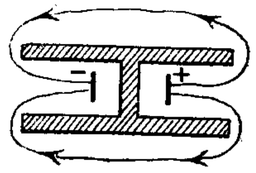
greater than in air, a more powerful attraction is observed than in air.

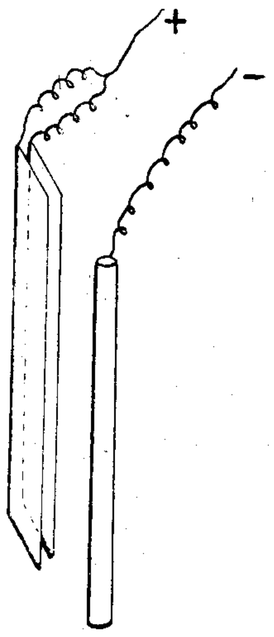
Fifth Experiment.—Two vertical strips of tinfoil, parallel to each other 4 or 5 mm. apart, are immersed in water, a plate of glass or of mica a little wider than the strips is interposed, and while the current is on, a repulsion of the strips is observed. The electrostatic tubes coincide with the lines of electrolytic current, and as the plate deviates the tubes uniting the interior and opposite faces, the resultant of the attractions becomes smaller than that of the repulsions due to the tubes applied to the exterior faces. To direct the Faraday tubes so as to give preponderance to those which pull the strips apart, it is necessary to arrange as in fig. 8, that is, to fix to the diaphragm two perpendicular plates which do not allow the tubes (and lines of current) to scatter laterally; the divergence of the leaves is thus increased several fold.

Fig. 8.



Sixth Experiment.—Two vertical strips of tinfoil are immersed in water (fig. 9). They are parallel, and as near each other as is possible consistent with not being drawn together by capillarity. The pair of strips constitutes one electrode, while the other is a vertical metallic wire, placed in the plane of the first electrode, and 3 cm. distant from it. On the passage of the current, the strips move a little towards the wire, and at the same time diverge from each other just as if they were in air before an electrified conductor.

Fig. 9.



The 4th, 5th, and 6th experiments show the existence of the electrostatic field inside an electrolyte.

Seventh Experiment.—If the two linear conductors in Herz's experiment are replaced by two flexible loops 15 or 20 cm. apart, they attract each other powerfully. Here the tubes are in motion between the linear conductors along which they slide by their extremities, and this is the cause of the equality of velocity of propagation in the medium and in conductors.

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St. Petersburg.

XII. *Molecular Dynamics of a Crystal.* *By* Lord Kelvin *.

§ 1. THE object of this communication is to partially realise the hope expressed at the end of my paper of July 1 and July 15, 1889, on the "Molecular Constitution of Matter †":—"The mathematical investigation must be deferred for a future communication, when I hope to give it *with some further developments.*" The italics are of present date.

Following the ideas and principles suggested in §§ 14–20 of that paper (referred to henceforth for brevity as M. C. M.), let us first find the work required to separate all the atoms of a homogeneous assemblage of a great number n of molecules to infinite distances from one another. Each molecule may be a single atom, or it may be a group of i atoms (similar to one another or dissimilar, as the case may be) which makes the whole assemblage a group of i assemblages, each of n single atoms.

§ 2. Remove now one molecule from its place in the assemblage to an infinite distance, keeping unchanged the configuration of its constituent atoms, and keeping unmoved every atom remaining in the assemblage. Let W be the work required to do so. This is the same for all the molecules within the assemblage, except the negligible number of those (§ 30 below) which are within influential distance of the surface. Hence $\frac{1}{2}n\mathrm{W}$ is the total work required to separate all the n molecules of the assemblage to infinite distances from one another. Add to this n times the work required to separate the i atoms of one of the molecules to infinite distances from one another, and we have the whole work required to separate all the in atoms of the given assemblage.

Another procedure, sometimes more convenient, is as follows:—Remove any one atom from the assemblage, keeping all the others unmoved. Let w be the work required to do so, and let Σw denote the sum of the amounts of work required to do this for every atom separately of the whole assemblage. The total amount of work required to separate all the atoms to infinite distances from one another is $\frac{1}{2}\Sigma w$. This (not subject to any limitation such as that stated for the former procedure) is rigorously true for any assemblage whatever of any number of atoms, small or large. It is, in fact, the well-known theorem of potential energy in the

* From the Proceedings of the Royal Society of Edinburgh for 1901–2, communicated by the Author.

† Proc. Roy. Soc. Edin., and vol. iii. of Mathematical and Physical Papers, art. xcvii.

dynamics of a system of mutually attracting or repelling particles; and from it we easily demonstrate the item $\frac{1}{2}n\mathrm{W}$ in the former procedure.

§ 3. In the present communication we shall consider only atoms of identical quality, and only two kinds of assemblage.

I. A homogeneous assemblage of N single atoms, in which the twelve nearest neighbours of each atom are equidistant from it. This, for brevity, I call an equilateral assemblage. It is fully described in M. C. M., §§ 46, 50 . . . 57.

II. Two simple homogeneous assemblages of $\frac{1}{2}$N single atoms, placed together so that one atom of each assemblage is at the centre of a quartet of nearest neighbours of the others.

For assemblage II., as well as for assemblage I., w is the same for all the atoms, except the negligible number of those within influential distance of the boundary. Neglecting these, we therefore have $\Sigma w = \mathrm{N}w$, and therefore the whole work required to separate all the atoms to infinite distances is—

$$\tfrac{1}{2}\mathrm{N}w \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

§ 4. Let $\phi(\mathrm{D})$ be the work required to increase the distance between two atoms from D to ∞; and let $f(\mathrm{D})$ be the attraction between them at distance D. We have

$$f(\mathrm{D}) = -\frac{d}{d\mathrm{D}}\phi(\mathrm{D}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

For either assemblage I. or assemblage II. we have

$$w = \phi(\mathrm{D}) + \phi(\mathrm{D}') + \phi(\mathrm{D}'') + \text{etc.} \quad . \quad . \quad . \quad (3);$$

where D, D′, D″, etc., denote the distances from any one atom of all neighbours, including the farthest in the assemblage, which exercise any force upon it.

§ 5. To find as many as we desire of these distances for assemblage I. look at figs. 1 and 2. Fig. 1 shows an atom A, and neighbours in one plane in circles of nearest, next-nearest, next-next-nearest, etc. Fig. 2 shows an equilateral triangle of three nearest neighbours, and concentric circles of neighbours in the same plane round it. The circles corresponding to r_4 and r_8 of § 7 below, are not drawn in fig. 2. In all that follows the side of each of the equilateral triangles is denoted by λ.

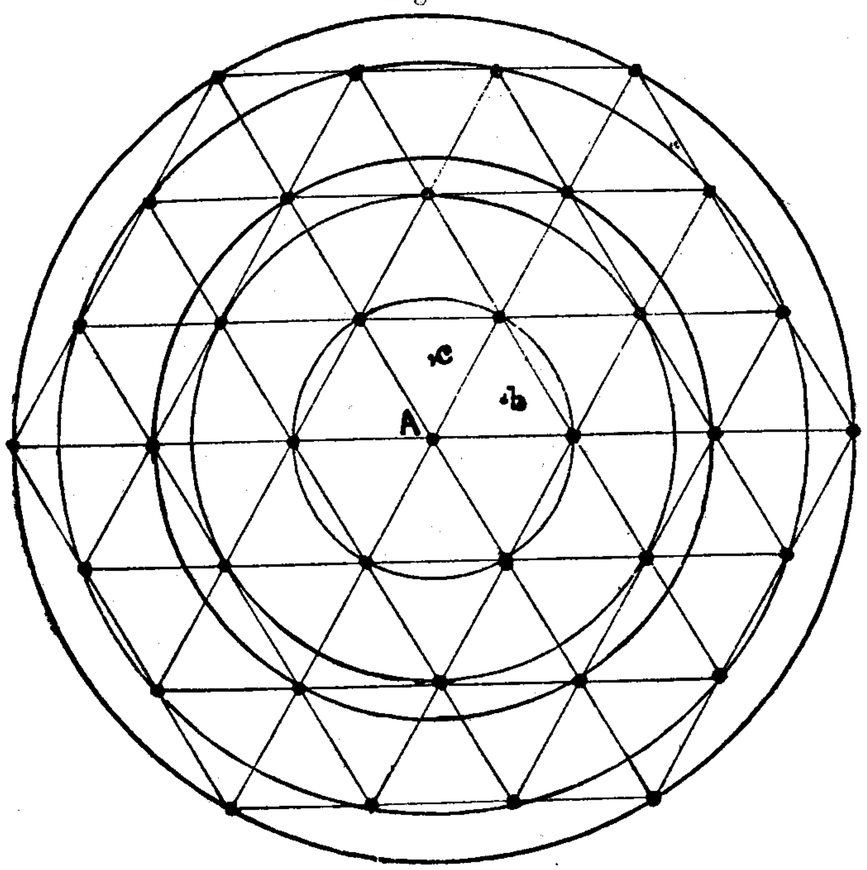
§ 6. All the neighbours in assemblage I. are found by aid of the diagrams as follows:—

(*a*) The atoms of the net shown in fig. 1. The plane of this net we shall call our "middle plane." Let lines be

drawn perpendicular to it through the atom A, and the points marked *b*, *c*, to guide the placing of nets of atoms in parallel planes on its two sides.

(*b*) Two nets of atoms at equal distances $\lambda\sqrt{\frac{2}{3}}$ on the two sides of the "middle plane." These nets are so placed that an atom of one of them, say the near one as we look at the diagram, is in the guide line *b*; and an atom of the far one is in the guide line *c*.

Fig. 1.



(*c*) Two parallel nets of atoms at equal distances, $2\lambda\sqrt{\frac{2}{3}}$, on the two sides of the "middle plane," so placed that an atom of the near one is in the guide line *c*, and an atom of the far one is in the guide line *b*.

(*d*) A third pair of parallel planes at equal distances, $3\lambda\sqrt{\frac{2}{3}}$, from the "middle plane," and each of them having an atom in guide line A.

(*e*) Successive triplets of parallel nets with their atoms cyclically arranged Abc Abc . . at greater and greater distances from A on the near side of the paper, and Acb Acb . . at greater and greater distances on the far side.

§ 7. Let $q_1, q_2, q_3 \ldots$ be the radii of the circles shown in fig. 1, and $r_1, r_2, r_3 \ldots$ be the radii of the circles shown in

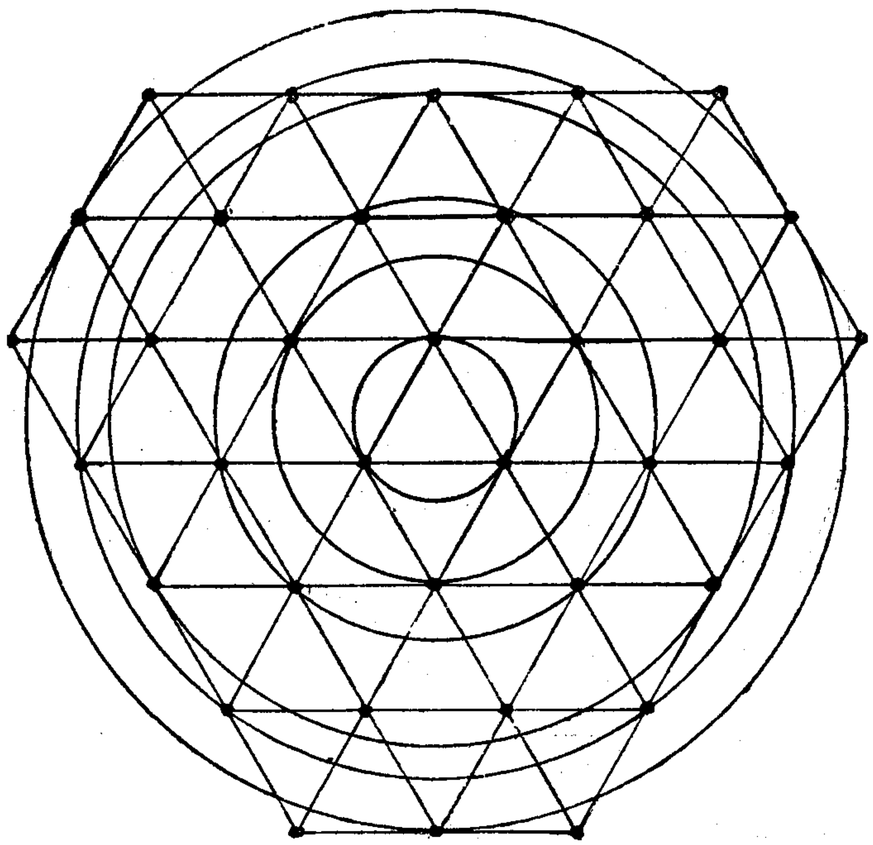
fig. 2; and for brevity denote $\lambda\sqrt{\frac{2}{3}}$ by κ. The distances from A of all the neighbours around it are:—

In our "middle plane": 6 each equal to q_1; 6, q_2; 6, q_3; 12, q_4; 6, q_5; . . . .

In the two parallel nets at distances κ from middle: 6 each equal to $\sqrt{(\kappa^2+r_1^2)}$; 6, $\sqrt{(\kappa^2+r_2^2)}$; 12, $\sqrt{(\kappa^2+r_3^2)}$; 12, $\sqrt{(\kappa^2+r_4^2)}$; 6, $\sqrt{(\kappa^2+r_5^2)}$; 12, $\sqrt{(\kappa^2+r_6^2)}$; 6, $\sqrt{(\kappa^2+r_7^2)}$.

In the two parallel nets at distances 2κ from middle: the same as (B) altered by taking 2κ everywhere in place of κ.

Fig. 2.



In the two parallel nets at distances 3κ from centre: the same as (A) altered by taking $\sqrt{(9\kappa^2+q_1^2)}$, $\sqrt{(9\kappa^2+q_2^2)}$, etc., in place of q_1, q_2, etc.

In nets at distances on each side greater than 3κ: distances of atoms from A, found as above, according to the cycle of atomic configuration described in (*e*) of § 6.

§ 8. By geometry we find

$$\left.\begin{array}{l} q_1=\lambda;\ q_2=\sqrt{3}\lambda=1{\cdot}732\lambda;\ q_3=2\lambda;\ q_4=\sqrt{7}\lambda=2{\cdot}646\lambda;\ q_5=3\lambda: \\ r_1=\sqrt{\frac{1}{3}}\lambda={\cdot}577\lambda;\ r_2=2\sqrt{\frac{1}{3}}\lambda=1{\cdot}154\lambda;\ r_3=\sqrt{\frac{7}{3}}\lambda=1{\cdot}527\lambda;\ r_4=\sqrt{\frac{13}{3}}\lambda=2{\cdot}082\lambda; \\ r_5=4\sqrt{\frac{1}{3}}\lambda=2{\cdot}308\lambda;\ r_6=\sqrt{\frac{19}{3}}\lambda=2{\cdot}517\lambda;\ r_7=5\sqrt{\frac{1}{3}}\lambda=2{\cdot}887\lambda. \end{array}\right\}(4).$$

§ 9. Denoting now, for assemblage I., distances from atom A of its nearest neighbours, its next-nearests, its next-next-nearests, etc., by D_1, D_2, D_3, etc., and their numbers by j_1, j_2, j_3, etc., we find by §§ 7, 8 for distances up to 2λ, for use in § 12 below,

$$D_1=\lambda,\ D_2=1{\cdot}414\lambda,\quad D_3=1{\cdot}732\lambda,\quad D_4=2\lambda,$$
$$j_1=12;\quad j_2=6;\qquad j_3=18;\qquad j_4=6.$$

§ 10. Look back now to § 5, and proceed similarly in respect to assemblage II., to find distances from any atom A to a limited number of its neighbours. Consider first only the neighbours forming with A a single equilateral assemblage: we have the same set of distances as we had in § 9. Consider next the neighbours which belong to the other equilateral assemblage. Of these, the four nearest (being the corners of a tetrahedron having A at its centre) are each at distance $\frac{3}{4}\sqrt{\frac{2}{3}}\lambda$, and these are A's nearest neighbours of all the double assemblage II. Three of these four are situated in a net whose plane is at the distance $\frac{1}{4}\sqrt{\frac{2}{3}}\lambda$ on one side of our "middle plane" through A, and having one of its atoms on either of the guide lines b or c. The distances from A of all the atoms in this net are, according to fig. 2,

$$\sqrt{(\tfrac{1}{16}\kappa^2+r_1^2)},\ \sqrt{(\tfrac{1}{16}\kappa^2+r_2^2)},\text{ etc.}\quad .\quad .\quad .\quad (5).$$

The remaining one of the four nearests is on a net at distance $\frac{3}{4}\sqrt{\frac{2}{3}}\lambda$ from our "middle plane," having one of its atoms on the guide line through A. The distances from A of all the atoms in this net are, according to fig. 1,

$$\tfrac{3}{4}\sqrt{\tfrac{2}{3}}\lambda,\ \sqrt{(\tfrac{9}{16}\kappa^2+q_1^2)},\ \sqrt{(\tfrac{9}{16}\kappa^2+q_2^2)},\text{ etc.}\quad .\quad .\quad (6).$$

All the other atoms of the equilateral assemblage to which A does not belong lie in nets at successive distances κ, 2κ, 3κ, etc., beyond the two nets we have already considered on the two sides of our "middle plane"; the atoms of each net placed of course according to the cyclical law described in (*e*) of § 6.

§ 11. Working out for the double assemblage II. for A's nearest neighbours according to § 10, we find four nearest neighbours at equal distances $\frac{3}{4}\sqrt{\frac{2}{3}}\lambda={\cdot}613\lambda$; twelve next-nearests at equal distances λ; and twelve next-next-nearests at equal distances $\sqrt{\frac{11}{8}}\lambda=1{\cdot}173\lambda$. These suffice for § 12 below. It is easy and tedious, and not at present useful, to work out for D_4, D_5, D_6, etc.

§ 12. Using now §§ 9, 11 in (3) of § 4 we find,—

for assemblage I.,

$$w = 12\phi(\lambda) + 6\phi(1{\cdot}414\lambda) + 18\phi(1{\cdot}732\lambda) + 6\phi(2\lambda) + \ldots$$

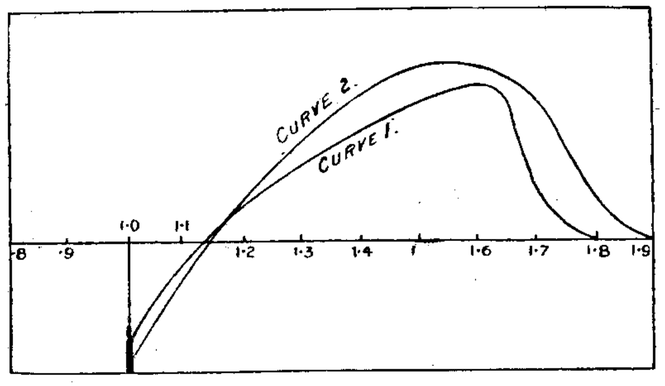
for assemblage II.

$$w = 4\phi({\cdot}613\lambda) + 12\phi(\lambda) + 12\phi(1{\cdot}173\lambda) + \ldots \quad (7).$$

These formulas prepare us for working out in detail the practical dynamics of each assemblage, guided by the following statements taken from §§ 18, 16 of M. C. M.

§ 13. Every infinite homogeneous assemblage of Boscovich atoms is in equilibrium. So, therefore, is every finite homogeneous assemblage, provided that extraneous forces be applied to all within influential distance of the frontier, equal to the forces which a homogeneous continuation of the assemblage through influential distance beyond the frontier would exert on them. The investigation of these extraneous forces for any given homogeneous assemblage of single atoms—or groups of atoms as explained above (§ 1)—constitutes the Boscovich equilibrium-theory of elastic solids.

Fig. 3.

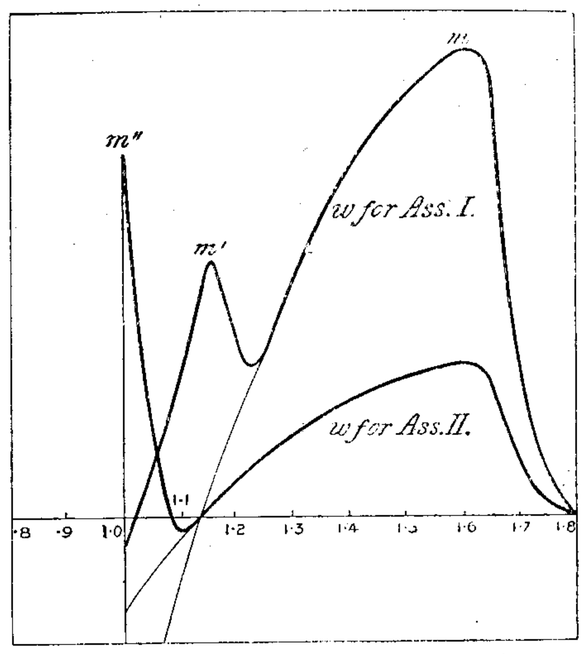


It is wonderful how much towards explaining the crystallography and elasticity of solids, and the thermo-elastic properties of solids, liquids, and gases, we find; without assuming, in the Boscovichian law of force, more than one transition from attraction to repulsion. Suppose, for instance, that the mutual force between two atoms is zero for all distances exceeding a certain distance I, which we shall call the diameter of the sphere of influence; is repulsive when the distance between them is $<\zeta$; zero when the distance is $=\zeta$; and attractive when the distance is $>\zeta$ and $<$ I.

§ 14. Two different examples are represented on the two curves of fig. 3, drawn arbitrarily to obtain markedly diverse conditions of equilibrium for the monatomic equilateral

assemblage (I.), and also for the diatomic assemblage (II.). The abscissa (x) of each diagram, reckoned from a zero outside the diagram on the left, represents the distance between centres of two atoms; the ordinates (y) represent the work required to separate them from this distance to ∞. Hence $-\frac{dy}{dx}$ represents the mutual attraction at distance x. This we see by each curve is $-\infty$ (infinite repulsion) at distance 1·0, which means that the atom is an ideal hard ball of diameter 1·0. For distances increasing from 1·0 the force is repulsive as far as 1·61 in curve 1, and 1·55 in curve 2. At these distances the mutual force is zero; and at greater

Fig. 4.



Law of Force according to Curve 1.

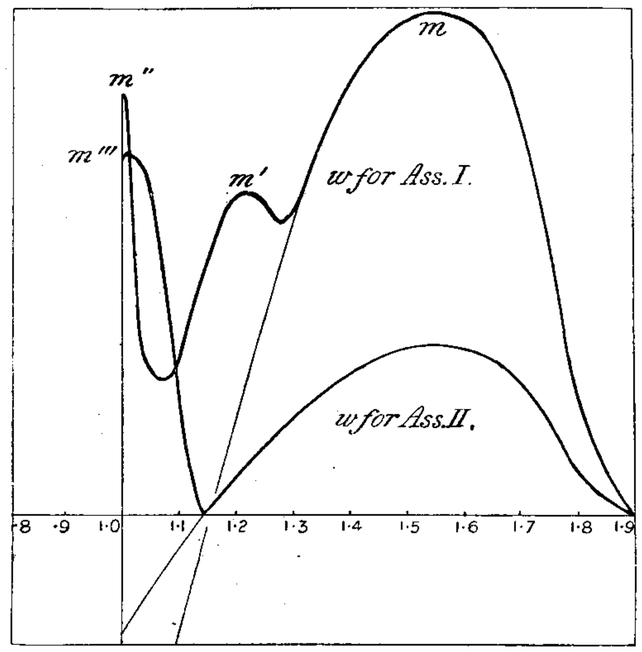
distances up to 1·8 in curve 1, and 1·9 in curve 2, the force is attractive. The force is zero for all greater distances than the last mentioned in the two examples respectively. Thus, according to my old notation, we have $\zeta = 1{\cdot}61$, $\mathrm{I} = 1{\cdot}8$ in curve 1; and $\zeta = 1{\cdot}55$, $\mathrm{I} = 1{\cdot}9$ in curve 2. The distances for maximum attractive force (as shown by the points of inflection of the two curves) are 1·68 for curve 1, and 1·76 for curve 2.

According to our notation of § 4 we have $y = \phi(\mathrm{D})$, if $x = \mathrm{D}$ in each curve.

§ 15. The two formulas (7), § 12, are represented in fig. 4 for curve 1, and in fig. 5 for curve 2; with $x = \lambda$ for Ass. I. and $x = {\cdot}613\lambda$ for Ass. II. In each diagram the abscissa, x,

is distance between nearest atoms of the assemblage. The heavy portions of the curves represent the values of w calculated from (7). The light portions of the curves, and their continuations in heavy curves, represent $4\phi(x)$ and $12\phi(x)$ respectively in each diagram. The point where the light curve passes into the heavy curve in each case corresponds to the least distance between neighbours at which next-nearests are beyond range of mutual force. All the diagrams here reproduced were drawn first on a large scale on squared paper for use in the calculations from (7); which included accurate determinations of the maximum and minimum values of w and the corresponding distances between nearest neighbours in each assemblage. The corresponding densities, given in the last column of the following table of results,

Fig. 5.



Law of Force according to Curve 2.

are calculated by the formula $\sqrt{2}/\lambda^3$ for assemblage I., and $2\sqrt{2}/\lambda^3$ for assemblage II.; "density" being in each case number of atoms per cube of the unit of abscissas of the diagram. This unit is (§ 14) equal to the diameter of the atom. For simplicity we assume the atom to be an infinitely hard ball exerting (§ 13) on neighbouring atoms, not in contact with it, repulsion at distance between centres less than ζ and attraction at any distance between ζ and I.

§ 16. To interpret these results, suppose all the atoms of the assemblage to be subjected to guidance constraining them

either to the equilateral homogeneousness of assemblage I., or to the diatomic homogeneousness of assemblage II., with each atom of one constituent assemblage at the centre of an equilateral quartet of the other constituent assemblage. It is easy to construct ideally mechanism by which this may be done; and we need not occupy our minds with it at present. It is enough to know that it can be done. If the system, subject to the prescribed constraining guidance, be left to itself at any given density, the condition for equilibrium without extraneous force is that w is either a maximum or a minimum; the equilibrium is stable when w is a maximum,

Assemblage I.			Assemblage II.		
Distances between centres of nearest atoms for maximum and minimum values of w.	Maximum and minimum values of w.	Densities.	Distances between centres of nearest atoms for maximum and minimum values of w.	Maximum and minimum values of w.	Densities.
Law of Force according to Curve 1.					
1·16	8·28 (max.)	·904	1·00	11·52 (max.)	·652
1·23	5·22 (min.)	·759	1·10	·76 (min.)	·490
1·61	14·76 (max.)	·338	1·61	4·92 (max.)	·158
Law of Force according to Curve 2.					
1·00	11·58 (max.)	1·414	1·00	12·36 (max.)	·652
1·07	3·78 (min.)	1·146	1·15	0·16 (min.)	·433
1·22	10·44 (max.)	·774	1·53	5·20 (max.)	·184
1·28	9·36 (min.)	·671			
1·53	15·60 (max.)	·393			

unstable when a minimum. It is interesting to see the two stable equilibriums of assemblage I. according to law of force 1, and the three according to law of force 2; and the two stable equilibriums for assemblage II. with each of these laws of force.

§ 17. But we must not forget that it is only with the specified constraining guidance (§ 16) that we are sure of these equilibriums being stable. It is quite certain, however, that without guidance the monatomic assemblage would be stable for the small density corresponding to the point m of

each of the diagrams, because for infinitesimal deviations each atom experiences forces only from its twelve nearest neighbours, and these forces are each of them zero for equilibrium. It may conceivably be that each of the maximums of w, whether for the monatomic or the diatomic assemblage, is stable without guidance. But it seems more probable that, for assemblage I. and law of force 2, the intermediate maximum m' (close to a minimum) is unstable. If it is so, the assemblage left to itself in this configuration would fall away, and would (in virtue of energy lost by waves through ether, that is to say, radiation of heat) settle in stable equilibrium corresponding to the maximum m (single assemblage), or either of the maximums m'' (single assemblage), or m''' (double assemblage). It is also possible that for law of force 1 the maximum m' for the single assemblage is unstable. If so, the system left to itself in this configuration would fall away and settle in either of the configurations m (single assemblage) or m'' (double assemblage). Or it is possible that with either of our arbitrarily assumed laws of force there may be stable configurations of equilibrium with the atoms in simple cubic order (§ 21 below): and in double cubic order; that is to say, with each atom in the centre of a cube of which the eight corners are its nearest neighbours.

§ 18. It is important to remark further, that certainly a law of force fulfilling the conditions of § 13 may be found, according to which even the simple cubic order is a stable configuration; though perhaps not the only stable configuration. The double cubic order, which has hitherto not got as much consideration as it deserves in the molecular theory of crystals, is certainly stable for some laws of force which would render the simple cubic order unstable. Meantime it is exceedingly probable that there are in nature crystals of elementary substances, such as metals, or frozen oxygen or nitrogen or argon, of the simple cubic, and double cubic, and simple equilateral, and double equilateral, classes. It is also probable that the crystalline molecules in crystals of compound chemical substance are in many cases simply the chemical molecules, and in many cases are composed of groups of the chemical molecules. The crystalline molecules, however constituted, are, in crystals of the cubic class, probably arranged either in simple cubic, or double cubic, or in simple equilateral, or double equilateral, order.

§ 19. It will be an interesting further development of the molecular theory to find some illustrative cases of chemical compound molecules (that is to say, groups of atoms presenting different laws of force, whether between two atoms of the same kind or between atoms of different kinds), which are, and others which are not, in stable equilibrium at some density or densities of *equilateral* assemblage. In this last class of cases the molecules make up crystals not of the cubic class. This certainly can be arranged for by compound molecules with law of force between any two atoms fulfilling the condition of § 13; and it can be done even for a monatomic homogeneous assemblage very easily, if we leave the simplicity of § 13 in our assumption as to law of force.

§ 20. The mathematical theory wants development in respect to the conditions for stability. If, with the constraining guidance of § 16, w is either a maximum or a minimum, there is equilibrium with or without the guidance. For w a maximum the equilibrium is stable *with the guidance*; but may be stable or unstable without the guidance. A criterion of stability which will answer this last question is much wanted; and it seems to me that though the number of atoms is quasi infinite the wanted criterion may be finite in every case in which the number of atoms exerting force on any one atom is finite. To find it generally for the equilibrium of any homogeneous assemblage of homogeneous groups, each of a finite number of atoms, is a worthy object for mathematical consideration. Its difficulty and complexity is illustrated in §§ 21, 22 for the particularly simple case of similar atoms arranged in simple cubic order; and in §§ 23–29 for a still simpler case.

§ 21. Consider a group of eight particles at the eight corners of a cube (edge λ) mutually acting on one another with forces all varying according to the same law of distance. Let the magnitudes of the forces be such that there is equilibrium; and in the first place let the law of variation of the forces be such that the equilibrium is stable. Build up now a quasi infinite number of such cubes with coincident corners to form one large cube or a crystal of any other shape. Join ideally, to make one atom, each set of eight particles in contact which we find in this structure. The whole system is in stable equilibrium. The four forces in each set of four coincident edges of the primitive cubes become one force equal to the force between atom and atom at distance λ. The two forces in either diagonal of the coincident square faces of two cubes in contact make one force equal to the force between atoms at distance $\lambda\sqrt{2}$. The single force in each body-diagonal of any one of the cubes is the force between atom and atom at distance $\lambda\sqrt{3}$. The three moduluses of elasticity (compressibility-modulus, modulus with reference to change of angles of the square faces, and modulus with reference to change of

angles between their diagonals) are all easily found by consideration of the dynamics of a single primitive cube, or they may be found by the general method given in "On the Elasticity of a Crystal according to Boscovich"*. (In passing, remark that neither in this nor in other cases is it to be assumed without proof that stability is ensured by positive values of the elasticity moduluses.)

§ 22. Now while it is obvious that our cubic system is in stable equilibrium if the eight particles constituting a detached primitive cube are in stable equilibrium, it is not obvious without proof that this condition, though sufficient, is necessary for the stability of the combined assemblage. It might be that though each primitive cube by itself is unstable, the combined assemblage is stable in virtue of mutual support given by the joinings of eight particles into one at the corners of the cubes which we have put together.

§ 23. The simplest possible illustration of the stability question of § 20 is presented by the exceedingly interesting problem of the equilibrium of an infinite row of similar particles, free to move only in a straight line. The consideration of this linear problem we shall find also useful (§§ 28, 29 below) for investigation of the disturbance from homogeneousness in the neighbourhood of the bounding surface, experienced by a three-dimensional homogeneous assemblage in equilibrium. First let us find a, the distance, or one of the distances, from atom to atom at which the atoms must be placed for equilibrium; and after that try to find whether the equilibrium is stable or unstable.

§ 24. Calling $f(D)$ (as in § 4) the attraction between atom and atom at distance D, we have for the sum, P, of attractions between all the atoms on one side of any point in their line, and all the atoms on the other side, the following finite expression having essentially a finite number of terms, greater the smaller is a:

$$f(a)+2f(2a)+3f(3a)+\ldots\ldots=\mathrm{P} \quad \ldots \quad (8).$$

Hence a, for equilibrium with no extraneous force, is given by the functional equation

$$f(a)+2f(2a)+3f(3a)+\ldots\ldots=0 \quad \ldots \quad (9);$$

which, according to the law of force, may give one or two or any number of values for a: or may even give no value (all roots imaginary) if the force at greatest distance for which there is force at all, is repulsive. The solution or all the solutions of this equation are readily found by calculating

* Proc. R.S.L., vol. 54, June 8, 1893.

from the Boscovich curve representative of $f(D)$ a table of values of P, and plotting them on a curve, by formula (8), for values of a from $a=I$ (the limit above which the force is zero for all distances) downwards to the value which makes $P=-\infty$, or to zero if there is no infinite repulsion. The

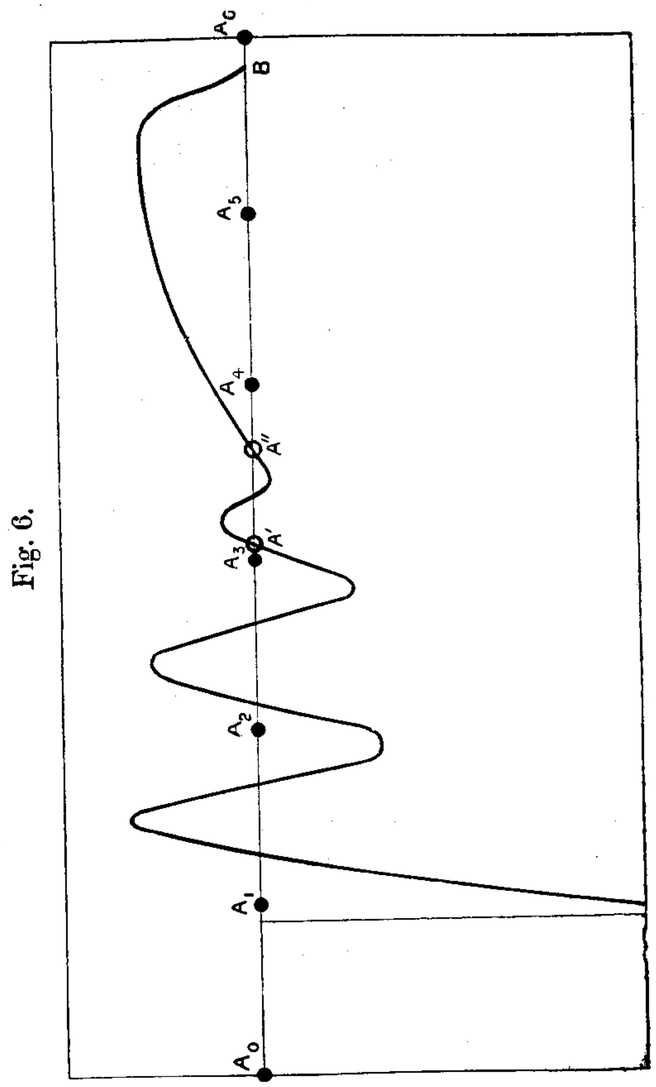


Fig. 6.

accompanying diagram, fig. 6, copied from fig. 1 of Boscovich's great book *, with slight modifications (including positive instead of negative ordinates to indicate attraction) to suit

* Theoria Philosophiæ Naturalis redacta ad unicam legem virium in natura existentium, auctore P. Rogerio Josepho Boscovich, Societatis Jesu, nunc ab ipso perpolita, et aucta, ac a plurimis præcedentium editionum mendis expurgata. Editio Veneta prima ipso auctore præsente, et corrigente. Venetiis, MDCCLXIII. Ex Typographia Remondiniana superiorum permissu, ac privilegio.

our present purpose, shows for this particular curve three of the solutions of equation (8). (There are obviously several other solutions.) In two of the solutions, respectively, A_0, A′, and A_0, A″, are consecutive atoms at distances at which the force between them is zero. These are configurations of equilibrium, because A_0B, the extreme distance at which there is mutual action, is less than twice A_0A', and less than twice A_0A''. In the other of the solutions shown, A_0, A_1, A_2, A_3, A_4, A_5, A_6 are seven equidistant consecutive atoms of an infinite row in equilibrium in which A_5 is within range of the force of A_0, and A_6 is beyond it. The algebraic sum of the ordinates with their proper multipliers is zero, and so the diagram represents a solution of equation (9).

§ 25. In the general linear problem to find whether the equilibrium is stable or not for equal consecutive distances, a, let (as in § 4) $\phi(D)$ be the work required to increase the distance between two atoms from D to ∞. Suppose now the atoms to be displaced from equal distances, a, to consecutive unequal distances—

$$\ldots . \; a+u_{i-2},\; a+u_{i-1},\; a+u_i,\; a+u_{i+1},\; a+u_{i+2},\; . \quad (10).$$

The equilibrium will be stable or unstable according as the work required to produce this displacement is, or is not, positive for all infinitely small values of $\ldots : u_{i-1}, u_i, u_{i+1}, \ldots .$ Its amount is $W_0 - W$; where W denotes the total amount of work required to separate all the atoms from the configuration (10) to infinite mutual distances.

According to § 2 above W is given by

$$W=\tfrac{1}{2}(\ldots + w_{i-1} + w_i + w_{i+1} + \ldots .) \quad (11);$$

where

$$\begin{aligned} w_i = {} & \phi(a+u_i) + \phi(2a+u_{i-1}+u_i) + \phi(3a+u_{i-2}+u_{i-1}+u_i) + \ldots \\ & + \phi(a+u_{i+1}) + \phi(2a+u_{i+1}+u_{i+2}) + \phi(3a+u_{i+1}+u_{i+2}+u_{i+3}) + \ldots \\ & + \ldots \qquad (12). \end{aligned}$$

Expanding each term by Taylor's theorem as far as terms of the second order, and remarking that the sum of terms of the first order is zero for equilibrium * at equal distances, a, and

* It is interesting and instructive to verify this analytically by selecting all the terms in W which contain u_i, and thus finding $\frac{dW}{du_i}$. This equated to zero, for zero values of $\ldots u_{i-1}, u_i, u_{i+1}, \ldots$ gives equation (9) of the text.

putting $\phi''(D) = -f'(D)$, we find

$$\begin{aligned} W_0 - W = \tfrac{1}{4}\Sigma \{ & f'(a)(u_i^2 + u_{i+1}^2) \\ & + f'(2a)[(u_{i-1}+u_i)^2 + (u_{i+1}+u_{i+2})^2] \\ & + f'(3a)[(u_{i-2}+u_{i-1}+u_i)^2 + (u_{i+1}+u_{i+2}+u_{i+3})^2] \\ & + \quad \text{etc.} \qquad \text{etc.} \qquad \text{etc.} \qquad \text{etc.} \} \quad (13); \end{aligned}$$

where Σ denotes summation for all values of i, except those corresponding to the small numbers of atoms (§§ 28, 29 below) within influential distances of the two ends of the row.

§ 26. Hence the equilibrium is stable if $f'(a)$, $f'(2a)$, $f'(3a)$, etc., are all positive; but it can be stable with some of them negative. Thus, according to the Boscovich diagram, a condition ensuring stability is that the position of each atom be on an up-slope of the curve showing attractions at increasing distances. We see that each of the atoms in each of our three equilibriums for fig. 6 fulfils this condition.

§ 27. Fig. 7 shows a simple Boscovich curve drawn arbitrarily to fulfil the condition of § 13 above, and with the further simplification for our present purpose, of limiting the sphere of influence so as not to extend beyond the next-nearest neighbours in a row of equidistant particles in equilibrium, with repulsions between nearests and attractions between next-nearests. The distance, a, between nearests is determined by

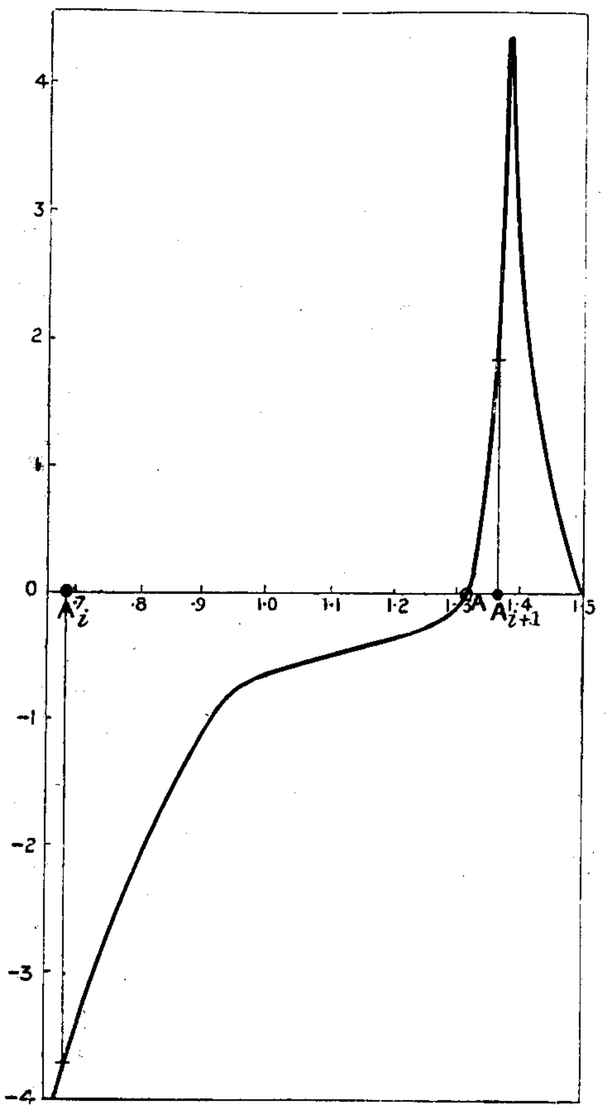
$$f(a) + 2f(2a) = 0 \quad . \quad . \quad . \quad . \quad . \quad (14),$$

being what (9) of § 24 becomes when there is no mutual force except between nearests and next-nearests. There is obviously one stable solution of this equation in which one atom is at the zero of the scale of abscissas (not shown in the diagram) and its nearest neighbour on the right is at A, the point of zero force with attraction for greater distances and repulsion for less distances. The only other configuration of stable equilibrium is found by solution of (14) according to the plan described in § 24, which gives $a = \cdot 680$. It is shown on fig. 7 by A_i, A_{i+1}, as consecutive atoms in the row.

§ 28. Consider now the equilibrium in the neighbourhood of either end of a rectilinear row of a very large number of atoms which, beyond influential distance from either end, are at equal consecutive distances a satisfying § 27 (14). We shall take for simplicity the case of equilibrium in which there is no extraneous force applied to any of the atoms, and no mutual force between any two atoms except the positive or negative attraction $f(D)$. But suppose first that ties or struts

are placed between consecutive atoms near each end of the row so as to keep all their consecutive distances exactly equal to a. For brevity we shall call them ties, though in ordinary language any one of them would be called a strut if its force is push instead of pull on the atoms to which it is applied. Calling A_1, A_2, A_3, . . . the atoms at one end of the row, suppose the tie between A_1 and A_2 to be removed, and A_1

Fig. 7.



allowed to take its position of equilibrium. A single equation gives the altered distance A_1A_2, which we shall denote by $a+{}_1x_1$. Let an altered tie be placed between A_1 and A_2 to keep them at this altered distance during the operations which follow. Next remove the tie between A_2 and A_3, and find by a single equation the altered distance $a+{}_1x_2$. After that

remove the tie between A_3 and A_4 and find, still by a single equation, the altered distance $a+{}_1x_3$, and so on till we find ${}_1x_7$ or ${}_1x_8$ or ${}_1x_i$, small enough to be negligible. Thus found, ${}_1x_1$, ${}_1x_2$, ${}_1x_3$, ... ${}_1x_i$ give a first approximation to the deviations from equality of distance for complete equilibrium. Repeat the process of removing the ties in order and replacing each one by the altered length as in the first set of approximations, and we find a second set ${}_2x_1$, ${}_2x_2$, ${}_2x_3$ . . . . Go on similarly to a third, fourth, fifth, sixth . . . . approximation till we find no change by a repetition of the process. Thus, by a process essentially convergent if the equilibrium with which we started is stable, we find the deviations from equality of consecutive distances required for equilibrium when the system is left free in the neighbourhood of each end, and all through the row (except always the constraint to remain in a straight line). By this proceeding applied to the curve of fig. 7 and the case of equilibrium $a=\cdot680$, the following successive approximations were found:—

	x_1	x_2	x_3	x_4	x_5	x_6	x_7
1st Approximation .	+·018	−·009	+·004	−·002	+·001	−·001	·000
2nd ,, .	+·026	−·014	+·007	−·003	+·002		
3rd ,, .	+·031	−·018	+·009	−·005	+·003		
4th ,, .	+·034	−·020	+·011	−·006			
5th ,, .	+·036	−·022	+·012	−·007			
6th ,, .	+·037	−·023	+·013				
7th ,, .	+·038	−·024					
8th ,, .	+·039						

Thus our final solution, with $a=\cdot680$, is

$$x_1=+\cdot039,\ x_2=-\cdot024,\ x_3=+\cdot013,\ x_4=-\cdot007,\ x_5=+\cdot003,$$
$$x_6=-\cdot001,\ x_7=\cdot000.$$

§ 29. It is exceedingly interesting to remark that the deviations of the successive distances from a are alternately positive and negative, and that they only become less than one-seventh per cent. of a for the distance between A_7 and A_8. Thus, if we agree to neglect anything less than one-seventh per cent. in the distance between atom and atom, the influential distance from either end is $7a$, although the mutual force between atom and atom is null at all distances exceeding $2{\cdot}2a$.

§ 30. If, instead of $f(D)$ denoting the force between two atoms in a rectilinear row, it denotes the mutual force between two parallel plane nets in a Bravais homogeneous assemblage

of single atoms, the work of §§ 27, 28 remains valid; and thus we arrive at the very important and interesting conclusion that when there is repulsion between nearest nets, attraction between next-nearests, and no force between next-next-nearests or any farther, the disturbance from homogeneousness in the neighbourhood of the bounding plane consists in alternate diminutions and augmentations of density becoming less and less as we travel inwards, but remaining sensible at distances from the boundary amounting to several times the distance from net to net.

XIII. *On Spectra arising from the Dissociation of Water Vapour and the Presence of Dark Lines in Gaseous Spectra.* By JOHN TROWBRIDGE *.

[Plate III.]

IN passing from the study of the light emitted by gases under the effect of electrical discharges to the investigation of the light produced by discharges of great quantity, one enters a new field of research. In previous papers on the spectra of hydrogen I have stated my convictions of the importance of the rôle played by water-vapour in glass spectrum-tubes. The results of further study emphasize these convictions. With powerful discharges in hydrogen, oxygen, and rarefied air, even when these gases are dried with the utmost care, I always obtain the same spectrum, which I regard as that arising from the dissociation of water-vapour which is always present in glass tubes. The bright-line spectrum, moreover, at high temperatures is accompanied by a faint continuous spectrum on which are dark lines which indicate a selective reversibility in the silver salt. This reversibility, it seems to me, is of great significance in the application of photography to astrophysics.

It has long been recognized that spectrum analysis is an extremely delicate method of recognizing the presence of a gas or the vapour of a metal under the excitation of heat; and when the improvements in photography enabled us to obtain permanent records of the spectra of gases, it was supposed that we had a means of escaping from the fallacies of eye-observations which arose from personal idiosyncracies. If the photographic plate were a perfect instrument for recording the infinite number of vibrations which light can communicate to atoms of matter, we should certainly feel that we had made a great advance in physical science. When

* Communicated by the Author.

we reflect, however, on the supposition that emulsions containing silver salts are capable of responding and giving a permanent record of all waves of light, even in the portion of the spectrum considered most actinic, when the waves exceed a certain intensity, we are conscious that we rely without proof upon an infinite range of photochemical action; and indeed I show in this paper the existence of a selective reversibility produced on the photographic plate by powerful discharges producing light of great intensity.

Realizing the importance of studying the behaviour of gases under different forms of excitation, I have collected in the rooms devoted to spectrum analysis in this laboratory three forms of apparatus: an induction-coil actuated by a very efficient liquid break, giving a spark of 30 inches in air; a step-up transformer, excited by an alternating current, producing with glass condensers of about ·3 microfarad discharges of an inch in length of great body; and a storage-battery of twenty thousand cells. A plant of this nature I conceive to be necessary in the present stage of spectrum analysis; for molecular motions excited in rarefied gases vary greatly with the kind of electrical discharge. In the application of photography to spectrum analysis one is immediately confronted with the necessity of submitting the gas to a comparatively long electrical stimulus in order to obtain a negative. Even with a concave grating of short focus several discharges are necessary with a narrow slit. Each discharge is capable of modifying the condition of the gas. This fact is well recognized by taking successive photographs upon the same plate with different strengths of current. A simple form of plate-holder enables this to be done. One obtains a striking example of the instability of a spectrum-tube filled, apparently, with dry hydrogen when one subjects it first to very powerful discharges from a glass condenser of ·6 microfarad charged by a storage-battery of twenty thousand cells, with practically no self-induction in the circuit, and follows this excitation by an alternating current of much less quantity. The powerful discharge gives what I term the spectrum arising from the dissociation of water-vapour; and the alternating current gives the spectra of argon. This results, I suppose, from the oxidization of traces of air in the tube under the action of the dissociation of the water-vapour. The presence of hydrogen is concealed. On cooling, the tube again shows the four-line spectrum of hydrogen. The period of the condenser-discharges which I have employed varied from one five-hundred thousandth of a second to one millionth. The practically instantaneous current, therefore, varied from five