatise of Descriptive Geometry has been compiled with painstaking conscientiousness in the effort to make its matter clear to those classes of students.

The first fourteen chapters, terminating with the Plane Sections

of Spheres, Cones, Cylinders, and Pyramids, together with the "development" of the surfaces of the two last-named solids,—reference being made for other cases to the "Crystallography" of the Series—contain what is regarded as the more elementary portion of the subject. More advanced problems on the Line and Plane: on the Projections and Plane Sections of Solids: on the less easy determination of the Intersections of Solids, as exemplified by two simple cases: on the Determination of Tangent Planes to Cylinders, Cones, and Spheres: on the Projection of Shadows: on Isometric Projection, cursorily treated, and stated to be "a branch of Orthographic," which latter adjective is barely explained as "*G. orthos*, right, straight; *grapho*, I write"—for "draw:" the six cases of the Spherical Triangle: lastly, on "Horizontal Projection."

It would be unreasonable to expect that so extensive a programme could be treated with an adequate amount of demonstration within the limits prescribed to the author. Student-life is short; and it is deemed necessary to train a certain number of proficient in the correct performance of the constructions, whether "the reason why" is known or not: "*Est quadam prodiere tenus, si non datur ultra.*" The diagrams inserted amidst the text are copious and generally clear; while each chapter is accompanied by a number of examples for exercise.

The second part of the volume of 48 pages, numbered anew, gives solutions of the most elementary problems of Constructive Geometry (pp. 1–10): the constructive performance of the four rules of Arithmetic, of involution and extraction of square roots (12 pp.): the representation of areas and volumes by straight lines (15 pp.): the elementary parts of "Graphical Statics" as far as the Equilibrium of Coplanar Forces and the determination of Centres of Gravity of Plane Areas: finally, a selection of Exercises taken from the Science Examination Papers "with hints and solutions" (21 pp.)—a section requiring careful revision. J. J. W.

XLIX. *Intelligence and Miscellaneous Articles.*

ON THE STRENGTH OF THE ELECTRICAL WAVES WHEN THE SPARK PASSES IN OIL. BY H. BAUERNBERGER.

THE author pursues the experiment of Sarassin and De la Rive and shows by quantitative measurement how in Lester's arrangement the electric resonance is increased if the primary spark passes in oil instead of in air. The investigation of different oils shows that petroleum gives the best results not only as regards the strength of the resonance, but chiefly because in it the change in the electrodes and the dielectric is least. In the preliminary experiments the influence of the capacity of the electrometer used in the measurements is investigated, and the author finds that in comparative measurements the changes in capacity of the electrometer have no influence on the changes of capacity, but that for each distance of the electrodes a definite current-strength is required to produce a maximum of electrical resonance. In conclusion it is shown that the length of the conducting wires to the primary condenser is of little influence.—*Wien. Ber.*, July 13, 1893.

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[FIFTH SERIES.]

DECEMBER 1893.

L. *The Dissociation of Compounds in Water as Measured by the Lowering of the Freezing-Point, and some Investigations with Organic Compounds.* By HARRY C. JONES*.

[Plates IV. to IX.]

THAT the molecules of compounds like the common salts dissociate into parts when dissolved in water has been shown by such independent lines of evidence that it can no longer be reasonably doubted. It has also been found that alkalies, acids, and many other compounds conduct themselves in a similar manner. The qualitative fact being established, it is of interest and importance to determine the *amount* of dissociation which compounds undergo when different quantities are dissolved in water. The problem, then, is to measure the dissociation of compounds in solutions of different concentrations.

There are several possible methods which can be applied for this purpose with more or less accuracy. These are—the osmotic pressure of the solution, the raising of the boiling-point of the solvent, the lowering of the freezing-point of the solvent, the effect of one compound on the solubility of another, and the conductivity of the solutions. Other methods, as “inversion” of sugar, and “saponification” of ethers, are

* Communicated by the Author.

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more special, and can be employed for determining particular kinds of ions.

The "osmotic-pressure" and "boiling-point" methods are at present, however, not sufficiently accurate to admit of extensive application for this purpose. Some doubt has recently been cast on the accuracy of the "solubility" method for measuring dissociation, but it seems probable that the method will be capable of yielding fair results in a limited number of cases. The freezing-point method has hitherto been open to the same objections as apply to the boiling-point and osmotic-pressure methods.

The "conductivity" method has been then, up to the present time, by far the most accurate and general method for measuring dissociation. It has this particular advantage, that it can be applied to very dilute solutions.

The "freezing-point" method, as improved by Beckmann*, is of limited application, since it cannot be used for very dilute solutions; indeed, it can scarcely be applied to solutions more dilute than $0.01n$. It has now, however, been so developed that the dissociation of solutions as dilute as 0.004 or $0.005n$ can be fairly well determined.

The Apparatus.

The apparatus employed was essentially the same in principle as that devised by Beckmann, in which every part was very greatly enlarged. The thermometer used was made especially for this work, and the scale was divided directly into *thousandths of a degree*, so that with a small lens one could read accurately to a ten-thousandth part of a degree. This thermometer was very carefully calibrated. The entire scale corresponded to only 0.6°C .

The vessel in which the solution whose freezing-point was to be determined was placed had a capacity of about 1200 cub. centim., and just a litre of the solution was used in each determination. The remainder of the apparatus, designed for the gradual cooling of the solution and for maintaining constant temperature, is shown in drawings, figs. 1, 2, and 3, *Zeits. phys. Chem.* xi. p. 532.

The form of stirrer there described has been found to be very efficient. All currents produced on the upward stroke of the stirrer were completely reversed on the downward. In the later work, when solutions of alkalies and acids were

* Beckmann, *Zeits. phys. Chem.* ii. p. 638, and vii. p. 324.

investigated, a stirrer of silver plated with gold by electrolysis was employed. A glass cover was also used for the inner vessel instead of a plate of brass covered with asphalt.

The Method of Work.

The compounds used were purified by the methods best adapted to the different substances and standard solutions prepared.

The freezing-point of exactly a litre of distilled water, which had been cooled nearly to zero before it was placed in the inner vessel, was determined each morning. This was found to differ very slightly from day to day. This slight difference was doubtless due to small changes in the large bulb of the thermometer, which was about 14 centim. long and 1.5 centim. in width.

A convenient number of cubic centimetres was removed from the litre of water by means of a graduated and calibrated pipette, and an equal volume of the standard solution added. The freezing-point of this new solution was then determined after it had been carefully mixed.

The vessel containing the solution was then removed from the cold bath and the ice which had formed was allowed to melt. Again a certain number of cubic centimetres was removed from this solution, and exactly an equal number of the standard solution added, and the freezing-point of this new solution determined. This was continued as long as it seemed desirable to concentrate the solution to be investigated. Thus all solutions were prepared directly from the original standardized solution. It was not possible to measure the freezing-point of more than four or five concentrations in one day. Every evening the vessel containing the solution was emptied, and on the following morning the freezing-point of a litre of pure water determined. A sufficient volume of the water was removed and of the standard solution added to make the concentration slightly greater than the last employed. This new solution was then concentrated and the freezing-points determined as on the preceding day.

The change in volume produced when the solution of the compound to be investigated was added to the water was so slight for the very dilute solutions employed that it can be entirely neglected.

During the cooling the solution must be stirred gently but continuously. With the form of stirrer employed, a very gentle movement was quite sufficient to keep the liquid

thoroughly mixed. The amount of cooling below the freezing-point was determined for all the substances employed. This was accomplished at first by means of an ordinary Beckmann's thermometer divided into hundredths of a degree, but it could also be done with the large thermometer which extended only over 0.6°C . by determining the time required by the solution to cool 0.6° , and the time between the moment when the mercury thread passed the zero of the thermometer and the moment when the ice separation began. During this entire time the stirring must be continued as uniformly as possible. Since the undercooling was in general only a little more than a degree, this was found to be quite accurate enough. Indeed, with the organic compounds this undercooling was usually less than a degree. Whenever it amounted to more than 1.2° , the solution was made to freeze by the addition of a minute fragment of pure ice.

The readings as made on the thermometer were in every case corrected for the change in concentration produced by the separation of the ice. This correction was based on the latent heat of water = 80 cal. The separation of one gram of ice would liberate enough heat to warm 80 cub. centim. of water 1° . Since the volume of the solution is known (1 litre) and the amount of undercooling determined, the calculation of the amount of ice is as follows:—Let S = specific heat of the liquid; U = the amount of undercooling in degrees Celsius; W = heat of solidification of unit weight of the liquid; T = fraction of the liquid which solidifies:

$$T = \frac{SU}{W}.$$

In all the solutions thus far investigated, water was the solvent, where $S=1$ and $W=80$. For every degree of undercooling 12.5 grs. ice separated from the litre of liquid. The original solution was thus concentrated a given amount by the separation of the ice, and the freezing-point as read from the thermometer is that of the solution thus concentrated. The lowering of the freezing-point of the water by the salt is thus too great, and must be diminished in proportion as the original solution was concentrated. This would then give the correct lowering of the freezing-point for the original solution. The correction is, however, not absolutely exact, since the lowering of the freezing-point does not change in exactly the same relation as the concentration, owing to an increase in dissociation with increase in dilution. But the amount of dissociation for very dilute solutions which have

been concentrated, only 1.5 per cent. remains so nearly constant that the error would be entirely inappreciable.

Further, this correction does not take into account the ice which separated during the time required for the thermometer to become constant. But on account of the form of the apparatus and the large volume of solution employed, the cooling proceeded so slowly that the amount of ice which separated during this time was comparatively small, and no serious error could have been introduced from this source.

A great advantage in the regulation of the temperature was derived from the use of such a large volume of the solutions. The surface of the solution exposed to the cold layer of air was relatively very much diminished, and the solution itself would therefore be affected much less by external changes in temperature. The cooling of the solution proceeded very slowly; therefore the accuracy of the measurement at any given time would be much increased. When small volumes of solutions are employed, the continued separation of the ice is comparatively rapid, and the solutions are thus ever concentrated by a large and unknown amount. This necessarily affects the accuracy of such determinations very considerably.

A number of duplicate determinations of the freezing-point of the same solution were made with this enlarged apparatus and improved method, and in no case did the individual determinations differ from each other by more than 0.0004° . For the most dilute solutions duplicate measurements were made, and the figure given is the mean result.

Whenever an acid was used, a drop of a dilute solution of the same acid was added to the litre of water each morning before the freezing-point of the water was determined. This was for the purpose of neutralizing any trace of ammonia present, and to convert all traces of salts in the distilled water into salts of the acid under investigation, so that no part of the acid to be measured might be neutralized by such impurities. That the water used contained only a mere trace of any alkaline substance was shown by the fact that one drop of dilute acid in a litre of water produced a perceptible acid reaction. The zero of the water containing the trace of salts and free acid was then determined. The very minute quantity of these substances present could not have appreciably affected the dissociation of the acid to be investigated.

When the alkalis were used, a drop of the same alkali was added to the water before the freezing-point was determined, that any carbon dioxide present might be neutralized.

The results with the three alkalies cannot be regarded as so accurate as those with the acids and salts. The solutions were of necessity in contact with the air and must have absorbed small amounts of carbon dioxide. The solutions were, however, so very dilute that the magnitude of the error could not have been great.

The Results with Electrolytes.

On account of the method of preparing the solutions, the concentrations actually investigated are not those which are commonly employed in work: they are not simple fractional parts of a normal solution. The results with the solutions used have already been partly recorded*, and the remainder will appear later in the same journal. For convenience in comparison and for future work, the results obtained have been plotted as curves, and the lowering of the freezing-point for simple decimal parts of a normal solution read off from the curves. The remaining values for each concentration have been calculated from this lowering.

In the Tables, column 1 contains the strength of the solutions in terms of gram-molecular normal. This was employed instead of gram-equivalent normal, because a molecule produces the same lowering of the freezing-point whatever the equivalence of the acid or base may be. Column 2 contains the corrected lowerings of the freezing-point. Column 3, the lowerings of the freezing-point which would have been produced by a gram-molecular weight of the compound = gram-molecular lowering. Column 4, the different values for i ,

$$i = \frac{\text{gr. molec. lowering}}{1.89},$$

1.89 being the constant for water, *i. e.* the amount of the lowering of the freezing-point of water produced by a gram-molecular normal solution of a completely undissociated compound. Column 5, the dissociation, $= i - 1$ when the molecule dissociates into two ions, and $\frac{i-1}{2}$ when the molecule dissociates into three.

When the molecule yields two ions the dissociation is calculated thus:

$$1 - \alpha + 2\alpha = i,$$

$$\alpha = i - 1.$$

* Jones, *Zeits. phys. Chem.* xi. pp. 112, 536.

When it yields three, thus :

$$1 - \alpha + 3\alpha = i,$$

$$\alpha = \frac{i-1}{2},$$

where α is the amount of the dissociation.

The experimental results have been plotted as curves (Plates IV. to IX.), in which the ordinates represent concentrations, and the abscissas lowering of the freezing-point. In the first curve of each set, the ordinate unit = 0.0005 normal, and the abscissa unit = 0.0015° lowering of freezing-point for the electrolytes, and 0.0010° lowering of freezing-point for the non-electrolytes. In the second the units are increased ten times, and in the same ratio as the concentrations are increased. In the third the units are the same as in the second. That the third curve may be placed in a convenient position with respect to the others, 0.1 normal is subtracted from the ordinates, and the lowering produced by 0.1 normal from the abscissas for the third curve.

The first curve extends from about 0.001 normal to about 0.01 normal; the second from this point to about 0.1 normal; and the third from here to about 0.2 normal, when the investigations were carried so far.

The points marked on the curves correspond to the concentrations actually used in the experiments, and the lowerings of the freezing-point produced by these concentrations. For the organic compounds, the first curve extends from the most dilute solution used to about 0.01 normal.

NaCl = 58.4. (KCl = 74.4, NH₄Cl = 53.4.)

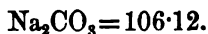
| 1. Normal. | 2. Lowering. | 3. Gram-molec. Lowering. | 4. <i>i</i> . | 5. Dissociation. |
|---------------|-----------------|--------------------------------|------------------|---------------------|
| | | | | per cent. |
| 0.001 | 0.00375 | 3.7500 | 1.984 | 98.4 |
| 0.002 | 0.0075 | 3.7500 | 1.984 | 98.4 |
| 0.004 | 0.0146 | 3.6500 | 1.931 | 93.1 |
| 0.006 | 0.0220 | 3.6666 | 1.937 | 93.7 |
| 0.008 | 0.0290 | 3.6250 | 1.916 | 91.6 |
| 0.01 | 0.0360 | 3.6000 | 1.905 | 90.5 |
| 0.02 | 0.0715 | 3.5750 | 1.892 | 89.2 |
| 0.04 | 0.1422 | 3.5550 | 1.881 | 88.1 |
| 0.06 | 0.2106 | 3.5100 | 1.857 | 85.7 |
| 0.08 | 0.2794 | 3.4925 | 1.848 | 84.8 |
| 0.1 | 0.3480 | 3.4800 | 1.841 | 84.1 |

| $K_2SO_4 = 174.335.$ | | | | |
|----------------------|-----------------|--------------------------------|----------|---------------------|
| 1. Normal. | 2. Lowering. | 3. Gram-molec. Lowering. | 4. i. | 5. Dissociation. |
| | | | | per cent. |
| 0.001 | 0.00545 | 5.4500 | 2.884 | 94.2 |
| 0.002 | 0.0107 | 5.3500 | 2.831 | 91.5 |
| 0.004 | 0.0211 | 5.2750 | 2.791 | 89.5 |
| 0.006 | 0.0313 | 5.2166 | 2.760 | 88.0 |
| 0.008 | 0.0413 | 5.1625 | 2.731 | 86.5 |
| 0.01 | 0.0501 | 5.0100 | 2.651 | 82.5 |
| 0.02 | 0.0984 | 4.9200 | 2.603 | 80.1 |
| 0.04 | 0.1886 | 4.7125 | 2.493 | 74.6 |
| 0.06 | 0.2736 | 4.5600 | 2.413 | 70.6 |
| 0.08 | 0.3526 | 4.4075 | 2.332 | 66.6 |
| 0.1 | 0.4323 | 4.3230 | 2.287 | 64.3 |
| $BaCl_2 = 207.94.$ | | | | |
| 0.001 | 0.00545 | 5.4500 | 2.884 | 94.2 |
| 0.002 | 0.0109 | 5.4500 | 2.884 | 94.2 |
| 0.004 | 0.0210 | 5.2500 | 2.777 | 88.3 |
| 0.006 | 0.0310 | 5.1666 | 2.730 | 86.5 |
| 0.008 | 0.0412 | 5.1500 | 2.725 | 86.2 |
| 0.01 | 0.0510 | 5.1000 | 2.698 | 84.9 |
| 0.02 | 0.1002 | 5.0100 | 2.651 | 82.5 |
| 0.04 | 0.1950 | 4.8750 | 2.579 | 78.9 |
| 0.06 | 0.2869 | 4.7816 | 2.530 | 76.5 |
| 0.08 | 0.3783 | 4.7287 | 2.502 | 75.1 |
| 0.1 | 0.4675 | 4.6750 | 2.474 | 73.7 |
| $MgSO_4 = 120.44.$ | | | | |
| 0.001 | 0.00845 | 3.4500 | 1.825 | 82.5 |
| 0.002 | 0.0068 | 3.4000 | 1.799 | 79.9 |
| 0.004 | 0.0129 | 3.2250 | 1.706 | 70.6 |
| 0.006 | 0.0191 | 3.1833 | 1.684 | 68.4 |
| 0.008 | 0.0250 | 3.1250 | 1.653 | 65.3 |
| 0.01 | 0.0307 | 3.0700 | 1.624 | 62.4 |
| 0.02 | 0.0597 | 2.9850 | 1.579 | 57.9 |
| 0.04 | 0.1090 | 2.7250 | 1.442 | 44.2 |
| 0.06 | 0.1538 | 2.5633 | 1.356 | 35.6 |
| 0.08 | 0.1975 | 2.4687 | 1.306 | 30.6 |
| 0.1 | 0.2344 | 2.3440 | 1.240 | 24.0 |
| $CdCl_2 = 183.00$ | | | | |
| 0.001 | 0.00495 | 4.9500 | 2.619 | 80.9 |
| 0.002 | 0.0098 | 4.9000 | 2.593 | 79.6 |
| 0.004 | 0.0193 | 4.8250 | 2.553 | 77.6 |
| 0.006 | 0.0286 | 4.7666 | 2.522 | 76.1 |
| 0.008 | 0.0373 | 4.7250 | 2.500 | 75.0 |
| 0.01 | 0.0463 | 4.6300 | 2.449 | 72.4 |
| 0.02 | 0.0926 | 4.6300 | 2.449 | 72.4 |
| 0.04 | 0.1731 | 4.3275 | 2.289 | 64.4 |
| 0.06 | 0.2430 | 4.0500 | 2.143 | 57.1 |
| 0.08 | 0.3150 | 3.9375 | 2.083 | 54.1 |

| CdBr ₂ = 272·00. | | | | |
|---|---------------------|--------------------------------|----------|---------------------|
| 1. Normal. | 2. Lowering. | 3. Gram-molec. Lowering. | 4. i. | 5. Dissociation. |
| | | | | per cent. |
| 0·002 | 0·0102 ⁸ | 5·1000 | 2·698 | 84·9 |
| 0·004 | 0·0195 | 4·8750 | 2·579 | 78·9 |
| 0·006 | 0·0281 | 4·6833 | 2·477 | 73·8 |
| 0·008 | 0·0369 | 4·6125 | 2·440 | 72·0 |
| 0·01 | 0·0454 | 4·5400 | 2·402 | 70·1 |
| 0·02 | 0·0822 | 4·1100 | 2·175 | 58·7 |
| 0·04 | 0·1501 | 3·7525 | 1·985 | 49·2 |
| 0·06 | 0·2089 | 3·4816 | 1·842 | 42·1 |
| 0·08 | 0·2659 | 3·3237 | 1·758 | 37·9 |
| 0·1 | 0·3252 | 3·2520 | 1·721 | 36·0 |
| CdI ₂ = 365·81. | | | | |
| 0·001 | 0·00456 | 4·5600 | 2·413 | 70·6 |
| 0·002 | 0·00891 | 4·4550 | 2·357 | 67·8 |
| 0·004 | 0·0173 | 4·3250 | 2·288 | 64·4 |
| 0·006 | 0·0242 | 4·0333 | 2·134 | 56·7 |
| 0·008 | 0·0315 | 3·9375 | 2·083 | 54·1 |
| 0·01 | 0·0385 | 3·8500 | 2·037 | 51·8 |
| 0·02 | 0·0705 | 3·5250 | 1·862 | 43·1 |
| 0·04 | 0·1180 | 2·9500 | 1·561 | 28·0 |
| 0·06 | 0·1539 | 2·5650 | 1·357 | 17·8 |
| 0·08 | 0·1938 | 2·4225 | 1·282 | 14·1 |
| 0·1 | 0·2283 | 2·2830 | 1·208 | 10·4 |
| Cd(NO ₃) ₂ = 236·16. | | | | |
| 0·001 | 0·00545 | 5·4500 | 2·884 | 94·2 |
| 0·002 | 0·0108 | 5·4000 | 2·857 | 92·8 |
| 0·004 | 0·0214 | 5·3500 | 2·831 | 91·5 |
| 0·006 | 0·0317 | 5·2833 | 2·795 | 89·7 |
| 0·008 | 0·0419 | 5·2375 | 2·766 | 88·3 |
| 0·01 | 0·0522 | 5·2200 | 2·762 | 88·1 |
| 0·02 | 0·1036 | 5·1800 | 2·741 | 87·0 |
| 0·04 | 0·2062 | 5·1550 | 2·727 | 86·3 |
| ZnCl ₂ = 136·28. | | | | |
| 0·001 | 0·0055 | 5·5000 | 2·910 | 95·5 |
| 0·002 | 0·0109 | 5·4500 | 2·884 | 94·2 |
| 0·004 | 0·0213 | 5·3250 | 2·817 | 90·8 |
| 0·006 | 0·0315 | 5·2500 | 2·777 | 88·8 |
| 0·008 | 0·0416 | 5·2000 | 2·751 | 87·5 |
| 0·01 | 0·0519 | 5·1900 | 2·746 | 87·3 |
| 0·02 | 0·1035 | 5·1750 | 2·738 | 86·9 |
| 0·04 | 0·1995 | 4·9875 | 2·639 | 81·9 |
| 0·06 | 0·2878 | 4·7966 | 2·538 | 76·9 |
| 0·08 | 0·3774 | 4·7175 | 2·495 | 74·7 |

| HCl = 36.45. | | | | |
|---|-----------------|--------------------------------|----------|---------------------|
| 1. Normal. | 2. Lowering. | 3. Gram-molec. Lowering. | 4. i. | 5. Dissociation. |
| | | | | per cent. |
| 0.002 | 0.0075 | 3.7500 | 1.984 | 98.4 |
| 0.004 | 0.0150 | 3.7500 | 1.984 | 98.4 |
| 0.006 | 0.0225 | 3.7500 | 1.984 | 98.4 |
| 0.008 | 0.0297 | 3.7125 | 1.964 | 96.4 |
| 0.01 | 0.0370 | 3.7000 | 1.958 | 95.3 |
| 0.02 | 0.0739 | 3.6950 | 1.955 | 95.5 |
| 0.04 | 0.1470 | 3.6750 | 1.944 | 94.4 |
| 0.06 | 0.2196 | 3.6600 | 1.937 | 93.7 |
| 0.08 | 0.2875 | 3.5937 | 1.902 | 90.2 |
| 0.1 | 0.3565 | 3.5650 | 1.886 | 88.6 |
| H ₂ SO ₄ = 98.06. | | | | |
| 0.002 | 0.0104 | 5.2000 | 2.751 | 87.5 |
| 0.004 | 0.0203 | 5.0750 | 2.685 | 84.2 |
| 0.006 | 0.0300 | 5.0000 | 2.645 | 82.2 |
| 0.008 | 0.0386 | 4.8250 | 2.550 | 77.5 |
| 0.01 | 0.0475 | 4.7500 | 2.513 | 75.6 |
| 0.02 | 0.0907 | 4.5350 | 2.399 | 69.9 |
| 0.04 | 0.1734 | 4.3350 | 2.294 | 64.7 |
| 0.06 | 0.2454 | 4.0900 | 2.164 | 58.2 |
| 0.08 | 0.3195 | 3.9937 | 2.113 | 55.6 |
| 0.1 | 0.3945 | 3.9450 | 2.087 | 54.3 |
| HNO ₃ = 63.04. | | | | |
| 0.002 | 0.0075 | 3.7500 | 1.984 | 98.4 |
| 0.004 | 0.0150 | 3.7500 | 1.984 | 98.4 |
| 0.006 | 0.0225 | 3.7500 | 1.984 | 98.4 |
| 0.008 | 0.0300 | 3.7500 | 1.984 | 98.4 |
| 0.01 | 0.0372 | 3.7200 | 1.968 | 96.8 |
| 0.02 | 0.0745 | 3.7250 | 1.971 | 97.1 |
| 0.04 | 0.1486 | 3.7150 | 1.966 | 96.6 |
| 0.06 | 0.2197 | 3.6616 | 1.937 | 93.7 |
| 0.08 | 0.2889 | 3.6112 | 1.911 | 91.1 |
| 0.1 | 0.3550 | 3.5500 | 1.878 | 87.8 |
| H ₃ PO ₄ = 98.04. | | | | |
| 0.002 | 0.0070 | 3.5000 | 1.852 | 85.2 |
| 0.004 | 0.0137 | 3.4250 | 1.812 | 81.2 |
| 0.006 | 0.0199 | 3.3166 | 1.755 | 75.5 |
| 0.008 | 0.0260 | 3.2500 | 1.720 | 72.0 |
| 0.01 | 0.0319 | 3.1900 | 1.688 | 68.8 |
| 0.02 | 0.0595 | 2.9750 | 1.574 | 57.4 |
| 0.04 | 0.1132 | 2.8300 | 1.497 | 49.7 |
| 0.06 | 0.1597 | 2.6616 | 1.408 | 40.8 |
| 0.08 | 0.2001 | 2.5012 | 1.323 | 32.3 |
| 0.10 | 0.2392 | 2.3920 | 1.266 | 26.6 |
| 0.15 | 0.3480 | 2.3200 | 1.228 | 22.8 |

| KOH = 56.14. | | | | |
|--|---------------------|--------------------------------|----------|---------------------|
| 1. Normal. | 2. Lowering. | 3. Gram-molec. Lowering. | 4. i. | 5. Dissociation. |
| | | | | per cent. |
| 0.002 | 0.0075 ⁹ | 3.7500 | 1.984 | 98.4 |
| 0.004 | 0.0150 | 3.7500 | 1.984 | 98.4 |
| 0.006 | 0.0223 | 3.7166 | 1.966 | 96.6 |
| 0.008 | 0.0295 | 3.6875 | 1.951 | 95.1 |
| 0.01 | 0.0366 | 3.6600 | 1.937 | 93.7 |
| 0.02 | 0.0723 | 3.6150 | 1.913 | 91.3 |
| 0.04 | 0.1437 | 3.5925 | 1.901 | 90.1 |
| 0.06 | 0.2133 | 3.5550 | 1.881 | 88.1 |
| 0.08 | 0.2800 | 3.5000 | 1.852 | 85.2 |
| 0.1 | 0.3460 | 3.4600 | 1.831 | 83.1 |
| NaOH = 40.06. | | | | |
| 0.002 | 0.0075 | 3.7500 | 1.984 | 98.4 |
| 0.004 | 0.0150 | 3.7500 | 1.984 | 98.4 |
| 0.006 | 0.0222 | 3.7000 | 1.958 | 95.8 |
| 0.008 | 0.0294 | 3.6750 | 1.944 | 94.4 |
| 0.01 | 0.0366 | 3.6600 | 1.937 | 93.7 |
| 0.02 | 0.0730 | 3.6500 | 1.931 | 93.1 |
| 0.04 | 0.1438 | 3.5950 | 1.902 | 90.2 |
| 0.06 | 0.2104 | 3.5000 | 1.852 | 85.2 |
| 0.08 | 0.2760 | 3.4500 | 1.825 | 82.5 |
| NH ₄ OH = 35.06. | | | | |
| 0.003 | 0.0067 | 2.2333 | 1.181 | 18.1 |
| 0.004 | 0.0087 | 2.1750 | 1.151 | 15.1 |
| 0.006 | 0.0126 | 2.1000 | 1.111 | 11.1 |
| 0.008 | 0.0165 | 2.0625 | 1.091 | 9.1 |
| 0.01 | 0.0202 | 2.0200 | 1.080 | 6.9 |
| 0.02 | 0.0394 | 1.9700 | 1.042 | 4.2 |
| 0.04 | 0.0787 | 1.9675 | 1.041 | 4.1 |
| 0.06 | 0.0981 | 1.9620 | 1.038 | 3.8 |
| K ₂ CO ₃ = 138.27. | | | | |
| 0.002 | 0.0111 | 5.5500 | 2.937 | 96.8 |
| 0.004 | 0.0221 | 5.5250 | 2.923 | 96.1 |
| 0.006 | 0.0330 | 5.5000 | 2.910 | 95.5 |
| 0.008 | 0.0440 | 5.5000 | 2.910 | 95.5 |
| 0.01 | 0.0550 | 5.5000 | 2.910 | 95.5 |
| 0.02 | 0.1056 | 5.2800 | 2.794 | 89.7 |
| 0.04 | 0.2001 | 5.0025 | 2.647 | 82.3 |
| 0.06 | 0.2847 | 4.7450 | 2.511 | 75.5 |
| 0.08 | 0.3748 | 4.6850 | 2.479 | 73.9 |



| 1. Normal. | 2. Lowering. | 3. Gram-molec. Lowering. | 4. i. | 5. Dissociation. |
|---------------|---------------------|--------------------------------|----------|---------------------|
| | | | | per cent. |
| 0.002 | 0.0111 ^o | 5.5500 | 2.937 | 96.8 |
| 0.004 | 0.0222 | 5.5500 | 2.937 | 96.8 |
| 0.006 | 0.0331 | 5.5166 | 2.919 | 95.9 |
| 0.008 | 0.0440 | 5.5000 | 2.910 | 95.5 |
| 0.01 | 0.0546 | 5.4600 | 2.889 | 94.4 |
| 0.02 | 0.1069 | 5.3450 | 2.828 | 91.4 |
| 0.04 | 0.1968 | 4.9200 | 2.603 | 80.1 |
| 0.06 | 0.2769 | 4.6150 | 2.442 | 72.1 |
| 0.08 | 0.3625 | 4.5312 | 2.397 | 69.8 |
| 0.1 | 0.4464 | 4.4640 | 2.362 | 68.1 |

DISCUSSION OF THE RESULTS.

The chlorides of potassium, sodium, and ammonium have been found to give the same dissociation within the limits of experimental errors. The same fact was found by Noyes* from his "Solubility" investigations. Two complete series of measurements have been made with solutions of sodium chloride, and the mean results are given as the most exact for the three chlorides. A number of solutions of potassium and ammonium chlorides have, however, been measured†. The curve from the results with sodium chloride (Pl. IV. curves 1, 2) can also be regarded as expressing the results in all three cases. The dissociation of the chlorides and other salts decreases more or less regularly with the increase in concentration. Certain apparent exceptions will be noticed here and there, especially in the dilute solutions. Thus the dissociation of 0.004 *n* sodium chloride is 93.1 per cent., while the dissociation of 0.006 *n* is 93.7 per cent. This is caused by experimental errors, which are much greater for the dilute solutions, because the lowering of the freezing-point here is the least. An error of 0.0001° at 0.001 *n* solution will affect the dissociation some per cent. This error, however, diminishes very rapidly with increase in concentration, and could be entirely disregarded at 0.1 *n* concentration.

As evidence that these small deviations are caused by experimental errors, when two series of measurements are made with solutions of the same salt, they do not appear constant to the two series.

These three alkali chlorides dissociate into two ions each,

* Noyes, *Zeits. phys. Chem.* ix. p. 609.

† Jones, *ibid.* xi. p. 114.

a monovalent anion and a monovalent kation. Each ion contains only one element, with the exception of the kation NH_4 , which resembles so closely the alkali elements. This is the simplest kind of dissociation, and regularities which appear with these salts might not be found when the molecules are more complicated and yield more complex ions. It may be said in advance that such regularities do exist in general, and will be seen from an examination of the following compounds.

Potassium Sulphate.—The molecules of potassium sulphate dissociate into two univalent kations and one bivalent anion. The molecules here, as with other compounds which give three ions, may dissociate at first into K and KSO_4 , and then with increase in dilution the ion KSO_4 dissociate into K and SO_4 . The freezing-point method is not capable of deciding this point, since it has to do with the quantity and not the quality of the ions present. This problem must be solved by a study of some property of the particular ions, electrical or otherwise.

The complete dissociation of potassium sulphate into three ions is less than the complete dissociation of potassium chloride for all the dilutions measured. This difference increases rapidly with the concentration. At $0.01\text{ }n$ it is about 8 per cent., while at $0.1\text{ }n$ it is about 20 per cent. This rapid decrease in dissociation with increase in concentration for potassium sulphate is seen in curve 4, Plate IV., which rapidly rises from the abscissa and approaches curve 3.

The comparison between the isotonic coefficients from osmotic pressure and the molecular lowering of the freezing-point for this and other salts has been made by de Vries*.

Barium Chloride.—The molecules of barium chloride, like the molecules of potassium sulphate, dissociate into three ions, but into one bivalent kation and two univalent anions. The complete dissociation here is less than for the alkali chlorides, and this difference also increases with the concentration. The decrease in dissociation with increase in concentration is less rapid than for potassium sulphate.

Magnesium Sulphate.—The molecules of this salt dissociate into two ions, a bivalent kation and a bivalent anion. This differs from the alkali chlorides, which also yield two ions, in that both ions in the former case are bivalent, in the latter univalent. It also differs from the two salts just considered, which give three ions, one bivalent and two univalent.

The compounds thus far considered can be regarded as typical representatives of four different ways in which molecules dissociate into ions :—

* de Vries, *Zeits. phys. Chem.* ii. p. 427.

- I. Into one univalent kation and one univalent anion.
- II. Into two univalent kations and one bivalent anion.
- III. Into one bivalent kation and two univalent anions.
- IV. Into one bivalent kation and one bivalent anion.

No new kind of ion formation from molecules will be found among the remaining compounds with possibly the exception of phosphoric acid, and they can all be referred to one of the four classes.

Magnesium sulphate dissociates much less than any compound thus far examined. The decrease in the dissociation with increase in concentration is very rapid. This decrease from $0.001\ n$ to $0.01\ n$ is about 20 per cent., while from $0.01\ n$ to $0.1\ n$ about 28.4 per cent. This is why curve 8 (Plate IV.) rises so rapidly and approaches curve 7.

Cadmium Chloride.—The cadmium salts were studied, because the conductivity results showed an abnormally small dissociation. These results also show that the chloride of cadmium dissociates much less than the chloride of barium.

Cadmium Bromide.—The bromide and iodide were measured that the effect of the three halogens combined with the same kation might be seen. The bromide appears to have about the same dissociation as the chloride in very dilute solutions, but much less in more concentrated. At $0.01\ n$ the difference is but 2.3 per cent., while at $0.08\ n$ this difference amounts to 16.2 per cent.

Cadmium Iodide.—The iodide dissociates much less than the bromide, and this difference is greater than between the bromide and chloride. That the bromide occupies a position between the chloride and iodide in reference to the amount of dissociation was also found by Grotrian and Wershoven*, in their work on the "Conductivity" of these salts. The curves 3, 4 (Plate V.) for the bromide, and 5, 6 (Plate V.) for the iodide, are not as smooth as the curves for the other compounds. The irregularities show some slight experimental error, at some points increasing the lowering of the freezing-point, at others diminishing it. The nature of this error with these two salts is at present not apparent.

Cadmium Nitrate.—The nitrate of cadmium dissociates to a much greater degree than the chloride, and to nearly the same extent as the alkali chlorides.

Zinc Chloride.—The chlorides of barium and of zinc dissociate to very nearly the same extent, while the chloride of cadmium is much less dissociated than either.

Hydrochloric Acid.—The solution of pure hydrochloric acid

* Wershoven, *Zeits. phys. Chem.* v. p. 481.

used was standardized against sodium and potassium carbonates, both of which had been repeatedly recrystallized. The chlorine was also determined as silver chloride.

It will be of interest to compare the amount of the dissociation of the acids with that of their salts, to ascertain whether the hydrogen of the acid or the replacing metal has the greater tendency to dissociate from the molecules into ions.

The chlorides of sodium, potassium, and ammonium dissociate less than hydrochloric acid. At 0.1 *n* this difference amounts to about 4.5 per cent. The difference is still greater when the acid is compared with the chlorides of barium, cadmium, and zinc, which dissociate much less than the univalent alkali chlorides.

Sulphuric Acid.—The solution was titrated against an alkali which had been titrated against the standardized hydrochloric acid. The sulphur was also determined as barium sulphate. Like the sulphates, it is quite possible that the acid dissociates first into H and HSO₄, and with increased dilution HSO₄ dissociates into H and SO₄. Sulphuric acid dissociates less than the potassium salt, which is the reverse to that observed with hydrochloric acid. The dissociation of the acid is much greater than that of the sulphate of magnesium, but the dissociation of this salt is abnormally small, as will be shown later.

Nitric Acid.—The solution was compared with alkalis which had been standardized against both hydrochloric and sulphuric acids. Nitric acid dissociates slightly more than its alkali salts; it is also a little more dissociated than hydrochloric acid, but the difference is slight.

Phosphoric Acid.—The phosphoric acid used was prepared by the oxidation of phosphorus with nitric acid. The arsenic present was precipitated by hydrogen sulphide. A qualitative analysis of the preparation showed it to be free from those impurities which would be expected to accompany the phosphorus, or to be introduced by the method of preparation. The solution was standardized by determining the phosphorus as magnesium pyrophosphate. The acid is of special interest, because the conductivity shows very small dissociation. It shows, further, that the acid probably dissociates into only two ions, H and H₂PO₄, since the greatest conductivity is less than if the dissociation into two ions were complete. The freezing-point results lead to the same conclusions as the conductivity. For the concentrations studied, the decrease in dissociation is over 60 per cent.

These results show very satisfactorily the rate of change in the dissociation. The rate of change is slow as we approach

complete dissociation, then becomes greater and greater with increase in concentration, and finally diminishes as we approach no dissociation. This is clearly seen in curve 8 (Plate VI.), which rapidly approaches curve 7, while curve 9 rises much less rapidly.

Of the four acids investigated, the two monobasic (HCl and HNO_3) dissociate to a greater degree than the dibasic (H_2SO_4), and this in turn more than the tribasic (H_3PO_4).

Potassium Hydroxide.—The preparation was freed from carbonate, with special care, by solution in alcohol. As has been pointed out, these results from the hydroxides cannot be regarded as thoroughly accurate, on account of the exposure to the air and the absorption of small amounts of carbon dioxide. When the hydroxides were under investigation, all the water was boiled just previous to using and before the drop of alkali was added. The water used in the preparation of the original solution was also boiled and cooled, protected from the carbon dioxide of the air, that the above error might be reduced to a minimum.

The results show that potassium hydroxide is dissociated to very nearly the same degree as potassium chloride, while both are dissociated less than the hydrochloric acid. The dissociation of the hydroxide is greater than that of the sulphate, which in turn is more dissociated than the free sulphuric acid.

Sodium Hydroxide.—The hydroxide used was prepared by allowing sodium to act upon water. The difference in the dissociation of sodium and potassium hydroxide is so slight that it is probably the result of error caused by the presence of unequal small quantities of carbonate. This difference increases somewhat with increase in concentration; but this increase is so small that doubt exists as to whether it represents an actual difference. The relation between the degree of dissociation of the hydroxides, acids, and salts, which exist in the case of potassium, hold also for sodium.

Ammonium Hydroxide.—The conductivity of ammonium hydroxide has shown that the dissociation is only a small part of that of the other hydroxides. The freezing-point results lead to the same conclusion, yet the chloride of ammonium undergoes the same dissociation as the chlorides of sodium and potassium. This very small dissociation is seen in curves 5 and 6 (Plate VII.), which rise very rapidly as compared with the curves for the other hydroxides.

The solutions of ammonium hydroxide were exposed to the same error from the carbon dioxide of the air as the other hydroxides, and an additional error from the volatility of the base. This can be disregarded for the most dilute solutions,

but is considerable for the more concentrated. After the four most concentrated solutions had been measured, which required several hours, the solution was titrated against standard acid, and found to have lost about $\frac{1}{3}$ per cent. of the calculated concentration. This error increased rapidly with increase in concentration, and prevented the use of more concentrated solutions than those which were employed.

Potassium Carbonate.—The carbonate is slightly more dissociated than the sulphate. The carbon dioxide was also removed from the water used in preparing the solutions of the carbonates to prevent the formation of acid carbonates. The solutions of the carbonates must have also been slightly affected by the carbon dioxide of the air. The hydrolysis of the carbonate molecules into KOH and KHCO_3 by the water in dilute solution, and the subsequent dissociation of these products of hydrolysis, would give slightly too great lowerings of the freezing-point and consequently a dissociation somewhat too high.

Sodium Carbonate.—Three compounds of potassium and sodium have then been investigated—the chlorides, hydroxides, and carbonates. The chlorides dissociate to the same degree, within the limit of error; the hydroxides to very nearly the same extent; sodium hydroxide possibly a little less in the more concentrated solutions. The carbonates have about the same dissociation in the most dilute solutions, but the difference noticed with the hydroxides increases here. Sodium carbonate dissociates less with increased concentration, and this difference amounts to 4 per cent. at 0.1 n.

*Comparison with Kohlrausch's Results from
Conductivity.*

The Conductivity method is probably the most exact hitherto employed for determining dissociation. It admits of wide application, and has the advantage over the Freezing-point method that it can be applied to more dilute solutions. It will suffice to compare a few of the results obtained by the two methods.

Most of the compounds discussed thus far in this communication have been studied by Kohlrausch*, as to their conductivity, with that care which characterizes his work. He has employed equivalent-normal solutions throughout, while I have used gram-molecular normal. Where the two do not coincide, Kohlrausch's results have been reduced to molecular normal and compared directly with mine. This applies to

* Kohlrausch, Wied. Ann. xxvi. p. 160.

potassium sulphate, barium chloride, magnesium sulphate, zinc chloride, sulphuric and phosphoric acids, and potassium and sodium carbonates. The comparison will only be carried to 0.002 or 0.003 molec. normal, beyond which the error in my results is necessarily large, from the very small lowering of the freezing-point to be measured.

Since the following comparison is only approximate, and does not demand the greatest accuracy, the highest molecular conductivity found will be taken as μ_{∞} in the calculation—

$$\text{dissociation} = \frac{\mu\nu}{\mu_{\infty}}.$$

The results from the two methods are given in the Table on the opposite page, where column 1 contains the names of the compounds investigated, with the values used as μ_{∞} ; 2, concentrations of solutions compared, in gram-molecular normal; 3, the dissociation as calculated from Kohlrausch's results, using Conductivity method; 4, the dissociation calculated from my results, using the improved Freezing-point method.

The general agreement between the results from the two methods is unmistakable. Indeed, it is as close as could be expected when it is considered that such widely different properties of the ions as the lowering of the freezing-point of the solvent and the conduction of electricity are utilized in the two cases. Again, each method is doubtless affected by small errors peculiar to itself. It has been pointed out that a slight difference in the amount of dissociation would be produced by the difference in temperature at which the two series of measurements were made*.

The dissociation of some of the salts as calculated from the lowering of the freezing-point is slightly greater than that calculated from the "Conductivity." A possible explanation in the case of the carbonates is to be found in the hydrolysis produced by the water. Shields† has shown that the amount of hydrolysis is at least nearly proportional to the square root of the dilution. The products of the hydrolysis would conduct better than the carbonate molecules, and μ_{∞} at the greater dilution would be too large relative to $\mu\nu$. This would give too little dissociation from the conductivity results for those concentrations where the results are compared. This would also explain why the difference increases with the concentration. The dissociation of magnesium sulphate, as calculated from the freezing-point results, is considerably lower for the concentrated solutions. This has been explained

* Jones, *Ber. d. deutsch. Chem. Gesell.* xxvi. p. 550.

† Shields, *Phil. Mag.* [5] xxxv. p. 377.

| Compounds. | Concentration gr.-molec. normal. | Kohlrausch's results from "Conductivity." | My results from Low. Freezing- point. |
|--|--|---|---|
| NaCl, $\mu\infty = 1029$. | 0.001 | 98.0 % | 98.4 % |
| " | 0.01 | 93.5 | 90.5 |
| " | 0.1 | 84.1 | 84.1 |
| K ₂ SO ₄ , $\mu\infty = 1280$. | 0.001 | 92.3 % | 94.2 % |
| " | 0.005 | 85.8 | 88.7 |
| " | 0.05 | 70.1 | 72.6 |
| BaCl ₂ , $\mu\infty = 1144$. | 0.001 | 93.9 % | 94.2 % |
| " | 0.005 | 87.9 | 87.6 |
| " | 0.05 | 75.3 | 77.7 |
| MgSO ₄ , $\mu\infty = 1056$. | 0.001 | 83.4 % | 82.5 % |
| " | 0.005 | 67.7 | 69.5 |
| " | 0.05 | 44.9 | 39.9 |
| ZnCl ₂ , $\mu\infty = 1036$. | 0.001 | 94.5 % | 95.5 % |
| " | 0.005 | 88.3 | 89.8 |
| " | 0.05 | 74.1 | 79.4 |
| HCl, $\mu\infty = 3455$. | 0.002 | 100.0 % | 98.4 % |
| " | 0.01 | 98.9 | 95.8 |
| " | 0.1 | 93.9 | 88.6 |
| H ₂ SO ₄ , $\mu\infty = 3342$. | 0.003 | 89.8 % | 86.0 % |
| " | 0.005 | 85.4 | 83.8 |
| " | 0.05 | 62.3 | 60.7 |
| HNO ₃ , $\mu\infty = 3448$. | 0.002 | 100.0 % | 98.4 % |
| " | 0.01 | 98.5 | 96.8 |
| " | 0.1 | 93.5 | 87.8 |
| H ₃ PO ₄ , $\mu\infty = 977$. | 0.002 | 87.8 % | 85.2 % |
| " | 0.01 | 63.5 | 68.8 |
| KOH, $\mu\infty = 2141$. | 0.002 | 100.0 % | 98.4 % |
| " | 0.01 | 99.2 | 93.7 |
| " | 0.1 | 92.8 | 83.1 |
| NaOH, $\mu\infty = 1880$. | 0.002 | 98.9 % | 98.4 % |
| " | 0.01 | 99.5 | 93.7 |
| " | 0.05 | 90.4 | 88.4 |
| NH ₄ OH, $\mu\infty = 700$. | 0.006 | 16.6 % | 11.1 % |
| " | 0.01 | 13.0 | 6.9 |
| " | 0.05 | 6.1 | 3.8 |
| K ₂ CO ₃ , $\mu\infty = 1222$. | 0.003 | 92.0 % | 96.6 % |
| " | 0.005 | 88.6 | 96.0 |
| " | 0.05 | 71.9 | 77.5 |
| Na ₂ CO ₃ , $\mu\infty = 1046$. | 0.003 | 91.4 % | 96.3 % |
| " | 0.005 | 86.0 | 95.9 |
| " | 0.05 | 65.2 | 73.0 |

by Arrhenius* as probably due to the formation of double molecules of sulphate in the more concentrated solutions, and these are partly broken down with increase in dilution.

The dissociation of the acids and alkalies as calculated from the lowering of the freezing-point is in general slightly lower than from the conductivity. This would be expected, since the highest conductivity in Kohlrausch's results is probably not that representing complete dissociation. The conductivity value decreases from 0.001 or 0.002 equivalent normal to the greatest dilutions employed †. Doubtless the same cause which produces this real decrease also diminishes the highest value to some extent. A decrease in the true value of μ_{∞} would increase the dissociation calculated from $\frac{\mu v}{\mu_{\infty}}$.

It is to be regretted that the freezing-point method could not be extended beyond that dilution where the conductivity value began to decrease. But on account of the very small lowering produced by such dilute solutions, it is even at present impossible. The cause of this decrease in conductivity for the very dilute solutions has been thought to be the carbon dioxide and ammonia in the water. These form compounds with the alkalies and acids respectively, and the molecules of these compounds dissociate into ions with smaller "velocity" than the ions of the original compounds, decreasing the conductivity. The amount of such impurities required to neutralize a considerable per cent. of the acid or base in such dilute solutions would be extremely small. Whether such impurities are the real cause is not positively established by the work of Kohlrausch, as will appear from his own statements ‡. This explanation is, however, regarded by many as entirely satisfactory.

Before concluding this division of my paper, which has to do especially with "electrolytic dissociation," it may be of interest to add a word in reference to the so-called "Breaks" which have been claimed to appear when the results from the freezing-point method are plotted as curves. This is the more desirable because of the large number of communications which have recently appeared from Mr. S. Pickering against the "Dissociation Theory." I have carefully examined his results in the case of dilute solutions of sodium chloride, and have shown that the "breaks" are caused only by the experimental errors in his results §. Mr. Pickering || has applied

* Arrhenius, *Zeits. phys. Chem.* ii. p. 497.

† Kohlrausch, *Wied. Ann.* xxvi. p. 196.

‡ Kohlrausch, *tom. cit.* p. 204.

§ Jones, *Ber. d. deutsch. Chem. Gesell.* xxvi. p. 551.

|| Pickering, *ibid.* p. 1221.

his method of curve-drawing to my results from sodium chloride, which differ from his to the extent of more than 50 per cent., and with it claims to have found the same "breaks" as in his own results. He has thus shown the true value of his method, which seems to be largely independent of the experimental data.

I have since * shown that his curve contains the following fundamental errors:—

- I. At least some of the points in his curve are wrong.
- II. The choice of points through which he has drawn the curve is purely arbitrary.

Organic Compounds.

Many of the organic compounds are known to undergo little or no electrolytic dissociation. These would be expected to give molecular lowerings of the freezing-point not widely different from the constant for the solvent, at least in fairly dilute solutions. The chief object in mind at first in studying some of the organic substances was to determine experimentally and with some care the constant for water. The work was begun with cane-sugar, and it was found that the most dilute solutions gave a molecular lowering much greater than the constant calculated for water, and that this high molecular lowering decreased fairly regularly with increase in concentration. It was thought at first that this was probably due to some inorganic impurity in the sugar, but that this was not the cause was shown when the same results were obtained from sugar as pure as it could be prepared. It was then thought that such results might be peculiar to sugar and bodies of similar chemical constitution. It was possible that the cane-sugar molecules conducted themselves in the very dilute solutions as if inverted into two molecules. Dextrose was then investigated, the molecules of which could not apparently conduct themselves in this way. When results of the same general character were obtained from the dilute solutions of dextrose, it was decided to study a number of organic compounds whose chemical composition and constitution were as widely different from each other as possible. One could then see whether this property were more or less general among the organic compounds, or limited to certain classes of them. In addition to cane-sugar and dextrose, urea, phenol, ethyl and propyl alcohols have been studied in reference to this point. Acetic and succinic acids have also been investigated, but the organic acids are known to undergo electrolytic dissociation.

* Jones, *Ber. d. deutsch. Chem. Gesell.* xxvi, p. 1035.

Results with Organic Compounds.

The tabulation of the results from the organic compounds is perfectly analogous to that used with the inorganic. For those organic compounds which do not undergo electrolytic dissociation, of course column 5, giving the amounts of such dissociation, is omitted.

| $C_{12}H_{22}O_{11} = 342.11.$ | | | |
|---|---------------------|--------------------------------|----------|
| 1. Normal. | 2. Lowering. | 3. Gram-molec. Lowering. | 4. i. |
| 0.003 | 0.0071 ^o | 2.3666 | 1.252 |
| 0.004 | 0.0094 | 2.3500 | 1.243 |
| 0.006 | 0.0139 | 2.3166 | 1.226 |
| 0.008 | 0.0184 | 2.3000 | 1.217 |
| 0.01 | 0.0229 | 2.2900 | 1.212 |
| 0.02 | 0.0455 | 2.2750 | 1.204 |
| 0.04 | 0.0894 | 2.2350 | 1.183 |
| 0.06 | 0.1286 | 2.1433 | 1.134 |
| 0.08 | 0.1633 | 2.0412 | 1.080 |
| 0.1 | 0.1976 | 1.9760 | 1.046 |
| 0.2 | 0.3998 | 1.9990 | 1.058 |
| $C_6H_{12}O_6 = 180.06.$ | | | |
| 0.003 | 0.0072 ^o | 2.4000 | 1.270 |
| 0.004 | 0.0095 | 2.3750 | 1.257 |
| 0.006 | 0.0139 | 2.3166 | 1.226 |
| 0.008 | 0.0182 | 2.2750 | 1.204 |
| 0.01 | 0.0226 | 2.2600 | 1.196 |
| 0.02 | 0.0442 | 2.2100 | 1.169 |
| 0.04 | 0.0874 | 2.1850 | 1.156 |
| 0.06 | 0.1262 | 2.1033 | 1.113 |
| 0.08 | 0.1592 | 1.9900 | 1.063 |
| 0.10 | 0.1910 | 1.9100 | 1.011 |
| 0.15 | 0.2889 | 1.9260 | 1.019 |
| $CO \begin{matrix} \nearrow NH_2 \\ \nwarrow NH_2 \end{matrix} = 60.1.$ | | | |
| 0.003 | 0.0068 ^o | 2.2666 | 1.199 |
| 0.004 | 0.0090 | 2.2500 | 1.190 |
| 0.006 | 0.0133 | 2.2166 | 1.173 |
| 0.008 | 0.0176 | 2.2000 | 1.164 |
| 0.01 | 0.0218 | 2.1800 | 1.153 |
| 0.02 | 0.0434 | 2.1700 | 1.148 |
| 0.04 | 0.0847 | 2.1175 | 1.120 |
| 0.06 | 0.1228 | 2.0466 | 1.083 |
| 0.08 | 0.1602 | 2.0025 | 1.059 |
| 0.10 | 0.1920 | 1.9200 | 1.016 |
| 0.15 | 0.2843 | 1.8963 | 1.003 |

| $C_6H_5OH = 94.04.$ | | | |
|-----------------------------|-----------------|-------------------------------|----------|
| 1. Normal. | 2. Lowering. | 3. Gram-mole. Lowering. | 4. i. |
| 0.003 | 0.0067 | 2.2333 | 1.182 |
| 0.004 | 0.0089 | 2.2250 | 1.177 |
| 0.006 | 0.0132 | 2.2000 | 1.164 |
| 0.008 | 0.0174 | 2.1750 | 1.151 |
| 0.01 | 0.0215 | 2.1500 | 1.138 |
| 0.02 | 0.0427 | 2.1350 | 1.130 |
| 0.04 | 0.0842 | 2.1050 | 1.114 |
| 0.06 | 0.1237 | 2.0616 | 1.091 |
| 0.08 | 0.1594 | 1.9925 | 1.054 |
| 0.10 | 0.1932 | 1.9320 | 1.022 |
| 0.15 | 0.2759 | 1.8393 | 0.973 |
| $C_2H_5OH = 46.03.$ | | | |
| 0.003 | 0.0071 | 2.3666 | 1.252 |
| 0.004 | 0.0093 | 2.3250 | 1.230 |
| 0.006 | 0.0136 | 2.2666 | 1.199 |
| 0.008 | 0.0177 | 2.2125 | 1.170 |
| 0.01 | 0.0218 | 2.1800 | 1.153 |
| 0.02 | 0.0414 | 2.0700 | 1.095 |
| 0.04 | 0.0812 | 2.0300 | 1.074 |
| 0.06 | 0.1197 | 1.9950 | 1.056 |
| 0.08 | 0.1563 | 1.9537 | 1.034 |
| 0.10 | 0.1940 | 1.9400 | 1.026 |
| 0.15 | 0.2788 | 1.8587 | 0.983 |
| $CH_3.CH_2.CH_2OH = 60.04.$ | | | |
| 0.003 | 0.0064 | 2.1333 | 1.129 |
| 0.004 | 0.0085 | 2.1250 | 1.124 |
| 0.006 | 0.0126 | 2.1000 | 1.111 |
| 0.008 | 0.0165 | 2.0625 | 1.091 |
| 0.01 | 0.0205 | 2.0500 | 1.085 |
| 0.02 | 0.0406 | 2.0300 | 1.074 |
| 0.04 | 0.0811 | 2.0275 | 1.073 |
| 0.06 | 0.1198 | 1.9966 | 1.056 |
| 0.08 | 0.1567 | 1.9587 | 1.036 |
| 0.10 | 0.1922 | 1.9220 | 1.017 |
| 0.15 | 0.2818 | 1.8787 | 0.994 |

Cane-Sugar.—Since these more or less unexpected results were obtained first with cane-sugar, great care was taken to secure a specimen as pure as possible. Two samples were obtained, one from the sugar refinery in Berlin, and the other through the kindness of Dr. Lippmann from the refinery in Halle. Both were tested with Fehling's solution and found

to be completely free from dextrose. The specimen from Berlin was purified by alcohol, and was in the form of a powder. That from Halle consisted of small crystals. The latter sample was on the whole to be preferred, and although measurement of solutions prepared from each were made, only those results obtained from the Halle sugar have been given here.

From the table of results it will be seen that the molecular lowering at $0.003\ n$ is about 2.36. This decreases with increase in concentration to about $0.1\ n$, and then increases again as the solution becomes more and more concentrated.

This increase in the molecular lowering with increase in concentration for the more concentrated solutions of cane-sugar was found by Arrhenius *. His method was, however, not sufficiently accurate to enable him to employ solutions dilute enough to detect the corresponding increase in this region.

Raoult †, using an improved method, has found that the molecular lowering of cane-sugar increases with increase in dilution from about $0.1\ n$, and also increases with the concentration in the more concentrated solutions. He did not use solutions more dilute than $0.02\ n$. These determinations of Raoult are probably the most accurate hitherto made for cane-sugar solutions.

I am entirely unable to understand the results of Loomis ‡, who has found the smallest molecular lowering for the most dilute solutions employed ($0.01\ n$), and that this increased throughout with the concentration. He has also found similar results with other organic compounds.

Since the results with cane-sugar were of an unsuspected character, it was determined to test the last apparent possibility of experimental error being their cause. It was barely possible that some considerable change in the bulb of the large thermometer had taken place and escaped notice. To test this it was decided to remeasure a series of solutions of sodium chloride. The results of these measurements agreed with the results obtained several months before, in every case to within a few ten-thousandths of a degree.

The facts with cane-sugar are then : 1st, the molecular lowering increases from a certain concentration (about $0.1\ n$) with increase in dilution, and also increases from this same concentration with increase in concentration.

A possible explanation of the latter fact has been furnished

* Arrhenius, *Zeits. phys. Chem.* ii. p. 491.

† Raoult, *ibid.* ix. p. 343.

‡ Loomis, *Ber. d. deutsch. Chem. Gesell.* xxvi. p. 797.

by Arrhenius *, in reference to osmotic pressure, and then he has shown the relation between osmotic pressure and lowering of the freezing-point. In the formula for osmotic pressure,

$$\pi = AK + BK^2,$$

π = osmotic pressure, A = product of gas constant R with the absolute temperature, B a new constant, a measure of the difference between the attractions of the solvent-dissolved body and the dissolved body-dissolved body, K = concentration. When the concentration K is small, BK^2 vanishes with respect to AK , and we have the law for ideal gases. But as K increases, the osmotic pressure would increase or decrease relatively, depending on whether B is positive or negative. But with water as a solvent, B is generally positive. Thus as solutions which satisfy the above condition increase in concentration, the osmotic pressure would increase more rapidly, and $\frac{\pi}{K}$ would increase. Later in the same communication he has shown the proportionality between osmotic pressure and lowering of the freezing-point. Since the lowering of the freezing-point is proportional to the osmotic pressure, $\frac{\epsilon}{K}$ (ϵ = lowering of freezing-point) would increase, and this agrees with the facts of experiment.

On the other hand, Bredig † has pointed out that when $\frac{K}{v_1}$

for very dilute solutions is great as compared with $\frac{a}{v}$, non-electrolytes may show too great a lowering of the freezing-point. K = the attraction between the molecules of the solvent and those of the dissolved body ; v = volume of the dissolved body ; a = attraction of the molecules of the dissolved body for each other ; and v_1 = volume of the solvent.

Natanson ‡ has also discussed results from freezing-point, boiling-point, and osmotic-pressure determinations.

These theoretical considerations may prove to be competent to explain all the facts which may be brought to light. On the other hand, it may be necessary to supplement the present theories to account for them. In reference to this it seems that we must wait until many more compounds have been investigated, and more facts are at hand.

Dextrose.—The molecular lowering for dextrose agrees

* Arrhenius, *Zeits. phys. Chem.* x. p. 51.

† Bredig, *ibid.* iv. p. 444.

‡ Natanson, *Zeits. phys. Chem.* x. p. 748.

very closely with that of cane-sugar for the most dilute solutions. The minimum value here also is very nearly reached at $0.1\ n$, but for dextrose is slightly lower than for cane-sugar. As the concentration increases from about $0.1\ n$ the molecular lowering of dextrose increases, but the change is much less rapid than for cane-sugar. In general the same qualitative changes in the molecular lowering with changes in the concentration of the solution are observed with dextrose as with cane-sugar, and for the more dilute solutions the results from the two compounds agree very well with each other.

Urea.—Urea shows the same variations in molecular lowering with concentration as the other compounds for the more dilute solutions. This value is somewhat less for urea for the same concentrations. The molecular lowering of this compound becomes constant at about $0.1\ n$, and remains unchanged as the concentration is increased, at least as far as my experiments were carried. There exists, then, this marked difference between the more concentrated solutions of urea and of the two carbohydrates which have been considered.

Since the molecular lowering of urea reaches a constant, this can be taken as the constant for water. This value determined experimentally can then be compared with that calculated by van't Hoff.

Phenol.—Here also the same general results are obtained from the more dilute solutions, but the molecular lowering does not reach a minimum for the most concentrated solutions used. This decreases below the calculated constant for water, being only about 1.714 at $0.619\ n$. That phenol may possibly undergo a very slight electrolytic dissociation has been shown by Bader*.

Ethyl and Propyl Alcohol.—Results of the same general character as above considered were found for the more dilute solutions of both alcohols. The molecular lowering of ethyl alcohol for the same concentrations is considerably greater than that of propyl, and agrees fairly well with that of dextrose and cane-sugar. The molecular lowering of both alcohols becomes practically constant at a concentration slightly greater than $0.1\ n$.

All the organic compounds thus far examined show, then, this increase in the molecular lowering with increase in dilution. Since compounds have been selected which differ chemically so widely from one another, this can scarcely depend on chemical composition or constitution, but seems to be more or less general. Investigations have not as yet

* Bader, *Zeits. phys. Chem.* vi. p. 291.

been carried far enough to justify a final statement on this point. The molecular lowerings for the different compounds agree fairly well with each other in many cases for the more dilute solutions, and in general reach a minimum or become constant at about $0.1n$. The two carbohydrates, dextrose and cane-sugar, are the only two compounds thus far studied which show an increase in the mol. lowering with increase in concentration from about $0.1n$.

Of the organic compounds which undergo electrolytic dissociation two acids have been investigated, acetic and succinic acids.

| $\text{CH}_3 \cdot \text{COOH} = 60.02.$ | | | | |
|--|-----------------|--------------------------------|-------------|---------------------|
| 1. Normal. | 2. Lowering. | 3. Gram-molec. Lowering. | 4. i . | 5. Dissociation. |
| | | | | per cent. |
| 0.003 | 0.0082 | 2.0666 | 1.093 | 9.3 |
| 0.004 | 0.0082 | 2.0500 | 1.085 | 8.5 |
| 0.006 | 0.0122 | 2.0333 | 1.076 | 7.6 |
| 0.008 | 0.0163 | 2.0375 | 1.078 | 7.8 |
| 0.01 | 0.0202 | 2.0200 | 1.069 | 6.9 |
| 0.02 | 0.0402 | 2.0100 | 1.064 | 6.4 |
| 0.04 | 0.0798 | 1.9950 | 1.056 | 5.6 |
| 0.06 | 0.1187 | 1.9783 | 1.047 | 4.7 |
| 0.08 | 0.1565 | 1.9662 | 1.035 | 3.5 |
| 0.10 | 0.1927 | 1.9270 | 1.019 | 1.9 |
| 0.15 | 0.2805 | 1.8700 | 0.989 | |
| $\begin{array}{c} \text{CH}_2 \cdot \text{COOH} \\ \\ \text{CH}_2 \cdot \text{COOH} \end{array} = 118.03.$ | | | | |
| 0.003 | 0.0067 | 2.2333 | 1.182 | 18.2 |
| 0.004 | 0.0089 | 2.2250 | 1.177 | 17.7 |
| 0.006 | 0.0133 | 2.2166 | 1.173 | 17.3 |
| 0.008 | 0.0175 | 2.1875 | 1.157 | 15.7 |
| 0.01 | 0.0216 | 2.1800 | 1.143 | 14.3 |
| 0.02 | 0.0437 | 2.1850 | 1.156 | 15.6 |
| 0.04 | 0.0871 | 2.1775 | 1.152 | 15.2 |
| 0.06 | 0.1293 | 2.1550 | 1.140 | 14.0 |
| 0.08 | 0.1643 | 2.0537 | 1.087 | 8.7 |
| 0.10 | 0.2010 | 2.0100 | 1.063 | 6.3 |
| 0.15 | 0.2864 | 1.9093 | 1.010 | 1.0 |

Acetic Acid.—Acetic acid is only slightly dissociated; at $0.002n$, being only about 11 per cent., and at $0.1n$, 1 per cent. When the dissociation of this acid is compared with that of the common inorganic acids, the difference is very striking. The mol. lowering for the most concentrated solution is

slightly less than the constant 1.89, but the difference is so slight that it is doubtless without important significance.

Succinic Acid.—This acid, like the other dibasic organic acids, dissociates into two ions, and the amount of dissociation is considerably greater than that of acetic acid. The results with succinic acid do not run as smoothly as could be desired, and without knowing the cause for this I am inclined to regard them as less exact than the other results.

Comparison with the Conductivity Results of Ostwald.

Ostwald has determined the conductivity of a large number of organic acids, as is well known, and among them are acetic and succinic acid*. The dissociation of these acids, as calculated from his conductivity results and from mine on the lowering of the freezing-point, are given below :—

Acetic Acid.

| Concentration gr.-mol. normal. | Ostwald's results from Conductivity. | My results from Low. Freezing-point. |
|-----------------------------------|---|---|
| 0.004 | per cent. 6.47 | per cent. 8.5 |
| 0.02 | 2.92 | 6.4 |
| 0.1 | 1.30 | 1.9 |

Succinic Acid.

| Concentration gr.-mol. normal. | Ostwald's results from Conductivity. | My results from Low. Freezing-point. |
|-----------------------------------|---|---|
| 0.004 | per cent. 12.08 | per cent. 17.7 |
| 0.02 | 5.53 | 15.6 |
| 0.1 | 2.72 | 6.3 |

Ostwald's results are obtained by interpolation. The figure for 0.1 succinic acid by extrapolation. The agreement between the two series of results is fairly good for acetic acid, but for succinic acid my results are considerably higher.

* Ostwald, *Zeits. phys. Chem.* iii. pp. 174 and 272.

The Constant for Water.

If all substances were completely undissociated, molecular solutions for any given solvent should give very nearly the same lowering of the freezing-point of that solvent. Gram-molecular normal solutions in water would give a certain lowering of the freezing-point, and this would be the constant for water. As we have seen, certain compounds like urea and alcohol behave thus, except for very dilute solutions, and enable one to determine this value experimentally.

The same value has been calculated by van't Hoff* from the latent heat of fusion of the solvent. The calculation has been developed rather more fully by Ostwald† thus:—

Let us take a solution consisting of n molecules of the dissolved substance and N molecules of the solvent (molecule = gr.-mol. wt.). Let T = temperature of solidification of the solvent, and Δ = the lowering of the freezing-point. Here as much of the solvent is allowed to solidify as would serve for the solution of one molecule of the substance, = $\frac{N}{n}$ molecules.

Let λ = the molecular heat of fusion of the solvent; the amount of heat liberated would be $\frac{N}{n}\lambda$. If now the ice be separated from the solution, warmed to temperature T and melted, and finally allowed to mix with the solution by passing through a semipermeable membrane, it will exert an osmotic pressure p . If v = volume of solvent which had solidified, the work = pv , the heat = $\frac{N}{n}\lambda$; from which

$$\frac{pvn}{N\lambda} = \frac{\Delta}{T};$$

but $pv = RT$ and $R = 2$ cal. Substituting, we have

$$\Delta = \frac{n}{N} \cdot \frac{2T^2}{\lambda}.$$

Let M = mol. wt. of the solvent, and substituting $N = \frac{100}{M}$ we have

$$\Delta = \frac{nM}{100} \frac{2T^2}{\lambda} \dots \dots \dots (1)$$

* van't Hoff, *Zeits. phys. Chem.* i. p. 496.

† Ostwald, *Lehrb.* i. p. 759.

the value found by Bunsen * being 79.7. This would diminish the constant as calculated from the formula $\frac{2T^2}{100L}$. Using

the above value, 79.7, the constant as calculated would be 1.87. The value found is in reality divided by 10 for the sake of direct comparison.

The agreement, then, is very satisfactory between the constant as calculated and that found from the above three compounds.

Very recently Mr. C. Dieterici† has suggested some points which he thinks would slightly affect the accuracy of my results as obtained from this improved freezing-point method. The very sensitive thermometer, he thinks, would detect the changes in the freezing-point of the solution produced by the changes in the barometric pressure. A change of an entire atmosphere would alter the freezing-point only about 0.0075°. The maximum time between the determination of the freezing-point of the water and of the last solution in which that water was used was six hours, since a new litre of water was employed and its freezing-point determined at the beginning of each day's work. The freezing-point of the pure water was determined about 12 noon, and the last determination with this water as solvent was made about 6 P.M. The barometer is read at 2 P.M. and 8 P.M. daily at the meteorological station, near the laboratory, so I am enabled to calculate the magnitude of the error from this source. From the data which have been kindly furnished me at the station, the greatest change in the barometer between 2 P.M. and 8 P.M., from the 1st of November, 1892, to the 1st of August, 1893, the time during which my measurements were made, was less than 10 millim. Hg (7.8 millim.). A change of 10 millim. Hg would alter the freezing-point only 0.0001°, and this is greater than the maximum change even for one day. The average change during this same time was less than 2 millim. Hg, and the mean error from this cause was therefore less than 0.00002°.

The second point, that different layers of the solution have slightly different freezing-points due to hydrostatic pressure, has no application whatsoever to my work, because the thermometer remained always at the same depth in the solution. The thermometer was firmly fixed in cork *c* (*Zeits. phys. Chem.* xi. p. 532, fig. 1), and was not removed from it during the entire time in which this work was in progress.

* Bunsen, Pogg. *Ann.* cxli. p. 1.

† Dieterici, Wied. *Ann.* l. p. 77.

It then passed loosely through cork G, on which *c* rested, and was never raised or lowered to the extent of 5 millim. The freezing-point of the water was thus determined at a certain depth, and that of the solution at the same depth. The lowering was the difference between these two determinations made under the same hydrostatic pressure. The difference between the specific gravity of the water and that of the very dilute solutions employed producing slight differences in pressures, is almost too small to consider. The difference *e.g.* for a 0.2 normal solution of cane-sugar at 20 centim. beneath the surface would be about $\frac{1}{2}$ millim. Hg, and this would alter the freezing-point 0.000005° .

The third point, as to whether the thermometer had reached the same temperature as the solution, can only be decided by the results. Several solutions were determined several times each to test this point. In some of these determinations twice as much time was allowed as in others, and the maximum difference between the readings was only a few ten-thousandths of a degree. While I could not wait an unlimited time to make the readings, because the solution became more concentrated as more and more ice separated, yet Mr. Dieterici must remember that in the apparatus which was employed the litre of solution cooled very slowly, and the time at my disposal to make the readings seems to have been quite sufficient, as shown by the results.

Thus the three points suggested by Mr. Dieterici, as probably introducing slight errors into my results, are almost entirely of a theoretical character, as shown by the calculation of the exact amount of error introduced by each. From his final statements the author himself does not seem to attach any great significance to them.

I suggested the error 0.0002° * simply as the half of the maximum difference between the results in a series of determinations of the same solution. Of course any error either of weight or measurement in the preparation of the solutions, or any traces of impurity in the compounds, which always exist to some slight degree, would not be included in this maximum error in the determination of the freezing-point.

To briefly summarize :—

The dissociation of the electrolytes investigated, as calculated from the lowering of the freezing-point, agrees in general with that calculated from the conductivity. The

* Jones, *Zeits. phys. Chem.* xi. p. 112.

results by the former method for the acids and alkalies are slightly lower than by the latter, but I think that this has been fairly satisfactorily explained. The slight difference for the carbonates can be accounted for by hydrolysis. The freezing-point method, as here improved, is probably as accurate a measure of dissociation as the conductivity method for all those dilutions, except the most dilute to which it has been applied. The lowering of the freezing-point produced by the most dilute solutions is so small that the error of measurement is necessarily relatively great.

The organic compounds which do not undergo electrolytic dissociation have all given more or less unexpected results. The molecular lowering for the most dilute solutions is much greater than the constant for water. As the concentration is increased the molecular lowering decreases to a minimum, and then either remains constant or, as with the two carbohydrates, increases. The minimum for phenol was, apparently, not reached. The dissociation of acetic acid, as calculated from the freezing-point, agrees moderately well with that from conductivity, but for succinic acid the freezing-point results are considerably higher. The constant for water, which I have found from urea and ethyl and propyl alcohols, agrees very closely with that calculated by van't Hoff.

I hope to apply this method in the future to a large number of more complicated inorganic compounds, for the purpose of measuring their dissociation in water and other solvents; also to a much larger number of organic compounds and classes of compounds, to determine whether the peculiarities presented by those already examined are of a general character. This method can also, apparently, be used to measure the dissociation of organic acids.

In conclusion, I wish to express my thanks to Prof. Ostwald, in whose laboratory this work has been carried out and to whom I am indebted for many valuable suggestions during its progress.

Leipzig, Phys. Chemical Laboratory,
September 1893.

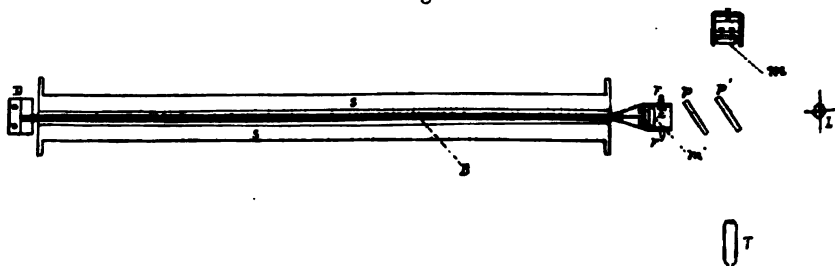
LI. *On the Elongation produced in Soft Iron by Magnetism.*
 By SIDNEY J. LOCHNER, *Fellow, Clark University, Worcester, Mass.**

HAD it not been for recent experiments by M. Alfonse Berget †, which apparently contradicted those of Mr. Shelford Bidwell ‡, I should have deemed it a waste of energy to have attempted to contribute anything further to our knowledge of the subject.

My original purpose was to confirm the experiments of either one or the other, not expecting in any way to reconcile the two. But I am led to believe that I have in general verified the experimental results of both.

The instrument which I employed for this investigation is in its essential features a Michelson interferential refractometer. It consists (fig. 1) of two mirrors, m and m' , the latter being

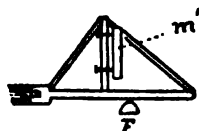
Fig. 1.



fastened to the free end of the bar B; and of two parallel plates of optical glass, P and P', the plate P' being lightly silvered on the side away from the light L.

The solenoid S contains 2100 turns of number 17 copper wire, wound in 7 layers on a glass cylinder 70 cm. long and 1.9 cm. in external diameter. The fixed end of the bar was screwed firmly to the brass tail-piece D, which in turn was both screwed and wedged in position. The free end of the bar carried the brass slide E, which carried the mirror m' . This slide, shown in cross section in fig. 2, rested very lightly on the bearings F and F'. Every precaution was taken to make this bearing as free from friction as possible. The object of the bearing was to prevent any side-motion of the mirror and at the same time deaden the vibrations which would

Fig. 2.



* Communicated by the Author.

† *Comptes Rendus*, Nov. 7, 1892.

‡ *Proc. Roy. Soc.* vol. xL

otherwise result from so long a bar, and destroy the definition of the fringes.

A telescope T was used to observe the displacement of the fringes due to the forward or the backward motion of the mirror *m'*. A motion of one wave-length produces a displacement of two fringes; so by observing in the telescope the number of fringes-displacement relative to the cross wires, it is an easy matter, knowing the wave-length of sodium light, to compute the actual expansion or contraction of the bar.

I had also at my disposal a single-thread magnetometer, the magnet being suspended by an exceedingly fine quartz fibre.

There were six different bars used in these experiments. We will hereafter refer to them by number.

No. I. was 70 cm. long, 0.952 cm. in diameter.

No. II. was 70 cm. long, 1.082 cm. in external and 0.714 cm. in internal diameter.

No. III. was 70 cm. long, 0.635 cm. in diameter.

No. IV. „ 43.5 cm. „ 0.635 cm. „

No. V. „ 19.5 cm. „ 0.635 cm. „

No. VI. „ 70 cm. „ 0.752 cm. „

With the exception of bar II., soft unannealed Norway iron was used. No. II. was a piece of ordinary wrought-iron gas-tubing. Nos. IV. and V. were made from No. III. by cutting off one end. No. VI. was made from No. I. by turning it down in diameter.

In the case of the short bars, brass rods were soldered to both ends. To make certain that brass was not at all affected by magnetic influence, I tested a brass rod and found no effect whatever.

With this instrument I found it an easy matter to measure to a tenth of a fringe, which means about $\frac{1}{1,000,000}$ of an inch.

In making these observations the only difficulty which I found at all troublesome were certain effects due to hysteresis.

The expansion due to the heating of the coil being slow in its action while the magnetic expansion was rapid, the two could be easily distinguished from each other. The object of using the glass tubing for my solenoid being to retard as much as possible the heat action, the heaviest currents used could remain on at least 5 seconds without showing any effect, then the bar would slowly begin to expand.

Mr. Shelford Bidwell, in mentioning the difficulties which he encountered, states that he found it absolutely necessary to centre the bar in the coil. He finally adopted the method of suspending the coil on one end of his bar, so that it moved with the bar. In this way the effect was entirely obviated.

I made some experiments with my instrument to ascertain whether any uncertainties entered into my observations from this cause. I found that when the centre of the bar fell even two or three centimetres from the centre of the coil, the measurements were the same as when it was centred as nearly as possible. When, however, the bar was thrown completely off from the centre, as much, for instance, as 10 or 15 centimetres, I found a slight but measurable effect amounting to about 0.2 of a fringe, or .000002 of an inch.

Early in the experiment I found that for a given magnetic field I could produce different amounts of expansion depending upon the manner in which the current had been applied—for instance, whether the full amount of the current had been turned on suddenly or, on the other hand, had been applied gradually, then again whether the current had been gradually *increased* from zero or had been *decreased* from a higher point.

Let me here mention that it was observed that the second and following contacts did not give the same expansion as the first contact; this has already been well shown by Prof. A. M. Mayer's observations.

In the following table the values dealing with the second and following contacts show some of these peculiarities quite conclusively. Column I. gives the amount of expansion in fringes, column II. the corresponding current when it was suddenly turned on at its full strength, column III. when gradually increased, and column IV. when gradually decreased from the current which produced the maximum expansion.

Bar No. I. was here used All currents were measured with a direct-reading ammeter.

| I. | II. | III. | IV. |
|------|-------|-------|------|
| 1 | 0.22 | 0.22 | |
| 2 | 0.27 | 0.27 | |
| 3 | 0.33 | 0.30 | |
| 4 | 0.37 | 0.33 | |
| 5 | 0.46 | 0.38 | 0.18 |
| 6 | 0.49 | 0.44 | 0.22 |
| 7 | 0.56 | 0.51 | 0.25 |
| 8 | 0.66 | 0.57 | 0.30 |
| 9 | 0.84 | 0.75 | 0.40 |
| 10 | 1.17 | 1.02 | 0.55 |
| 10.3 | 1.84 | 1.72 | 0.67 |
| 11.0 | | | 1.00 |

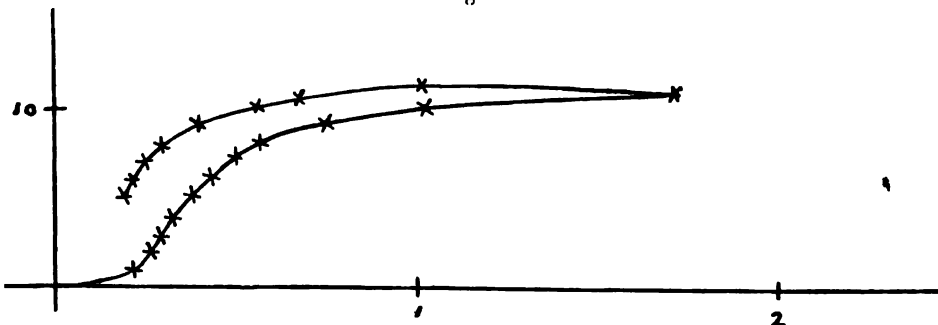
Here must be noted a peculiarity which was observed in every bar that I experimented with.

If the current be gradually increased from zero up, at a certain point we reach a maximum amount of expansion: now a further increase in current will produce a decrease from that maximum; but if, on the other hand, we gradually decrease the current, we are able to obtain a still greater expansion.

This increase in the case of soft iron is from $\cdot 05$ to $\cdot 20$ of the total amount of expansion otherwise obtained.

Mr. Bidwell has noted a peculiarity in the behaviour of a steel bar which will come under this head. At lower points in the expansion this peculiarity does not seem to exist. I have plotted (fig. 3) from the above table columns I.,

Fig. 3.



III., and IV., which give a graphical illustration of this phenomenon.

I have adopted, as the method which gives the most uniform and certain results, that of quickly but gradually *increasing* my currents (not using the first contact), counting my fringes from the zero point for my lighter currents and from the turning, or maximum, point for my heavier currents. For attaining this end I constructed a resistance out of fine platinum wire placed in water to prevent fusing, with a sliding metallic contact. By using this resistance directly, and as a shunt for the smaller currents, I have been able to have the current perfectly under control.

The following tables give the detail results for the different bars. Column I. gives the total amount of expansion in fringes. Column II. gives the corresponding currents. Column III. gives the intensity of the field computed by the

ordinary formula $4\pi nI$. Column IV. the magnetic moments computed by the formula $\frac{M}{H} = \frac{1}{2}(d^2 - d'^2 + 1/4 \frac{d'^4}{d}) \tan \alpha$.

I have adopted for my value of H , '1645, the mean of numerous observations made by Mr. B. F. Ellis, of this University, who is at present engaged upon work which involves a frequent determination of that quantity.

TABLE I.

| I. | II. | III. | IV. |
|------|------|-------|--------|
| 1 | 0.22 | 8.3 | 18890 |
| 2 | 0.27 | 10.2 | 28559 |
| 3 | 0.30 | 11.3 | 2966.0 |
| 4 | 0.33 | 12.4 | 31811 |
| 5 | 0.38 | 14.3 | 33782 |
| 6 | 0.44 | 16.6 | 37200 |
| 7 | 0.51 | 19.2 | 38700 |
| 8 | 0.57 | 21.5 | 41700 |
| 9 | 0.75 | 28.3 | 43800 |
| 10 | 1.02 | 38.5 | 46700 |
| 10.3 | 1.72 | 64.8 | 51500 |
| 9.3 | 2.46 | 92.7 | 54296 |
| 8.3 | 3.42 | 128.9 | 56839 |
| 7.3 | 4.40 | 165.0 | 59700 |
| 6.3 | 5.35 | 201.7 | 61371 |
| 5.3 | 6.20 | 233.7 | 62188 |
| 4.3 | 7.17 | 270.3 | 64671 |
| 3.3 | 8.15 | 307.3 | 65718 |
| 2.3 | 9.09 | 342.7 | |

TABLE II.

| I. | II. | III. | IV. |
|------|------|-------|-------|
| 1 | 0.18 | 6.8 | 15011 |
| 2 | 0.27 | 10.2 | 17805 |
| 3 | 0.37 | 13.9 | 18516 |
| 4 | 0.50 | 18.8 | 19936 |
| 5 | 0.68 | 25.6 | 21251 |
| 5.6 | 1.23 | 46.4 | 24375 |
| 4.6 | 2.38 | 89.7 | 26258 |
| 3.6 | 3.14 | 118.4 | 27536 |
| 2.6 | 3.94 | 148.5 | 28297 |
| 1.6 | 4.69 | 176.8 | 29087 |
| 0.6 | 5.55 | 209.2 | 29615 |
| -0.4 | 6.35 | 239.4 | 30077 |
| -1.4 | 7.18 | 270.7 | 30595 |
| -2.4 | 8.23 | 310.3 | 31169 |
| -3.4 | 9.29 | 350.2 | 31591 |

TABLE III.

| I. | I. | III. | IV. |
|-----|------|-------|-------|
| 1 | 0.18 | 6.8 | 11294 |
| 2 | 0.24 | 9.0 | 13257 |
| 3 | 0.30 | 11.3 | 17780 |
| 4 | 0.36 | 13.6 | 18422 |
| 5 | 0.47 | 17.7 | 19034 |
| 6 | 0.62 | 23.4 | 19685 |
| 7 | 0.90 | 33.9 | 21102 |
| 7.4 | 1.49 | 56.2 | 23528 |
| 6.4 | 2.63 | 99.2 | 25315 |
| 5.4 | 3.34 | 125.9 | 26453 |
| 4.4 | 4.01 | 151.2 | 27007 |
| 3.4 | 4.60 | 173.4 | 27350 |
| 2.4 | 5.27 | 198.7 | 27770 |

TABLE IV.

| I. | II. | III. | IV. |
|-----|------|-------|-------|
| 1 | 0.25 | 9.4 | 9800 |
| 2 | 0.37 | 13.9 | 10800 |
| 3 | 0.49 | 18.5 | 11700 |
| 4 | 0.60 | 22.6 | 12700 |
| 5 | 0.72 | 27.1 | 14100 |
| 6 | 1.23 | 46.4 | 14700 |
| 6.2 | 1.75 | 66.0 | 16000 |
| 5.7 | 3.35 | 126.3 | 17700 |
| 4.7 | 4.71 | 177.6 | 20900 |

TABLE V.

| I. | II. | III. | IV. |
|-----|------|-------|-------|
| 0.5 | 0.67 | 25.3 | 2500 |
| 1.0 | 0.96 | 36.2 | 3740 |
| 2.0 | 1.32 | 49.8 | 4060 |
| 2.5 | 1.89 | 71.3 | 4880 |
| 3.0 | 3.15 | 118.8 | 5310 |
| 2.5 | 5.97 | 225.1 | 10690 |

TABLE VI.

| I. | II. | III. | IV. |
|-----------------------------|------|-------|-------|
| 1 | 0.18 | 6.8 | 17750 |
| 2 | 0.28 | 9.8 | 19420 |
| 3 | 0.33 | 12.4 | 20890 |
| 4 | 0.42 | 15.8 | 22160 |
| 5 | 0.53 | 20.0 | 25390 |
| 6 | 0.67 | 25.3 | 27220 |
| 7 | 1.05 | 39.6 | 29610 |
| 7.2 | 1.65 | 62.2 | 31960 |
| 6.2 | 2.68 | 101.0 | 34250 |
| 5.2 | 3.43 | 129.3 | 34880 |
| 4.2 | 4.05 | 152.7 | 36300 |
| 3.2 | 4.70 | 177.2 | 36580 |
| 2.2 | 5.60 | 211.1 | 37240 |
| 1.2 | 6.33 | 238.6 | 37960 |
| Backward maximum. 7.8 | 0.92 | 34.7 | 28800 |

In order to determine the effect of the thickness of his bar upon the amount of expansion, Mr. Bidwell selects for the purpose three rods of 100 millim. length and 2.65, 3.65, and 6.25 millim. in diameter. He assumes that the iron in the three bars may be regarded as similar, and that the differences in the expansion are due only to their diameters. He finds that the expansion "varies inversely as the square root of the diameter" (the length remaining the same). I regret to say that my results do not in any way confirm his conclusions. Instead of finding that larger bars give less expansion than smaller bars, I find just the opposite.

At first I thought that the best way to make this test would be to take my largest bar and turn it down to successively smaller diameters. In fact, I did this with bar I. The resultant bar, which I have called No. VI., showed a falling off of the expansion from 10.3 fringes to 7.2 fringes. I found it a very difficult matter to turn so long a bar perfectly true in the lathe which I had at my disposal; and at the same time I was not certain about the effect of the strains due to the turning. Further, there was no certainty that the inside of my bar would behave in the same manner as the outside.

Taking into consideration these factors, I determined that the most feasible method of avoiding the difficulties would be

to vary the ratio between the diameter and the length, not by diminishing the diameter but by changing the length. This I did, as has already been mentioned, by taking bar III. and, after testing its expansion, cutting off a portion of it. The result is shown in Tables III., IV., and V. Lest, perchance, bar III. of less diameter be compared with bar VI., which although larger gives less expansion, I took the precaution to turn bar VI. down again until it was about the same size as No. III. As a result, the expansion was then less than 5 fringes, while bar III. gave 7.4 fringes, and this although the iron in the two bars was very nearly alike in magnetism.

The following table will show clearly that the expansion varies directly as some function of the ratio between the diameter and length, possibly the square root. Joule's bars were rectangular, and I have computed a mean diameter. His tests were confined to four bars, and I have taken the mean value of the temporary elongations in the four bars.

I have dealt entirely with the temporary elongations, or the elongation produced by the second or following contacts, because both Mr. Bidwell's observations and my own deal with these maxima.

Prof. A. M. Mayer tested six different bars, and in this case I have taken the mean value on the second contact.

Shelford Bidwell tested three bars of different diameters. I have used the mean of the two observations which he himself quotes in a comparison between his results and those formerly obtained. I have taken the mean of the diameters, and likewise the mean expansion.

Mr. Barrett's observation in 'Nature' (1882) I do not give, as he has furnished so few details of his experiment that one can form no judgment in regard to value.

Although I have quoted M. Alfonse Berget's single experiment, because the ratio in this case was exceedingly large, yet, as the length of his bar was so short, and as he tells us nothing as to whether he has given us the elongation from the first or second contact, one must feel compelled to give it little weight except for showing the main point in the discussion.

It must also be borne in mind that the iron used by different observers could of itself produce variations of as much as 25 per cent., due to a difference of permeability.

| Diameter, in millim. | Length, in millim. | Ratio of D to L. | Elongation in fraction of length. | Observer. | Magnetic field. |
|-------------------------|-----------------------|---------------------|---|-----------|--------------------|
| 12.7 | 1526.5 | .0083 | .0000019 | Mayer. | |
| 9.5 | 914.4 | .0104 | .0000028 | Joule. | |
| 7.9 | 700.0 | .0113 | .0000038 | Lochner. | 60 |
| 3.15 | 100.0 | .0315 | .0000042 | Bidwell. | 59 |
| 19.5 | 52.0 | .3750 | .0000108+ | Berget. | 540+ |
| 6.35 | 700.0 | .0090 | .0000031 | Lochner. | 56 |
| 6.35 | 435.0 | .0146 | .0000042 | Lochner. | 66 |
| 6.35 | 195.0 | .0326 | .0000045 | Lochner. | 119 |

Bars I., II., III., and VI. were all of the same length ; their respective weights were 350, 192, 160, and 217 grams.

The following table seems to indicate that the expansion varies with the magnetic moment per unit volume or mass as well as with the form of the bar.

| Bar. | Moment per grm. Field 200. | Ratio D : L. | $\sqrt{\frac{D}{L}}$ | Fringes, Maximum Expansion. |
|----------|----------------------------------|-----------------|----------------------|-----------------------------------|
| I. ... | 175.3 | .0136 | .117 | 10.3 |
| II. ... | 153.1 | .0101 | .100 | 5.6 |
| III. ... | 173.6 | .0091 | .095 | 7.4 |
| VI. ... | 170.6 | .0107 | .107 | 7.2 |

It may be stated briefly that my observations furnish the following evidence in regard to the expansion which takes place in soft iron bars :—

1st. They confirm the general form of Mr. Shelford Bidwell's curves.

2nd. They indicate that the expansion is a function of the ratio between the diameter and length, and that the elongation varies *directly* as possibly the square root of this ratio.

3rd. They further indicate that the expansion varies directly as the permeability.

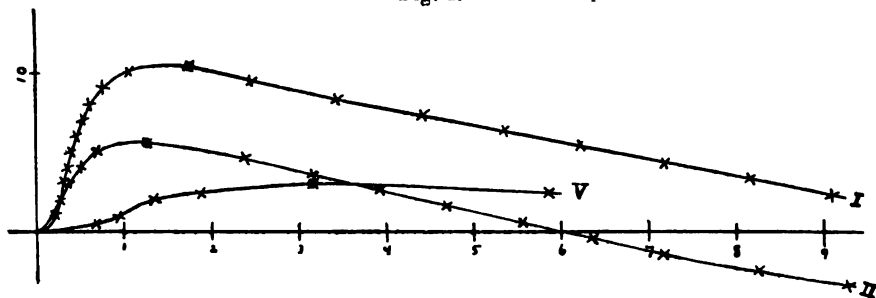
4th. That the amount of current required to produce the maximum expansion, and also the point of no expansion,

likewise depends upon the ratio between the diameter and length.

5th. That there are two maxima: one produced by increasing the current, another by decreasing the current from that point which produced the first maximum.

6th. They confirm Prof. A. M. Mayer's observations, that the first contact gives more expansion than the second and following contacts, and, further, even these seem to disagree slightly among themselves, the expansion falling off with subsequent contacts.

Fig. 4.



In fig. 4 I have plotted the expansion-curves of three of the bars which show the greatest differences.

Mr. Bidwell's curves are similar in form to those produced by bars I. and II., while M. Alfonse Berget's curve, as would be expected, agrees more closely in form with that of bar V.

The experiments were carried on in the physical laboratory of Clark University, under the direction of Prof. A. G. Webster, to whom acknowledgment should be made for frequent suggestions.

LII. *The Viscosity of Gases and Molecular Force.*

By WILLIAM SUTHERLAND*.

IT is now well known that a full acceptance of the kinetic theory of gases was suddenly accelerated by the experimental verification of Maxwell's theoretical discovery of the paradoxical independence of the coefficient of viscosity of a gas on pressure. Contrary to the general sentiment of physicists, the premisses of the kinetic theory were found to lead to the conclusion that a vibrating pendulum would be just as much hindered by gaseous friction in an environment under one twentieth of an atmo pressure as under twenty atmos, and experiment soon afterwards showed the coefficient of viscosity

* Communicated by the Author.

of gases to be actually constant down to pressures as low as one thousandth of an atmo. Naturally this confirmation gave a great stimulus to the development of the kinetic theory; and as the same equation which asserted that the viscosity of a gas is independent of its pressure also asserted it to be proportional to the square root of the absolute temperature, the experimental examination of the relation between viscosity and temperature was taken up with enthusiasm. When the first experimental difficulties had been overcome, it was proved quite clearly that with the natural gases the variation of viscosity with temperature is more rapid than was asserted by theory; instead of the relation $\eta \propto T^{\frac{1}{2}}$ it was found that $\eta \propto T^n$, where n ranges from its lowest value of about .7 for hydrogen to about 1.0 for the less perfect gases.

Maxwell, by some inaccurate experiments, was led to believe that for the perfect natural gases $\eta \propto T$, and recast the kinetic theory in a special form to bring it into harmony with this supposed fact of nature. In the original form of the kinetic theory the molecules are supposed to collide with one another as small actual spherical bodies do, only with a coefficient of restitution unity, to which actual bodies approximate but never attain. Maxwell now supposed the molecules to behave as centres of repulsive force, and deduced that if $\eta \propto T$ the centres of force must repel one another with a force inversely as the fifth power of the distance between them. But as more accurate experiments proved that η does not vary as T , the hypothesis of repulsion inversely as the fifth power had to be abandoned. It is to be remembered that Maxwell probably worked out the details of this hypothesis more for the sake of illustrating the mathematical methods to be applied to centres of force than for the actual results obtained.

The only other hypothesis which has hitherto been advanced to account for the discrepancy between theory and experiment is that of O. E. Meyer, who pointed out that if the molecules, instead of being regarded as of constant size, were supposed to shrink with increase of temperature, then the experimental results would be explained. But the great objection to this explanation was that it made the size of the molecules vary far too much with temperature: for instance, if σ is the sectional area of the sphere by which the hydrogen molecule may be supposed to be replaced, $\eta \propto T^{\frac{1}{2}}/\sigma$, that is $T^{\frac{1}{2}} \propto T^{\frac{1}{2}}/\sigma$, or the sectional area varies inversely as the fifth root of the absolute temperature. No independent confirmation of such great variability of molecular size has been given, and has been tacitly regarded as hardly possible.

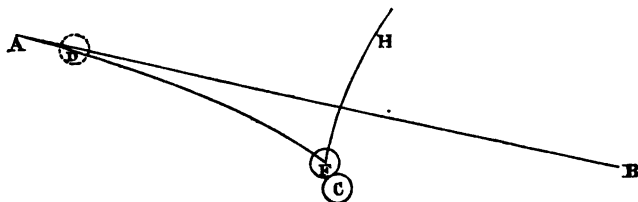
The object of the present paper is to show that the whole of the discrepancy between theory and experiment disappears if in the theory account is taken of molecular force. According to the usual presentation of the kinetic theory, the molecules are supposed to be spheres colliding with coefficient of restitution unity, molecular force is neglected because at the average distance apart of the molecules in a gas it is very small. Now molecular attraction has been proved to exist, and, though negligible at the average distance apart of molecules in a gas, it is not negligible when two molecules are passing quite close to one another, it can cause two molecules to collide which in its absence might have passed one another without collision; and the lower the velocities of the molecules, the more effective does molecular force become in bringing about collisions which would be avoided in its absence: thus molecular force cannot be neglected in investigating the relation between viscosity and molecular velocity or temperature.

Molecular force alone without collisions will not carry us far in the explanation of viscosity of gases as known to us in nature, because in all experiments on the viscosity of gases there is a solid body which either communicates to the gas motion parallel to its surface or destroys such motion, so that the molecules of the gas must collide with the molecules of the solid; for if the molecules of gas and solid act on one another only as centres of force, then each molecule of gas when it comes out of the range of the molecular force of the solid must have the same kinetic energy as when it went in, so that without collision between molecules of gas and solid there can be no communication of motion to the gas. If, then, molecules of gas and solid collide, molecules of gas must collide amongst themselves.

Of course, if this difficulty about communicating motion to a number of centres of force is ignored, then, as Maxwell does, we can proceed to trace viscosity in the gas as due to the fact that when two centres pass close to one another they deflect each other's path through an angle depending on the relative velocity and nearness of approach: thus the centres which leave the surface of a moving solid with their thermal velocities of agitation compounded with the velocity v of the solid, have the resultant velocities deflected in so haphazard a manner that at a certain distance from the solid they are uniformly distributed in all directions, and thus the energy of the velocity v is converted into heat, and there is viscous action between the successive layers of gas. And this holds whether the force be attractive or repulsive; hence we see

that in the case of molecules which do collide amongst themselves a portion of the viscosity will be due to molecular attraction on account of mutual deflection of paths experienced by those pairs of molecules which pass close to one another without actual collision.

It is thus apparent that a full mathematical theory of the viscosity of a medium composed of colliding molecules which attract one another would be a complicated affair, but to anyone familiar with the available knowledge of the size of molecules and the strength of molecular attraction, the following considerations lend themselves to simplify the problem of the viscosity of actual gases:—First, that where the average relative velocity is so low and the molecular force is so strong that it happens in a large number of cases that a pair of molecules describe closed paths relative to their centre of mass, then there must be a still larger number of cases of pairs of molecules which deflect each other's path through a large angle. In other words, deflection of paths, on account of molecular attraction and irrespective of collisions, may become an appreciable factor in viscosity in the case of vapours below their critical temperatures. Second, that where a closed path is of rare occurrence, that is, in the case of gases above the critical temperature and at no great pressure, the effect of deflection due to molecular attraction is negligible in comparison with that due to collision as a factor in the production of viscosity, except in so far as molecular attraction causes collisions to occur which would not happen in its absence. This effect of molecular force is illustrated by the figure, where AB represents the relative



path of the two spheres C and D when no molecular force is supposed to act between them, C being considered to be at rest: according to the figure no collision can occur in the absence of molecular attraction; but if molecular attraction acts a collision can occur as in the position C F, and the relative path is changed into the two curved branches AF and FH, AB being the asymptote to the branch AF, if in respect to molecular force A is practically at an infinite distance from C. It is evident that this effect of molecular

force in increasing the number of collisions is fundamental; and we will proceed to determine the number of collisions that occur amongst the molecules of a gas when molecular force is in operation, in comparison with the number when there is no molecular force. Let b be the perpendicular distance from the centre of molecule C to AB the asymptote to the relative path of the molecule D, both molecules being supposed to be spheres of radius a ; let V be the relative velocity of D when it is so far from C as to be moving almost along the asymptote, then with the usual notation for orbits under central forces $h=bV$, where h is twice the area described in unit time by the vector CD denoted by r , and $1/r$ being denoted by u .

Let $m^2F(u)$ be the molecular attraction, and $m^2f(u)$ be the mutual potential energy of two molecules of mass m at distance r apart, then the usual differential equation of the orbit is

$$\frac{d^2u}{d\theta^2} + u - \frac{mF(u)}{h^2u^2} = 0,$$

with its first integral the equation of energy,

$$\frac{1}{2}h^2 \left\{ \left(\frac{du}{d\theta} \right)^2 + u^2 \right\} = \frac{1}{2}v^2 = mf(u) + \frac{1}{2}V^2,$$

v being the velocity at any reciprocal-distance u .

Now when this orbit is such that there is no collision, we can determine the nearest distance to which the molecules approach one another (an apsidal distance) by the condition $du/d\theta=0$; denote the reciprocal of this distance by w , it is then given by

$$\frac{1}{2}h^2w^2 = mf(w) + \frac{1}{2}V^2,$$

or

$$mf(w) - \frac{1}{2}b^2V^2w^2 + \frac{1}{2}V^2 = 0.$$

Now there will be a collision if $1/w$ is less than $2a$, that is, if w is greater than $1/2a$; hence the greatest value of b for which a collision is possible is given by

$$\left. \begin{aligned} mf(1/2a) - \frac{1}{2}b^2V^2/(2a)^2 + \frac{1}{2}V^2 &= 0 \\ \text{or } b^2 &= (2a)^2 \left(1 + \frac{2mf(1/2a)}{V^2} \right) \end{aligned} \right\}, \quad \dots (1)$$

and there is a collision for every value of b from 0 up to that given by the last equation. Testing this assertion by applying it to the case when there is no molecular force, we put $mf(1/2a)=0$, and find that there is a collision for all values of b from 0 up to $2a$, which is correct. Hence, molecular force

causes the spheres to behave as regards collisions as if they were larger spheres devoid of force, the diameter-squared $(2a)^2$ being enlarged in the proportion $1 + 2mf(1/2a)/V^2 : 1$.

Hence, in the theory of viscosity as worked out for forceless molecules, we need only increase the square of the molecular sphere-diameter in this proportion to take account of molecular force. As the expression diminishes with increasing V^2 , that is with increasing temperature, we see at once why the apparent result of increasing temperature was to make the molecules shrink: increase of temperature does not make the real molecules shrink (at least to the extent imagined), but produces shrinkage of the imaginary enlarged forceless spheres which could exhibit the same viscosity as the real molecules.

So far we have considered only a typical case of two molecules: to obtain the effect of molecular force in the average case we should have to calculate, in accordance with Maxwell's law of the distribution of velocities amongst the molecules, the number of pairs that have relative velocities between V and $V + dV$ and sum for all values of V . This process can easily be carried out when necessary, but it will be quite accurate enough for our purpose to assume that the pair of molecules we have studied is an average pair, that is, a pair which has the square of the relative velocity equal to the average value of the square of the relative velocities for all the molecules; this is proportional to the mean squared velocity, and according to Maxwell's law of velocities is equal to twice it, in the usual notation $\bar{V}^2 = 2\bar{v}^2$.

Now if there are n spheres of radius a moving about in unit volume with Maxwell's distribution of velocities of which the average is \bar{v} , then the average number of collisions per second per sphere is $2^{\frac{1}{2}}n\pi a^2\bar{v}$ when the spheres are forceless; when the spheres attract one another it becomes

$$2^{\frac{1}{2}}n\pi a^2\bar{v}\left(1 + \frac{2mf(1/2a)}{V^2}\right).$$

This number is fundamental in the kinetic theory of matter, though more spoken of under another form, namely the mean free path of a sphere; accordingly we can state the highly convenient result that all the investigations of the founders and developers of the kinetic theory on the properties of gases which depend on the mean free path or mean number of collisions of forceless molecules can be applied to attracting molecules by simply replacing a^2 by $a^2 \left(1 + 2mf(1/2a)/V^2\right)$. The chief properties depending on number of collisions are

viscosity, thermal conduction, diffusion, and characteristic equation.

The coefficient of viscosity for forceless spheres with the Maxwell distribution of velocities is given by Tait (Trans. Roy. Soc. Edin. vols. xxxiii. and xxxv.) as

$$\eta = .882 \times .838 \frac{m}{3\pi(2a)^2} \left(\frac{2\bar{v}^2}{3} \right)^{\frac{1}{2}} = .064 \frac{m(\bar{v}^2)^{\frac{1}{2}}}{(2a)^2} :$$

hence when we take account of molecular force, the coefficient of viscosity is

$$\eta = \frac{.064 m (\bar{v}^2)^{\frac{1}{2}}}{(2a)^2 \left(1 + \frac{2m^2 f(1/2a)}{V^2} \right)} ;$$

but $m\bar{v}^2$ is proportional to absolute temperature ; let $m\bar{v}^2 = cT$, and therefore $mV^2 = 2cT$, then

$$\eta = \frac{.064 c^{\frac{1}{2}} m^{\frac{1}{2}} T^{\frac{1}{2}}}{(2a)^2 \left(1 + \frac{m^2 f(1/2a)}{cT} \right)} (2)$$

Now for a given substance $.064 c^{\frac{1}{2}} m^{\frac{1}{2}}$, $2a$, and $m^2 f(1/2a)/c$ remain constant ; denote $m^2 f(1/2a)/c$ by C ; and then

$$\eta \propto \frac{T^{\frac{1}{2}}}{1 + \frac{C}{T}} (3)$$

is the law of variation of viscosity with temperature in the case of gases at temperatures not below the critical, and at pressures for which the departure from Boyle's law is not great.

There is some fine experimental material for testing the above theoretical law, for Holman (Phil. Mag. 5th ser. vol. xxi.), in the light of results already obtained by O. E. Meyer, Puluj, Obermayer, and E. Wiedemann, made special measurements of great exactness of the variation of the viscosity of air and carbonic dioxide at temperatures from 0° C. to 124° and from 0° to 225° . Barus for air and hydrogen pushed the temperature range up to 1400° C. (Amer. Journ. Sc. 3rd ser. vol. cxxxv.).

If η_0 is the value of η at 0° C., then, from our equation (3),

$$\frac{\eta}{\eta_0} = \left(\frac{T}{273} \right)^{\frac{1}{2}} \frac{1 + C/273}{1 + C/T} ; (4)$$

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so that from each of Holman's values of η/η_0 we can calculate a value of C, which is now given.

| | | | | | | |
|---------------------|--------|--------|--------|--------|--------|--------|
| Temp. C. | 14° | 43° | 67·8° | 88·8° | 99·2° | 124·4° |
| η/η_0 | 1·0377 | 1·1180 | 1·1850 | 1·2411 | 1·2698 | 1·3306 |
| C | 88 | 104 | 111 | 114 | 118 | 116 |

There appears to be a tendency for the values of C to increase with the temperature-interval; but it is of no importance, because the smaller temperature-intervals are too small to give a reliable measure of C. Giving each of the values of C a weight in proportion to the temperature-interval from which it is derived, we get the mean value of C as 113. With this value of C in the theoretical equation, the following values of η/η_0 have been calculated for comparison with Holman's experimental results :—

| | | | | | | |
|---------------|-------|-------|-------|-------|-------|--------|
| Temp. C. | 14° | 43° | 67·8° | 88·8° | 99·2° | 124·4° |
| Exper. | 1·038 | 1·118 | 1·185 | 1·241 | 1·270 | 1·331 |
| Calcul. | 1·040 | 1·120 | 1·186 | 1·241 | 1·267 | 1·329 |

The agreement is within the limits of experimental error.

Barus's results for air are now given with the values of C derived from them :—

| | | | | | | | | |
|---------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| Temp. C.... | 442° | 565° | 569° | 592° | 982° | 995° | 1210° | 1216° |
| η/η_0 | 1·901 | 2·083 | 2·149 | 2·117 | 2·711 | 2·693 | 3·214 | 3·147 |
| C | 118 | 84 | 101 | 83 | 99 | 93 | 118 | 107 |

The range in the values of C is about the same as in Holman's experiments, but the mean value is less, namely 100, but in this mean the values at certain temperatures get undue weight; and seeing that the measurement of temperature is the most difficult part of the experiment, it would be fairer to take for instance the mean of 84 and 101 at 565° and 569° as 92 at 567°, and in this way to get the values 118, 92, 83, 96, 118, and 107, of which the mean is 102. But to compare theory with experiment we will retain the value 113 already found from Holman's results.

| | | | | | | | | |
|--------------|-------|-------|-------|-------|-------|-------|-------|-------|
| Temp. C.... | 442° | 565° | 569° | 592° | 982° | 995° | 1210° | 1216° |
| Exper. ... | 1·991 | 2·083 | 2·149 | 2·117 | 2·711 | 2·693 | 3·214 | 3·147 |
| Calcul. | 1·976 | 2·183 | 2·190 | 2·225 | 2·781 | 2·799 | 3·179 | 3·185 |

It is evident, from a comparison of the experimental numbers among themselves, that the agreement between theory and experiment is within the limit of experimental error in these difficult experiments, and the theoretical law is

proved to hold over the great range of temperature up to 1216° C. Barus found that his results for air could be well represented by the empirical form $\eta/\eta_0 = (T/273)^{\frac{1}{2}}$, and, further, that the results for hydrogen could be equally well represented by the same form: hence for hydrogen the value of C in our theoretical equation would from his experiments have the same value as for air, namely 113; and the theoretical law applies to hydrogen as well as to air up to high temperatures.

Holman's experiments on carbonic dioxide furnish a still better test of the theory. Here are his values of η/η_0 at the given temperatures with the values of C calculated therefrom:—

| | | | | | | |
|----------------------------|-------|-------|-------|-------|--------|--------|
| Temp. C. | 18° | 41° | 59° | 79.5° | 100.2° | 119.4° |
| η/η_0 exper. | 1.068 | 1.146 | 1.213 | 1.285 | 1.351 | 1.415 |
| C. | 315 | 265 | 236 | 292 | 277 | 274 |
| η/η_0 calcul. | 1.066 | 1.148 | 1.211 | 1.280 | 1.351 | 1.414 |

| | | | | |
|----------------------------|-------|-------|-------|-------|
| Temp. C. | 142° | 158° | 181° | 224° |
| η/η_0 exper. | 1.484 | 1.537 | 1.619 | 1.747 |
| C. | 266 | 270 | 284 | 279 |
| η/η_0 calcul. | 1.490 | 1.541 | 1.614 | 1.746 |

Giving each value of C a weight proportional to the temperature-interval from which it is found, we get the mean value $C=277$, with which the calculated values of η/η_0 in the last table were obtained. The agreement between the experimental and calculated numbers is again within the limits of experimental error.

The law of the connexion of viscosity and temperature being thus established, we can now examine some important consequences of the theoretical formula (2),

$$\eta = \frac{.064c^{\frac{1}{2}}m^{\frac{1}{2}}T^{\frac{1}{2}}}{(2a)^2 \left(1 + \frac{m^2 f(1/2a)}{cT}\right)}.$$

The value of C, that is of $m^2 f(1/2a)/c$, is proportional to the potential energy $m^2 f(1/2a)$ of two molecules in contact, and it is therefore desirable to obtain values of C for as many substances as possible; and as C is a function of 2a it will be advantageous to use the values of C to calculate relative values of 2a for different substances by means of the above formula, so that we may be in possession of relative values of the diameters of molecules and of the mutual potential energy of two molecules whose centres are at the distance apart of a diameter. The equation of the kinetic theory of forceless molecules, $\eta \propto m^{\frac{1}{2}}T^{\frac{1}{2}}/(2a)^2$, was applied by

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Naumann and L. Meyer (*Lieb. Ann. Suppl. Bd. v. p. 253*, and *Phil. Mag.* 1867, xxxiv. p. 551) to the calculation of the relative sizes of molecules, and with considerable success; but when the same method was applied to vapours of liquids, certain discrepancies arose which have caused this method of inquiry as to molecular size to come to a standstill. We can now see that the reason for these discrepancies lies in the fact that the form of relation for the viscosity of vapours is different from that for gases, and also in the fact that with gases also inaccuracies are introduced by ignoring molecular force in the factor $1 + C/T$ by which it expresses itself.

The published data from which values of C for other substances can be obtained are those of Obermayer (*Sitz. Akad. Wien*, lxxiii.) on the variation of viscosity with temperature; the following values are calculated from his results.

Values of C .

| N_2 | O_2 | CO. | C_2H_4 | N_2O |
|-------|-------|-----|----------|--------|
| 84 | 127 | 100 | 272 | 260 |

The mean value of C for hydrogen from Obermayer's experiments with different capillary tubes comes out 79, ranging from 88 to 69, which is much smaller than the value given by Barus's experiments, namely 113, the same value as for air; but it is to be remembered that the viscosity of hydrogen is a difficult physical constant to measure on account of the large effect of impurities, and moreover in Barus's experiments at very high temperatures the hydrogen began to pass through the walls of the platinum capillary tube, and it is possible that a slight similar action at lower temperatures might interfere with the apparent variation of viscosity with temperature. As Barus's experiments were carried out with a different object from that of getting the best value of a constant for pure hydrogen, it is probable that Obermayer's value, though derived from a temperature-interval of only 40° , is more nearly the value for pure hydrogen. For nitrogen the value 84, obtained from Obermayer's experiments, is too different from the value 113 for air to be quite satisfactory; so that I think it is better to derive the value for nitrogen from those for air and oxygen, thus $C_{4/5} + 127/5 = 113$, whence $C = 109$.

In the case of C_2H_4 and N_2O , the values of the viscosity found by Obermayer at -21° have been excluded in the calculation of C as coming from a region too near the vaporous.

To get relative values of $(2a)^2$ for the substances for which we know C and η_0 , we may write our relation (2) thus

$$(2a)^2 = \frac{0.064 (273 \text{ cm})^{\frac{1}{2}}}{\eta_0 (1 + C/273)} = \frac{k m^{\frac{1}{2}}}{\eta_0 (1 + C/273)},$$

where k is the same for all bodies. As we do not know the actual masses m , but only the molecular mass M compared to that of the hydrogen atom, we will take

$$M^{\frac{1}{2}} / \{10^2 \eta_0 (1 + C/273)\}$$

as giving relative values of the square of molecular diameters. Subjoined are the data and the results calculated from them; the values of η_0 are those given by Obermayer, and the numbers given as $(2a)^2$ (relative) are the values of

$$M^{\frac{1}{2}} / \{10^2 \eta_0 (1 + C/273)\}.$$

| | H ₂ . | N ₂ . | O ₂ . | CO. | CO ₂ . | N ₂ O. | C ₂ H ₄ . |
|---------------------------|------------------|------------------|------------------|------|-------------------|-------------------|---------------------------------|
| $10^6 \eta_0$ | 86 | 166 | 187 | 162 | 138 | 135 | 92 |
| M | 2 | 28 | 32 | 28 | 44 | 44 | 28 |
| C | 79 | 109 | 127 | 100 | 277 | 260 | 272 |
| $(2a)^2$ (relative) | 127 | 228 | 206 | 239 | 239 | 261 | 288 |
| $(2a)^3$ (relative) | 1440 | 3440 | 2963 | 3698 | 3686 | 4230 | 4884 |

Now in the characteristic equations given in my paper on the "Laws of Molecular Force" (Phil. Mag. March 1893), there is a limiting volume in the liquid state denoted by β and values of β are given for a gramme of each of the above substances except CO, so that multiplying them by the molecular masses (weights) we get numbers giving other relative values of the volumes of the molecules which should stand in a constant ratio to those already tabulated as $(2a)^3$ (relative). The following are the values of $M\beta$ and the ratio of $(2a)^3$ (relative) to $M\beta$:—

| | H ₂ . | N ₂ . | O ₂ . | CO ₂ . | N ₂ O. | C ₂ H ₄ . |
|--------------------------------|------------------|------------------|------------------|-------------------|-------------------|---------------------------------|
| $M\beta$ | 8.6 | 22.7 | 19.3 | 30.3 | 29.0 | 42.8 |
| $(2a)^3$ (relative) / $M\beta$ | 167 | 153 | 153 | 121 | 137 | 114 |

The value of the ratio is larger for the elements than for the compounds; but considering that $M\beta$ ranges from 8.6 to 42.8, the ratio approaches near enough to constancy to show that the theory is right in its essentials, while it is possible that departure of shape of molecules from the assumed spherical form will have to be taken account of

before perfect constancy can be attained in the ratio just considered.

But fortunately we can test our theory in a more complete manner in another direction, namely, in that of the values of C which are proportional to the potential energy of two molecules in contact. Now, if the law of molecular force is that discussed by me in various papers, namely, that of the inverse fourth power, or, if the force between two molecules of mass m at distance r apart is $3Am^2/r^4$, where A is a constant characteristic of each substance, then $m^2f(1/r)$ becomes Am^2/r^3 , and C or $m^2f(1/2a)/c$ becomes $Am^2/(2a)^3c$, so that $(2a)^3 C$ is proportional to Am^2 .

In the characteristic equations alluded to (Phil. Mag. March 1893) there is a term representing the virial of the attractions of the molecules, which by definition is $\frac{1}{2} \cdot \frac{1}{2} \sum \sum 3Am^2/r^3$, where the summations are extended to all the molecules in unit mass, and this is shown to be proportional to $3A\pi\rho$ where ρ is the density; when this is written in the form $l\rho$, l is called the virial constant and is proportional to $3A$, and as values of M^2l have been tabulated for a large number of substances ("Laws of Molecular Force," Phil. Mag. March 1893), we can use them for relative values of Am^2 . If, then, the law of molecular force is that of the inverse fourth power, the ratio of the values of $(2a)^3 C$, from this paper, to the values of M^2l , from that paper, must be constant. As $M\beta$ has been seen to be approximately proportional to $(2a)^3$, and there are means of getting its value for substances for which $(2a)^3$ cannot at present be found, we will use $M\beta$ in place of $(2a)^3$, and study the relation of $M\beta C$ to M^2l . The following table contains the values of $M\beta C$, M^2l , and the ratio $M\beta C/M^2l$:

| | H ₂ . | N ₂ . | O ₂ . | CO ₂ . | N ₂ O. | C ₂ H ₄ . |
|--------------------------|------------------|------------------|------------------|-------------------|-------------------|---------------------------------|
| $M\beta C/10$ | 67.9 | 247 | 245 | 839 | 755 | 1167 |
| M^2l | .22 | 1.23 | 1.16 | 7.1 | 8.8 | 6.5 |
| $M\beta C/10^2 M^2l$... | 31 | 20 | 21 | 12 | 8.6 | 18 |

The values of the ratio as they stand do not look promising, but in the paper on the "Laws of Molecular Force" it is shown that while in the elements l retains its value from the gaseous to the liquid state, in most compounds it attains in the liquid a value one half of the limiting value in the gas, and CO₂ and N₂O conform to this, while in the case of ethylene, which is peculiar, l falls in the liquid to $4.15/5.79$ of its value in the gas, that is to $.7166l$. If, then, we use the values of M^2l which hold in the above substances as liquids,

we get the following values of the above ratios:—

31 20 21 24 17 25

Excepting in the case of hydrogen, where through experimental difficulties the value of C is uncertain, the values of the ratio now show a satisfactory approach to constancy if all the difficulties of the comparison are allowed for, and they furnish satisfactory confirmation of the truth of the inverse fourth power law of force. In view of the importance of this confirmation, it will be well to extend it to as many substances as possible, and although we have exhausted the direct experimental determinations of C , there is an indirect method of obtaining some more by means of the results already established.

For CO_2 , N_2O , and C_2H_4 , $(2a)^3(\text{relative})/M\beta$ has the values 121, 137, and 114, of which the mean is 124; and assuming this to be the value for all compounds, we can obtain from the values of β and M the values of $(2a)^3(\text{relative})$, then those of $(2a)^2(\text{relative})$ which stands for

$$M^{\frac{1}{2}}/\{10^2\eta_0(1+C/273)\},$$

so that with values of η_0 it is possible to calculate those of C . The following are the data for the gases CH_4 , NH_3 , and SO_2 , the values of η_0 being those given by Obermayer from Graham's transpiration experiments.

| | CH_4 . | NH_3 . | SO_2 . |
|---------------------------------|-----------------|-----------------|-----------------|
| β | 1.59 | 1.22 | .55 |
| M | 16 | 17 | 64 |
| $M\beta$ | 25.4 | 20.7 | 35.2 |
| $(2a)^3(\text{relative})$ | 215 | 188 | 267 |
| $10^2\eta_0$.. | 104 | 96 | 122 |
| C | 215 | 352 | 397 |

As before, we can compare $M\beta C$ and $M^{\frac{1}{2}}$:

| | CH_4 . | NH_3 . | SO_2 . |
|---------------------------------------|-----------------|-----------------|-----------------|
| $M\beta C/10$ | 547 | 729 | 1399 |
| $M^{\frac{1}{2}}$ | 2.2 | 8.5 | 15 |
| $M\beta C/10^2 M^{\frac{1}{2}}$ | 25 | 8.6 | 9.3 |

As before, we must double the value of the ratio for the compounds NH_3 and SO_2 , but not for CH_4 , because I have shown its characteristic equation to be of the same form as

that for the elements which have an unchanging virial constant; thus we get the numbers

25

17

19

in agreement with the previous series of ratios. The fact that here CH_4 behaves as an element gas is noteworthy.

Exact values of β are at present lacking for other gases, but sufficiently exact ones for the present comparison can be got by reducing the volume of a gramme of the gas when liquefied at its boiling-point under one atmo in the ratio .64, and thus we get:—

| | Cl_2 | HCl | H_2S | C_2N_2 |
|---------------------------------|---------------|--------------|----------------------|------------------------|
| β | .48 | .75 | .70 | .73 |
| M | 70.8 | 36.4 | 34.0 | 52.0 |
| $M\beta$ | 33.6 | 27.1 | 23.9 | 38.2 |
| $(2a)^2(\text{relative})$ | 259 | 224 | 206 | 282 |
| $10^6\eta_0$ | 129 | 138 | 115 | 95 |
| C | 410 | 256 | 395 | 461 |

With these values we get:—

| | Cl_2 | HCl | H_2S | C_2N_2 |
|---------------------------|---------------|--------------|----------------------|------------------------|
| $M\beta C/10$ | 1377 | 695 | 944 | 1762 |
| M^2 | 5.8 | 7.9 | 10.5 | 17.7 |
| $M\beta C/10^2 M^2$ | 24.0 | 8.8 | 9.0 | 10.0 |

Here, again, the ratio for the element chlorine is about what it ought to be, while for the compounds it is about half of what it is for elements; doubling its value for compounds we get the values 24, 17, 20, which again harmonize with the previous values, the complete series being

31 20 21 24 17 25 25 17 19 24 17 18 20: Mean 21.

Thus of the available data there is not one at variance with the theory, while the distinction between the elements with methane on the one hand and compounds on the other, which was drawn in the study of characteristic equations, is borne out here. In the paper on the "Laws of Molecular Force" it was suggested that the difference in characteristic equations between compounds and elements is due to molecular pairing in compounds, all the molecules being in pairs in the liquid state, but in the gaseous state only a certain portion of them depending on the volume occupied. Now in considering viscosity we seem to have taken no account of such a phenomenon as that of pairing, but we have found that the

mutual potential energy of two compound molecules in contact in the gaseous state is affected in the same way as the virial (or potential energy) of all the molecules when brought close to one another in the liquid state. With our present knowledge the simplest explanation of this fact is got by supposing that in a compound gas each collision of two molecules is of the nature of a brief pairing with formation of a temporary bimolecule, rearrangement of atomic energy, and alteration of constant of mutual energy, all in a reversible manner when the molecules can get out of one another's influence, as in a gas, but not reversible in the limited free range of a molecule in a liquid. Thus, as in the theory of viscosity we have been dealing only with the mutual potential energy of two molecules in contact, the possibility of pairing in this manner has not been excluded. In connexion with a more complete testing of the theory of this paper, it may be pointed out that approximate values of C have been given on theoretical grounds for CH_4 , NH_3 , SO_2 , Cl_2 , HCl , H_2S , and C_2N_2 , the experimental determination of which would supply a further check on the sufficiency of the theory.

Although it is not proposed to deal fully in this paper with the viscosity of vapours, still, as the cause of a difference in the cases of gases and vapours has been pointed out, it may be as well to indicate what is the degree of importance of that cause, namely the deflexion of molecular paths produced by molecular attraction without the occurrence of actual collisions. The best way to do this will be to calculate the part of the viscosity of vapours due to collisions, and compare it with the total viscosity found by experiment. Determinations of viscosity have been made for the following substances:—Ethyl chloride by Obermayer, with the capillary-tube method (*Sitzb. Akad. Wien*, lxxiii.); ethyl oxide, ethyl alcohol, steam, benzene, acetone, chloroform, and carbon disulphide, by Puluji, with the vibration method (*ibid.* lxxviii.); and a number of esters by O. Schumann by the vibration method (*Wied. Ann.* xxiii.). A still greater number of esters had been previously examined by L. Meyer and O. Schumann with the capillary-tube method (*Wied. Ann.* xiii.), with results which brought out the viscosities much larger than they were afterwards found by Schumann with the vibration method; and as the reason for the discrepancy has not been demonstrated (though we can see on theoretical grounds that it is probably due to the use of pressures too near that of saturation), we will not use these doubtful data.

The viscosity of any substance as a gas at any temperature

is given by the formulæ

$$(2a)^2(\text{relative}) = \frac{M^{\frac{1}{2}}}{10^2 \eta_0 (1 + C/273)},$$

$$\eta/\eta_0 = (T/273)^{\frac{1}{2}} \frac{1 + \frac{C}{273}}{1 + \frac{C}{T}},$$

and we have seen that for compounds

$$(2a)^3(\text{relative}) = 124 M\beta \quad \text{and} \quad M\beta C 10^{-2} = 21 M^{\frac{1}{2}}/2;$$

so that with values of β and $M^{\frac{1}{2}}$ we can calculate the viscosities of substances as gases. Values of $M^{\frac{1}{2}}$ are tabulated (Phil. Mag. March 1893), and the method of calculating them from chemical composition is also given, and values of β , the limiting volume of a gramme of the above substances, are calculable from existing data by means of the characteristic equation for liquids given in the same paper, or by a much simplified unpublished equation which gives the same values to the degree of accuracy required for the present purpose. Here are the values of M , $M\beta$, and $M^{\frac{1}{2}}$ for the above substances:—

| | C_2H_5Cl | $(C_2H_5)_2O$ | C_2H_5OH | H_2O | C_6H_6 | $(CH_3)_2CO$ |
|-------------------------|------------|---------------|------------|-----------|----------|--------------|
| M | 64.4 | 74 | 46 | 18 | 78 | 58 |
| $M\beta$ | 55.5 | 82.1 | 46 (near) | 16 (near) | 75.5 | 56 (near) |
| $M^{\frac{1}{2}}$ | 27.4 | 40.2 | 17.6 | 6.8 | 43.8 | 31.1 |

| | $CHCl_3$ | CS_2 | Methyl formate. | Propyl acetate. | Methyl isobutyrate. | Ethyl propionate. |
|-------------------------|----------|--------|-----------------|-----------------|---------------------|-------------------|
| M | 119.2 | 76 | 60 | 102 | 102 | 102 |
| $M\beta$ | 72 | 50 | 46 | 97 | 97 | 97 |
| $M^{\frac{1}{2}}$ | 36.9 | 26.9 | 22.9 | 58.5 | 58.5 | 58.5 |

With these the following values of the viscosity at $0^\circ C$., due to collisions only, have been calculated, and will be denoted by H_0 to distinguish them from η_0 , the total viscosity of the vapour.

| | C_2H_5Cl | $(C_2H_5)_2O$ | C_2H_5OH | H_2O | C_6H_6 | $(CH_3)_2CO$ |
|-----------|------------|---------------|-----------------|-----------------|---------------------|-------------------|
| H_0 ... | 76.6 | 63.5 | 92 | 102 | 61.7 | 65.6 |
| | $CHCl_3$ | CS_2 | Methyl formate. | Propyl acetate. | Methyl isobutyrate. | Ethyl propionate. |
| H_0 ... | 85.5 | 84.3 | 83.4 | 58.1 | 58.1 | 58.1 |

With these values the part of the viscosity due to collisions

only (to be denoted by H) at any temperature can be calculated by the formula (4) above, where the symbol H is represented by η .

In the following table t denotes temperature C. and η is the viscosity of the vapour found by experiment at that temperature, while H is the part of the viscosity calculated as due to collisions, and then the difference between the two expressed as percentage of the calculated numbers is denoted by diff. %.

| (C ₂ H ₅) ₂ O. | | | | | | | |
|--|-----------------|-------------------|-----------------------------------|---|-------|-------|------|
| <i>t</i> | 7.2 | 10 | 15.5 | 18.9 | 25.8 | 31.4 | 36.5 |
| η | 71.2 | 71.6 | 73.2 | 73.5 | 75.5 | 77.1 | 79.3 |
| H | 65.5 | 66.2 | 67.7 | 68.6 | 70.3 | 71.9 | 73.3 |
| Diff. %. | 9 | 8 | 8 | 7 | 7 | 7 | 8 |
| C ₂ H ₅ Cl. | | | | | | | |
| <i>t</i> | 16.4 | 53.5 | 157 | C ₂ H ₅ . (CH ₃) ₂ CO. CHCl ₃ . | | | |
| η | 94.1 | 105.8 | 144.0 | 17 | 17 | 17 | |
| H | 81.7 | 93.8 | 126.7 | 76 | 78 | 103 | |
| Diff. %. | 15 | 13 | 14 | 66.2 | 71 | 92 | |
| Methyl formate. | | | | | | | |
| <i>t</i> | CS ₂ | H ₂ O. | C ₂ H ₅ OH. | 20 | 100 | | |
| η | 17 | 17 | 17 | 92.3 | 135.2 | | |
| H | 99 | 97 | 88.5 | 90.8 | 119.0 | | |
| Diff. %. | 90 | 109 | 98.2 | 2 | 13 | | |
| Propyl acetate. | | | | | | | |
| <i>t</i> | 15 | 77.8 | 100 | Methyl isobutyrate. | | | |
| η | 74.3 | 95.4 | 109.6 | 24 | 65.5 | 100 | |
| H | 62.0 | 77.8 | 83.6 | 75.4 | 99.9 | 112.2 | |
| Diff. %. | 20 | 23 | 31 | 64.3 | 74.5 | 83.6 | |

The comparison, except in the case of water and alcohol, establishes the theoretical provision that the viscosity of a vapour is greater than that due to the collisions of its molecules, and water and alcohol have been proved to be exceptional as regards molecular force, both as vapours and liquids, so that we have no right to expect them to be otherwise than exceptional here; indeed, we see here another opening towards the elucidation of the exceptional nature of these substances.

Excepting the esters, we can say that at ordinary temperatures the part of viscosity due to deflexion of paths by molecular attraction without collision is between 8 and 16 per

cent. of that due to collisions; with rising temperature and diminishing pressure, that is with nearer approach to the gaseous state, this difference ought to diminish towards 0 as a limit; in the case of the esters the reverse of this appears to hold, but the experiments are perhaps at fault. For the complete elucidation of this part of the subject further experiments are required, in which the various values of the viscosity of a substance are followed from the one limit when it is a gas to other limits when it is a saturated vapour. The theoretical investigation of this part of the subject would not be difficult, though it might be tedious, and not very interesting unless hand in hand with experiment.

The other main properties of a gas besides viscosity which depend on the molecular free path or number of collisions are the coefficient of diffusion into other gases, the thermal conductivity and the characteristic equation, in all of which molecular attraction plays as fundamental a part as in viscosity, and in the theory of which molecular attraction can be taken account of on the same simple principle as has been applied to viscosity, namely, imagine the molecular spheres to have their sections increased in the proportion $(1 + C/T) : 1$, and then proceed with the theory of them as if they were forceless.

The difficulties that confront us in diffusion and conductivity arise entirely from the fact that the theory of these phenomena, even for forceless molecules, is incomplete; in the case of diffusion chiefly on account of mathematical difficulties, and in that of conductivity because it is not known what provision there is for the transmission of other forms of molecular kinetic energy besides that of translatory motion. However, this much may be said in general terms, that experiment has shown that if theory and experiment were brought into harmony for viscosity they would be in as good harmony for diffusion and conductivity as could be expected in the confessedly incomplete state of theory. In the case of diffusion the question is still further complicated by the fact that we have to deal with the attractions of unlike molecules, a subject which will yet become of great importance, but too large to open in this paper, so it must suffice to repeat that, assuming the attractions of unlike molecules to be of about the same strength as those of like, then the experiments of Loschmidt and Obermayer show that when the temperature-variation of viscosity is correctly explained by theory the temperature-variation of diffusion must also be correctly accounted for. A complete theoretical discussion of diffusion would come in more naturally in connexion with a general

investigation of the properties of mixed gases (viscosity, conductivity, and characteristic equation), where the attraction of unlike molecules would be an essential element in the question. The experimental investigation of the properties of mixed gases could also be extended with advantage.

With regard to conduction, the kinetic theory of forceless, smooth, spherical molecules leads to the result that in a first approximation the thermal conductivity $k = \cdot 826 \eta m \bar{v}_0^2 / m T_0$, where $m \bar{v}_0^2 / 2$ is the mean kinetic energy of a molecule of mass m at temperature T_0 . But if in order to come nearer to what must be the conditions of conduction in natural gases, we assume that the natural molecules transmit the whole of their molecular kinetic energy in the same proportion as they would transmit their translatory kinetic energy if they were smooth spheres, then $k = \cdot 826 \eta c$, where c is the specific heat of the gas at constant pressure. According to this formula the effect of molecular force on conductivity is found by putting for η the value obtained when molecular force is allowed for. The temperature-variation of the conductivity of only three gases has been thoroughly investigated, namely of air, hydrogen, and CO_2 . The temperature-variation of c for air and hydrogen is so small that within ordinary temperature-ranges it can be neglected, but for CO_2 c_{100}/c_0 according to E. Wiedemann is 1.11, and according to Regnault 1.147. For these three gases the theoretical ratio of the conductivities at 100°C . and 0°C . is calculable according to the relation

$$\frac{k_{100}}{k_0} = \frac{c_{100}}{c_0} \frac{\eta_{100}}{\eta_0} = \frac{c_{100}}{c_0} \left(\frac{373}{273} \right)^{\frac{1}{2}} \frac{1 + C/273}{1 + C/373}$$

using for each the appropriate value of C already found, namely 113 for air, 79 for hydrogen, and 277 for CO_2 , with which we get :—

| Authority. | Date. | Air. | Hydrogen. | CO_2 . |
|----------------------|-------|-------|-----------|-----------------|
| Theory | 1893 | 1.268 | 1.243 | 1.50 or 1.55 |
| Winkelmänn | 1876 | 1.277 | 1.277 | 1.50 |
| Graetz | 1881 | 1.185 | 1.160 | 1.22 |
| Winkelmänn | 1883 | 1.208 | 1.208 | 1.38 |
| Winkelmänn | 1886 | 1.206 | 1.206 | 1.366 |
| Schleiermacher | 1888 | 1.289 | 1.275 | 1.548 |
| Richborn | 1890 | 1.199 | 1.199 | 1.367 |
| Winkelmänn | 1891 | 1.190 | 1.175 | 1.401 |

It will be noticed that the theoretical numbers agree best with Winkelmänn's determinations of 1876 and with Schleiermacher's ; but Winkelmänn, returning with great devotion to these difficult measurements, obtains persistently smaller

results, and if the experimental difficulties were not so great, we should be led to the conclusion that the theory is inadequate; but the variation of the individual numbers from which these means are derived is so great that we cannot yet accept so definite a conclusion.

Schleiermacher's results are obtained by a special and apparently very appropriate method, namely that of measuring the heat conducted through a gaseous envelope from a wire heated by an electric current, and yet his values of k_{100}/k_0 range from 1.256 to 1.318 for air, from 1.200 to 1.315 for hydrogen, and from 1.485 to 1.584 for CO_2 , and the separate measurements of other experimenters vary in the same manner. Under the circumstances of the case all that we can say is that when molecular force is taken account of in the theory of the conductivity of gases, the theoretical variation of conductivity with temperature is brought within the range of present experimental determinations in a manner which is not possible when molecular force is ignored. The direction in which further experimental work is desirable is that of testing for other compound gases where c is largely variable with temperature, whether $k \propto cT^{1/2}/(1 + C/T)$.

The whole theory of the conduction of heat in gases awaits development; it has been touched on here in only one aspect, namely that of its dependence on molecular force.

The last property of a gas which we shall take as being affected by molecular force in a manner hitherto ignored is its characteristic equation. I have shown (Phil. Mag., March 1893) that the equation of Van der Waals applies only to the element gases and methane and not to compounds; but if it only applied to a single substance it would still be of great interest in relation to the kinetic theory. In the theoretical deduction which Van der Waals gave of his characteristic equation $(p + a/v^2)(v - b) = RT$ the number of encounters of a molecule was shown to have the important effect of introducing the constant b into the equation, b being (when molecular force is ignored as affecting the number of collisions) equal to four times the volumes of all the sphere-molecules in volume v ; but when the influence of molecular force on the number of collisions is allowed for, then b can no longer be regarded as a constant equal to four times the volumes of the molecules, and the theoretical form of the characteristic equation of gases is rather profoundly affected.

In tracing this effect of molecular force it will be most convenient to reproduce the essentials of Tait's method of presenting the establishment of the characteristic equation for forceless molecules (Trans. Roy. Soc. Edinb. xxxiii. and

xxxv.) and introduce the necessary modifications for attracting molecules.

The starting-point is Clausius's equation of the Virial,

$$\frac{3}{2}pv = \Sigma \frac{1}{2}mv^2 - \frac{1}{2} \cdot \frac{1}{2} \Sigma \Sigma Rr,$$

where R is the force acting between two molecules at distance r apart. Now the forces R consist of two sets, first the continuously acting attractions to be denoted by R_a , and second, the discontinuous repulsions that act during the collision of two molecules to be denoted by R_b , thus

$$\Sigma \Sigma Rr = \Sigma \Sigma R_a r - \Sigma \Sigma R_b r.$$

Of the actual values of R_b we know nothing, but if ν is the number of encounters of a molecule in a second and μ is the average momentum communicated to a molecule in an encounter, then we can treat the virial of the unknown impulsive forces as equivalent to that of an average continuous force of repulsion $\mu\nu$ acting at points $2a$ apart (the distance of two centres at collision), so that $\Sigma \Sigma R_b r$ becomes $\Sigma 2a\mu\nu$. The value of μ for forceless spheres is $m(\pi\bar{v}^2/3)^{\frac{1}{2}}$.

When molecular attraction acts, the molecules at the instant of collision have on the average a relative velocity greater than that which rules amongst molecules that are remote from one another's influence; calling it V_* , then

$$\frac{1}{2}mV_*^2 = \frac{1}{2}mV^2 + m^2f(1/2a) - m^2f(1/D),$$

where D is the distance apart of molecules remote from one another's influence, so that $m^2f(1/D)$ can be neglected, and then

$$V_* = \{V^2 + 2mf(1/2a)\}^{\frac{1}{2}} = V\{1 + 2mf(1/2a)/V^2\}^{\frac{1}{2}}.$$

Thus, then, for attracting molecules the value of μ is got by supposing the velocities of forceless molecules increased in the ratio $\{1 + mf(1/2a)/\bar{v}^2\}^{\frac{1}{2}}$. The value of ν for N forceless molecules in volume B when the diameter of a molecule is so small that it can be neglected in comparison to the mean free path is $2\frac{N}{B}\pi(2a)^2(4\bar{v}^2/3\pi)^{\frac{1}{2}}$. But when the diameter $2a$ cannot be so neglected this must be increased in the ratio $1 : 1 - \frac{2}{3}\frac{N}{B}\pi(2a)^3$, so that

$$\nu = 2\frac{N}{B}\pi(2a)^2(4\bar{v}^2/3\pi)^{\frac{1}{2}} / \{1 - \frac{2}{3}\frac{N}{B}\pi(2a)^3\};$$

hence for forceless molecules,

$$\frac{1}{2} \cdot \frac{1}{2} \Sigma \Sigma R_b r = \Sigma \frac{\pi N m (2a)^2 \bar{v}^2 / 3B}{1 - \frac{2}{3} N \pi (2a)^3 / 3B} = m \frac{\bar{v}^2 N}{2B} \frac{b}{1 - b/B},$$

where b is four times the volume of the N spheres ; with the usual notation of v for B the volume, the last expression becomes

$$\frac{1}{2} \cdot \frac{1}{2} \Sigma \Sigma R_i r = N \frac{\bar{mv}^2}{2} \frac{b}{v-b}.$$

We have now to take up the evaluation of ν for attracting molecules. In the first place, if we neglect molecular diameter compared to free path and also neglect curvature of path and acceleration of velocity due to molecular force, then the number of encounters per second of each of N molecules in volume B is obtained, according to our principle, from that given for forceless molecules by increasing $(2a)^2$ to $(2a)^2(1 + mf(1/2a)/\bar{v}^2)$. But it may not appear legitimate to neglect curvature of path and acceleration of velocity due to molecular force, even although they tend to neutralize one another, so we will prove them to be practically negligible in determining the average time taken by a molecule starting with relative velocity V from distance D to reach distance $2a$ from the centre of attraction. Neglecting $m^2f(1/D)$, $v^2 = V^2 + 2mf(1/r)$ gives the velocity v at distance r ; but

$$v^2 = \left(\frac{ds}{dt}\right)^2 = \left(\frac{dr}{dt}\right)^2 + r^2 \left(\frac{d\theta}{dt}\right)^2,$$

and with the usual notation for orbital motion,

$$r^2 \frac{d\theta}{dt} = h = Vb,$$

b being the perpendicular from the centre of attraction on the asymptote to the orbit ; hence

$$\begin{aligned} \frac{dr}{dt} &= \left(V^2 + 2mf(1/r) - \frac{V^2 b^2}{r^2} \right)^{\frac{1}{2}}; \\ t &= \int_{2a}^D \frac{dr}{V \left(1 + \frac{2mf(1/r)}{V^2} - \frac{b^2}{r^2} \right)^{\frac{1}{2}}}. \end{aligned}$$

Now in the case of molecules collisions occur for all values of b from 0 up to $2a(1 + 2mf(1/2a)/V^2)^{\frac{1}{2}}$, to be denoted by b' ; hence the average value of t under these conditions is

$$\bar{t} = \frac{1}{\pi b'^2} \int_0^{b'} 2\pi b db \int_{2a}^D \frac{dr}{V \left(1 + \frac{2mf(1/r)}{V^2} - \frac{b^2}{r^2} \right)^{\frac{1}{2}}}.$$

Integrating first with respect to b , we get

$$\begin{aligned} \bar{t} &= \frac{2}{V^2 \sqrt{V}} \int_{2a}^D r^2 dr \left[\{1 + 2mf(1/r)/V^2\}^{\frac{1}{2}} - \{1 + 2mf(1/r)/V^2 - b^2/r^2\}^{\frac{1}{2}} \right] \\ &= \frac{2}{V^2 \sqrt{V}} \int_{2a}^D \frac{r^2 dr \, b^2/r^2}{\{1 + 2mf(1/r)/V^2\}^{\frac{1}{2}} + \{1 + 2mf(1/r)/V^2 - b^2/r^2\}^{\frac{1}{2}}} \\ &= \frac{D-2a}{V} + \frac{2a}{V} \int_{2a}^D \frac{dr}{2a} \left[\frac{1}{\{1 + 2mf(1/r)/V^2\}^{\frac{1}{2}} + \{1 + 2mf(1/r)/V^2 - b^2/r^2\}^{\frac{1}{2}}} - \frac{1}{2} \right]. \end{aligned}$$

We could proceed no farther without a knowledge of the law of force, but if it is that of the inverse fourth power,

$$f(1/r) = A/r^3.$$

Even with this substitution the handling of the last integral in a general way would occupy too much space, and for present purposes we shall be better served by a consideration of its values in particular typical cases, say those of hydrogen, oxygen, or nitrogen at particular temperatures : $2mf(1/r)/V^2$ takes the form $(2a)^3 C/r^3 T$, and $b^2 = (2a)^2 (1 + C/T)$. For hydrogen $C=79$, and taking T as 173, 273, 373, 473, and ∞ , we get by approximation the following numerical values of the last integral, assuming $1/D=0$:—

| | | | | | | |
|----------|-----------|-------|-------|-------|-------|----------|
| T | | 173° | 273° | 373° | 473° | ∞ |
| Integral | . . . | ·1647 | ·1652 | ·1658 | ·1664 | ·1666 |

I do not guarantee the fourth figure of these values to be accurate, but the main result is clear enough, namely, that for hydrogen as a gas the integral is almost independent of V^2 or temperature ; and as the integral has for nitrogen ($C=109$) the above values at temperatures 239°, 377°, 515°, 653°, and ∞ , and for oxygen at 278°, 439°, 600°, 760°, and ∞ , we can say that for the element gases the value of the integral is $1/6$, and thus

$$\bar{t} = \frac{D-2a}{V} + \frac{2a}{3V},$$

which, of course, is the result also for forceless molecules, as it is exactly true when $V=\infty$, in which case finite force becomes negligible. Accordingly it has been shown that the effect which curvature of path and acceleration due to molecular force have on the time between two encounters or on the number of encounters may be neglected, and the number ν for attracting molecules is

$$2 \frac{N}{B} \pi (2a)^2 \left(1 + \frac{mf(1/2a)}{v^2} \right) (4v^2/3\pi)^{\frac{1}{2}} \left\{ 1 - \frac{2}{3} \frac{N}{B} \pi (2a)^2 \right\},$$

and

$$\mu = m(\pi \bar{v}^2/3)^{\frac{1}{2}}(1 + mf(1/2a)/\bar{v}^2)^{\frac{1}{2}};$$

hence

$$\begin{aligned} \frac{1}{2} \cdot \frac{1}{2} \Sigma \Sigma R_{\mu} r &= \frac{1}{4} \Sigma 2a\mu v = \Sigma \frac{N\pi(2a)^3 \{1 + mf(1/2a)/\bar{v}^2\}^{\frac{1}{2}}/3B}{1 - \frac{2}{3} \frac{N}{B} \pi(2a)^3} \cdot m\bar{v}^2 \\ &= \left(1 + \frac{mf(1/2a)}{\bar{v}^2}\right)^{\frac{1}{2}} \frac{N}{B} \frac{m\bar{v}^2}{2} \frac{b}{1-b/B}, \end{aligned}$$

showing that for attracting molecules the virial of the collisional forces is $(1 + mf(1/2a)/\bar{v}^2)^{\frac{1}{2}}$ times its value when the effect of molecular force on the number of collisions is neglected. The form of the characteristic equation is soon obtained in both cases, for the virial of the molecular attractions $\frac{1}{2} \cdot \frac{1}{2} \Sigma \Sigma R_{\mu} r$ reduces to the form $3a/2B$ or $3a/2v$; hence when the effect of molecular force on collisions is neglected,

$$\frac{3}{2}pv = N \frac{m\bar{v}^2}{2} + N \frac{m\bar{v}^2}{2} \frac{b}{v-b} - \frac{3}{2} \frac{a}{v};$$

$$\begin{aligned} \therefore \left(p + \frac{a}{v^2}\right)v &= N \frac{m\bar{v}^2}{3} \left(1 + \frac{b}{v-b}\right) = RT \frac{v}{v-b} \\ \text{or} \quad \left(p + \frac{a}{v^2}\right)(v-b) &= RT; \end{aligned} \quad \left. \vphantom{\begin{aligned} \therefore \left(p + \frac{a}{v^2}\right)v \\ \left(p + \frac{a}{v^2}\right)(v-b) \end{aligned}} \right\} \quad (A)$$

this form depending on the fact that the coefficient of $b/(v-b)$ is unity. When the effect of molecular force on the number of collisions is allowed for, the coefficient of $b/(v-b)$ becomes $\{1 + mf(1/2a)/\bar{v}^2\}^{\frac{1}{2}}$ or $(1 + C/T)^{\frac{1}{2}}$, and thus the characteristic equation is

$$pv = RT \left\{ 1 + (1 + C/T)^{\frac{1}{2}} \cdot \frac{b}{v-b} \right\} - \frac{a}{v} \quad \dots (B)$$

Now of the two forms (A) and (B), it has been shown (Phil. Mag., March 1893) that (A) represents fairly well the facts of Amagat's experiments down to the critical volume, so that (B) cannot do so, seeing that it implies at low volumes or high pressures a considerable variation of $\partial p/\partial T$ with T , which does not occur at volumes above the critical.

How are we to explain that the more accurate equation represents the experimental facts worse than the less accurate? Simply in this way, that we have no right to expect to get the virial of the collisional forces of actual molecules by treating them as smooth spheres. There are certain properties of

molecules that can be explained by representing the molecules as smooth spheres, but there are others which cannot be so explained, the best known of the latter being the specific heat. It is well to see how far a simplifying hypothesis such as that of smooth spherical molecules can lead us ; but it is also well to recognize when the hypothesis has got to the end of its tether. Van der Waals's theoretical equation agrees closely with experiment for the element gases only through an accidental compensation in the effects of two neglected causes, namely, the effect of molecular force on the number of collisions of molecules and the effect of a difference between the forces called into play in the collision of molecules and of smooth spheres. It must also be remembered that the empirical equation given for compound gases in my paper on the "Laws of Molecular Force" is quite different in form from that for elements, and that a theoretical explanation of it must involve considerations beyond the range of the spherical molecule. Indeed it appears to me that a combined and collated study of specific heat, characteristic equation, and thermal conductivity of gases might now be expected to yield some of that knowledge of the internal dynamics of molecules which is absolutely necessary for the advancement of the kinetic theory in the most interesting directions.

Melbourne, June 1893.

LIII. *On the Passage of Electric Wave-trains through Layers of Electrolyte.* By G. UDNY YULE*.

Introduction.

THE attempt to compare the resistances of electrolytes with rapidly alternating currents, by utilizing for that purpose electric radiation, was first made by Prof. J. J. Thomson in 1888†. The method he used was as follows :—Between a circular oscillator and a resonator was placed a large shallow dish, into which an electrolyte was poured, forming an absorbent layer which greatly weakened the resonator-sparks and finally extinguished them. So long as the layer be thin, the thickness of liquid necessary to *just* extinguish the sparks is inversely proportional to its conductivity. In this way the conductivities of several different solutions were compared, and the ratios found were approximately those of the conduc-

* Communicated by the Author. A preliminary note was published, Proc. Roy. Soc. liv. p. 96, May 1893.

† Proc. Roy. Soc. xlv. p. 269 (1889).

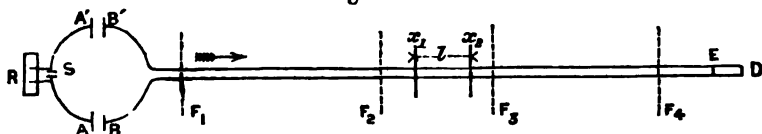
tivities determined by ordinary methods. No absolute determinations, however, could be made, and the measurements were naturally somewhat rough.

Since it would be important to make certain of even a slight variation in the resistance with increasing rapidity of oscillation, I decided last winter to take up these experiments again, with such alterations as might suggest themselves to render measurements more exact. After several unsuccessful attempts to directly improve the procedure used by Prof. J. J. Thomson, the following method was adopted:—The waves were propagated along (or between) a pair of long wires instead of being allowed to scatter in all directions through space; a certain length of these wires was then immersed in an electrolyte, and the ratio determined in which the wave-trains were weakened by their passage through this absorbent layer. Measurements could be fairly accurately made with an electrometer. It would have been easy from a series of observations to calculate the conductivity of the electrolyte used, if the change in the transmitted intensity were only a consequence of absorption. But the matter proved not so simple. As the thickness of the absorbent layer increased, the transmitted intensity, so far from decreasing logarithmically, did not continuously decrease at all, but decreased and increased periodically. The effect was obviously analogous to the interference-phenomena of thin plates by transmitted light: independently of any slight absorption a layer a quarter wave-length thick transmitted a minimum, a half wave-length thick a maximum, and so on. This disturbance made the matter too complex to permit of an exact determination of the conductivity, but its intrinsic interest was quite sufficient to warrant further investigation, and I give in the following pages the detailed results of my experiments.

Apparatus.

Fig. 1 represents the actual apparatus diagrammatically. The primary and secondary conductors were given the form

Fig. 1.



and dimensions previously used by Bjerknes*. The primary oscillator consisted of two circular zinc plates, A A', connected

* Wied. *Ann.* xlv. p. 513 (1891).

to the spark-gap, S, by wires, A S, A' S, and was worked by a Ruhmkorff coil, R. Opposite the plates A A' stood similar plates B B', from which a pair of long wires B F D were led off, stretched parallel to each other. These wires serve simply as guides for the radiation, which travels straight up the space between them and through the electrolyte x_1, x_2 .

The principal dimensions of the oscillator &c. were as follows :—

| | |
|---|------------|
| Diameter of plates A A', B B' | 40 centim. |
| Distance A B, A' B' | 30 " |
| Length of wire A S A' (diam. 2 millim.) | 200 " |
| Wave-length λ | 900 " |

The wires B F D (about 1 millim. diam.) were spanned 6 centim. apart. If these wires be made too short, a wave-train emitted from B B' may be reflected at the electrolyte x_1 or the bridge D and arrive back at B before the primary has finished oscillating. If this occur, alterations in the state of the secondary may react on the primary somewhat as in an alternate-current transformer, and inconvenient interference takes place. But if B x_1 be made longer than half the effective length of the wave-train, the reflected waves will not reach B until the primary has practically finished oscillating, and the latter can then know nothing of any alterations in the secondary at or beyond x_1 . Such a reaction of the secondary on the primary was noticed to a very serious extent by Herr von Geitler* with a Blondlot oscillator†.

In my apparatus the wires were led out at F₁ in a circuit of about 50 metres circumference round a garden next the laboratory. They re-entered the room at F₂, and were then run vertically through the vessel containing the electrolyte x_1, x_2 . A second length of 50 metres, F₃ F₄, round the garden, completed the circuit, the wires re-entering the room at F₄ and being bridged at D. The electrometer was connected at E a quarter wave-length (2.25 metres) from the end of the wires, at the crest of the standing waves formed by interference of the direct and reflected trains. If we accept, at least as an approximation, the value of the primary damping determined by Bjerknes (*loc. cit.*) for his apparatus, these dimensions should suffice to exclude any sensible reaction.

The electrometer was the one employed by Bjerknes for his researches in the same laboratory. It is a simple quadrant-electrometer with only one pair of quadrants and an

* Doctor-Dissertation : Bonn, Jan. 1893, p. 22.

† *Comptes Rendus*, cxiv. p. 283 (1892).

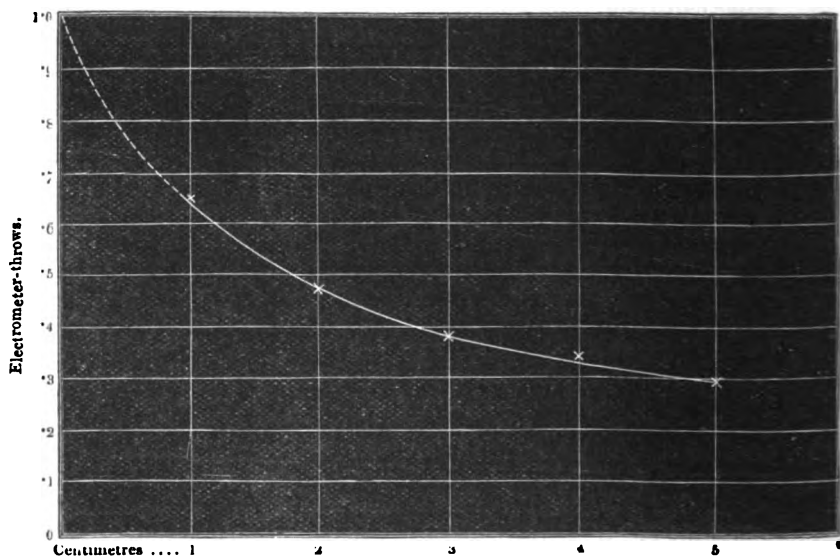
aluminium needle of the usual shape suspended by a quartz fibre. One quadrant is connected to each wire. The needle not being charged, throws are always in the same direction, and are directly proportional to the time-integral of the energy, or to the intensity of the radiation. First throws, not steady deflexions, are read.

Various glass jars were used for holding the electrolyte. The wires were run vertically through holes in the bottom of the jar, strained straight, and cemented in.

Experiments.

Electrometer-readings were taken in pairs alternately with the dish empty and with, say, 1 centim. of liquid in it, then alternately with the dish empty and with 2 centim. of liquid, and so on, a good many readings being taken at each point to get a good average and eliminate spark-variations. By this means one gets a curve showing the variation in the transmitted intensity as the thickness of the layer is increased, the intensity transmitted when the thickness is zero being always taken as unity.

Fig. 2.



Transmission-curve for a thin layer CuSO_4 solution.

The first trials of the apparatus were made with dilute solutions of copper sulphate, some five or six centimetres of solution being the greatest depth used, as the dish was only a shallow one. One of the first curves obtained is given in fig. 2, and may serve as a type of two or three similar ones. The curve is by no means logarithmic, and if the conductivity of the solution be calculated from a pair of points on it arbitrarily chosen near the beginning and end it comes out very high.

It appeared possible that this irregularity might be due to the existence of interference-effects analogous to Newton's rings or the phenomena of thin plates by transmitted light, especially in view of a somewhat similar effect observed just previously by Mr. Barton in the same laboratory*; but I felt doubtful at first whether it might not be ascribed to some other disturbance—to the fact that a part of the radiation passes round outside the jar instead of through the electrolyte, or to mutual induction between the two halves of the long wire circuit in the garden. The second disturbance proved, however, to be nonexistent, and the first quite inadequate to explain such a distortion of the curve.

To see if the effect were really due to interference phenomena, it was necessary to determine a transmission-curve for a great length of liquid, and consequently to avoid absorption as far as possible. Distilled water presented itself naturally as the best liquid for the purpose.

A tall glass cylinder, about 114 centim. high and 12 centim. internal diameter, was used as the containing vessel, the wires being strained straight down the middle of it, and passing through holes drilled in the bottom.

In order to avoid having to remove all the water between every pair of readings, the method of observation was slightly altered: each point was compared with one previously determined, instead of directly with the zero. As before, ten or twelve readings were taken at every point to cover variations in the effectiveness of the primary sparks. As a specimen of the usual variations, I give two series of observations in Table I. The first was for the determination of the ratio between the intensities transmitted at 40 and at 55 centim., the second for the determination of the same ratio at 60 and 80 centim.

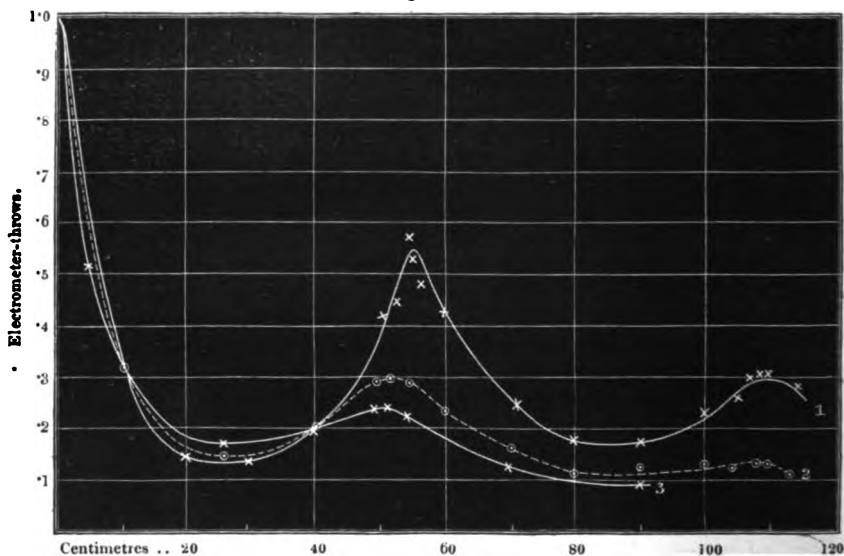
* Proc. Roy. Soc. liv. p. 85 (1893).

TABLE I.

| 40 centim. | 55 centim. | 60 centim. | 80 centim. |
|------------|------------|------------|------------|
| 4.6 | 11.4 | 6.8 | 3.0 |
| 4.9 | 11.4 | 6.4 | 3.0 |
| 5.0 | 11.0 | 6.5 | 2.8 |
| 4.2 | 11.9 | 6.1 | 2.7 |
| 4.3 | 11.5 | 6.1 | 2.3 |
| 3.9 | 11.2 | 6.1 | 2.5 |
| 4.0 | 11.6 | 5.9 | 2.7 |
| 4.3 | 11.4 | 5.7 | 2.5 |
| 4.6 | 10.4 | 5.8 | 2.0 |
| 4.4 | 11.2 | 6.6 | 2.1 |
| 4.5 | 10.4 | 5.8 | 2.7 |
| 4.6 | 10.0 | 6.8 | 2.7 |

The readings for each thickness are grouped separately, but it will be understood that they were taken in pairs alternately as described above.

Fig. 3.



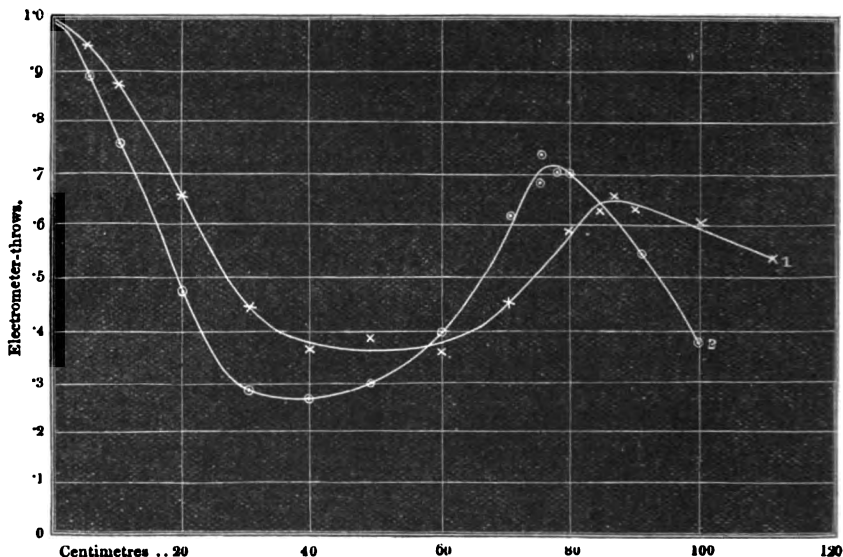
Transmission-curves (1) for water.
 " " (2) for ZnSO_4 solution.
 " " (3) for " "

The complete results for distilled water are given in curve 1, fig. 3. It is seen that, at least for such a poor conductor as distilled water, any slight absorption is completely masked by the interference. As I mentioned in the introduction, the intensity of the transmitted ray does not uniformly decrease, but the transmission follows the same general law as for light with a thin plate: we are in fact dealing with a "thin plate"—a plate whose thickness is comparable with the wave-length of the radiation used. A minimum is transmitted by a plate a quarter wave-length thick, a maximum by a plate a half wave-length thick, and so on. The fact that the maxima in our curve (1. fig. 3) get successively lower is only in part due to the absorption: it is chiefly owing to the fact that we are here dealing, not with a steady wave-train like light, but with a rapidly damped wave-train. If the head of such a wave-train be only interfered with by the tail, it is not much affected: complete interference is quite impossible.

It was desirable to know how far the phenomenon would still be noticeable with electrolytes of higher conductivity. To test this question, a few drops of a strong solution of zinc sulphate were added to the jarful (some 14 litres) of distilled water, and the relative intensities of the transmitted radiation determined as before. The results are given in curve 2, fig. 3. Curve 3 of the same figure was determined with a slightly stronger solution. In both curves the first maximum is very well marked. Both solutions were, however, very dilute: their specific gravities with reference to water at the same temperature were approximately 1.00028 and 1.00038, and their specific resistances 5100 and 4030 ohms \times cm. respectively, as measured with the Kohlrausch bridge and telephone. To give an idea of the corresponding opacities I may add that radiation traversing the first solution would be reduced to 0.41 of its initial intensity in a metre, or to 0.32 of its initial intensity in traversing a metre of the second solution.

With a view to making certain of the nature of the periodic effect, experiments were also carried out with liquids of a different specific inductive capacity. Curve 1, fig. 4, was determined with 95 per cent. alcohol, and curve 2 with a mixture of three volumes of the same alcohol with one volume of water. In both cases the maxima are very well marked.

Fig. 4.



Transmission-curve (1) for 95 per cent. alcohol.

" " (2) for { 3 vols. 95 per cent. alcohol.
1 vol. water.

Numerical Results.

For the very low conductivities with which we are here dealing, we may safely regard the values given by the maxima of the curves as the true wave-lengths, a correction for conductivity being quite negligible. As the wave-length in air is known to us, we may determine the coefficients of refraction (n) and the dielectric constants (k) of the various liquids used by the ordinary relation

$$k = n^2 = \left(\frac{\lambda_a}{\lambda_l} \right)^2,$$

where λ_a , λ_l are the wave-lengths in air and the liquid respectively. These wave-lengths are given in the first column of Table II., and the corresponding values of the two constants in the second and third columns.

The experiments with zinc-sulphate solution show that an addition of salt which largely affects the conductivity of a

TABLE II.

| | λ cms. | n . | k . |
|-------------------------------------|----------------|-------|-------|
| Water | 108 | 8.33 | 69.5 |
| (1) ZnSO_4 solution | 106 | 8.49 | 72.0 |
| (2) ZnSO_4 solution | 104 | 8.65 | 74.9 |
| 95 per cent. alcohol..... | 174 | 5.17 | 26.7 |
| 3 vols. alcohol } 1 vol. water } | 154 | 5.84 | 34.1 |
| Air..... | 9.00 | — | — |

solution only slightly increases its dielectric constant, thus confirming entirely the similar result published in 1892 by Cohn* (to whom we are also indebted for the first determination of the high constant of water†).

For comparison with my figures I give in Table III. the dielectric constants of water and alcohol found by other investigators.

TABLE III.

| Method used. | Authority. | Dielectric Constants. | |
|---------------------------------------|-------------------------------|-----------------------|----------|
| | | Water. | Alcohol. |
| Alternated or interrupted currents. { | Heerwagen ¹ . | 79.56 | ... |
| | Rosa ² . | 75.70 | 25.7 |
| | Rosa ³ . | 70 | 30.9† |
| | Bouty ⁴ . | ... | 7.93 |
| Rubmkorff coil { | Tereschin ⁵ . | 83.8 | 27* |
| | Cohn & Arons ⁶ . | 76 | 26.5* |
| Hertzian oscillations. { | Ellinger ⁷ . | 81 | 24 |
| | Cohn ⁸ . | 73.5 | ... |
| | Stacheghtineff ⁹ . | 1.75 | 1.62 |

* 98 per cent.

† 93 per cent.

¹ Wied. *Ann.* xlviii. p. 35 (1893). ² Phil. Mag. xxxi. p. 200 (1891).

³ Ibid. xxxiv. p. 344 (1892).

⁴ *Jour. de Phys.* 3^e série, tome i. p. 445 (1892).

⁵ Wied. *Ann.* xxxvi. p. 792 (1889). ⁶ Ibid. xxxiii. p. 13 (1888).

⁷ Ibid. xlv. p. 513 (1892). ⁸ Ibid. xlv. p. 370 (1892).

⁹ Phil. Mag. xxxiv. p. 388 (1892), or *Journ. de Phys.* June 1892.

* Wied. *Ann.* xlv. p. 370 (1892).

† Cohn & Arons, *ibid.* xxxiii. p. 13 (1888).

The figures given by Stschehtiaeff agree so nicely with Maxwell's law that one regrets being compelled to treat them as negligible; and the low value found for alcohol by Bouty is also in a minority and requires explanation. It should be noted that it was not determined directly, but deduced from the constants found for mixtures of small proportions of alcohol with other liquids.

My figures agree roughly with the high values given in the table, but are somewhat low. This is very likely to be ascribed to the fact that a certain portion of the wave always flows through the dielectric outside the jar instead of going through the liquid. This portion interferes with the first in such a way as to shift the maximum of the curve forwards; *i. e.* the whole arrangement behaves as if the wave had flowed through a layer of air and water mixed instead of through pure water.

The indefinite error arising from this cause might have been avoided in one way, namely, by making a certain length AB (fig. 5) of the one wire into a tube surrounding the other, and using this tube ABCD also for holding the liquids. The whole of the induction must then lie between the inside wire and the tube, and, consequently, the whole of the radiation must pass through the liquid.

This was in fact the arrangement that I originally wished to use. It possesses, however, several serious disadvantages which finally led to its rejection in favour of the simple wires and glass jar. For one thing, such a condenser as the tube forms reflects of itself a considerable portion of the incident energy. Again, the variations in the position of the electrolyte surface, with reference to the top of the jar, would introduce fresh interference phenomena, as wave-trains are reflected equally well from the latter and the former (as in the apparatus used by Mr. Barton*). The large surface of metal in contact with the liquid would cause additional inconvenience, as it would rapidly render distilled water or very dilute electrolytes impure.

In addition to the liquids I have mentioned, salt and soda crystals were used with a view to try and determine their dielectric constants. No definite results were, however,

Fig. 5.

* *Loc. cit.*

obtained. With salt absolutely no effect could be observed, and soda gave only a slight drooping of the curve. This shows at all events that the constants of these substances approximate to normal values, and not to the very high figures found for water and alcohol.

Note on the Theory.

It was my original intention to calculate from the curves, not the dielectric constants, but the conductivities of the liquids. At first sight one might claim that this should be possible, but practically the matter is too complex to serve the purpose. On the assumption that the conductivity be very small, so that one may neglect the phase alteration on reflexion and the increase in the reflected fraction, the equation to the curve may be calculated by a procedure recently described by Mr. Barton*. I will only give the principal equations here, and refer to his paper for a more complete sketch of this method and discussion of fundamental points†. We may write the equation of the incident wave-train in the form

$$y = ae^{-\alpha t + a_1 x} \sin(\beta t - \beta_1 x), \dots (1)$$

where

$$\alpha/\alpha_1 = \beta/\beta_1 = v_1, \dots (2)$$

v_1 being the velocity of propagation in the ordinary portion of the long leads. Similarly, for the waves in the liquid,

$$\alpha/\alpha_2 = \beta/\beta_2 = v_2, \dots (2a)$$

For the primary damping γ , or time-rate of decrease of the amplitudes of oscillations in the primary, we have

$$\gamma = \frac{2\pi\alpha}{\beta} = \alpha\tau, \dots (3)$$

where τ is the period.

Secondary damping, or damping out of the whole wave-train, owing to the leads between which it travels not being perfect conductors, is legitimately neglected in this part of the theory as it is known to be small.

We assume the electrolyte to have a certain, though small,

* Proc. Roy. Soc. liv. p. 85 (1893), *vide* more particularly p. 80. I am deeply indebted to Mr. Barton for full explanations of his theory prior to publication.

† The case discussed by him is one of similar interference where there is *no absorption* in the medium.

conductivity. Let the damping of wave-trains in their passage through it be given by a factor p , such that

$$a_2 = a_1 e^{-px}, \dots \dots \dots (4)$$

where a_1 is the initial amplitude, and a_2 the amplitude of the same wave after traversing a length x of electrolyte. From Maxwell's theory it follows that

$$p = 2\pi\mu CV, \dots \dots \dots (5)*$$

where V = velocity of propagation in the electrolyte,
 C = conductivity of the electrolyte.
 μ = magnetic permeability of the electrolyte.

Taking the second surface of the electrolyte (x_2 , fig. 1) as origin of coordinates, and carrying out the summation of successively emergent rays, we arrive, after sundry transformations, at the expression for the curve

$$\frac{I_t}{I_0} = \frac{(1-b^2)^2 e^{-2pt}}{1-b^4 e^{-4pt}} \left\{ 1 + \frac{2Q}{\beta} \right\}, \dots \dots (6)$$

where

$$Q = b^2 e^{-2pt-t_2\alpha} \left\{ \frac{\alpha \sin t_2\beta + \beta \cos t_2\beta - \beta b^2 e^{-2pt-t_2\alpha}}{1 - 2b^2 e^{-2pt-t_2\alpha} \cos t_2\beta + b^4 e^{-4pt-2t_2\alpha}} \right\}, \dots (7)$$

and

I_0 = intensity transmitted when the absorbent layer vanishes.

I_t = intensity transmitted for a thickness l of the layer.

b = fraction of the incident amplitude reflected at the first surface.

$t_2 = \frac{2l}{v_2}$, i. e. = the time taken by radiation to traverse twice the thickness of the layer.

On putting the conductivity, or p , = zero the above expression (6) reduces to that given by Mr. Barton for the case of no absorption.

On analysing (6) we see that the expression on the right-hand side may be split into two terms: the first gives us a continuous drooping curve which may be considered as a centre line, on which the humps formed by the second, periodic, term are imposed. If we put the primary damping $\gamma = \infty$, interference is impossible, the periodic terms vanish, and we have

$$\frac{I_t}{I_0} = \frac{(1-b^2)^2 e^{-2pt}}{1-b^4 e^{-4pt}}, \dots \dots \dots (8)$$

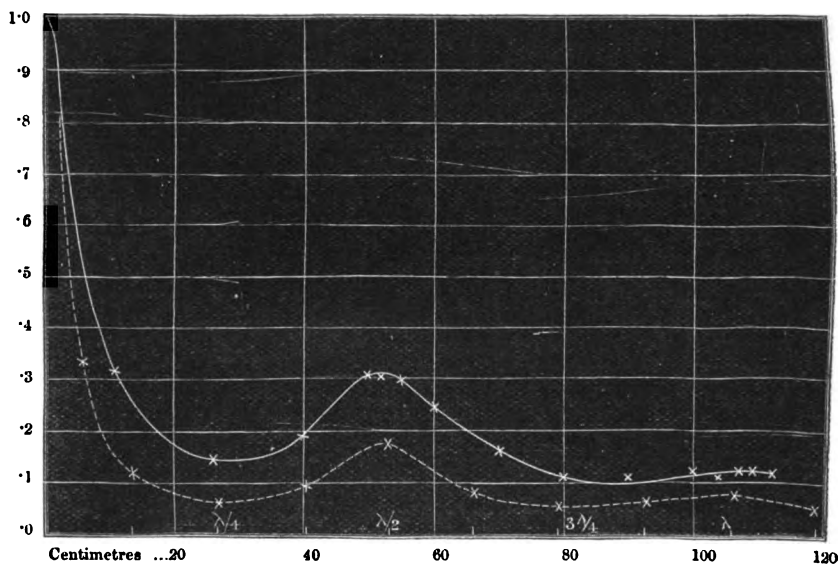
* Maxwell, ii. [798].

an equation which would give the form of the curve if no interference took place. It is not a simple logarithmic curve, inasmuch as we have to take account of multiple reflexions inside the absorbent layer. If we again put the conductivity $=0$, the centre line becomes a straight line parallel to the base instead of a drooping curve.

If we put in (7) $l=\infty$, Q vanishes; *i.e.* as the length of the layer is increased the humps on the curve disappear. As I have already mentioned, this is due to the fact that the wave-train is a rapidly damped one so that interference is not perfect.

I have calculated a curve for the first zinc-sulphate solution by these equations; the theoretical and experimental curves are shown together in fig. 6. The dielectric constant of the

Fig. 6.



Comparison of experimental ——— and theoretical curves
for the first zinc-sulphate solution.

Data for Theoretical Curve.

Wave-length $\lambda = 106$ cms.
By Kohlrausch bridge $\sigma = 5100$ ohm. cms.
Assumed log. dec. $\gamma = 0.4$.

solution is known from the experimental curve; this gives us b , r_2 , and t_2 . The primary damping γ we do not know, but an

approximate value can be found by trial and error ;

$$\gamma = 0.4$$

was found to be suitable. γ furnishes us with α and β from equations (2) and (3). The conductivity of the solution was measured with the Kohlrausch bridge (*vide* p. 537), and hence p was known. We have, then, all the necessary data.

The two curves, calculated and experimental, disagree considerably ; the experimental curve stands all along much higher than the other. Now this shift could not be caused by any variation in the conductivity : that only causes a quicker or slower downward trend of the curve. It could be approximately brought about by an alteration in the reflected fraction, but by a *decrease* of it ; *i. e.* if we took the conductivity into account in calculating the amplitude of the reflected ray, it would only make matters worse.

The fact of the matter is that we have all along neglected the multiple reflexions that occur in all parts of the circuit. The fraction reflected from the first surface of the electrolyte is not lost for good, but is turned back again when it reaches the secondary plates B B' (fig. 1), and is given another chance of getting through the liquid layer. Similar multiple reflexions occur not only between B and x_1 (fig. 1), but between x_2 and D, and B and D. The matter becomes too complex for calculation as we have a fresh unknown—the secondary damping—introduced. The fact that the experimental curve trends downwards towards the theoretical agrees with the above explanation : as the thickness of the absorbent layer is increased the waves are so weakened by their passage through it that multiple reflexions are of less account.

Though, as I have said, calculation is impossible, a comparison of the two curves in fig. 6 shows at least that no great alteration of conductivity has taken place.

Conclusion.

This investigation was carried out during the winter and summer semesters (1892–93) in the Physical Institute of the University at Bonn. It is with great pleasure that I take this opportunity of expressing my thanks to Prof. Hertz for his most useful advice and suggestions, and for the interest he showed in the work throughout.

LIV. *Notices respecting New Books.*

A Treatise on the Analytical Geometry of the Point, Line, Circle, and Conic Sections, containing an account of its most recent extensions, with numerous examples. By Dr. J. CASEY, F.R.S. Second Edition. London: Longmans, 1893. (Pp. xxxii + 564.)

THE mathematical world was informed, on the occasion of Dr. Casey's death in 1891, that he had himself passed 400 pages of this second edition through the press, and that the concluding portion was in manuscript. Dr. Casey received considerable assistance in the preparation of this edition from Prof. Neuberg, of Liège; and we learn from the preface, supplied by the editor, Prof. Dowling, that the final proof-sheets, which had not received the author's revision, have been submitted to the same gentleman for correction and approval. The book brought out under such auspices is, as might naturally be expected, quite up to date, and will amply repay a careful study. How greatly the work has been enlarged will be seen when we mention that the first edition extended to 331 pages as against the 564 pages of this volume.

The first seven chapters have identical headings in the two editions. The subject-matter has grown from 227 pages to 279. There are new articles on biradial and biangular coordinates; the treatment of anharmonic and harmonic ratio is advanced and now concludes the section on Cartesian Coordinates (applied to the line), and in place of the section on Trilinear Coordinates we have an enlarged one on "Systems of Three Coordinates." This section gives a clear account of many of the modern terms which have come into vogue with the rise of the *modern geometry* of the triangle. In fact this is the book to which a student will naturally turn who wishes to read in English what has been done in this direction. A glance at the "Contents" will put in evidence how deeply Dr. Casey had explored this new field, and how fully he had adopted the ways of the "surname" geometers. Chapter VIII. is still headed "miscellaneous investigations," but its sections are now devoted to figures inversely similar, pencils inversely equal, twin-points (the *Zwillingspunkte* of Artzt), triangles derived from same triangle and tripolar coordinates. Chapter IX. discusses special relations of the Conic Sections, and much of the matter of chapter VIII. of the first edition is now rearranged and rewritten in chapters X.-XIII. A long chapter (XIV.) is devoted to the recent geometry, and in it will be found almost all that is known at present of the numerous circles which stud the firmament of the *modern* geometer.

It is to this subject, as well as to the theories of the Mean Centre, of Anharmonic Ratios, and of Homographic Division and Involution, that the principal additions have been made. But perhaps the fullest and most important additions are contained in

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the final chapter (xv.) on the Invariant Theory of Conics, a subject previously lightly touched in 15 pages, now extended to 60 pages. We know of no text-book, in English, in which so many developments of this branch are given. Our statement at the beginning of this notice is, we believe, fully justified by this bald sketch of the contents, when it is borne in mind that the proofs are all that one could desire, and that the principles are fully illustrated by a copious and excellent collection of exercises. The specially numbered results, for reference, have grown from 641 to 1085.

There is a large printed list of errata, but to this should be added at least ninety more which we have come across; and why, in an English text-book, should we repeatedly meet with such forms as "orthique," "orthologique," "symétrique"? For "antipolar" in many places "autopolar" should be read: in a few instances this slip is indicated in the *Errata*. Again, there is the uncertainty of the first edition in the spelling of proper names, Simpson and Simson, Coates' and Cotes,' Appolonian and Apollonian, de Jonquiers and de Jonquières, where in each case the latter is the proper form. All the above errata are easily corrected by the reader, but we dwell upon them because the proof-sheets passed through three or four hands at least. More important are the following slips:—On p. 7, line 6, insert — before $x' - x''$; on p. 299, line 8, insert $\frac{1}{2}$ after the =; on p. 425, line 1, for *Brocard* read *Neuberg*. We do not think that the figures of the conic sections are anywhere discussed: of course by tracing it is readily seen that they are as drawn in the text. In the next edition, which we hope will be soon called for, a few such statements as "subject matter are," "become infinity large," and the definitions of the conics (see pp. 173, 201, compared with p. 250), should be amended. The figures which accompany the text, as well as the type, leave little to be desired. The utility of the work is greatly enhanced by an excellent index.

Practical Chemical Physics (Physikalisch-chemische Methoden).

By Dr. J. TRAUBE. Hamburg: Leopold Voss, 1893.

THE great modern development of organic physical chemistry is mainly due to three important discoveries. These are (1) that organic compounds can be arranged in series ascending by increments of CH_2 ; (2) that for each increment there is generally a corresponding equal change in physical properties; and (3) that bodies of the same molecular composition have often very different physical character, even when their chemical properties are nearly identical. It follows that a chemist wishing to obtain a complete knowledge of new compounds must study their physical properties, and the volume before us has been written to satisfy the needs of such seekers after knowledge. It does not trouble them with physical theories but describes in plain (German) language the apparatus

necessary and the method of using it, for most of these determinations. The formulæ for calculations are also quoted; and in the case of several determinations the working-out of results is facilitated by tables given in the Appendix to the book. The author indicates the use in chemical research of each physical constant whose evaluation he describes, and in so doing he suggests several new fields for research.

The methods of determining the surface-tension of a solution are mentioned, although they have not yet received much attention from chemists. We believe, with the author, that an investigation of the capillary constants of liquids containing known quantities of organic bodies in solution would amply repay the time spent upon it. In the volume before us the methods described only serve to determine the component of the surface-tension resolved along the plane to which the liquid surface clings. If T be the surface-tension and α the angle of contact, they only give $T \cos \alpha$. By measuring the size of large globules of liquid on a horizontal plane, or of bubbles of air in the liquid, T and α can be obtained separately, as Quincke has shown. The size of a globule of liquid formed in another liquid with which it does not mix furnishes a simple means of obtaining the surface-tension between the two, which may possibly be of value in chemical investigations. For those who desire fuller details on the subjects of the experiments, the author gives copious references to text-books and original papers.

JAMES L. HOWARD.

Arbeitsmethoden für Organisch-chemische Laboratorien; ein Handbuch für Chemiker, Mediziner und Pharmazeuten. By Dr. LASSAR-COHN, Privatdocent in the University of Königsberg. Hamburg and Leipzig: Leopold Voss, 1893.

ALTHOUGH not a large volume, considering the wide scope of the subject dealt with, the present work will be found most valuable by the practical worker in organic chemistry. Its very terseness is, in fact, a point in its favour. That it has been found serviceable may also be inferred from the fact that the present is a second edition, the first edition having been enlarged and improved by the incorporation of much new matter representing the more recently discovered processes for bringing about the transformation of organic compounds. As is so generally the custom with German writers, the author divides the work into a general and a special part. The former treats of the operations generally carried on by those who are engaged in practical organic chemical work, such as extraction, distillation, decolorizing solutions, filtering, crystallizing, sublimation, and the determination of molecular weights and melting-points.

The special part is divided into what may be considered eleven divisions or sections, the scope of which will be gathered from their headings: brominating, chlorinating, &c. (methods of halo-

genizing generally), preparation of salts, diazotizing, preparation of ethers and esters, potash and soda fusion, condensation, nitration, oxidation, reduction, sulphonation, saponification. A few pages at the end are devoted to some hints on elementary analysis and the detection and estimation of nitrogen, the halogens, and sulphur in organic compounds.

Among the numerous books on practical organic chemistry now at the disposal of laboratory workers there is none which occupies exactly the same position as the work under consideration. It is literally a "handbook" in the best sense. The various processes described under their respective headings are introduced by a list of the reagents employed, and then the more important special methods of applying the reagents are described in some detail. It will thus be seen that the book supplies the working chemist with much about the same kind of information that a book on workshop-recipes supplies to the mechanic. As such it will be found most serviceable, and we have no hesitation in recommending its adoption by chemists in this country.

LV. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 380.]

November 8th, 1893.—W. H. Hudleston, Esq., M.A., F.R.S.,
President, in the Chair.

THE following communications were read:—

1. 'The Geology of Bathurst, New South Wales.' By W. J. Clunies Ross, Esq., B.Sc., F.G.S.

After sketching the physiography of the Bathurst district, the Author describes in detail its stratigraphy. The oldest sedimentary rocks are Silurian, but the floor on which they rest is unknown, and the author states that it was probably fused up and incorporated in the granite which is described in the paper. The Silurian rocks may have been folded before the granite was erupted; in any case the granite produced a zone of contact-metamorphism, whilst almost all the Silurian rocks may be considered to be examples of regional metamorphism, though the agents producing the metamorphism were least active to the east of Bathurst, where the Silurian limestones are very little altered. An anticlinal was probably produced at the time of the granitic intrusion. After a time there was subsidence, but at first it need not have been very extensive, since the Devonian conglomerates, sandstones, and shelly limestones were probably deposited in a comparatively shallow sea. They contain *Lepidodendron australe*. At Rydal they abut against the uplifted Silurian rocks of the Bathurst area. At the end of Devonian times there appears to have been a long interval, during which both Silurian and Devonian rocks were greatly denuded, and the granite exposed in places. The Upper Carboniferous and Permian rocks

were deposited in the Lithgow district, but it is doubtful if they ever extended to Bathurst. There is nothing to show what happened in this region during Mesozoic and early Tertiary times. The Hawkesbury Sandstone (probably Triassic) may have approached nearer to Bathurst than it does now. In late Tertiary times stream-deposits were formed on the granitic rocks, and afterwards covered with thick basaltic lava-flows, which have since undergone much denudation.

2. 'The Geology of Matto Grosso (particularly of the region drained by the Upper Paraguay).' By J. W. Evans, D.Sc., LL.B., F.G.S.

The district includes a portion of the Brazilian hill-country, and also of the low-lying plains to the south-west.

The rocks principally dealt with are unfossiliferous, and of unknown age, except that they appear to be older than the Devonian. They may be classified as follows:—

5. Matto Sha'es.
(Relations not shown.)
4. Rizama Sandstone.
(Perhaps some unconformity.)
3. Curumbá and Arara Limestones.
(Very marked unconformity.)
2. Cuyabá Slates.
(Strong unconformity.)
1. Ancient crystalline rocks.

The Devonian and later rocks are briefly described.

3. 'Notes on the Occurrence of Mammoth-remains in the Yukon District of Canada and in Alaska.' By George M. Dawson, C.M.G., LL.D., F.R.S., F.G.S.

LVI. Intelligence and Miscellaneous Articles.

ABERRATION PROBLEMS.

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN,

NOW that my paper of March 1892 on Aberration and Ether Motion has been published by Messrs. Kegan Paul & Co. for the Royal Society (Phil. Trans.), I ask permission to state that reference to an experimental investigation made at Leipzig in 1889 by Th. des Coudres was unwittingly omitted (Wied. Ann. vol. xxxviii. p. 73).

It consisted in observing the mutual inductance of a pair of coils when their common axis made different angles with the Earth's motion through space; the apparatus used being a kind of induction-balance. So far as I remember it is the first electrical experiment

in this subject actually tried, and its result is as negative as all the optical ones have been. I am not prepared to admit that there ought to be a first-order effect; but anyhow the experiment is an interesting modification of the thermopile experiment suggested in 1833 by Fizeau, which so far as I know has not yet in that form been attempted.

It happens that Herr des Coudres in the same communication suggests the possible aberration of a mountain-top as seen from a valley, referred to in a footnote to § 32 of my paper.

I would also take this opportunity of mentioning a mathematical memoir by Professor H. A. Lorenz, "*La Théorie Électromagnétique de Maxwell, et son application aux corps mouvants,*" which appeared in the *Archives Néerlandaises*, vol. xxv. in 1892. There are also various short communications by Mr. Heaviside on the same subject in his collected papers.

Yours faithfully,
OLIVER J. LODGE.

October 28th, 1893.

ON A SIMPLE METHOD OF INVESTIGATING THE CONDUCTING
POWER OF DIELECTRIC LIQUIDS. BY K. R. KOCH.

In recent times many investigations have been made as to the coexistence of dielectric power and electrical conductivity. Engaged myself on an investigation in which I desired to ascertain qualitatively the power of insulation, I have found the following method very useful and rapid in its execution.

If it be assumed that electrical conductivity in dielectric liquids is of the nature of electrolysis, we must look for galvanic polarization in two electrodes inserted in it and connected with a galvanic battery. In ordinary circumstances this could not of course be galvanometrically or electrometrically measured. Yet a capillary electrometer, in which the electrolyte is the liquid itself to be investigated, may in a suitable manner be made so sensitive that the existence of a polarization, and therewith of electrolytic conductivity, may be demonstrated. An ordinary Lippmann's capillary electrometer could not be used for this purpose; Dewar's* form is much more sensitive. This consists of a horizontal tube about 1 mm. in the clear, which on each side is connected with mercury cups; the mass of mercury in the tube is separated by a drop of dilute sulphuric acid, if the instrument is to be used in the ordinary way for measuring electrolytic forces; in the present case the dilute acid was replaced by a drop of the substance to be investigated. If, now, the two mercury cups are connected with the poles of a battery the drops move in one way or the other, according to the direction of the current, if the liquid conducts electrolytically, and thus when polarization takes place at the opposite surfaces of the mercury.

* 'Nature,' vol. xv. p. 210 (1877).

With these badly conducting liquids the drop should not exceed $\frac{1}{2}$ mm. in length.

Investigated in this way, all dielectric liquids, without exception, exhibit polarization, and, so far as my observations extend, always in the direction of an increasing surface-tension at the kathode due to polarization. It is, however, probable that this phenomenon, in the case of benzole for instance, is due to the presence of impurity; this seems to follow from the following observations. If the current is closed for a long time, the mobility of the drop is considerably diminished. In like manner, when the apparatus is left for some time at rest, the conductivity of the dielectric liquid is considerably diminished.

If this idea is correct it ought to be possible, by carefully purifying the substance, to diminish as much as possible the polarization and therefore also the conductivity. I used for my experiments benzole (not benzine, for this is no well-defined body), which Dr. Haussermann was good enough to prepare for me in the greatest state of purity. When this was examined in the electrometer in the manner described, it showed, like a commercial specimen, strong polarization, notwithstanding that the electrometer had previously been carefully purified and dried, and mercury used which had been repeatedly distilled. Only when, in addition to the other precautions, the mercury was filled hot (about 120°) into the hot apparatus, did the benzole show no polarization, even with high electromotive forces. Benzole in its greatest purity appears therefore to be a perfect insulator for electricity; the conductivity observed depends on impurities and particularly moisture, which in these experiments may have been on the surface of the mercury. Those methods of determining the dielectric constants of dielectric liquids, the result of which is influenced by a possible conductivity of the liquid, must therefore lead to wrong results, for in the ordinary arrangement and with the comparatively large masses and surfaces which come into play, it must be difficult to prevent the impurities and the presence of moisture.

As regards sensitiveness the method is equal, if not superior to a galvanometric method with a very sensitive astatic Thomson's galvanometer.—Wiedemann's *Annalen*, No. 11, 1893.

ON THE EMISSION OF HEATED GASES. BY F. PASCHEN.

The chief results of his investigation of this subject are thus summarized by the author:—

Gases can in consequence of their temperature emit a discontinuous spectrum; hence the opposite view of M. Pringsheim fails. This emission has been investigated for CO_2 and aqueous vapours at different temperatures. A displacement of the intensity within the maxima of emission was observed with decrease of temperature. This fact could be demonstrated but not explained.

The maxima of emission of flames are to be regarded as due to pure radiation of temperature for which the chemical process is non-essential.—Wiedemann's *Annalen*, No. 11, 1893.

ON THE CONDITION OF MATTER NEAR THE CRITICAL POINT.

BY B. GALITZINE.

The following is a summary of the results obtained by the author :—

1. The temperature t_c of the actual appearance of the meniscus on cooling must be lower, and even considerably so than the true critical temperature T_c of the substance. Accordingly the optical method, at any rate in its ordinary form—observation of the formation of mist—must lead to incorrect results for the critical temperature.

2. With very slow and regular cooling the frequently discussed peculiar formation of mist is no necessary condition of the phenomenon.

3. The temperature at which the meniscus actually appears, and the temperature t_c' at which the last traces of want of homogeneity disappear, must be assumed to be *independent* of the quantity of substance in the tube.

4. The density ρ of a liquid (in contact with its vapour) and the density δ of its saturated vapour change at exactly the same temperature with the time, and with frequent heating beyond the critical temperature, in which ρ decreases and δ increases.

5. Both magnitudes are therefore *not* completely and unequivocally defined by the temperature alone.

6. At temperatures which lie considerably higher than the critical temperature, a body at almost exactly the same temperature may have two (or perhaps more) different densities. The differences of density may amount to 21–25 per cent.

7. The remarkable anomalies observed by various experimenters, which are with difficulty brought into harmony, may be very well recognized and justified on the basis of the modern views as to molecular processes in liquid and vapour.—Wiedemann's *Annalen*, No. 11, 1893.

NOTE ON THE ATOMIC WEIGHT OF CARBON.

BY J. ALFRED WANKLYN.

An investigation which has occupied me for the greater part of the year has yielded the following remarkable result. There is a series of hydrocarbons the successive members of which rise in molecular weight—not by $\text{CH}_2=14$ —but by $\frac{1}{2}(\text{OH}_2)=7$. If this result cannot be overturned, the consequence follows that the atomic weight of carbon is 6.

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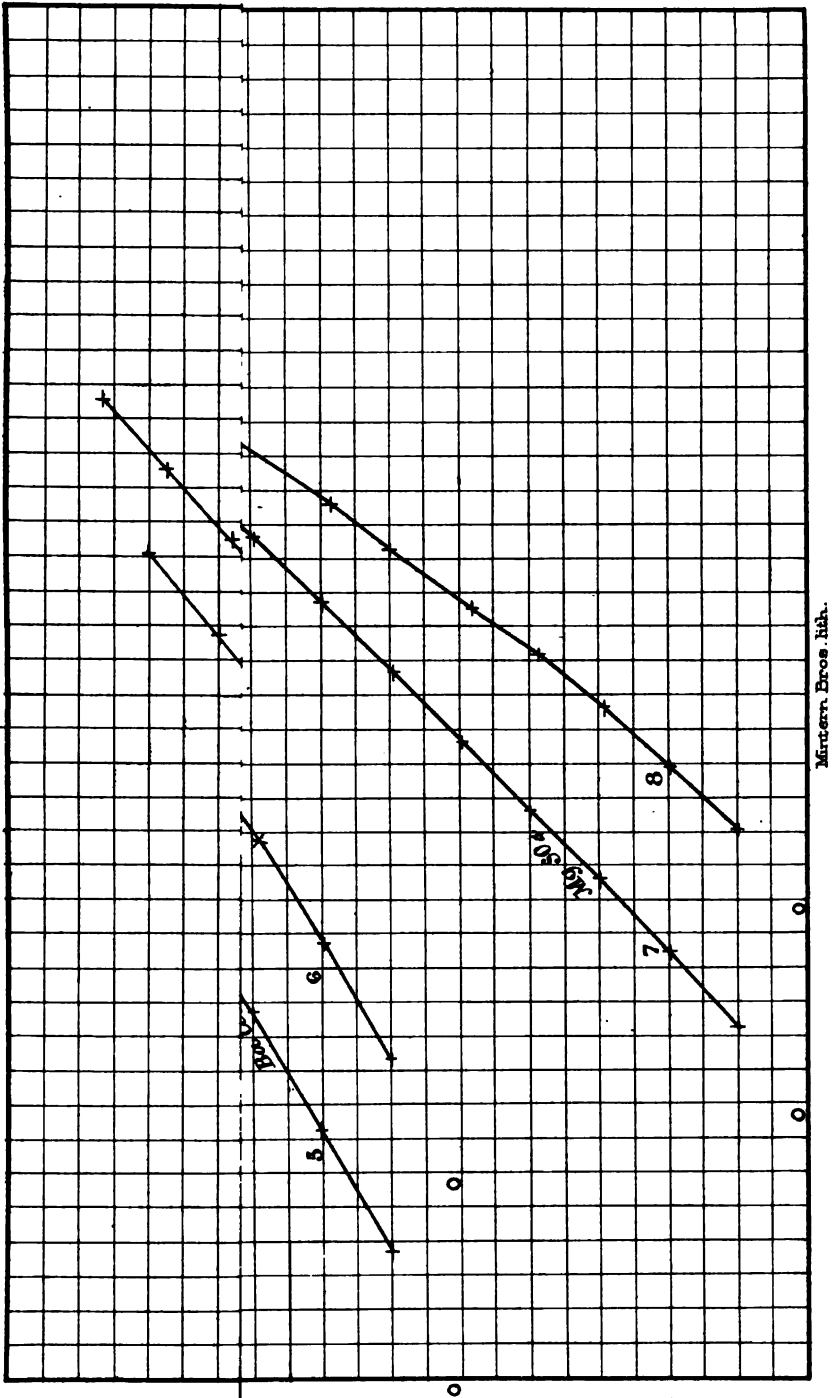
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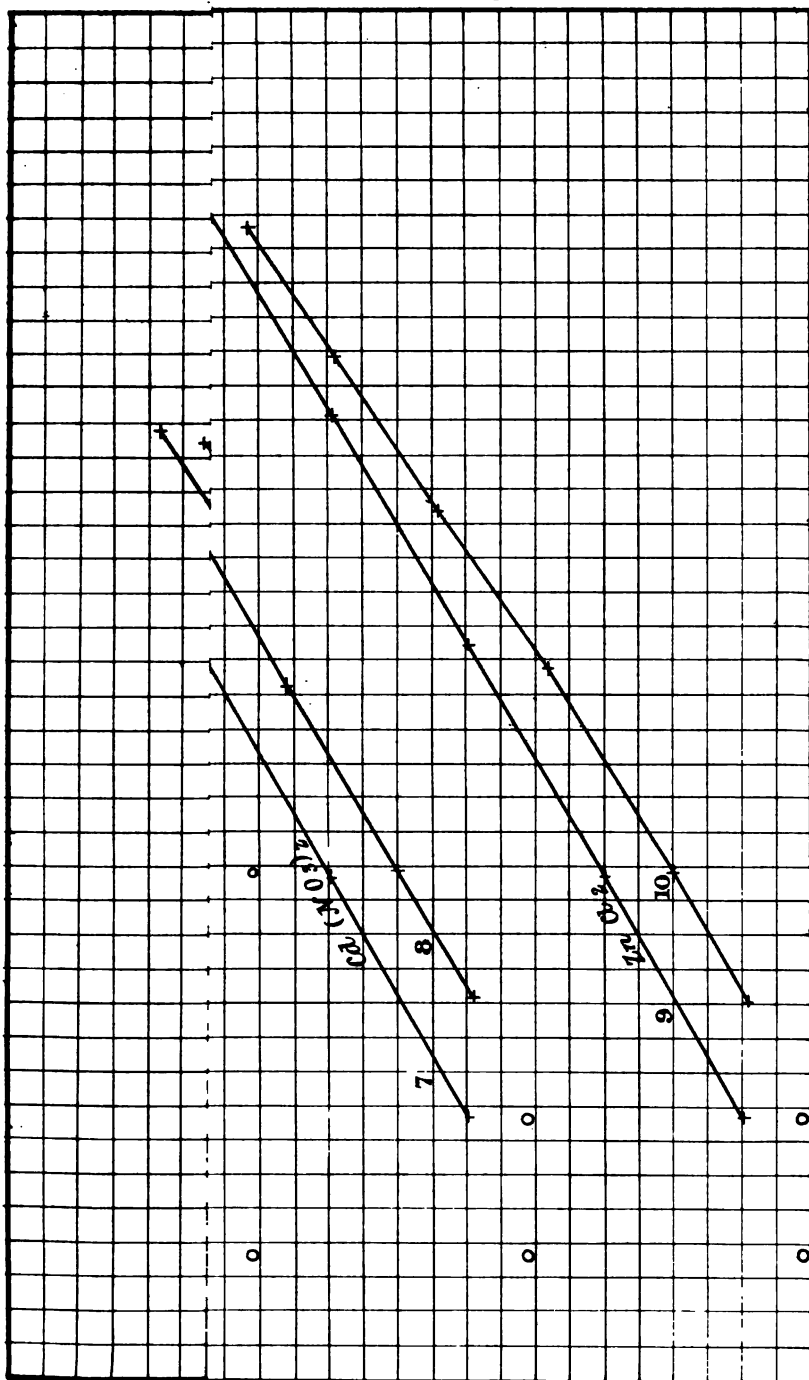
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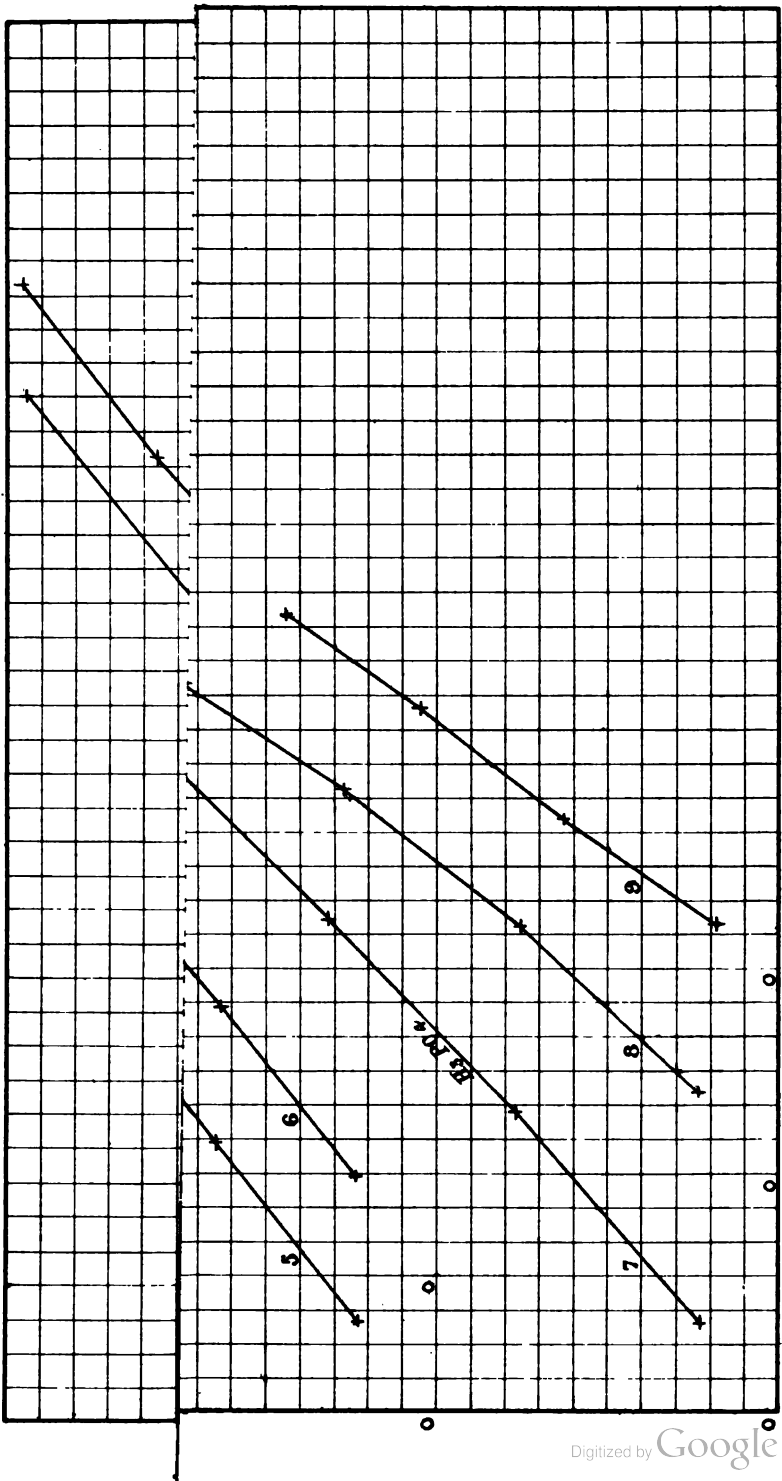
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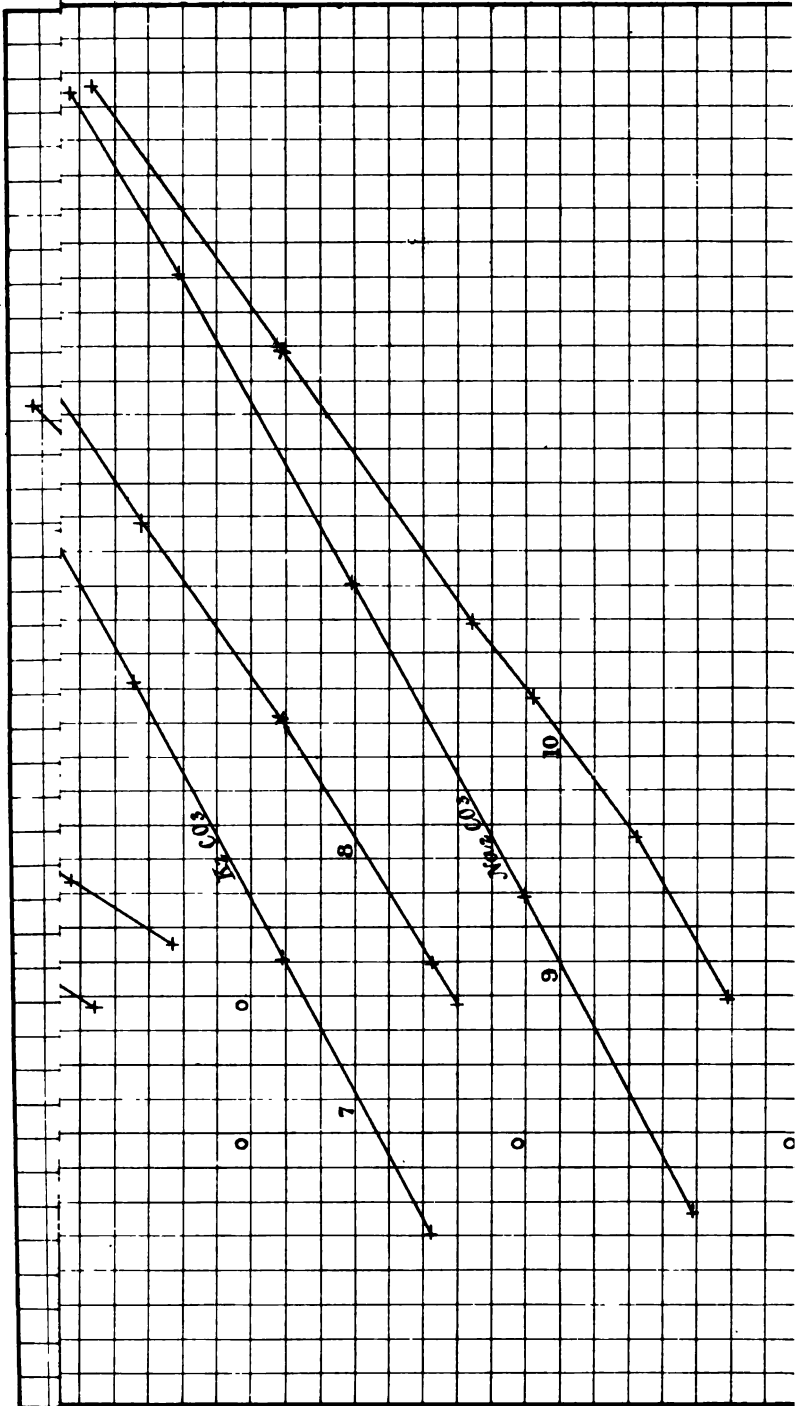


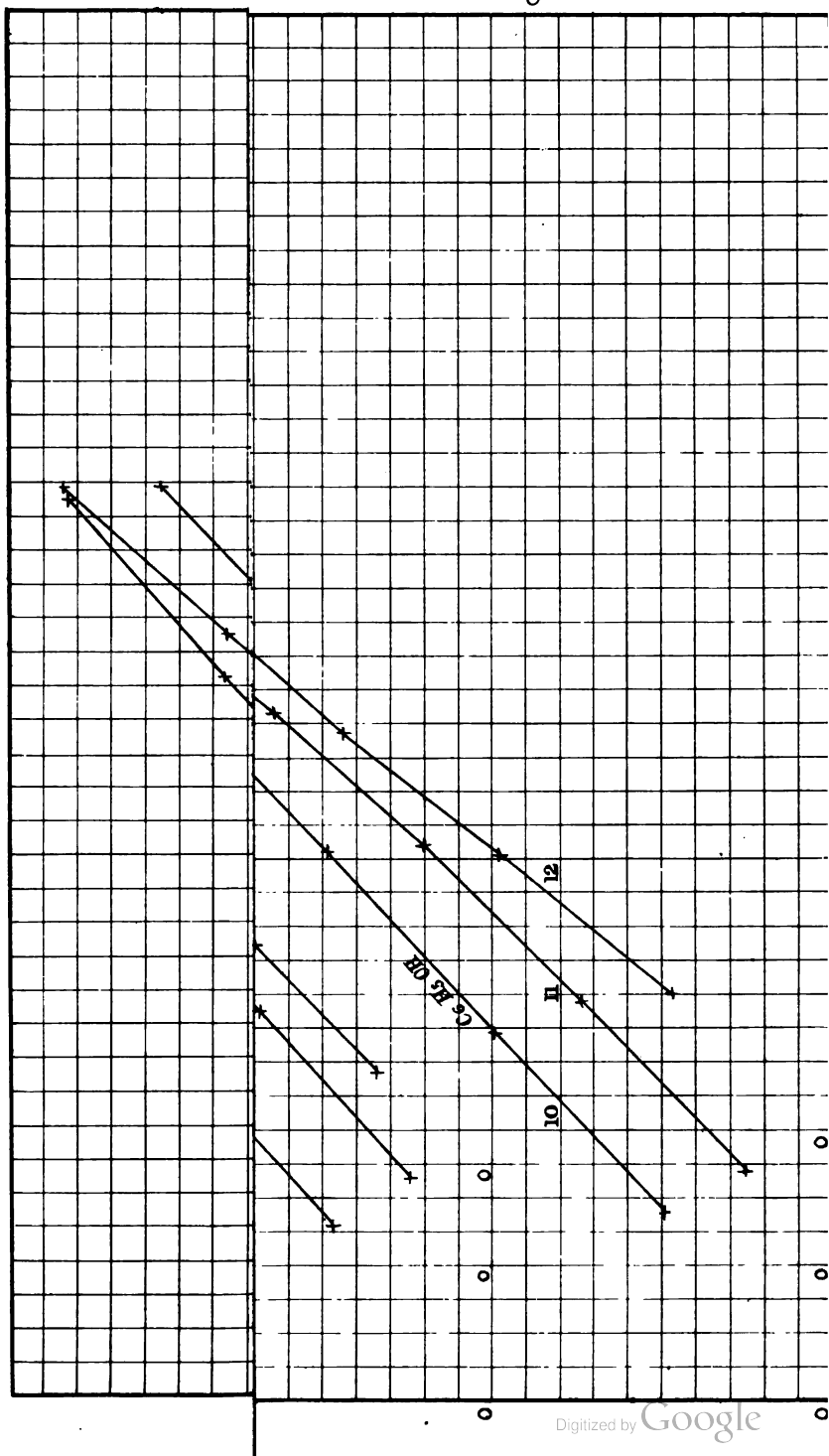


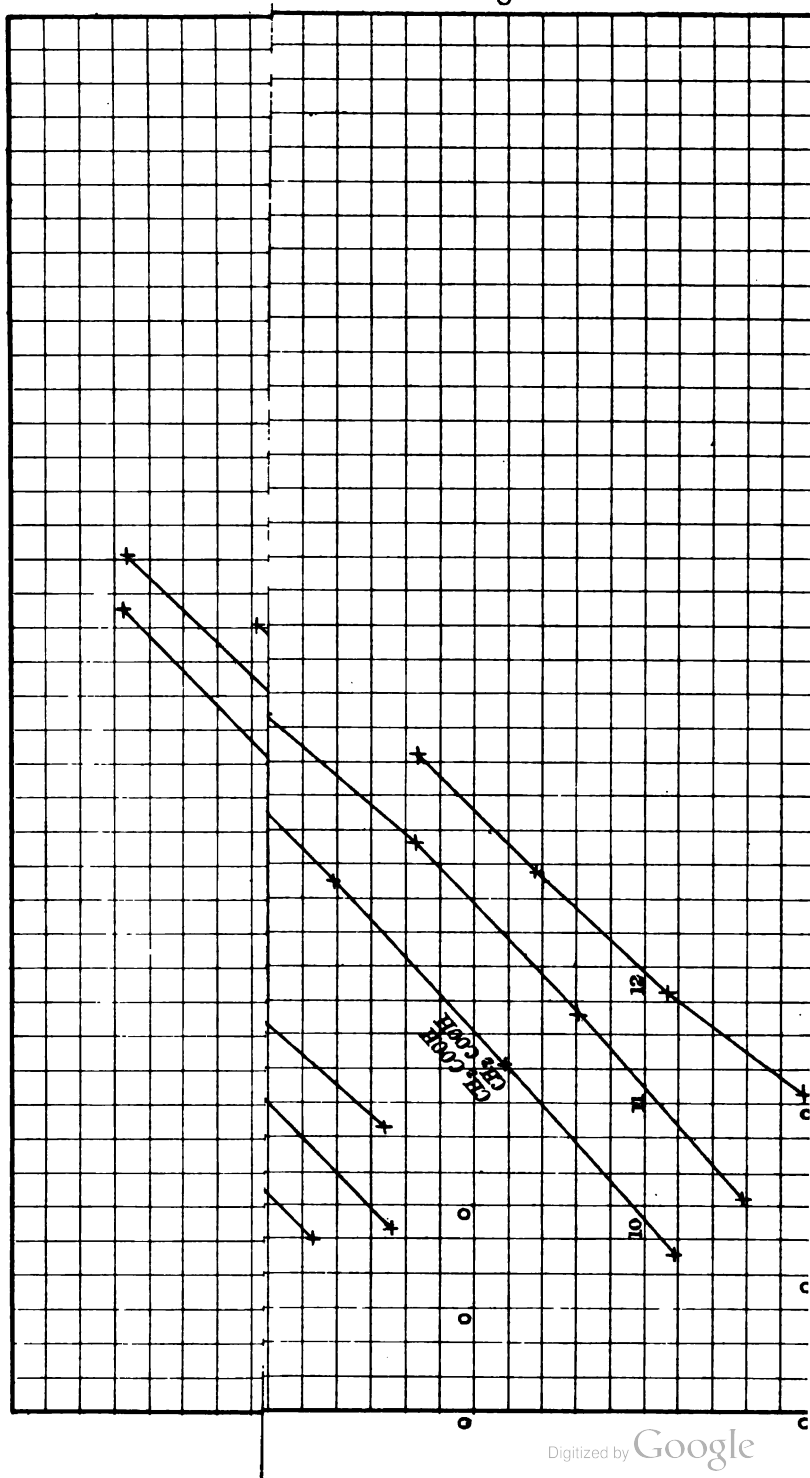
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