

While the rigid investigation of facts is no doubt one of the great methods of science, we must not forget that by asking questions as to the use or value of a particular physiological arrangement, we may obtain light as to the road along which investigations are to be pursued. This is the guiding star of Fleischl von Marxow's speculation, and it has led him and other physiologists to scrutinize anew the theories of respiration now in vogue.

In this address we have had abundant evidence of the fact that physiology, in the solution of some of her problems, depends entirely upon the methods of chemistry and physics. The air-pump, the special advantages of the mercurial air-pump, the methods devised for collecting and analyzing the gases of the blood, the spectroscope, have all contributed important facts to our knowledge of respiration. The narrative placed before you also illustrates in a striking manner the relation of modern physiology to the physiology of our forefathers. The latter were engaged in observing and explaining the more obvious phenomena, whilst the modern physiologists are pushing their researches further, and are endeavouring to study the hidden phenomena, which, like a second order, lie behind these. I need scarcely add that even the results of modern research are not to be regarded as final. Although we see a little further and more clearly than those who went before, there is still uncertainty as to fact and obscurity as to explanation in most departments of physiological science, and not least as regards the function of respiration. Enough has been said to show that in the study of respiratory mechanisms we meet with numerous examples of the same wonderful adaptation of organic structure to physical conditions as may be traced in the mechanism of the eye and of the ear. The structure of a lung or of a gill is just as much adapted for the play of the physical laws regulating gases as the retina is tuned to the vibrations of the ether, or as the organ of Corti responds sympathetically to the waves of musical tone.

*List of Experiments in illustration of the Lecture.*

1. Appearance of blood after having been shaken with carbonic acid.
2. Appearance of blood after having been shaken with hydrogen.
3. Appearance of blood after having been shaken with nitrogen.
4. Appearance of blood after having been shaken with oxygen.
5. *Fas-simile* model of Leeuwenhoek's syringe, by which gases were first demonstrated in the blood.
6. Absorption of ammonia by water.
7. Gases escaping from water in Torricellian vacuum.
8. Gases escaping from blood in Torricellian vacuum.
9. Spectrum of oxyhæmoglobin shown by electric light.
10. Spectrum of reduced hæmoglobin; the reduction effected by ammonium sulphide.
11. Spectrum of oxyhæmoglobin changing into that of reduced hæmoglobin by heating blood *in vacuo*.
12. Demonstration of a new gas-pump for the physiological lecture table (Figs. 1, 2, and 3).
13. Demonstration of the use of Pflüger's gas-pump.
14. Collection of blood-gases and demonstration of the existence of carbonic acid and of oxygen.
15. Carbonic acid collected from a solution of carbonate of soda *in vacuo*.
16. Method, by use of thermo-electric piles with galvanometer, of observing thermal changes attending formation of oxyhæmoglobin.
17. Demonstration of Fleischl von Marxow's experiments, not with a syringe, but with the fluid in a Torricellian vacuum so arranged as to receive a shock.

Dr. McKendrick asks us to direct the attention of our readers to a statement in his address which he wishes to correct. He stated: "If the union of oxygen with the colouring matter is an example of oxidation, it must be attended with the evolution of heat, but, so far as I know, this has not been measured." He then referred to a method by which Mr. J. T. Bottomley and he had been able to observe the heat produced. Dr. McKendrick was not then aware of an important research on this subject conducted in 1871 by his friend Dr. Arthur Gamgee, and contained in a Report to the British Association for the Advancement of Science in 1871. Dr. Gamgee, both by the use of thermometers and by thermo-electric arrangements, demonstrated the important fact that an evolution of heat accompanies the union of oxygen with hæmoglobin, and in the Report referred to there is ample evidence that the research was conducted with

great skill and with an appreciation of the difficulties to be surmounted. He arrived at the conclusion "that the mean rise of temperature during the absorption of oxygen amounted to 0°·0976 C. The maximum heating found was 0°·111 C., and the minimum 0°·083 C."

MOLECULAR PHYSICS: AN ATTEMPT AT A COMPREHENSIVE DYNAMICAL TREATMENT OF PHYSICAL AND CHEMICAL FORCES.<sup>1</sup>

I.

THE author states that his attention was drawn to the subject in the first place by personal intercourse with Sir William Thomson, and by his opening address to the Mathematical and Physical Section of the British Association at the Montreal meeting in 1884, followed by the study of the lithographed report of his lectures on "Molecular Dynamics" at the Johns Hopkins University.

The opening paragraph of the paper contains a restatement of the portions of Thomson's theory applicable to the explanation of optical phenomena. Thomson did not succeed in arriving at a satisfactory explanation of the fact that metallic reflection and double refraction are accompanied by little or no dispersion. The author believes that he has overcome this difficulty by a more complete discussion of the formulæ by expansion in series. He then proceeds to apply the theory to the explanation of chemical phenomena on a purely dynamical basis, and arrives at a method of determining the spectrum of a compound from the spectra of its constituents.

The second portion of the paper is quite independent of the first, and also of Thomson's theories, except that it gives a complete explanation of the manner in which the ether vibrations can be taken up by the molecules of a body.

The author endeavours to explain electrical phenomena by transverse vibrations of the ether, which are very small compared to the diameter of a molecule or of an atom, and one of the most remarkable and interesting results of his investigation is that the theory leads to Weber's law expressing the mutual action of two electric currents, subject to a restriction which excludes exactly those cases the consideration of which led Helmholtz to the conclusion that the law was untenable. A further confirmation of the theory is given by its explanation of a number of other phenomena, such as fluorescence, magnetism, and diamagnetism, and the electro-magnetic rotation of the plane of polarization.

PART I.—LIGHT, HEAT, AND CHEMICAL AFFINITY.

§ 1.—*The Internal Structure of Molecules.*<sup>2</sup>

The ether is assumed to fill the whole of space, and to be everywhere of equal elasticity and density. It is further assumed that, with respect to vibrations of periods comparable with those of light-waves, the ether behaves like a perfectly elastic solid; while with respect to slower vibrations, such as those due to the motion of gaseous molecules, it behaves like a perfect fluid, so that the molecules can traverse it freely.

A molecule is supposed, on Thomson's<sup>3</sup> theory, to consist of a solid core inclosed within a series of spherical shells. Between the core and the innermost shell there is supposed to be an elastic action of a nature which might be represented by a series of symmetrically disposed elastic springs.

A similar elastic action is supposed to take place between every pair of adjacent shells, and also between the outermost shell and the external ether.

Let  $j$  be the number of shells in a molecule, and let their masses, beginning with the outermost one, be

$$\frac{M_1}{4\pi^2}, \frac{M_2}{4\pi^2}, \dots, \frac{M_j}{4\pi^2}.$$

The centres of the core and shells may be supposed to lie in a straight line and to be capable of oscillations along this line. The elastic force between each pair of shells is assumed to be proportional to the relative displacement of their centres; and that between the outermost shell and the external ether, proportional

<sup>1</sup> A Paper read before the Physico-Economic Society of Königsberg, by Prof. F. Lindemann, on April 5, 1888.

<sup>2</sup> The author generally uses the term molecule to denote either an atom or a molecule except when he is considering chemical compounds.—G. W. T.

<sup>3</sup> "Lectures on Molecular Dynamics and the Wave Theory of Light," by Sir William Thomson. (Baltimore, 1884.)



to the displacement of the centre relatively to the external ether. Let  $x_1, x_2, \dots, x_j$ , be the absolute displacement of the  $j$  shells, and  $\xi$  the displacement of the ether; and let  $c_1, c_2, \dots, c_j$ , be the magnitudes of the elastic forces. We then have the following equations:—

$$\begin{aligned} \frac{M_1}{4\pi^2} \frac{d^2x_1}{dt^2} &= c_1(\xi - x_1) - c_2(x_1 - x_2), \\ \frac{M_2}{4\pi^2} \frac{d^2x_2}{dt^2} &= c_2(x_1 - x_2) - c_3(x_2 - x_3), \\ &\dots \dots \dots \end{aligned} \quad (1)$$

Let the point  $\xi$  have a periodic motion given by

$$\xi = a \cos \frac{2\pi t}{T} \dots \dots \dots (2)$$

Then this motion will gradually be communicated to the centres of the shells in a manner which has been fully worked out by Thomson. The value of  $T$  will vary, and after a certain interval a steady condition will be arrived at in which all the points will have periodic motions, so that

$$x_i = a_i \cos \frac{2\pi t}{T} \dots \dots \dots (3)$$

where  $T$  is now arbitrary.

Writing  $a_1 = M_i/T^2 - c_i - c_{i+1}$ , equations (1) give

$$-c_1 \xi = a_1 - \frac{c_2^2}{a_2 - \frac{c_3^2}{a_3 - \dots - \frac{c_{j-1}^2}{a_{j-1} - \frac{c_j^2}{a_j}}}}$$

which may be written in the form—

$$-\frac{x_1}{c_1 \xi} = \frac{T^2}{m_1} \left\{ \frac{K_1^2 R_1}{K_1^2 - T^2} + \frac{K_2^2 R_2}{K_2^2 - T^2} + \dots + \frac{K_j^2 R_j}{K_j^2 - T^2} \right\} \dots (4)$$

The constant  $R_1$  represents the ratio of the energy of the shell  $m_i$  to the total energy of the system. The quantity  $K_i$  is determined by the condition that when  $T = K_i$  the ether remains at rest, or  $\xi = 0$ ; and it may be called a critical period of the molecule, which will accordingly have  $j$  critical periods, and the molecule may undergo vibrations corresponding to any or all of them simultaneously without affecting the external ether.

Instead of this somewhat artificial structure, the molecule may be regarded as consisting of a sphere filled with continuous matter of density varying with the radius, the density having different values for each of  $j$  assigned values of the radius, but though this would be a simpler physical representation, it would lead to great difficulties in the mathematical treatment, though the results would necessarily be of a similar nature to those obtained for the discrete molecule, and it is therefore preferable to retain this representation.

To apply the theory to transparent media let  $M_i/4\pi^2$  represent the thickness instead of the mass of a shell, and let  $\rho/4\pi^2$  and  $l/4\pi^2$  be the density and elasticity respectively of the ether.

The vibrations of the ether will then be given by the equation

$$\rho \frac{d^2\xi}{dt^2} = l \frac{d^2\xi}{dx^2} \dots \dots \dots (5)$$

And the vibrations of the outermost shell will, in virtue of the assumptions which have been made, be connected with those of the neighbouring ether particle  $\xi$  by an equation of the form

$$\rho \frac{d^2\xi}{dt^2} = l \frac{d^2\xi}{dx^2} + c_1(x_1 - \xi)4\pi^2 \dots \dots \dots (6)$$

in which  $c_1$  only differs from its former value by an unimportant factor. The axis of  $x$  is here supposed to be perpendicular to the line of centres, or diameter, of the molecule.

Suppose a light-wave in a direction perpendicular to this axis, and given by the equation

$$\xi = a \sin 2\pi \left( \frac{x}{\lambda} - \frac{t}{T} \right) \dots \dots \dots (7)$$

to strike the molecule; then on the assumption that within a definite interval only one wave strikes the molecule, or that the diameter of the molecule is small in comparison with the wave-

length, where  $\mu$  is the index of refraction of the medium, and  $v$  the velocity of the wave in it, equation (6) gives the equation

$$\begin{aligned} \mu^2 &= \frac{l}{v^2} = \frac{T^2}{\lambda^2} = \frac{l}{\lambda} \left\{ \rho - c_1 T^2 \left( l - \frac{x_1}{\xi} \right) \right\} \\ &= \frac{l}{\lambda} \left\{ \rho - c_1 T^2 \left[ 1 + c_1 \frac{T^2}{m_1} \sum \frac{K_i^2 R_i}{K_i^2 - T^2} \right] \right\} \dots (8) \end{aligned}$$

expressing the index of refraction as a function of the period of vibration of the ray. For waves of period equal to one of the critical periods of the molecule,  $\mu$  becomes infinite, so that the medium is opaque for such waves, which are entirely absorbed in increasing the energy of the internal vibrations of the molecules. The critical periods of the molecule are therefore the vibration-periods of the dark lines of its absorption spectrum.

§ 2.—The Index of Refraction as a Function of the Wave-Length.

As a preliminary to the more general investigation, it will be advisable to trace the dependence of the index of refraction upon the period of vibration in the simple cases  $j = 1$  and  $j = 2$ .

For  $j = 1$  the molecule will consist of a core and a single shell, and equation (8) will reduce to

$$\mu^2 = \frac{\rho}{l} - \frac{c_1 T^2}{l} - \frac{c_1^2 T^4}{l m_1} \frac{K^2 R}{K^2 - T^2} \dots \dots (9)$$

Writing

$$\frac{\rho}{l} = a, \quad -\frac{c_1}{l} = \beta, \quad -\frac{c_1^2 K^2 R}{l m_1} = \gamma, \quad T^2 = x, \quad \mu^2 = y,$$

this may be written in the form

$$y(K^2 - x) = (a + \beta x)(K^2 - x) + \gamma x^2 \dots (10)$$

the equation of a hyperbola having the asymptotes

$$x = K^2, \quad y = (\beta - \gamma)x + a - \gamma K^2 \dots (11)$$

The former represents the single critical period, and the latter practically determines by its direction whether the index of refraction increases or diminishes as  $T$ , the period of vibration, increases, and this the more exactly the more nearly the curve coincides with its asymptotes—that is, the more nearly the value of its determinant, which reduces to  $-\gamma K^2/4$  approaches the value zero.

There will therefore be three cases to consider—

- (a)  $\beta - \gamma > 0$ ,  $\mu$  increases as  $T$  increases.
- (b)  $\beta - \gamma = 0$ ,  $\mu$  approximately constant.
- (c)  $\beta - \gamma < 0$ ,  $\mu$  diminishes as  $T$  increases.

There will be two expansions for  $\mu^2$  in powers of  $T$ , viz.: For  $T < K$ ,

$$\begin{aligned} \mu^2 &= a + \beta x + \frac{\gamma x^2}{K^2} \left\{ 1 + \frac{x}{K^2} + \frac{x^2}{K^4} + \&c. \right\} \\ &= \frac{\rho}{l} - \frac{c_1}{l} T^2 - \frac{c_1^2 R}{l m_1} T^2 \left\{ 1 + \frac{T^2}{K^2} + \frac{T^4}{K^4} + \&c. \right\} \dots (12) \end{aligned}$$

For  $T > K$ ,

$$\begin{aligned} \mu^2 &= a + \beta x - \gamma x \left\{ 1 + \frac{K^2}{x} + \frac{K^4}{x^2} + \&c. \right\} \\ &= \frac{\rho}{l} + \frac{c_1^2 K^4 R}{l m_1} - \frac{c_1}{l} \left( 1 - \frac{c_1 K^2 R}{m_1} \right) T^2 \\ &\quad + \frac{c_1^2 K^6 R}{l m_1 T} \left\{ 1 + \frac{K^2}{T^2} + \&c. \right\} \dots (12a) \end{aligned}$$

The coefficient of  $T^2$  must be very small in order that the formulæ may be in accordance with experimental results.

Both the equations (12) and (12a) give, as a first approximation to the relation between wave-length and period of vibration in the medium considered—

$$T = \lambda \sqrt{\frac{\rho}{l} + \frac{c_1^2 K^4 R}{l m_1}} \dots \dots (13)$$

But  $\lambda$  is approximately proportional to  $T$ , so that

$$\mu^2 = A + B\lambda^2 + \frac{C\lambda^4}{\lambda^2 - \lambda_0^2}$$

where  $\lambda_0$  is the wave-length corresponding to the period  $T = K$ . This agrees with the results of Helmholtz's theory, and with experiment.<sup>1</sup>

For values of  $T$  not in the neighbourhood of  $K$ , the hyperbola

<sup>1</sup> Wüllner's "Experimental-Physik," vol. ii. p. 161, fourth edition.



may be replaced by its non-vertical asymptote, and then it follows from (11) that

$$\mu^2 = \frac{\rho}{l} + \frac{c_1^2 K_1^4 R}{lm_1} - \frac{c_1}{l} \left( 1 - \frac{c_1^2 K_1^2 R}{m_1} \right) T^2 \dots (13a)$$

the right-hand expression consisting of the first two terms of (12a). When  $j = 2$ , or the molecule consists of a core and two shells, equation (8) becomes

$$\mu^2 = \frac{\rho}{l} - \frac{c_1}{l} T^2 - \frac{c_1^2 T^4}{lm_1} \left( \frac{K_1^2 R_1}{K_1^2 - T^2} + \frac{K_2^2 R_2}{K_2^2 - T^2} \right) \dots (14)$$

or

$$y = \alpha + \beta x + \frac{\gamma x^2}{K_1^2 - x} + \frac{\delta x^2}{K_2^2 - x}$$

where  $x, \gamma, \alpha, \beta, \gamma$ , have the same meanings as before, and  $\delta = -c_1^2 R_2 / m_1$ . The curve is therefore of the third order with two vertical asymptotes,  $x = K_1$ , and  $x = K_2$ , and a third given by the equation

$$y = \alpha - \gamma K_1^2 - \delta K_2^2 + (\beta - \gamma - \delta)x \dots (15)$$

If the curve nearly coincides with its asymptotes,  $\mu^2$  will be given approximately in terms of  $T^2$  by (15), except near the critical periods, and as before there will be three cases, viz. :-

- (a)  $\beta - \gamma - \delta > 0$ ,  $\mu$  increases as  $T$  increases.
- (b)  $\beta - \gamma - \delta = 0$ ,  $\mu$  approximately constant.
- (c)  $\beta - \gamma - \delta < 0$ ,  $\mu$  diminishes as  $T$  increases.

Near the critical periods  $\mu^2$  will always diminish as  $T$  increases.

When the condition (a) is fulfilled, and the curve does not approximately coincide with its asymptotes,  $\mu$  may continue to decrease as  $T$  increases throughout the whole branch of the curve between the two vertical asymptotes, the curve running from the upper left-hand to the lower right-hand side.

The expansions in powers of  $T$  will be different for the three branches, viz. :-

For  $T < K_1$ ,

$$\mu^2 = \alpha + \beta x + x^2 \left( \frac{\gamma}{K_1^2} + \frac{\delta}{K_2^2} \right) + x^3 \left( \frac{\gamma}{K_1^4} + \frac{\delta}{K_2^4} \right) + \&c. \dots (16)$$

For  $T > K_2$ ,

$$\mu^2 = \alpha - \gamma K_1^2 - \delta K_2^2 + (\beta - \gamma - \delta)x - \frac{1}{x} (\gamma K_1^4 + \delta K_2^4) - \frac{1}{x^2} (\gamma K_1^6 + \delta K_2^6) + \&c. \dots (16a)$$

For  $K_1 < T < K_2$ ,

$$\mu^2 = \alpha - \gamma K_1^2 + (\beta - \gamma)x - \frac{\gamma K_2^4}{x} + \frac{\delta x^2}{K_1^2} - \frac{\gamma K_1^6}{x^2} + \frac{\delta x^3}{K_1^4} - \frac{\gamma K_1^8}{x^3} + \&c. \dots (16b)$$

The first terms of (16a) are identical with the right-hand side of (15), and therefore if the curve nearly coincides with its asymptotes, it will closely approximate to the curve (14), except near the critical periods. This explains why Cauchy's expansion of  $\mu^2$  in descending powers of  $T$ , or of  $\lambda$ , gives approximately correct results. In this expansion the coefficient of  $T^2$  vanishes if the asymptote is parallel to the axis of  $x$ , viz. if  $\beta = \gamma + \delta$ , or if

$$m_1 = c_1(K_1^2 R_1 + K_2^2 R_2) \dots (17)$$

If  $\delta = 0$  it reduces to the preceding case; the curve breaking up into the asymptote  $x = K_2^2$ , and a hyperbola. If  $\gamma = 0$  it breaks up into the asymptote  $x = K_1^2$  and a hyperbola.

In general, with a greater number of critical periods, if the curve is of the order  $n$ , it will have  $n - 1$  vertical, and one other asymptote. To the left of the first vertical asymptote and to the right of the last there will be a hyperbolic branch, and between every two of them will be a branch of the curve proceeding from the upper left-hand to the lower right-hand side, either falling continuously or reaching a minimum, then rising to a maximum, and again falling and approaching the next asymptote. There will be  $n$  distinct expansions for  $\mu^2$  in powers of  $T^2$ , one for each branch of the curve. In many cases the curve, except near the critical periods, will approximately coincide with its non-vertical asymptote, and there will then be the three cases, (a), (b), (c), to consider, as in the previous examples.

§ 3.—Dispersion and Reflection.

It is well known that the spectrum of light of a given kind depends on the function of  $T^2$  serving to express  $\mu^2$ . The

dispersion in a refracting medium will be designated as normal when, except near the critical periods,  $\mu^2$  diminishes without limit as  $T^2$  increases, and anomalous when  $\mu^2$  increases without limit, or passes through a series of maxima and minima. In the first case the colours of the spectrum will appear in their "natural" order, the smaller values of  $T^2$  corresponding to the blue, and the larger values to the red end of the spectrum. In the examples considered in § 2 the dispersion will accordingly be normal in case (c), and anomalous in case (d), while in case (b) the spectrum will be compressed into a line.

When the dispersion is anomalous throughout, the colours will appear in the inverse of the natural order, but it will be otherwise when it is alternately normal and anomalous.

Consider, for example, the non-vertical asymptote in case (c). Then if there are only two critical periods there will be to the left of the asymptote  $x = K_1^2$ , a hyperbolic branch, along which  $\mu^2$  will decrease continuously, giving normal dispersion at the blue end of the spectrum above the axis of  $x$ . Below this axis  $\mu^2$  will be negative, and therefore  $\mu$  will be imaginary, so that light of the corresponding period will be entirely reflected by the medium. From the point of intersection of the branch of the curve with the axis of  $x$  to the point  $x = K_2^2$  there will therefore be a dark space or absorption band. To the right of this point  $\mu^2$  will again decrease from positive infinity to a minimum.

Suppose this to be at a position for which  $x = \beta$  above the axis of  $x$ , the curve will then rise to a maximum, say for  $x = \gamma$ . For  $\beta < T^2 < \gamma$  the light will then be more strongly refracted than for  $T^2 < \beta$ , and therefore the corresponding colours will be displaced, and may overlap the colours for which  $T^2 < \beta$ . There will therefore be a dark band at the part of the spectrum which should be occupied by them, but this is not now an absorption band, and may be made to disappear by further dispersion. For  $T^2 < \gamma$  the dispersion will be normal up to the intersection of the branch with the axis of  $x$ , from which a dark band will extend to the point  $x = K_2^2$ , after which the dispersion will again become normal.

Phenomena of this kind have been observed by Kundt and others, and the fact that they follow from the formulæ was considered by Thomson to afford important confirmation of the theory. In fact, taking  $T$  proportional to  $\lambda$ , the preceding equations do not differ essentially from those obtained from quite different phenomena by Sellmayer, von Helmholtz, Lommel, and Ketteler, and which have been shown to be in complete accordance with experiment.<sup>1</sup>

Sir William Thomson, in his Baltimore lectures, came to the conclusion that according to his theory metallic reflection would necessarily cause dispersion. This would be the case if there were only a single expansion for  $\mu^2$ , but in the case of most of the metals there are so many lines, distributed over the whole spectrum, that there is no reason for selecting any one in preference to the others. The fact that all the colours are reflected to practically the same extent, which means that  $\mu^2$  must be a negative constant, may be completely explained by the assumptions that the corresponding curve of the  $n$ th order approximates very closely to its  $n$  asymptotes, and that the single non-vertical asymptote is very nearly parallel to the axis  $\mu = 0$ . The essential portion of the curve may then be replaced by its horizontal asymptote, as in the cases previously considered, in which  $\beta - \gamma$  and  $\beta - \gamma - \delta$  respectively were assumed to be nearly zero. The non-existence of dispersion does not therefore afford an objection to the theory.

It is easy to see that by a suitable choice of the disposable constants, the curve may be made to practically coincide with its asymptotes, for consider the curve of the third order given by (14). This may be written in the form

$$(K_1^2 - x)(K_2^2 - x)(y - \alpha - \beta x) = \gamma x^2(K_2^2 - x) + \delta x^2(K_1^2 - x);$$

$$\text{or}$$

$$(K_1^2 - x)(K_2^2 - x)(y - \alpha - \beta x + \gamma K_1^2 + \delta K_2^2 + \gamma x + \delta x) = x^3(\gamma + \delta - \gamma K_1^2 - \delta K_2^2) - x(\gamma K_1^4 + \delta K_2^4) + K_1^2 K_2^2 (\gamma K_1^2 + \delta K_2^2),$$

and it is evident that when  $K_1^2$  and  $K_2^2$  are given, the right-hand member may be made to vanish by taking  $\gamma$  and  $\delta$  small enough, and the required condition will then be fulfilled, since the left-hand member equated to zero represents the three asymptotes.

<sup>1</sup> See Willner, "Experimental-Physik," vol. ii. pp. 105 and 169, fourth edition. An outline of the various theories of reflection and refraction will be found in the British Association Reports for 1835 and 1837.



## § 4.—Spectra of Luminous Gases.

It was first shown by Kirchhoff that glowing gases emit light of the same wave-length, and therefore also of the same period, as that which they absorb.

In the modern theory of gases it is assumed that the molecules of a luminous gas move over a certain distance, the length of the "free path," in straight lines, until they collide with other molecules, or with the sides of the containing vessel, when they move off rectilinearly in another direction.

At every collision the molecule is subjected to an elastic impulse in a direction passing through its centre, causing internal elastic vibrations. The periods of these vibrations could, on the analogy of a corresponding problem in the theory of elasticity, be calculated from a transcendental equation, if the interior of the molecule were uniformly filled with matter; according to Thomson's theory of molecular structure they are determined *a priori*, being the critical periods of the molecule. In fact, during the collisions the external shells only are in contact, but the surrounding ether remains unaffected, and therefore the external vibrations must be of such a nature that  $\xi = 0$  (§ 1), which is the condition determining the critical periods. But according to § 1 these periods determine the wave-length of the light absorbed. Thus Kirchhoff's law is a consequence of the theory.

It has hitherto been assumed that the vibrations in a molecule, arising from the collisions, take place along a fixed diameter, and therefore that the vibrations due to one encounter are not disturbed by a later one in another direction. If the temperature or the density of the gas is so great that the encounters follow one another very rapidly, the investigation of § 1 is no longer applicable, and light-waves of other than the critical periods will be emitted. If a second encounter takes place only after the vibration due to the first has nearly subsided, the period of the emitted light will only differ slightly from a critical period. As the density and temperature increase, the bright lines will therefore gradually increase in width.<sup>1</sup> If a molecule receives impulses in different directions in rapid succession, very few of the vibrations will have the critical periods, and therefore the dark spaces between the bright lines will ultimately disappear, and the spectrum become continuous, as is well known to be experimentally true.

## § 5.—Applications to the Theory of Heat.

It will be of interest to see what explanation Thomson's molecular hypothesis can give of the manner in which the velocity of gaseous molecules can be increased by the action of heat, as has been assumed in what precedes.

The energy due to the internal molecular vibrations cannot possibly exceed a definite maximum value, for the amplitudes and therefore the velocities of the centres of the shells must have fixed upper limits, since the shells must remain one within the other. This maximum may be attained either for vibrations of a single critical period, or of all the critical periods. Suppose this maximum value to have been nearly reached, then any further disturbance of the internal equilibrium, tending to increase the amplitude of motion of one of the centres beyond the maximum value possible while the centre of gravity remains fixed, will necessarily displace the centre of gravity, whether the disturbance be due to a wave of light or to a mechanical impulse.

This leads to the general and fundamental proposition that "A molecule will begin to move as soon as the energy of its internal vibrations has attained its maximum value, supposing the external influences to which the attainment of the maximum is due continue to act."<sup>2</sup>

The internal equilibrium of a molecule may be disturbed either by light or heat, the disturbance in the case of light being due to its action on the critical periods of the molecule. A medium will therefore be heated when traversed by light-rays; the rays of the critical periods set the molecular shells in vibration, and when the internal energy has reached its maximum value, the centres of gravity of the molecules will begin to move, and this motion will be perceived as heat.

<sup>1</sup> This result may be expressed by saying that the characteristic constant  $c_2$  of the molecule is a function of the temperature. It is preferable to regard the ideal spectrum, whether due to emission or absorption, as something definitely fixed; external circumstances merely assisting or hindering its formation.

<sup>2</sup> Sir W. Thomson also points out ("Lectures," p. 280) that a considerable increase in the internal vibrations of a molecule must set it in motion, and therefore cause a production of heat.

The energy of internal motions therefore accounts for a portion of the internal work of the mechanical theory of heat.<sup>1</sup>

The external work is effected by the motion of the centres of gravity of the atoms, and this takes place in different and known ways in solid, liquid, and gaseous bodies. Heat may act on a medium either by radiation or conduction. Radiant heat differs from light only in its action on our senses, so that what has been said about light will apply also to radiant heat. In the case of conduction of heat the process is exactly the reverse. The external work of the medium emitting the heat will be transmitted directly to the medium receiving it by contact—that is, by collisions of molecules.<sup>2</sup>

The disturbance of the internal equilibrium of the molecules is here merely a secondary effect, but in this case also the internal energy will gradually increase to the maximum value.<sup>3</sup>

The emission of light by a sufficiently heated solid is explained as in the case of gases, but the spectrum in the case of the solid is continuous.

Just as the action of heat may produce such violent molecular motion as to cause the emission of all possible kinds of light, so the action of light may produce a molecular motion giving rise to a special kind of light. This will only happen, however, when the molecule (owing to specially favourable values of the constants  $c_2$  and  $m_2$ ) is specially susceptible to some among its critical periods. In this way the phenomenon of fluorescence may be explained.

G. W. DE TUNZELMANN.

(To be continued.)

## SOCIETIES AND ACADEMIES.

## LONDON.

Royal Society, June 21.—"On the Determination of the Photometric Intensity of the Coronal Light during the Solar Eclipse of August 28-29, 1886. Preliminary Notice." By Captain W. de W. Abney, C.B., R.E., F.R.S., and T. F. Thorpe, Ph.D., F.R.S.

Attempts to measure the brightness of the corona were made by Pickering in 1870, and by Langley and Smith, independently, in 1878, with the result of showing that the amount of emitted light as observed at various eclipses, may vary within comparatively wide limits. These observations have been discussed by Harkness ("Washington Observations for 1876," Appendix III.) and they are again discussed in the present paper. Combining the observations, it appears that the total light of the corona in 1878 was 0.072 of that of a standard candle at 1 foot distance, or 3.8 times that of the full moon, or 0.0000069 of that of the sun. It further appears from the photographs that the coronal light varied inversely as the square of the distance from the sun's limb. Probably the brightest part of the corona was about 15 times brighter than the surface of the full moon, or 37,000 times fainter than the surface of the sun.

The instruments employed by the authors in the measurement of the coronal light on the occasion of the solar eclipse of August 28-29, 1886, were three in number. The first was constructed to measure the comparative brightness of the corona at different distances from the moon's limb. The second was designed to measure the total brightness of the corona, excluding as far as possible the sky effect. The third was intended to measure the brightness of the sky in the direction of the eclipsed sun. In all three methods the principle of the Bunsen photometric method was adopted, and in each the comparison-light was a small glow-

<sup>1</sup> The discrepancies occurring in the determination of the atomic weights of gases may therefore be explained by assuming that internal work is done by the motions of the atoms, instead of assuming, as would otherwise be necessary, that the internal work is only done by the motions of the molecules and a decrease in the attractive force between them. For "motion of the atoms" we should have to substitute "motion of the inner spherical shells."

<sup>2</sup> For the method of deducing the differential equation of heat-conduction from these considerations, see F. Neumann, "Vorlesungen über die Theorie der Elasticität," § 59.

<sup>3</sup> Dulong's law of atomic heat gives some information respecting the relative value of this maximum. This law states that the quantity of internal work due to heating is approximately the same, at any rate when in the gaseous state, for elementary bodies which are ordinarily solid or liquid, a given number of atoms always requiring the same quantity of heat to produce a given rise of temperature. It follows, then, that for these elements the maximum internal energy is very nearly the same. Carbon, silicon, sulphur, and phosphorus behave exceptionally in this, as in many other respects, and the law is not generally true for the elements which are ordinarily gaseous. Since the maximum value of the internal energy depends on the diameter of the molecule, as well as on the constants  $c_2$  and  $m_2$ , it may perhaps be concluded that the diameter of the molecules of these elements are approximately equal.