

Hence we see that the density of the saturated solution depends upon the extent of surface of the liquid, so that, if we alter the surface, we may either deposit or absorb salt. Effects of this kind have, I believe, been observed by chemists.

Let us now proceed to investigate the effects of pressure on the solubility. Let us suppose that the mixture of salt and solution is under a pressure p per unit area. The effect of the pressure will be due to two causes. The first is the change of volume which accompanies solution, and which causes the process of solution to be accompanied by an expenditure or absorption of work; the second cause is that the energy due to the strain in unit mass of the salt is not, in general, the same as that of an equal mass of the solution, so that there will be a change in the potential energy when the salt dissolves. If κ be the bulk modulus for the salt, κ' for the solution, the rest of the notation being the same as before, then the change in the potential energy due to strain is, when unit mass of salt dissolves,

$$\frac{1}{2}p^2 \left\{ \frac{1}{\kappa'\rho} + v' \frac{d}{dq'} \frac{1}{\kappa'} + \frac{v'}{\kappa'} \frac{d}{dq'} \frac{1}{\rho} - \frac{1}{\sigma\kappa} \right\};$$

the increase in the potential energy due to the change in volume is

$$p \frac{d}{dq'} (v + v'),$$

so that we have, by equation (37),

$$\theta \delta \left(\frac{w}{\rho} + w'q' \frac{d}{dq'} \frac{1}{\rho} + v' \frac{dw'}{dq'} \right) = p \frac{d}{dq'} (v + v') + \frac{1}{2}p^2 \left(\frac{1}{\kappa'\rho} + v' \frac{d}{dq'} \frac{1}{\kappa'} + \frac{v'}{\kappa'} \frac{d}{dq'} \frac{1}{\rho} - \frac{1}{\sigma\kappa} \right); \quad (42)$$

or, if the change due to pressure be the same as the change due to an increase $\delta\theta$ in the temperature, we have

$$\lambda \frac{\delta\theta}{\theta} = -p \frac{d}{dq'} (v + v') - \frac{1}{2}p^2 \left(\frac{1}{\kappa'\rho} + v' \frac{d}{dq'} \frac{1}{\kappa'} + \frac{v'}{\kappa'} \frac{d}{dq'} \frac{1}{\rho} - \frac{1}{\sigma\kappa} \right). \quad (43)$$

Thus we see that the effect of pressure consists of two parts, one of which is proportional to the pressure, and the other to the square of it. It will be well to try to gain some idea of the relative magnitude of these effects. Let us suppose that the pressure is n atmospheres, that is, in C.G.S. units, $n \times 10^6$. We do not know accurately the value of the second term on the left-hand side of equation, but, since κ for water is about 2×10^{10} , the multiplier of p^2 will be of about the order 10^{-11} , so that the ratio of the second term to the first will be of the order

$$\frac{n \times 10^{-5}}{\frac{d}{dq'} (v + v')}.$$

If the alteration in the volume of the saturated solution amounts to a cubic millimetre per gramme of salt dissolved, $d(v + v')/dq'$ is 10^{-3} , so that

$$\frac{n \times 10^{-5}}{\frac{d}{dq'}(v + v')} = n/100,$$

so that with this amount of alteration in volume the terms proportional to the pressure will be the most important for pressures up to 100 atmospheres, while for pressures greater than this the term proportional to the square of the pressures will be the most important. In the case of a solution of sal-ammoniac the increase in volume is enormously greater than that stated, so that for such a salt the effect of pressure on the solubility ought to be very nearly proportional to the pressure. This agrees with SORBY'S experiments on the solubility of certain salts.*

In this case the effect of pressure is expressed by the equation

$$\lambda \frac{\partial \theta}{\theta} = -p \frac{d(v + v')}{dq'}. \quad \dots \dots \dots (44)$$

We can test the formula by comparing it with the result of SORBY'S experiments on the effect of pressure upon the solubility. The two salts we shall take are potassium sulphate and sodium chloride, as we can get approximate values for these salts for all the quantities involved in equation (44).

According to J. THOMSEN, the heat absorbed when 174 grammes of K_2SO_4 dissolve in water is 6380 gramme-degree units, so that the heat absorbed for one grain of K_2SO_4 will be about 36 gramme-degrees or $36 \times 4.2 \times 10^7$ C.G.S. units. We may take this as an approximation to the value of λ , though it must be remembered that λ is the heat absorbed when one gramme of salt is dissolved in a nearly saturated solution.

According to SORBY, when K_2SO_4 crystallises out of a saturated solution, the volume increases from 100 to 134, so that, when a cubic centimetre of salt dissolves, the volume diminishes by about .25 c.c. The specific gravity of K_2SO_4 is about 2.5, so that, when one gramme of salt dissolves, the volume diminishes by .1 c.c., and $d(v + v')/dq' = -10^{-1}$, so that for 100 atmospheres the change in temperature required to produce the same change in solubility is at the temperature 15° C. given by the equation

$$\begin{aligned} \delta\theta &= \frac{288 \times 10^8 \times 10^{-1}}{36 \times 4.2 \times 10^7} \\ &= 2^\circ. \end{aligned}$$

SORBY found that the K_2SO_4 dissolved increased by about 3 per cent. According to KOPP, 100 parts of water dissolve 8.36 parts of K_2SO_4 at 0° , and .1741 part

* SORBY, 'Roy. Soc. Proc.,' vol. 12, 1863, p. 538.

for every degree above 0° , so that at 15° C. an increase of 2 per cent. would cause an increase of $\cdot 348$ part in $10\cdot 9$, which is about 3 \cdot 2 per cent., so that in this case the agreement is almost closer than we could have expected.

In the case of NaCl we have, getting the data from the same sources as before—

$$\lambda = 20 \times 4\cdot 2 \times 10^7,$$

$$d(v + v')/dq' = \cdot 05;$$

hence the change in temperature required to produce the same change as 100 atmospheres at 15°

$$= \frac{288 \times 10^8 \times 5 \times 10^{-2}}{20 \times 4\cdot 2 \times 10^7}$$

$$= 1\cdot 6^{\circ} \text{ approximately.}$$

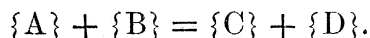
Now, according to the curve of solubility of NaCl given in OSTWALD'S 'Lehrbuch der Allgemeinen Chemie,' vol. 1, p. 380, about 34 parts dissolve at 15° , and the increase is about $\frac{1}{1\frac{1}{2}}$ of a part per degree Centigrade, so that for $1\cdot 6^{\circ}$ the increase would be about $\cdot 13$ in 34: this is $\cdot 40$ per cent. The value found by SORBY was $\cdot 419$ per cent., so that the agreement is again very close.

Chemical Combination.

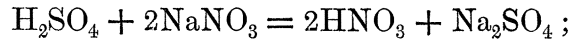
§ 11. We can apply HAMILTON'S principle to the case of chemical combination. Let us in the first place take cases of the type studied by GULDBERG and WAAGE in their theory of chemical combination ('Études sur les Affinités Chimiques').

In these cases there is equilibrium between various chemical actions which tend to reverse each other: a good example of such cases is that of a mixture of dilute solutions of sulphuric and nitric acids, sodium nitrate, and sodium sulphate. When the sulphuric acid acts on the sodium nitrate it produces nitric acid and sodium sulphate, while nitric acid by its action on sodium sulphate produces sulphuric acid and sodium nitrate. The problem is, given four substances of this kind, to find the quantity of each when there is equilibrium. Let us begin with the case of four gases, which we will call A, B, C, D, such that A by its action on B produces C and D, while C by its action on D produces A and B.

Let $p\xi$, $q\eta$, $r\zeta$, $s\epsilon$, be the number of molecules of A, B, C, D, respectively, when p , q , r , s , are the numbers of molecules in equivalent molecules. By equivalent molecules we mean molecules, or groups of molecules, such that, {A} being the equivalent molecule of the gas A, with a corresponding notation for the others, the chemical action which goes on may be expressed by the equation



Let us take as an example the case mentioned above, where the chemical action is expressed by the equation



here the equivalent molecules are H_2SO_4 , 2NaNO_3 , 2HNO_3 , and Na_2SO_4 ; and, if A, B, C, D, denote sulphuric acid, sodium nitrate, nitric acid, and sodium sulphate respectively, $p = 1$, $q = 2$, $r = 2$, $s = 1$.

Let m_1, m_2, m_3, m_4 , denote the masses of the molecules of A, B, C, D, respectively. Then, if these are gases, by what we have proved before (p. 486), the value of \bar{L} equals

$$\theta \left[m_1 p \xi \left(c_1 + R_1 \log \frac{\rho_0 Q}{m_1 p \xi} \right) + m_2 q \eta \left(c_2 + R_2 \log \frac{\rho_0' Q}{m_2 q \eta} \right) + m_3 r \zeta \left(c_3 + R_3 \log \frac{\rho_0'' Q}{m_3 r \zeta} \right) + m_4 s \epsilon \left(c_4 + R_4 \log \frac{\rho_0''' Q}{m_4 s \epsilon} \right) \right] - w, \quad \dots \quad (45)$$

where w is the mean potential energy of the four gases, and the remaining notation is the same as that on p. 486.

The quantities $\xi, \eta, \zeta, \epsilon$, are not independent of each other; in fact, there are three relations between them. Thus suppose, for example, that {A} consists of the two components α, β ; {B} of γ, δ ; {C} of α and γ ; {D} of β and δ , then the chemical reaction is expressed by the equation

$$(\alpha\beta) + (\gamma\delta) = (\alpha\gamma) + (\beta\delta),$$

so that we have evidently

$$\begin{aligned} \xi + \zeta &= \text{a constant,} \\ \xi + \epsilon &= \dots\dots\dots, \\ \eta + \zeta &= \dots\dots\dots, \end{aligned}$$

so that

$$d\xi = d\eta = -d\zeta = -d\epsilon. \quad \dots\dots\dots (46)$$

Thus, if ξ be increased by $d\xi$, the change in \bar{L} equals

$$d\xi \left[\theta \left\{ m_1 p \left(c_1 + R_1 \log \frac{\rho_0 Q}{m_1 p \xi} - R_1 \right) + m_2 q \left(c_2 + R_2 \log \frac{\rho_0' Q}{m_2 q \eta} - R_2 \right) - m_3 r \left(c_3 + R_3 \log \frac{\rho_0'' Q}{m_3 r \zeta} - R_3 \right) - m_4 s \left(c_4 + R_4 \log \frac{\rho_0''' Q}{m_4 s \epsilon} - R_4 \right) \right\} - \frac{dw}{d\xi} \right];$$

and by HAMILTON'S principle the quantity in square brackets must vanish when there is equilibrium.

For perfect gases (*i.e.*, gases which obey BOYLE'S Law)

$$R_1 m_1 = R_2 m_2 = R_3 m_3 = R_4 m_4. \quad \dots\dots\dots (47)$$

Let each of these quantities equal K ; then the equation of equilibrium becomes

$$\theta \left\{ m_1 p_1 c_1 + m_2 q c_2 - m_3 r c_3 - m_4 s c_4 + K \left(p \log \frac{\rho_0 Q}{m_1 p \xi} + q \log \frac{\rho_0' Q}{m_2 q \eta} - r \log \frac{\rho_0'' Q}{m_3 r \zeta} - s \log \frac{\rho_0''' Q}{m_4 s \epsilon} \right) - (p + q - r - s) \right\} = \frac{dw}{d\xi} \dots \dots \dots (48)$$

We see from this equation that anything which increases $d\omega/d\xi$ will increase $\log \rho_0 Q/m_1 p \xi + \dots$, and so will diminish ξ , so that, if there is any kind of potential energy which increases as ξ increases, the value of ξ when there is equilibrium will be smaller than it would have been if this energy had not been present; or, in more general terms, any circumstance which causes the potential energy to increase as chemical action goes on tends to stop the action, while, if it causes the energy to diminish, it will facilitate the action.

Equation (47) may be written

$$\frac{\zeta^r \epsilon^s}{\xi^p \eta^q} = C e^{\frac{dw}{d\xi} \frac{1}{K\theta}}, \dots \dots \dots (49)$$

where C is independent of $\xi, \eta, \zeta, \epsilon$.

In the case of gases combining in a vessel of constant volume, and when there is no action on the sides of the vessel, $d\omega/d\xi$, being the increase in the potential energy when one equivalent of C acts on one of D , to produce one each of A and B , may be measured by the heat developed in the reverse process, that is, when an equivalent of A acts on one of B to produce one each of C and D . Let us call this quantity of heat (measured in mechanical units) H ; then

$$\frac{\zeta^r \epsilon^s}{\xi^p \eta^q} = C e^{H/K\theta} \dots \dots \dots (50)$$

If H be positive, and θ zero, then either ξ or η must be zero, that is, the chemical action which is attended by the production of heat will go on as far as possible. This is **BERTHELOT'S** Law of Maximum Work, and we see from the above expression that it holds at the zero of absolute temperature, but only then. Equation (49) also shows that the tendency of any chemical reaction to take place is greater, the larger the amount of heat developed by it.

If all the equivalents contain the same number of molecules, we may put $p = 1, q = 1, r = 1, s = 1$, and equation (50) takes the simple form

$$\frac{\zeta \epsilon}{\xi \eta} = C e^{H/K\theta} \dots \dots \dots (51)$$

GULDBERG and **WAAGE** put $\zeta \epsilon = \kappa \xi \eta$, where κ is a constant. This agrees with equation (50) if the temperature remains constant. Equation (50) shows how the

equilibrium varies with the temperature, and shows that, the lower the temperature, the further that action which is attended by the evolution of heat goes on, and that the equilibrium will vary more quickly with the temperature when the heat developed by the reaction is great than when it is small. By determining the state of equilibrium at two different temperatures, we could determine H .

Since, by the kinetic theory of gases,

$$K\theta = R_1 m_1 \theta = p/N,$$

where p is the pressure and N the number of molecules, we see that $K\theta$ is one-third of the mean energy of the molecules at the temperature θ . In many cases of chemical combination the heat developed by the combination of the gases is enormously greater than that required to raise their temperature through 300° or 400° , and in these cases $H/K\theta$ will be very large, so that the combinations will nearly obey BERTHELOT'S Law at moderate temperatures. But this law will not nearly hold when only a small quantity of heat is developed in the reaction.

Equation (49) only agrees with that given by GULDBERG and WAAGE when the number of molecules in the equivalent is the same in each of the gases; and, if we look at the subject from another point of view, we shall also see reasons for supposing that GULDBERG'S and WAAGE'S equation is not likely to hold when the equivalents contain different numbers of molecules. Let us take first the case where the molecule and the equivalent molecule are identical. Then, calling the four substances A, B, C, D, as before, combinations will take place by a molecule of A pairing with one of B. The number of collisions in unit time between the A and B molecules is proportional to $\xi\eta$, and if combination takes place in a certain fraction of the number of cases of collision the number of A and B molecules which disappear in unit time through this combination, or, what is the same thing, the number of C and D molecules produced, is

$$p\xi\eta,$$

where p is a constant.

In a similar way we may show that the number of C and D molecules disappearing by their combination to form A and B molecules is

$$q\zeta\epsilon,$$

where q is again a constant quantity.

When there is equilibrium the number of A and B molecules which disappear must equal the number which appear, so that in this case

$$p\xi\eta = q\zeta\epsilon,$$

which, so long as the temperature is constant, agrees with equation (49) and with GULDBERG'S and WAAGE'S equation.

Let us now suppose that the equivalents of B and D each contain two molecules.

In this case, for chemical combination to take place, one molecule of A must come into collision with two of B simultaneously. The number of such collisions is proportional to $\xi\eta^2$, so that the number of equivalents of A and B destroyed and of C and D produced by this combination will be

$$p'\xi\eta^2,$$

where p' is a constant.

In a similar way we can show that the number of equivalents of C and D destroyed and of A and B produced in unit time by the combination of C and D is

$$q'\zeta\epsilon^2,$$

where q' is a constant.

In the state of equilibrium these quantities must be equal, so that

$$p'\xi\eta^2 = q'\zeta\epsilon^2,$$

which, so long as the temperature remains constant, agrees with equation (49), but not with GULDBERG and WAAGE'S equation.

In order to illustrate some important points connected with the theory of the combination of gases, we will consider the simpler case when two gases, A and B, combine to form a third, C, while C again splits up to form A and B. A particular case of this is dissociation, which we have already considered. Let ξ , η , ζ , be the number of equivalents of A, B, C, respectively, and let m_1 , m_2 , m_3 , be the masses of the molecules of A, B, C.

Then, with the same notation as the last case, the value of \bar{L} is

$$\theta \left\{ m_1 p \xi \left(c_1 + R_1 \log \frac{\rho_0 Q}{m_1 p \xi} \right) + m_2 q \eta \left(c_2 + R_2 \log \frac{\rho_0' Q}{m_2 q \eta} \right) + m_3 r \zeta \left(c_3 + R_3 \log \frac{\rho_0'' Q}{m_3 r \zeta} \right) \right\} - w,$$

where w is the mean potential energy of the three gases. We have, as before,

$$d\xi = d\eta = -d\zeta;$$

so that the condition that the value of \bar{L} should be unaltered when ξ is increased by $d\xi$ gives

$$\theta \left\{ m_1 p (c_1 - R_1) + m_2 q (c_2 - R_2) - m_3 r (c_3 - R_3) + m_1 p R_1 \log \frac{\rho_0 Q}{m_1 p \xi} + m_2 q R_2 \log \frac{\rho_0' Q}{m_2 q \eta} - m_3 r R_3 \log \frac{\rho_0'' Q}{m_3 r \zeta} \right\} = \frac{dw}{d\xi}. \quad \dots \dots \dots (52)$$

For perfect gases

$$R_1 m_1 = R_2 m_2 = R_3 m_3 = K.$$

Making this substitution, the equation of equilibrium becomes

$$\theta \left\{ m_1 p_1 c_1 + m_2 q c_2 - m_3 r c_3 + K (p + q - r) + K \left(p \log \frac{\rho_0 Q}{m_1 p \xi} + q \log \frac{\rho_0' Q}{m_2 q \eta} - r \log \frac{\rho_0'' Q}{m_3 r \zeta} \right) \right\} = \frac{d\omega}{d\xi} \dots \dots \dots (53)$$

This equation may be written

$$\frac{\xi^p \eta^q}{\zeta^r} = C Q^{p+q-r} e^{\frac{d\omega}{d\xi} \frac{1}{K\theta}} \dots \dots \dots (54)$$

If the combination takes place without alteration in the number of molecules,

$$p + q = r.$$

In this case the equilibrium state is independent of the volume of the vessel Q in which a given mass of gas is contained.

If $p + q > r$, that is, if the number of molecules after combination is less than that before, Q^{p+q-r} will increase with Q, so that $\xi^p \eta^q / \zeta^r$ will be larger, the greater the value of Q, so that for a given quantity of the gases there will not be so much combination in a large vessel when the pressure is small as in a smaller one when the pressure is large. If, on the other hand, $p + q < r$, then the amount of chemical combination will be greater at low than at high pressures.

We see from equation (54) that anything which affects the value of $d\omega/d\xi$ will affect the amount of the combination which takes place; anything which causes the potential energy to increase as chemical combination goes on, *i.e.*, which tends to make $d\omega/d\xi$ negative, increases, by equation (54), the value of $\xi^p \eta^q / \zeta^r$, that is, it increases the ratio of the number of uncombined atoms to the combined ones, and so tends to stop the combination; while, on the other hand, anything which makes the potential energy diminish as chemical combination goes on, since it tends to increase $d\omega/d\xi$, diminishes the ratio of the number of uncombined atoms to the number of combined ones, and so facilitates the combination.

If we define the coefficient of affinity, ω , of the gases A and B, to be the value of the steady state of

$$\frac{\zeta^r}{\xi^p \eta^q},$$

then

$$\omega = C Q^{p+r-r} e^{-\frac{d\omega}{d\xi} \frac{1}{K\theta}}; \dots \dots \dots (55)$$

and if the potential energy be increased by $\delta\omega$, the corresponding increment $\delta\omega$ in the coefficient of affinity is given by the equation

$$\frac{\delta\omega}{\omega} = - \frac{1}{K\theta} \frac{d \cdot \delta\omega}{d\xi}, \dots \dots \dots (56)$$

an equation which connects the alteration in the coefficient of affinity with the alteration in the potential energy.

The layers of gas condensed on the surfaces of solids in contact with the gas may, perhaps, be looked upon as corresponding to the surface films of liquids, and as possessing energy different from that possessed by the same volume of gas when not attached to the sides of the vessel. In this case part of the energy of the gas would depend upon the surface of the solids in contact with it, just as in a liquid the existence of surface-tension makes part of the energy of a fluid proportional to its surface. It is, perhaps, worthy of notice that, according to the vortex ring theory of gases, part of the energy of a gas at a given pressure and volume depends upon the surface (J. J. THOMSON, 'Treatise on the Motion of Vortex Rings,' p. 112). If the layer of condensed gas were to contain an abnormal amount of energy, we could easily explain the influence exerted in some cases of chemical combination by the walls of the vessel in which the combination takes place (J. H. VAN 'T HOFF, 'Études de Dynamique Chimique,' p. 58), and also the influence exerted by finely divided charcoal and platinum where a very large surface is exposed. For the explanation given above shows that, if the energy of unit area of the condensed gas varies as chemical combination goes on, the action of the surface layer will either promote or impede chemical combination. It will promote it if the energy per unit surface decreases as combination goes on ; impede it, if this energy increases.

If the specific inductive capacity of the mixture of gases alters as the chemical combination goes on, their combination will be effected by placing them in an electric field. The chemical action will be checked if the specific inductive capacity increases as combination goes on ; promoted, if it diminishes.

§ 12. The equations contained in the preceding investigation express the result of actions which are usually termed by the chemists "mass actions." These, however, have been chiefly studied in the case of very dilute solutions, so that it is important to endeavour to apply our results to this case.

If we regard a solution of one substance A in another B as equivalent to a distribution of the molecules of A through the volume occupied by B, then these molecules will behave with respect to each other very much like the molecules of a gas, and we may suppose that the value of \bar{L} is expressed by an equation of the same form. This view would have to be modified if the nature of the solvent should be found to influence the equilibrium of a mixture of various reagents, and we should have to apply the more general method which we shall discuss later on. In those cases, however, where the solvent is without influence the above assumption that the solvent only separates the molecules of the substances dissolved seems legitimate.

If this be so, the investigation by the Hamiltonian principle of the case, when dilute solutions of four reagents, A, B, C, D, act upon each other, is the same in form as that investigated on p. 503, where four gases, A, B, C, D, act upon each other. Let us suppose that when A acts on B it produces C and D, and when C acts on D it pro-

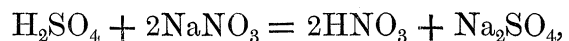
duces A and B. Then, if ξ , η , ζ , ϵ , be the number of equivalents of A, B, C, D, respectively, p , q , r , s , the number of molecules in these equivalents, w the mean potential energy of the mixture of the reagents, θ the absolute temperature, we have

$$\frac{\zeta^r \epsilon^s}{\xi^p \eta^q} = C Q^{r+s-p-q} e^{-\frac{dw}{d\xi} \frac{1}{K\theta}}, \quad \dots \dots \dots (57)$$

where Q is the volume of the solvent, and C and K are constants; we must not, however, assume without proof that the value of K is the same as that of the quantity denoted by the same letter for gases.

The same conclusions as to the coincidence of this law with that of BERTHELOT at the zero of absolute temperature, and the close approximation between the two at ordinary temperatures in those cases where a very large amount of heat is developed in the reaction, hold in this case as well as in that of the gases.

We will now apply this formula to some cases which have been experimentally investigated. The one to which most attention has been directed is that of a mixture of dilute solutions of nitric and sulphuric acids, sodium nitrate, and sodium sulphate. Here the reaction is represented by the equation



and equation (57) becomes

$$\gamma \zeta^r \epsilon^s = \xi^p \eta^q,$$

where γ depends upon the temperature, but not on ξ , η , ζ , or ϵ . Here ξ , η , ζ , ϵ , are respectively the number of equivalents of sulphuric acid, sodium nitrate, nitric acid, and sodium sulphate. In order to fix the values of p , q , r , s , we must know whether the molecules of sodium nitrate and nitric acid in the solution are to be represented by $\text{Na}_2\text{N}_2\text{O}_6$, $\text{H}_2\text{N}_2\text{O}_6$, or by NaNO_3 and HNO_3 ; if the first supposition is correct, then $p = q = r = s = 1$; if the latter, $p = 1$, $q = 2$, $r = 2$, $s = 1$. In the first case the equation is

$$\gamma \zeta \epsilon = \xi \eta;$$

in the second,

$$\gamma^1 \zeta^2 \epsilon = \xi \eta^2.$$

THOMSEN* has determined the state of equilibrium when solutions of nitric acid and sodium sulphate are mixed together in varying proportions. I have calculated from his results the corresponding value of γ and γ' . In the following Table n is the ratio of the number of equivalents of sodium sulphate to the number of equivalents of nitric acid before chemical combination commences.

* THOMSEN, 'Thermochemische Untersuchungen,' I., 112.

n	γ	γ'
8	1.93	28.1
4	2.89	28.9
2	2.90	13.05
1	3.47	6.8
$\frac{1}{2}$	4.1	3.2
$\frac{1}{4}$	4.1	1.0

It is evident from the above Table that, except when the amount of nitric acid originally present is very small, the second equation, which requires γ' to be constant, does not agree with the experiments, while the first, which requires γ to be constant, does agree fairly well, except in those cases where the quantity of nitric acid present is originally small.

Hence we conclude that, except in these cases, the molecule and the equivalent coincide, that is, the molecule of nitric acid in the solution is represented by $\text{H}_2\text{N}_2\text{O}_6$; a similar conclusion applies to the molecule of sodium nitrate, the molecule of which in the solution has to be represented by $\text{Na}_3\text{N}_2\text{O}_6$. When the quantity of nitric acid initially present is very small, the second equation seems to agree with the experiments better than the first, so that it might seem as if, when the quantity of nitric acid was very small, the molecule was HNO_3 and not $\text{H}_2\text{N}_2\text{O}_6$; but, as in this case a very small error in the experiments would make a large error in γ or γ' , too much weight must not be attached to it. It seems quite possible that there are molecules of both types, and that in concentrated solutions those of the type $\text{H}_2\text{N}_2\text{O}_6$ are by far the most numerous.

Cases when one or more of the Reagents are insoluble.

§ 13. Let us suppose that A is insoluble; then for A the positional part of the kinetic energy equals

$$\theta \frac{\overline{\partial p}}{\partial \theta} v,$$

where $\overline{\partial p / \partial \theta}$ is the mean value of $\partial p / \partial \theta$ (v constant), and v is the volume. If σ be the density of A, we may write this

$$\theta \frac{\overline{\partial p}}{\partial \theta} \cdot \frac{m_1 p \xi}{\sigma}.$$

Hence \bar{L} for the system equals

$$\theta \left\{ \frac{\overline{\partial p}}{\partial \theta} \frac{m_1 p \xi}{\sigma} + m_2 q c_2 \eta + K q \eta \log \frac{\rho_0' Q}{m_2 q \eta} + m_3 r c_3 \zeta + K r \zeta \log \frac{\rho_0'' Q}{m_3 r \zeta} + m_4 s c_4 \epsilon + K s \epsilon \log \frac{\rho_0''' Q}{m_4 s \epsilon} \right\} - w.$$

The condition that \bar{L} should be stationary is therefore

$$\theta \left\{ \frac{\partial p}{\partial \theta} \frac{m_1 p}{\sigma} + m_2 q c_2 - m_3 r c_3 - m_4 s c_4 + K (q - r - s) \right. \\ \left. + \kappa \left(q \log \frac{\rho_0 Q}{m_2 q \eta} - r \log \frac{\rho_0' Q}{m_3 r \zeta} - s \log \frac{\rho_0'' Q}{m_4 s \epsilon} \right) \right\} = \frac{dw}{d\xi}. \quad (58)$$

This equation may be written as

$$\frac{\zeta^r e^s}{\eta^q} = Q^{r+s-q} C e^{\frac{dw}{d\xi} \frac{1}{K\theta}}. \quad (59)$$

If two of the constituents, say A and C, are insoluble, then we can easily prove in a similar way that

$$\frac{\epsilon^s}{\eta^q} = Q^{s-q} C' e^{\frac{dw}{d\xi} \frac{1}{K\theta}}. \quad (60)$$

The Effect of Temperature on the Equilibrium.

§ 14. If we define the coefficient of the reaction to be the value of $\zeta^r e^s / \xi^p \eta^q$ when there is equilibrium, and denote it by the symbol ω , then we have

$$\omega = Q^{r+s-p-q} C e^{\frac{dw}{d\xi} \frac{1}{K\theta}}; \quad (61)$$

so that, if $\delta\omega$ be the alteration in the value of ω when the temperature is increased by $\delta\theta$, we have approximately, if $dw/d\xi$ does not change with the temperature, and if its ratio to $K\theta$ is large, so that the term in ω which varies most rapidly with the temperature is $e^{\frac{dw}{d\xi} \frac{1}{K\theta}}$,

$$\frac{\delta\omega}{\omega} = - \frac{1}{K\theta} \frac{dw}{d\xi} \frac{\delta\theta}{\theta}; \quad (62)$$

so that the percentage change in ω for a given change in θ varies inversely as the square of the absolute temperature, and directly as $dw/d\xi$, which, when the system is free from strain, electrification, &c., is the amount of heat given out when one equivalent of A combines with one of B to form one each of C and D.

The greater this amount of heat, the more quickly will the coefficient of the reaction vary with the temperature.

We shall now proceed to reduce this expression to numbers, assuming, as an approximate value of K, that it is the same as for gases. In this case

$$K\theta = \frac{pm}{\rho},$$

where p is the pressure and ρ the density.

Let H' be the amount of heat produced when c grammes of A combine, c being the combining weight of A, then

$$H' = Nc \frac{dw}{d\xi},$$

where N is the number of equivalents in a gramme of A. In order to simplify the reasoning, let us suppose that we are considering a case where the molecule and the equivalent are identical,

$$\begin{aligned} \frac{1}{K\theta} \frac{dw}{d\xi} &= \frac{H'}{Nm \frac{pc}{\rho}} \\ &= \frac{H'}{pc/\rho}, \end{aligned}$$

since

$$Nm = 1.$$

Since pc/ρ is the same for all gases, and since for Hydrogen it is about $10^{11}/4.5$, we have

$$\frac{1}{\kappa\theta} \frac{dw}{d\xi} = \frac{4.5 H'}{10^{11}},$$

and therefore, by equation (62),

$$\frac{\delta\omega}{\omega} = - \frac{4.5 H'}{10^{11}} \frac{\delta\theta}{\theta}.$$

In the case of hydrochloric acid, sulphuric acid, sodium sulphate, and sodium chloride THOMSEN* found $H' = 2 \times 10^3 \times 4.2 \times 10^7$, so that in this case

$$\frac{\delta\omega}{\omega} = 3 \frac{\delta\theta}{\theta} \text{ approximately;}$$

so that a temperature of about 30° C., an alteration of 1° C., would make a change of about 1 per cent. in the value of ω .

§ 15. The formula

$$\frac{\eta^r \epsilon^s}{\xi^p \eta^q} = Q^{r+s-p-q} C e^{\frac{dw}{d\xi} \frac{1}{K\theta}}$$

enables us to calculate readily the disturbing effect produced by any slight alteration in the external circumstances.

* LOTHAR MEYER: 'Theorien der Chemie,' 4th edit., p. 478.

Putting, as before,

$$\frac{\zeta^r \epsilon^s}{\xi^p \eta^q} \equiv \omega,$$

we see that $\delta\omega$, the change in ω due to a change δw in the value of the potential energy, is given by the equation

$$1 + \frac{\delta\omega}{\omega} = e^{\frac{d \cdot \delta w}{d\xi} \frac{1}{K\theta}}; \quad (63)$$

so that, if $d \cdot \delta w/d\xi$ is positive, $\delta\omega$ is positive, that is, in the state of equilibrium. ξ and η are smaller than they would have been if δw had been zero; so that, if an increase in ξ increases the additional potential energy, the value of ξ in the state of equilibrium will be diminished. If, on the other hand, the additional potential energy diminishes as ξ increases, the value of ξ in the state of equilibrium will be increased.

Effect of Capillarity.

§ 16. Let us first consider the case when the additional potential energy is due to capillarity; then

$$\delta w = TS,$$

where S is the area of the surface, and T the surface-tension.

Hence we have, from Equation (63),

$$1 + \frac{\delta\omega}{\omega} = \epsilon^{\frac{d(TS)}{d\xi} \frac{1}{K\theta}}. \quad (64)$$

Thus, if either the surface-tension or the area of the surface alters as chemical combination proceeds, the final state of equilibrium will depend upon the extent of surface. The state of equilibrium will be different when the solution is spread out over a large surface from that which exists when the solution exposes only a small free surface. Considerations of this kind would explain the experiments of Professor LIEBREICH on the precipitation of chloroform by the mixture of hydrate of chloral and an alkaline solution. ('Nature,' vol. 35, p. 264.) In these experiments it was observed that when the solutions were mixed in a test-tube the top layer remained clear, no precipitation taking place inside it, and the same phenomenon occurred in the capillary space between two plates; in short capillary tubes the reaction failed altogether. The equations obtained above apply to this case. Since the surface-tension of pure water is altered by the addition of other substances, the surface-tension of the mixture of chloral and alkaline solution will be altered by the withdrawal from the solution of chloral and alkali; let us suppose that it is increased; then the precipitation of the chloroform will increase the surface-tension, and therefore the potential energy due to it. Thus, if ξ in this case is the number of equivalents of chloroform, $d \cdot \delta w/d\xi$ is positive, and

therefore the existence of surface-tension diminishes the value of ξ , that is, it diminishes the precipitation. In the case mentioned above it seems to have been able to stop the precipitation altogether. The effects of surface-tension will be most noticeable when the heat developed by the chemical action is small. Some other effects produced by surface-tension on chemical action are considered in a paper read before the Cambridge Philosophical Society, February 1887, by Professor LIVEING.

Surface-tension will also affect the equilibrium when chemical combination produces a change in volume, even though the surface remains unaltered.

Effects of Pressure.

§ 17. If Q be the volume, p the pressure, κ the coefficient of compressibility of the solution, then, just as in the case of solution, we have

$$\frac{d \cdot \delta\omega}{d\xi} = p \frac{dQ}{d\xi} + \frac{1}{2} \frac{d}{d\xi} \left(\frac{Qp^2}{\kappa} \right). \quad \dots \dots \dots (65)$$

Thus pressure produces two effects, the one being proportional to the pressure, the other to the square of it.

If the volume increases as chemical combination goes on, external pressure will tend to stop the combination; and, *vice versa*, the change in the coefficient of reaction due to this case is given by the equation

$$1 + \frac{\delta\omega}{\omega} = e^{\frac{pdQ}{\kappa\theta d\xi}},$$

or, approximately,

$$\frac{\delta\omega}{\omega} = \frac{1}{K\theta} p \frac{dQ}{d\xi}. \quad \dots \dots \dots (66)$$

If the coefficient of compressibility increases as chemical action goes on, external pressure will tend to facilitate the combination, and the change in the coefficient of the reaction due to this cause is

$$\frac{\delta\omega}{\omega} = \frac{1}{2} \frac{1}{K\theta} \frac{d}{d\xi} \left(\frac{Qp^2}{\kappa} \right). \quad \dots \dots \dots (67)$$

HORSTMANN'S Experiments on the Division of Oxygen between Carbonic Oxide and Hydrogen.

§ 18. We shall now proceed to apply the Hamiltonian principle to this case, which is more complicated than any of the preceding. In these experiments hydrogen, carbonic oxide, and oxygen were mixed together and exploded, and the proportion of hydrogen, oxygen, carbonic oxide, carbonic acid, and water in the mixture after the explosion determined.

Let $\xi, \eta, \zeta, \epsilon, \omega$, be the number of molecules of hydrogen, oxygen, carbonic oxide, carbonic acid, and water respectively; then the value of \bar{L} will be

$$\theta \left\{ m_1 \xi R_1 \log \frac{\rho_0 Q}{m_1 \xi} + m_2 \eta R_2 \log \frac{\rho_0' Q}{m_2 \eta} + m_3 \zeta R_3 \log \frac{\rho_0'' Q}{m_3 \zeta} \right. \\ \left. + m_4 \epsilon R_4 \log \frac{\rho_0''' Q}{m_4 \epsilon} + m_5 \omega R_5 \log \frac{\rho_0'''' Q}{m_5 \omega} \right\} - w,$$

where m_1, m_2, m_3, m_4, m_5 are respectively the masses of the hydrogen, oxygen, carbonic oxide, carbonic acid, and water molecules respectively; $R_1, R_2, \dots R_5$ the value of $p/\rho\theta$ for these gases; w the mean potential energy of the mixture of gases, and Q the volume of the vessel in which they are contained.

Since the quantity of hydrogen in the mixture remains constant,

$$\left. \begin{aligned} &\xi + \omega = \text{a constant;} \\ \text{and, since the quantity of oxygen remains constant,} \\ &\eta + \frac{1}{2}\zeta + \epsilon + \frac{1}{2}\omega = \text{a constant;} \\ \text{since the quantity of carbon remains constant,} \\ &\zeta + \epsilon = \text{a constant.} \end{aligned} \right\} \dots \dots \dots (68)$$

Since there are three equations between these five quantities, we may take two of them as independent variables. Let us take ξ and ϵ as our independent variables; then we have from the above equations

$$\left. \begin{aligned} \frac{d\eta}{d\xi} &= \frac{1}{2}, & \frac{d\zeta}{d\xi} &= 0, & \frac{d\omega}{d\xi} &= -1, \\ \frac{d\eta}{d\epsilon} &= -\frac{1}{2}, & \frac{d\zeta}{d\epsilon} &= -1, & \frac{d\omega}{d\epsilon} &= 0. \end{aligned} \right\} \dots \dots \dots (69)$$

By the Hamiltonian principle we have

$$\frac{d\bar{L}}{d\xi} = 0, \\ \frac{d\bar{L}}{d\epsilon} = 0,$$

so that

$$\theta \left\{ m_1 R_1 \log \frac{\rho_0 Q}{m_1 \xi} - m_1 R_1 + \frac{1}{2} \left(m_2 R_2 \log \frac{\rho_0' Q}{m_2 \eta} - m_2 R_2 \right) \right. \\ \left. - \left(m_5 R_5 \log \frac{\rho_0'' Q}{m_5 \omega} - m_5 R_5 \right) \right\} = \left(\frac{dw}{d\xi} \right)_{\epsilon \text{ constant}} \dots \dots (70)$$

Since $m_1 R_1 = m_2 R_2 = m_3 R_3 = m_4 R_4 = m_5 R_5 = \kappa$, we may write this equation as

$$\frac{1}{2}\kappa\theta \left\{ \log \frac{\rho_0^2 \rho_0' Q \omega^2 m_5^2}{m_1^2 m_2 \rho_0'^2 \xi^2 \eta} - \frac{1}{2} \right\} = \left(\frac{dw}{d\xi} \right)_{\epsilon \text{ constant}},$$

or

$$\frac{\omega^2}{\xi^2 \eta} = \frac{C_1}{Q} e^{\frac{2}{\kappa\theta} \frac{dw}{d\xi}}, \dots \dots \dots (71)$$

where C_1 is a constant.

From the equation

$$\frac{d\bar{L}}{d\epsilon} = 0$$

we get, in a similar way,

$$\frac{\xi^2 \eta}{\epsilon^2} = Q C_2 \epsilon^{\frac{2}{\kappa\theta} \left(\frac{dw}{d\epsilon} \right)}. \dots \dots \dots (72)$$

Equations (71) and (72), along with the three equations (68), are sufficient to determine the five quantities $\xi, \eta, \zeta, \epsilon, \omega$.

If we multiply equations (71) and (72) together, we get

$$\frac{\omega^2 \zeta^2}{\xi^2 \epsilon^2} = C_1 C_2 \epsilon^{\frac{2}{\kappa\theta} \left\{ \left(\frac{dw}{d\xi} \right) + \frac{dw}{d\epsilon} \right\}}; \dots \dots \dots (73)$$

so that, as long as the temperature remains constant, $\omega\zeta/\xi\epsilon$ is constant; or, in words, the ratio of the quantities of water and carbonic acid formed by the explosion always bears a constant ratio to the ratio of the quantity of hydrogen left free to the quantity of free carbonic acid.

Since equations (71) and (72) involve Q , the amount of combination which goes on when a given quantity of the gases are exploded will depend upon the volume in which they are confined. The equations show that the amount of combination will increase as the volume diminishes. In a paper on the "Chemical Combination of Gases" * I arrived at similar results (except with regard to the effect of temperature, which I did not investigate) by a purely kinematical method.

Method applicable to Solutions of any Strength.

§ 19. When the solutions are too concentrated to permit us to assume that the energy possessed by the molecules of the salt is the same as the energy possessed by the same number of molecules in the gaseous state, we must use the more general expression given on p. 487 for the positional part of \bar{L} , viz.,

$$\theta \int_{v_0}^v \frac{\partial p}{\partial \epsilon} dv - w,$$

* 'Phil. Mag.,' vol. 19, 1884.

where, in finding the value of $\partial p/\partial \epsilon$, we suppose v to be constant, and w is the mean potential energy of the system.

If $\xi, \eta, \zeta \dots$ be the number of equivalent molecules of the substances A, B, C... in the solution, then, since \bar{L} must be stationary when the system is in equilibrium, we have

$$\theta \frac{d}{d\xi} \int_{v_0}^v \frac{\partial p}{\partial} dv - \frac{dw}{d\xi} = 0, \dots \dots \dots (74)$$

with as many equations of a similar type as there are independent variables. We can experimentally determine the way in which $\partial p/\partial \epsilon$ and ω vary with the quantities of the various substances in the solution ; and, if we have sufficient data to express these quantities as functions of ξ, η, \dots , the equations of the type (74) will enable us to find the values of ξ, η, \dots when there is equilibrium. The part of $dw/d\xi$ which depends upon the chemical affinity of the substances for each other can be measured by the heat developed when the chemical action which causes the diminution of the number of equivalents of the substance A by one goes on. But, just as in the case of the more dilute solutions, part of w may be the energy due to surface-tension, electrification, compression, &c., and the presence of this energy will affect the state of equilibrium.

The Velocity of Chemical Change.

§ 20. It is much easier in many cases to measure the rate at which chemical change takes place than to determine the final state of equilibrium. It seems desirable, therefore, in order to facilitate the comparison of theory with experiment, to endeavour to deduce some expression for the velocity of chemical change.

Let us suppose that, as before, we have a number of substances which can act chemically on each other. Let $\xi, \eta, \zeta \dots$ be the number of equivalents of these substances : these will be connected by various equations ; let us choose $\xi, \eta \dots$ as independent variables. Then, since when there is equilibrium $d\bar{L}/d\xi = 0, d\bar{L}/d\eta = 0$, we conclude that these quantities have something to do with the velocity with which chemical change goes on. Now the approach of a mixture of various reagents to its state of equilibrium is not like the approach of a vibrating body resisted by a frictional force to its position of equilibrium, for after the mixture has got to its position of equilibrium it stays there instead of vibrating about it like the ordinary dynamical system. Thus the mixture behaves like a system in which inertia is absent or comparatively unimportant ; we may, therefore, suppose that the accelerations ξ, η, \dots are absent from the equations of motion of the mixture, and we may assume, at any rate when $d\bar{L}/d\xi, d\bar{L}/d\eta$, are small, that

$$\left. \begin{aligned} \frac{d\xi}{dt} &= A \frac{d\bar{L}}{d\xi} \\ \frac{d\eta}{dt} &= B \frac{d\bar{L}}{d\eta} \end{aligned} \right\}, \dots \dots \dots (75)$$

where A and B are either constants or functions of ξ , η , &c., whose values we do not know. From the indeterminateness of A and B, we cannot use these equations to determine the absolute velocity of chemical change. We can, however, use them to determine the effect on this velocity of any alteration in the external circumstances. Thus, suppose that the circumstances are changed so that \bar{L} is increased by δL ; then, if $\delta \dot{\xi}$ denotes the change in the velocity of ξ , we have

$$\dot{\xi} + \delta \dot{\xi} = A \left\{ \frac{d\bar{L}}{d\xi} + \frac{d\delta L}{d\xi} \right\},$$

so that

$$\frac{\delta \dot{\xi}}{\dot{\xi}} = \frac{\frac{d\delta L}{d\xi}}{\frac{d\bar{L}}{d\xi}}; \quad \dots \dots \dots (76)$$

and we can measure all the quantities occurring in this equation, and so compare it with experiment.

If the change in the energy be due to surface-tension, then, if S be the area of the surface, T the surface-tension, we have

$$\frac{\delta \dot{\xi}}{\dot{\xi}} = - \frac{\frac{d}{d\xi}(ST)}{\frac{d\bar{L}}{d\xi}}. \quad \dots \dots \dots (77)$$

If the change in the circumstances be due to the action of the pressure p , then

$$\frac{\delta \dot{\xi}}{\dot{\xi}} = - \frac{p \frac{dv}{d\xi} - \frac{1}{2} p^2 \frac{d\kappa}{d\xi}}{\frac{d\bar{L}}{d\xi}}, \quad \dots \dots \dots (78)$$

where V is the volume of the mixture and κ its coefficient of compressibility. The value of $d\bar{L}/d\xi$ for gases is given by equation (14); for solids and liquids by equation (74).

Irreversible Effects.

§ 21. So far we have only considered those cases which involve nothing but reversible processes, and have left out of consideration the effect of such things as friction, electrical resistance, and so on, which destroy the reversibility of any process in which they play a part. If, however, as we have done in this paper, we take the view that the properties of matter in motion, as considered in abstract dynamics—when all the

processes are reversible—are sufficient to account for any physical phenomenon, then we must show how to explain irreversible processes as the effect of changes all of which are reversible. It would not be sufficient to explain these irreversible effects by means of ordinary dynamical systems with friction, as friction itself ought on this view to be explained by means of the action of frictionless systems.

If every physical phenomenon can be explained by means of frictionless dynamical systems, each of which is reversible, then it follows that, if we could only control the phenomenon in all its details, it would be reversible, so that the irreversibility of any system is due to the limitation of our powers of manipulation. It is because we only possess the power of dealing with the molecules *en masse* and not individually, while the reversal of these processes would require us to be able to reverse the motion of each individual molecule. This was pointed out by MAXWELL, who showed that an army of his “demons” would be able to prevent the dissipation of energy.

Our want of power of dealing with very minute portions of matter imposes one kind of limitation on our control of physical processes; another limitation to our power of interpreting them is caused by the time which our sensations last, causing any phenomenon which consists of events following one another with great rapidity to present a blurred appearance, so that what we perceive at any moment is not what is happening at that moment, but merely an average effect, which may be quite unlike the effect at any particular instant. In consequence of the finiteness of the time taken by our senses to act we are incapable of separating two events which happen within a very short interval of each other, just as the finiteness of the wave-length of light prevents us separating two points which are very close together. Thus, if we observe any effect, we cannot tell by our senses whether it represents a steady state of things or a state which is rapidly changing, and whose mean is what we actually observe. Thus we are at liberty, if it is more convenient for the purposes of explanation, to look upon any effect as the average of a series of other rapidly changing effects.

Let us consider the case of a system whose motion is such that, in order to represent it, “frictional terms” have to be introduced. Let us first assume that the motion is represented at each instant by the equations with these terms in, and that these equations are not equations which are only true on the average. Let us assume that any phenomenon is capable of explanation by the principle of abstract dynamics. Then, from our point of view, we shall have explained the phenomenon when we have found a frictionless system whose motion would produce the phenomenon.

It might at first sight appear as if we could explain the frictional terms in the equations of motion as arising from the connection of other subsidiary systems with the original system, just as in the first part of the Paper (‘Phil. Trans.’ 1885, p. 311) we explained the “positional” forces as due to changes in the motion of a system connected with the original system. Let us suppose for a moment that this is possible. Then, if T be the kinetic energy of the original system, and T' that of the subsidiary

system whose motion is to explain the frictional forces, then we have, by LAGRANGE'S equation,

$$\frac{d}{dt} \frac{dT}{dx} - \frac{dT}{dx} - \frac{d}{dt} \frac{dT'}{dx} - \frac{dT'}{dx} + \frac{dV}{dx} = \text{external force of type } x;$$

thus the term

$$- \frac{d}{dt} \frac{dT'}{dx} - \frac{dT'}{dx}$$

must be equal to the "frictional term" which is proportional to \dot{x} . For this to be the case, it is evident that T' must involve \dot{x} . The momentum of the system is, however, $d(T + T')/d\dot{x}$. This momentum must, however, be the same as that given by the ordinary expression in Rigid Dynamics, viz., $dT/d\dot{x}$. If these two expressions, however, are identical, $dT'/d\dot{x}$ must vanish for all values of \dot{x} , that is, T' cannot involve \dot{x} , which is inconsistent with the condition necessary in order that the motion of the subsidiary system should give rise to the "frictional" terms. Hence we conclude that the frictional terms cannot be explained by supposing that any subsidiary system with a finite number of degrees of freedom is in connection with the original system.

If we investigate the case of a vibrating piston in connection with an unlimited volume of air, we shall find that the waves starting from the piston dissipate its energy just as if it were resisted by a frictional force proportional to its velocity; this, however, is only the case when the medium surrounding the piston is unlimited; when it is bounded by fixed obstacles the waves originated by the piston get reflected from the boundary, and thus the energy which went from the piston to the air gets back again from the air to the piston. Thus the frictional terms cannot be explained by the dissipation of the energy by waves starting from the system and propagated through a medium surrounding it, for in this case it would be possible for energy to flow from the subsidiary into the original system, while, if the frictional terms are to be explained by a subsidiary system in connection with the original one, the connection must be such that energy can flow from the original into the subsidiary system, but not from the subsidiary into the original.

Hence we conclude that the equations of motion, with frictional terms in, represent the average motion of the system, but not the motion at any particular instant.

Thus, to take an example, let us suppose that we have a body moving rapidly through a gas; then, since the body loses by its impacts with the molecules of a gas more momentum than it gains from them, it will be constantly losing momentum, and this might on the average be represented by the introduction of a term expressing a resistance varying as some power of the velocity; but the equations of motion, with this term in, would not be true at any instant, neither when the body was striking against a molecule of the gas, nor when it was moving freely and not in collision with any of the molecules. Again, if we take the resistance to motion in a gas which arises from its own viscosity, the kinetic theory of gases shows that the equations of motion

of the gas, with a term included expressing a resistance proportional to the velocity, are not true at any particular instant, but only when the average is taken over a time which is large compared with the time a molecule takes to traverse its own free path.

The irreversible effects which have the closest connection with the phenomena we have been considering in this paper are those of electrical resistance, and we shall now go on to consider the application of dynamical principles to phenomena of this type. In accordance with what we have already stated, we regard the ordinary electrical equations containing the terms which express the effects of the resistance as equations which only apply to the average state of the system, the average being taken over a time which is too small to allow us to perceive the changes taking place inside it; about these changes the ordinary equations give us no information. It is evident from this point of view that we cannot hope to deduce directly the ordinary electrical equations from these dynamical equations, which are always true, and which, if we could solve them, would describe the whole history of the electrical configuration. We should expect the electrical equations to be obtained from the dynamical ones by some process of averaging.

If this view is right, the passage of a "steady" current is not, strictly speaking, a steady phenomenon; but only one in which the average effect, taken over some very small time, is steady. We must therefore take a view of the electric current somewhat different from that usually taken. In order to explain this view, let us begin by considering a case which is plainly discontinuous, but which, when the changes succeed each other sufficiently rapidly, will produce the same effect as a steady current. The case is that of the passage of electricity through a tube containing gas at a low pressure. In this case the electric force inside the tube increases until it gets too great for the electric strength of the gas, the field then breaks down, and for a moment the electric force either vanishes or is very much diminished, or, what is the same thing, a quantity of electricity passes from the one terminal to the other; after this the force increases until it gets great enough to again overcome the electric strength of the gas, when discharge again takes place. The constant succession of such discharges produces the same effect as a current flowing through a metallic conductor. In the case of metallic conductors we may suppose that very much the same kind of thing goes on, only that now the electric field is dissipated by the breaking up of molecular aggregations which split up independently of the electric field. Let us imagine a conductor placed in the electric field, and suppose that at first induction occurs in it as well as in the surrounding dielectric: then in each unit of volume of the conductor there is a certain amount of energy. If the molecules or the atoms in the molecules can move so that this energy diminishes, they will do so; in general, however, we should expect the forces existing between the atoms in the molecule to be so large that no very extensive re-arrangement of the atoms or molecules in the way suggested by the electric forces would take place unless the electric field were excessively strong. If, however, the molecules or the aggregations of molecules were to

break up independently of the electric field, then these inter-atomic or inter-molecular forces would be absent, and the atoms or molecules would be free to arrange themselves so as to diminish the potential energy due to the electric field. This diminution in the electrical energy would be equivalent to a discharge of the electric field, partial or total, according as the energy is only partially or totally exhausted. According to this view, the electric current is a discontinuous phenomenon, though there need not be anything corresponding to a definite period, as the field may not be simultaneously discharged at all points. We may suppose that much the same kind of thing occurs in electrolytes, and in this case the view has much in common with the WILLIAMSON-CLAUSIUS hypothesis. According to this view the electrolyte is not decomposed by the electric field, the function of the electric forces being merely to direct the motion of the components of the molecules dissociated by other means. According to our view it is the re-arrangement of the components of dissociated molecules or groups of molecules which produces the current. This view is in accordance with FARADAY'S remark that induction always precedes conduction. If, as in the case of the electric discharge through permanent gases, the electric field were strong enough to separate the molecules without any independent dissociation, we should expect the law connecting the current with the electromotive force to be different from the law connecting the same quantities when the electromotive force is too weak to decompose the molecule. There seems to be evidence for such a difference, for QUINCKE* has shown that when the E.M.F. is very large the current through badly conducting liquids, such as olive oil or benzene, does not obey OHM'S Law, while the experiments of Mr. NEWALL and myself have shown that when the E.M.F. is small, not more than a few hundred volts per centimetre, the current does obey OHM'S Law.

We shall now proceed to endeavour to represent the theory symbolically. To fix our ideas, let us consider the case of an air-condenser whose armatures are connected with the poles of a battery whose E.M.F. is greater than the air-space can stand: then, as soon as the armatures are connected to the poles of the battery, there is an electric displacement across the air-space in the direction of the E.M.F.; then the air breaks down, and there is the passage of a quantity of electricity—equal per unit area to the displacement across the unit area—from one armature to the other, and then the disappearance of the displacement. Now, whether we take the ordinary two-fluid theory, or MAXWELL'S displacement theory, the result is the same; let us take the two-fluid theory first—then the displacements count for nothing, and we have only to consider the passage of the electricity across the air-space. Let us next take MAXWELL'S theory—the effect of the disappearance of the displacement is equal and opposite to that of the passage of the electricity across the air-space—so that we are left with the effect of the establishment of the displacement, which is the same as that of the passage of the electricity, and the two theories lead to identical results; and we may conclude that when a field, such that the displacement across unit area

* 'WIEDEMANN'S Annalen,' vol. 28, p. 529.

is η , is established, and then breaks down by reason of the re-arrangement of the dielectric, the whole effect is the same as if a quantity of electricity equal to η passed through each unit area of the dielectric.

Let us suppose that in the expression for the electrical part of $T - V$ for unit volume of a conductor through which the electrical displacements are f, g, h , in addition to the usual term

$$\frac{1}{2} \left\{ L \frac{df}{dt} + M \frac{dg}{dt} + N \frac{dh}{dt} \right\},$$

where L, M, N , are the components of the electrical momentum parallel to the axes of x, y, z , respectively, there is the term

$$- \frac{1}{2} Q (f^2 + g^2 + h^2);$$

then LAGRANGE'S equations give

$$\begin{aligned} \frac{dL}{dt} + Qf &= \text{external electromotive force tending to increase } f, \\ &= X \text{ say.} \end{aligned}$$

Now, in the case of a conductor, f is changing very rapidly, while the other terms in this equation only change gradually. Let us then take the mean over unit time of each side of the equation, then we have

$$\overline{\frac{dL}{dt}} + Q \int_0^1 f dt = \bar{X}, \quad (79)$$

where a bar placed over a symbol denotes the mean value of that symbol, and we suppose that Q does not change quickly with the time.

Now let us suppose, as before, that the polarisation is continually being broken down and renewed; let it break down n times a second, and let the mean value of f over one of these intervals of $1/n$ of a second be \bar{f} , and the maximum value be $\alpha\bar{f}$: the breaking down of the field each time is equivalent to the passage of $\alpha\bar{f}$ units of electricity across unit area at right angles to the axis of x . Since the field breaks down n times a second, it is equivalent to the passage of $n\alpha\bar{f}$ across this unit section in unit time, or, if u be the component of currents parallel to the axis of x ,

$$u = n\alpha\bar{f}.$$

Now

$$\int_0^1 f dt = n \int_0^{\frac{1}{n}} f dt = n \cdot \frac{1}{n} \bar{f} = \frac{u}{\alpha n};$$

hence we have, from equation (79),

$$\frac{d\bar{L}}{dt} + \frac{Qu}{an} = \bar{X}, \quad \dots \dots \dots (80)$$

the ordinary electrical equation if the specific resistance of the substance equals Q/an . From this expression for the specific resistance we see that if Q remains constant, or nearly constant, the resistance will vary inversely as n , that is, the resistance will be inversely proportional to the number of discharges in unit time. Now, since the discharges are caused by the breaking up of the molecular aggregations, the number of discharges in unit time will be greater, the greater the ease with which the molecular aggregations break up. The formation and breaking up of these molecular aggregations in a solid would play in it very much the same part as that played by the collision between the molecules in a gas. But, the greater the number of collisions in unit time, the greater the rapidity with which inequalities in the kinetic energy, momentum, &c., in the different parts of a gas disappear, so that we may conclude that, the greater the ease with which molecular aggregations are broken up in a solid, the more rapidly will the inequalities in the kinetic energy disappear, that is, the better conductor of heat the solid will be. Thus the expression for the resistance of a solid conductor contains one term which is inversely proportional to the conductivity for heat of the substance. Hence we can understand why those metals which are good conductors of electricity are also good conductors of heat.

The term

$$-\frac{1}{2}Q(f^2 + g^2 + h^2),$$

which we have introduced into the expression for $T - V$ of unit volume of the conductor, corresponds to the term

$$\frac{2\pi}{K}(f^2 + g^2 + h^2)$$

in the expression for the potential energy of unit volume of a dielectric in which the electric displacement is f, g, h . Thus we may look on Q as equal to $4\pi/K$, where K is the specific inductive capacity of the conductor. The rapid way the resistance increases with the temperature for metals shows that of the term $-\frac{1}{2}Q(f^2 + g^2 + h^2)$ the great part must in this case be due to the kinetic energy. Let us suppose that in the kinetic energy we have the term

$$-\frac{1}{2}a\theta(f^2 + g^2 + h^2),$$

where θ is proportional to the absolute temperature, and in the potential energy the term

$$\frac{1}{2}b(f^2 + g^2 + h^2);$$

then

$$Q = a\theta + b,$$

and the specific resistance σ equals

$$\frac{a\theta + b}{na}.$$

Now n will probably depend on the temperature, and will probably in most cases increase as it increases, as it seems likely that the molecular aggregations will split up more easily at high than at low temperatures. Thus there are two influences which, when the temperature increases, oppose each other in the effect they produce upon the resistance. On the one hand there is a tendency for the resistance to increase in consequence of the greater change in the value of $T - V$ produced by a given electric displacement, and on the other hand there is a tendency for the conductivity to increase in consequence of the molecular aggregations breaking up with greater ease, and so increasing the number of discharges which take place in unit time. In the case of metals the first effect seems to be the most important, as the resistance of these substances increases with the temperature. In the case of electrolytes the second seems the most important, as the conductivity of these substances increases with the temperature. Anything which increases the complexity of the molecular aggregations will increase the importance of the second effect relatively to the first, hence we can understand why it is that alloys have so much smaller temperature coefficients than pure metals, as we should expect the molecular aggregations to be more complex in alloys than in pure metals, and therefore the second effect, which tends to make the resistance diminish as the temperature increases, is relatively more important.

It is evident that, if the view which we have taken of the electric discharge be correct, the specific inductive capacity of metals must alter more quickly with the temperature than the specific inductive capacities of dielectrics, as experiment has shown that these vary only slowly with the temperature.

The consideration of the term

$$-\frac{1}{2}Q(f^2 + g^2 + h^2),$$

which occurs in $T - V$, leads to many interesting results, of which we shall proceed to give one or two examples.

If we take the axis of x parallel to the electric displacement, and write σna for Q , where σ is the specific resistance, we may write this term as

$$-\frac{1}{2}\sigma n a f^2.$$

Now the experiments of Sir W. THOMSON and Mr. TOMLINSON show that the resistance of metals is affected by strain, so that σna must be a function of the strain.

Let us suppose that e is a strain coordinate ; then it follows, by LAGRANGE'S equations, that there is a force due to this term, tending to increase e , equal to

$$-\frac{1}{2} \frac{d}{de} (\sigma n \alpha) f^2.$$

Since f , according to our view, changes very rapidly, we must find the mean value of this term, that is, we must find the value of

$$\int_0^1 f^2 dt.$$

If the electric field breaks down and gets established n times in a second, this will equal

$$n \int_0^{\frac{1}{n}} f^2 dt.$$

Now

$$\int_0^{\frac{1}{n}} f dt = \bar{f}.$$

Let

$$\int_0^{\frac{1}{n}} f^2 dt = \beta \cdot (\alpha \bar{f})^2,$$

where, as before, αf is the maximum value of f , and β is a quantity which will depend upon the way f reaches its maximum ; then

$$\int_0^1 f^2 dt = n \beta (\alpha \bar{f})^2 = \frac{\beta}{n} u^2,$$

where u is the current through unit area of the section of the conductor. Then the average force tending to increase e equals

$$-\frac{1}{2} \frac{d}{de} (\sigma n \alpha) \frac{\beta}{n} u^2. \quad \dots \dots \dots (81)$$

If neither n nor α depend upon e , then this equals

$$-\frac{1}{2} \alpha \beta \frac{d\sigma}{de} u^2. \quad \dots \dots \dots (82)$$

Thus, if the specific resistance increases with the strain, there will be a tendency to diminish that strain when a current traverses the conductor.

We can apply precisely the same method to any other physical effect which influences the resistance. Suppose that an alteration in the configuration δp alters the resistance; then, when the current u passes through the conductor, there will be a force, tending to increase p , equal to

$$-\frac{1}{2} \frac{d}{dp} (\sigma n \alpha) \frac{\beta}{n} u^2. \quad \dots \dots \dots (83)$$

Let us now consider the effect which this term in the expression for $T - V$ will produce on the chemical phenomena which we discussed in the earlier part of this paper. The alteration in $\bar{T} - \bar{V}$ due to this term is

$$-\frac{1}{2} \sigma n \alpha \frac{\beta}{n} u^2$$

or

$$-\frac{1}{2} \sigma \alpha \beta u^2.$$

Now, if the specific resistance depends, as we know it does to a very large extent in the case of liquids, on the substances dissolved in them, the chemical equilibrium will be affected by the passage of an electric current through them.

Let us first take the case of solution; then, when we were considering that subject, we showed that, if $\bar{T} - \bar{V}$ were increased by $-\delta w$, the change $\delta\theta$ in the temperature, which would produce the same effect as that produced by this change in $\bar{T} - \bar{V}$, is given by the equation

$$\frac{\delta\theta}{\theta} = - \frac{dw}{\frac{dq'}{\lambda}},$$

where q' is the mass of the solution, and λ the amount of heat absorbed when one gramme of the salt dissolves at constant temperature. Applying this formula to our case, we have

$$\frac{\delta\theta}{\theta} = - \frac{\frac{1}{2} \alpha \beta u^2 \frac{d\sigma}{dq'}}{\lambda}, \quad \dots \dots \dots (84)$$

so that, if the specific resistance of the solution depends upon the amount of salt dissolved, then, if we make a current pass through a saturated solution, it will either absorb or deposit salt; if the specific resistance increases as the salt dissolves, it will deposit salt; if the resistance diminishes, it will absorb it. In trying the experiment, it would be well to use alternating currents to avoid any difficulty which might arise from the substances set free by electrolysis.

Again, if we have dilute solutions of any number of substances, and if the resistance of the solution depends upon the relative proportion of these substances, then the

proportion of these substances when there is equilibrium will be altered by passing an electric current through the solution. Thus the coefficient of reaction ω will be altered, and we see from equation (56) that the alteration $\delta\omega$ is given by the equation

$$\begin{aligned} \frac{\delta\omega}{\omega} &= \frac{1}{\kappa\theta} \frac{d}{d\xi} \frac{1}{2} \sigma \alpha \beta u^2 \\ &= \frac{1}{2\kappa\theta} \alpha \beta u^2 \frac{d\sigma}{d\xi}, \quad (85) \end{aligned}$$

where the notation is the same as that used on page 509.

Thus, if the specific resistance increases as any reaction goes on, the passage of an electric current through the solution will tend to stop that reaction.