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Some Applications of Dynamical Principles to Physical Phenomena. Part II

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XVI. *Some Applications of Dynamical Principles to Physical Phenomena.*—Part II.

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§ 1. The two laws of Thermodynamics have proved by far the most powerful, indeed almost the only, means we possess of connecting the phenomena in one branch of Physics with those in another. Though the two laws are usually grouped together, it should not be forgotten that they differ essentially in character. The First Law is a direct application to Physics of one of the most important dynamical principles, that of the Conservation of Energy; while the Second Law, which for the purpose of connecting various physical phenomena is even more important than the first, is not, strictly speaking, a dynamical principle at all, since its statement involves a reference to quantities which never occur in abstract Dynamics.

Clausius and Sir William Thomson, the two physicists to whom the Second Law owes its importance, have connected it with other principles which seem more axiomatic.

Thus Clausius bases the Second Law on the principle that "heat cannot by itself pass from a colder to a hotter body." In this statement too much depends upon the meaning to be attached to the words "by itself" for it to be regarded as axiomatic, and the following extract from Clausius seems to show that in his view it is the statement of a new physical principle, and not the necessary consequence of previously recognised ones. He says ('Mechanical Theory of Heat,' English translation, by W. R. Browne, p. 342), "If, however complicated the processes may be, it is maintained that without some other permanent change, which may be looked upon as a compensation, heat can never pass from a colder to a hotter body, it would seem that this principle ought not to be treated as one altogether self-evident, but rather as a newly propounded fundamental principle on whose acceptance or non-acceptance the validity of the proof depends."

Again Sir William Thomson has connected the Second Law with the principle that "it is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects." To follow out the connection between this principle and the Second Law, it is convenient to divide the energy of a body into two kinds, the one kind depending upon circumstances over which we have complete control, the other

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depending on circumstances which we cannot completely control. Take as an example the energy possessed by a stretched spring: part of the energy depends upon the extension of the spring; we have complete control over this, but another part of the energy (the heat energy) depends upon the motion of the molecules of the spring, and, although we have some control over the average motion of all the molecules, we have none over the motion of individual molecules. Let us for the moment call the energy of the first kind "controllable energy," that of the second "intrinsic energy." We may look on an engine as a means of converting intrinsic into controllable energy. Then, if we follow the connection between the axiom and the principle that the efficiency of a perfectly reversible engine is a maximum (which we may take as equivalent to the Second Law), we shall see that if the axiom is to cover all the cases to which the Second Law has been applied it must be equivalent to the statement that it is impossible to derive mechanical effect by abstracting intrinsic energy from the refrigerator. Now the intrinsic energy consists, in addition to sensible heat, of what CLAUSIUS calls the internal energy of the body, that is, energy depending upon the arrangement of the molecules, and, it may be, also upon their motion. If we consider the various forms which this intrinsic energy can take, the statement that it is impossible to derive mechanical effect by abstracting intrinsic energy from the refrigerator would seem to be hardly more axiomatic than the Second Law itself.

The Second Law of Thermodynamics, like the Law of Gravitation, seems then to be proved rather by the truth of its consequences than by any *à priori* considerations.

For this, among other reasons, I have thought it might perhaps be interesting to deduce by the use of purely dynamical principles many results which are usually obtained by the aid of the Second Law of Thermodynamics, as well as some others which, so far as I know, have not previously been obtained. This I have endeavoured to do in the following paper, as I did in one previously published under the same title in the 'Philosophical Transactions,' 1885, Part 1. In the first paper I considered the relation between thermal, elastic, and magnetic phenomena, but did not consider any phenomena in which chemical or quasi-chemical processes were concerned, such as dissociation, evaporation, solution, chemical combination: or any effects which are not reversible, such as those produced by the electric resistance of metals and electrolytes. In this paper I shall endeavour to apply the same or analogous principles to the phenomena mentioned above, as well as to a few additional phenomena of the kind discussed in the first paper.

Though the dynamical method is open to the objection that the quantities made use of are those which occur in abstract Dynamics, such as mass, velocity, energy, acceleration, and so require further knowledge before we can connect them with such things as temperature, electric current, resistance, and so on—a knowledge which, in many cases, we do not possess—while, in the Second Law, the results are expressed in terms of quantities which can be readily measured; still it has advantages which make it worthy of consideration.

In the first place, there is the mental satisfaction to be got by explaining things on dynamical principles; and, again, there is the certainty that the method is capable of completely solving the question (whether we can make it do so is another matter), while we have no certainty that all possible information is given by the two laws of Thermodynamics, or that some unknown third law might not enable us to arrive at results beyond the powers of the first and second.

§ 2. The researches of CLAUSIUS, SZILY, and BOLTZMANN have shown that the Second Law of Thermodynamics is closely connected with the principle of Least Action, and it might therefore be thought that the Second Law was only a more convenient way of stating this principle, so that no advantage could be gained by the direct use of dynamical principles. In the investigations on the connection between the Second Law and the principle of Least Action there are, as I shall endeavour to show later on, a good many assumptions implicitly made, so that it seems to be much preferable to proceed, if possible, in any special case by the direct use of dynamical principles.

Again, there can, I think, be no question that the principle of Least Action and the Second Law of Thermodynamics are not equivalent; for, in the first place, as is well known (see ROUTH's 'Advanced Rigid Dynamics,' p. 257), the principle of Least Action includes that of the Conservation of Energy, so that, if the Second Law of Thermodynamics included all that could be got from the principle of Least Action, it ought to include the First Law as a particular case.

Again, in the most general case, the principle of Least Action will for a system fixed by n coordinates give n equations; but the Second Law of Thermodynamics, which asserts that a certain function is a perfect differential, would, in the most general case, give rise to $\frac{1}{2}n(n-1)$ equations, as that is the number of conditions to be satisfied if

$$P_1 dx_1 + P_2 dx_2 + \quad . \quad .$$

is a perfect differential.

§ 3. The dynamical methods we shall most frequently use in the following paper are the Hamiltonian principles expressed by the equations

$$2\delta\int_0^i T\,dt = i\delta(T+V) + \left[\Sigma\frac{dT}{d\dot{q}}\delta q\right]_0^i, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$2\delta\int_0^i (T-V)\,dt = (T+V)\,\delta i + \left[\Sigma\frac{dT}{d\dot{q}}\delta q\right]_0^i, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where T and V are respectively the kinetic and potential energies of a system, q a typical coordinate helping to fix the configuration of the system, and t the time.

The first of these equations has been used to show the connection between the principle of Least Action which it expresses and the Second Law of Thermodynamics;

and it will be convenient to begin by considering the investigations which have been made on this connection.

The proof usually given is as follows (see ROUTH's 'Advanced Rigid Dynamics,' p. 254):—

Let us suppose that no external work is done by the system; then—

$$\delta(\mathrm{T} + \mathrm{V}) = \delta\mathrm{Q}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\delta\mathrm{Q}$ is a small quantity of work supplied to the system. The quantity $\delta(\mathrm{T} + \mathrm{V})$ occurs on the right-hand side of equation (1): let us now consider the term $[\Sigma\, \delta q\, d\mathrm{T}/d\dot{q}]_0^i$, which also occurs on the same side of the equation. If the motion be oscillatory, and i a period of complete recurrence; $\delta q\, d\mathrm{T}/d\dot{q}$ will have the same value at the lower as it has at the upper limit of the integral, and therefore the difference of the values will vanish. The case when the motion is oscillatory is not, however, the only, nor indeed the most important, case in which this term may be neglected. Let us suppose that the system consists of a great number of secondary systems, or, as they are generally called, molecules, and that the motion of these molecules is in every variety of phase; then the term $[\Sigma\, \delta q\, d\mathrm{T}/d\dot{q}]$, the sum being taken for all the molecules, will be small, and will not increase indefinitely with the time, but will continually fluctuate within narrow limits. This is evidently true if we confine our attention to those coordinates which fix the configuration of the molecule relatively to its centre of gravity; and, if we remember that the motion of the centre of gravity of the molecules is by collision with other molecules and with the sides of the vessel which contain them continually being reversed, we can see that the above statement remains true even when coordinates fixing the position of the centres of gravity of the molecules are included. Thus, if the time over which we integrate is long enough, we may neglect the term $[\Sigma\, \delta q\, d\mathrm{T}/d\dot{q}]_0^i$ in comparison with the other terms which occur in equation (1), as these terms increase indefinitely with the time, so that in this case, even though the motion is not entirely periodic, equation (1) may be written—

$$2\delta \int_0^i \mathrm{T}\, dt = i\, \delta\mathrm{Q},$$

or

$$2\delta(i\mathrm{T}_m) = i\, \delta\mathrm{Q}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where T_m is the mean kinetic energy. This equation may be written—

$$2\delta \log(i\mathrm{T}_m) = \delta\mathrm{Q}/\mathrm{T}_m, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

so that $\delta\mathrm{Q}/\mathrm{T}_m$ is a perfect differential.

One of the ways of stating the Second Law of Thermodynamics is that $\delta\mathrm{Q}/\theta$ is a perfect differential, θ being the absolute temperature; thus, if θ is a constant multiple of the mean kinetic energy, the Second Law of Thermodynamics can be deduced from the principle of Least Action. Thus even in the simplest case, when the system does no external work, we require the additional assumption that the absolute temperature is proportional to the mean kinetic energy. Now, in the only case in which the theory has been completely worked out, that of the kinetic theory of gases, the absolute temperature is measured, not by the mean total kinetic energy directly, but by the mean kinetic energy due to the translatory motion of the centres of gravity of the molecules. This is shown by the way in which BOYLE's Law is deduced from the kinetic theory. If the temperature depended upon the vibratory energy, we could not explain why the relation between pressure, density, and temperature is practically the same for all gases, while the ratio of the vibratory energy to the translatory energy varies from an exceedingly small fraction in the case of mercury vapour to more than half in the case of hydrogen, oxygen, and nitrogen. Thus in the case of gases we have strong reasons for supposing that the temperature is measured by the mean translatory energy, the mean being taken for all the molecules. In the case of solids and liquids this is not so clear, but even here there seem to be reasons for believing that the temperature is measured by the mean of some particular kind of energy rather than by the mean total kinetic energy. From the continuity of the solid, liquid, and gaseous states of matter we should expect the temperature to depend upon the kinetic energy in the solid or liquid as well as in the gaseous state. But, if in the case of a solid the temperature were measured by the mean total kinetic energy and not by the mean of some special kind of energy, then, if we have a gas and a solid at the same temperature, the mean total kinetic energy of the gas will be greater than that of the solid, for by our supposition the mean translatory energy of the molecules of the gas equals the mean total kinetic energy of the molecules of the solid. Now, the specific heat of water in the solid state is about the same as that of the same body when in the gaseous state, while for some substances it is double, as it would be if the kinetic energy in the solid state were equal to that in the gaseous, and if, as we should expect *à priori*, the work supplied to a solid is equally divided between the kinetic and potential energies. For this reason, we conclude that the mean kinetic energy of the molecules of a solid is not less than the mean kinetic energy of the molecules of a gas at the same temperature; and hence, that the temperature in the solid state is measured by the mean of some particular kind of energy. It would seem most probable that this particular kind would be the energy due to the translatory motion of the molecules; and that the temperature is measured by the mean energy due to the translatory motion of the molecules in the solid and liquid as well as in the gaseous states.

In the simple case we are considering, we have seen that it follows from the principle of Least Action that $\delta Q/T_m$ is a perfect differential.

If this is identical with the Second Law of Thermodynamics, then T_m must either be a constant multiple of θ, the absolute temperature, or T_m/θ must be a function of ϕ, where ϕ is given by the equation $d\phi = d\mathrm{Q}/\mathrm{T}_m$. Making the first supposition, and remembering that the absolute temperature measures the mean energy due to the translatory motion of the molecules, we see that it is equivalent to supposing that the mean total kinetic energy of the molecules is a constant multiple of their mean translatory energy. This is the assumption which was originally made by CLAUSIUS, and we see that it must be made if we are to derive the Second Law of Thermodynamics from the principle of Least Action.

BOLTZMANN, in his celebrated investigation* of the distribution of energy among the molecules of a gas, each molecule of which possesses n degrees of freedom, arrives at a much more definite result. According to this investigation the mean kinetic energy corresponding to each degree of freedom is the same, so that the mean kinetic energy due to the translatory motion of the centres of gravity of the molecules is only $3/n$ of the mean total kinetic energy of the molecules. The proof of this theorem given by the author seems to me to be open to grave objection, and the results to which it leads have certainly not been reconciled with the properties possessed by actual gases. According to this theorem, the result is the same, whatever be the constitution of the molecule, and whatever the forces exerted by one molecule on another when they come so close together as to be within the range of each other's action. BOLTZMANN shows that, if the number of molecules which have the coordinates $q_1, q_2, \ldots\ldots q_n$ and the corresponding momenta $p_1, p_2, \ldots\ldots p_n$ between the limits $q_1, q_1 + \delta q_1, q_2, q_2 + \delta q_2, \ldots q_n, q_n + \delta q_n, p_1, p_1 + \delta p_1, \ldots p_n, p_n + \delta p_n$, is

$$Ce^{-h(\mathrm{T}+\chi)}\, dq_1\, dq_2 \ldots dq_n \,.\, dp_1\, dp_2 \ldots dp_n,$$

where C and h are constants, and T and χ the kinetic and potential energies of such a molecule; then the number of such molecules will remain constant, as in a given time as many molecules pass out of that state as enter it. Thus, if this distribution is ever established, it will be a steady distribution, *i.e.*, the state of the gas will not change. To prove the theorem we have quoted above, BOLTZMANN integrates this expression, assuming that each velocity may have all values from *plus* infinity to *minus* infinity. It seems to me, however, that this assumption is not legitimate, and that before we can fix the limits of the velocity we must know the nature of the molecule and the forces between two molecules when they come within the sphere of each other's action. We can easily imagine cases in which the assumption is not true. Take, for example, the case of two bodies describing orbits about their centre of gravity under each other's attraction. If the relative velocity of the bodies exceeds a certain value, which depends upon the distance between them and the law of attraction, the two bodies will not remain together, but will separate until they are finally at an infinite distance apart. Thus, if the two bodies represent the atoms in a

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[*] BOLTZMANN, 'Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften,' vol. 63 (Abth. 2), Wien, 1871. See also MAXWELL, 'Transactions of the Cambridge Philosophical Society,' vol. 12, 1879.

molecule, the molecule will be split up when the relative velocity of the atom exceeds a certain value; so that in this case the limits of the relative velocity would be functions of the coordinates fixing the position of the atoms, and not *plus* and *minus* infinity, as in BOLTZMANN's investigation. We can, moreover, imagine a kind of molecule for which we can prove that the theorem itself is not true. We know that many dynamical theorems have their most elegant applications to systems of electric currents flowing through neighbouring circuits, and that if any dynamical theorem is true at all it must be true when interpreted in an electrical sense as well as in the mechanical one. This is evident, because we can apply the same method, that of LAGRANGE's equations, to both the electrical and mechanical problems. Thus BOLTZMANN's theorem, if it is true at all, must be true when some of the coordinates fixing the configuration of the molecule are coordinates which fix the distribution of electric currents flowing through circuits attached to the molecule. Let us suppose that these coordinates, which we will call $x_1, x_2, \ldots x_n$, fix currents flowing through perfectly conducting circuits in parallel planes in the molecule, the circuits being so close together that the magnetic force due to the currents round the other molecules, or to any other external source, may be taken as constant over the circuits. The kinetic energy due to the currents $\dot{x}_1, \dot{x}_2, \ldots$ circulating through these conductors is of the form

$$\tfrac{1}{2}(\mathrm{L}_{11}\dot{x}_1^2 + 2\mathrm{L}_{12}\dot{x}_1\dot{x}_2 + \ldots).$$

Let y_1, y_2, be the "principal" coordinates, fixing the same configuration as that fixed by $x_1, x_2, \ldots$; then, when the kinetic energy is expressed in terms of these coordinates, it is of the form

$$\tfrac{1}{2}(\mathrm{L}_1\dot{y}_1^2 + \mathrm{L}_2\dot{y}_2^2 + \ldots).$$

The electrical equations are:—

$\frac{d}{dt}(\mathrm{L}_1\dot{y}_1) =$ rate of diminution in the number of lines of force passing through the circuit corresponding to y,

$\frac{d}{dt}(\mathrm{L}_2\dot{y}_2) =$ the same thing for the circuit y_2,

Now, since all the circuits are parallel, and so close together that the magnetic force may be considered constant over them, the number of lines of force passing through y_1 will be in a constant ratio to the number passing through y_2. Let this ratio be λ; then

$$\frac{d}{dt}(\mathrm{L}_1\dot{y}_1) = \lambda\frac{d}{dt}(\mathrm{L}_2\dot{y}_2),$$

or, if $\dot{y}_1$ and $\dot{y}_2$ are each initially zero,

$$\mathrm{L}_1\dot{y}_1 = \lambda\,\mathrm{L}_2\dot{y}_2.$$

Now, the kinetic energy corresponding to $\dot{y}_1$ is

$$\tfrac{1}{2}\,L_1\dot{y}_1^2\,;$$

that corresponding to y_2 is

$$\tfrac{1}{2}\,L_2\dot{y}_2^2.$$

The ratio of these is $\lambda^2 L_2/L_1$; this is a quantity depending only on the configuration of the circuits, and, if the molecules are geometrically similar, will be the same for each molecule; thus the ratio of the mean kinetic energy corresponding to y_1 to that corresponding to y_2 is $\lambda^2 L_2/L_1$, and, by properly choosing the configuration of the circuits, this quantity may be made to have any positive value we please, whereas, if BOLTZMANN'S theorem were true, the ratio ought always to be equal to unity. Hence we conclude that BOLTZMANN'S theorem is not true. It ought to be noticed that in this case the ratio is constant, though not unity, and this is all that is assumed by CLAUSIUS.

The consideration of the collision of two vortex rings, according to the vortex ring theory of gases, would, I think, lead us to the conclusion that the energy corresponding to each mode of vibration is, when the gas is in a steady state, a function of the mean translatory energy of the molecules of the gas, the function being of such a kind that, the higher the mode of vibration, the smaller the ratio of the corresponding energy to the mean translatory energy.

The application of the Second Law to the case we have just discussed, which is the one investigated by SZILY and CLAUSIUS, does not include the application to the case (almost the only one of importance in the applications of the Second Law) when the system absorbs or expends work when heat is communicated to it. It would not include, for example, the case when heat is applied to a gas at constant pressure.

Let $P_1, P_2, \ldots$ be the external forces of type p_1, p_2, respectively, acting on the system, and let the points of application of these forces move through $\delta p_1, \delta p_2 \ldots$ Then, if δQ be the quantity of undirected energy supplied to the system, that is, energy that is not supplied by moving the system against definite external forces, δT and δV the increments in the kinetic and potential energies of the system,

$$\delta Q = \delta T + \delta V - P_1\,\delta p_1 - P_2\,\delta p_2 \ldots \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Thus, for example, in the case of a gas contained in a cylinder with a movable piston,

$$\delta Q = \delta T + \delta V + p\,\delta x,$$

where p is the total pressure on the piston, and x the distance of the piston from the bottom of the cylinder.

[* In considering this case it will be convenient to divide the kinetic energy into two parts, one part, which we shall denote by T_1, depending on the velocities of coordinates fixing the position of the molecule; the other, which we shall denote by T_2, depending on the velocities of coordinates of the type p, which we have completely under our control. The coordinates fixing the configuration of the system with respect to strain, electrification, magnetisation, &c., are coordinates of this class. T_2 will be a quadratic function of the velocities of the p coordinates, since the total kinetic energy of the system cannot involve the product of the velocity of a p coordinate with that of one fixing the position of a molecule; otherwise the kinetic energy of the system would be altered by reversing the motion of all the molecules.

We have, by LAGRANGE's equation,

$$\frac{d}{dt}\frac{dT}{d\dot{p}_1} - \frac{dT}{dp} + \frac{dV}{dp} = P;$$

now

$$T = T_1 + T_2,$$

and by definition

$$\frac{dT_1}{d\dot{p}_1} = 0,$$

we have also, by the Conservation of Energy,

$$\delta Q = \delta T_1 + \delta T_2 + \delta V - \Sigma P\, \delta p; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6^*)$$

now

$$\delta T_2 = \Sigma\left(\frac{dT}{dp}\,\delta p + \frac{dT}{d\dot{p}}\,\delta\dot{p}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

since T_2 is a homogeneous quadratic function of the velocities of the "p" coordinates,

$$2T_2 = \Sigma\,\dot{p}\,\frac{dT_2}{d\dot{p}},$$

and therefore

$$2\,\delta T_2 = \Sigma\left(\delta\dot{p}\,\frac{dT_2}{d\dot{p}} + \dot{p}\,\delta\,\frac{dT_2}{d\dot{p}}\right); \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

subtracting (7) from (8), we have

$$\delta T_2 = \Sigma\left(\dot{p}\,\delta\,\frac{dT_2}{d\dot{p}} - \delta p\,\frac{dT_2}{dp}\right).$$

If the change in the configuration is that which actually takes place, then we have

$$\dot{p}_1\,\delta t = \delta p_1,$$

so that

$$\delta T_2 = \Sigma\,\delta p\left(\frac{d}{dt}\frac{dT_2}{d\dot{p}} - \frac{dT_2}{dp}\right),$$

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* This portion within brackets re-written October 17, 1887.

so that equation (6) becomes

$$\delta Q = \Sigma\, \delta p \left(\frac{d}{dt}\frac{d\mathrm{T}_2}{d\dot{p}} - \frac{d\mathrm{T}_2}{dp} + \frac{d\mathrm{V}}{dp} - \mathrm{P} \right) + \delta \mathrm{V}_{p\ \mathrm{constant}} + \delta \mathrm{T}_1\,;$$

substituting for P from (5), we have

$$\delta Q = \Sigma \frac{d\mathrm{T}_1}{dp}\,\delta p + \delta \mathrm{T}_1 + \delta \mathrm{V}_{p\ \mathrm{constant.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Now, if p enters into the expression for the kinetic energy due to the motion of the molecules of the body, it must enter as a factor into all the terms expressing this energy, otherwise the phenomenon symbolised by p would be more affected by the motion of particular molecules than by that of others. Thus T_1 must be of the form

$$f(p)\,\mathrm{T}_3$$

when T_3 does not involve p.

Thus

$$\frac{d\mathrm{T}_1}{dp} = f'(p)\,\mathrm{T}_3$$

$$= \frac{f'(p)}{f(p)}\,\mathrm{T}_1,$$

and therefore, by (9),

$$\delta Q = \Sigma \frac{f'(p)}{f(p)}\,\mathrm{T}_1\,\delta p + \delta \mathrm{T}_1 + \delta \mathrm{V}_{(p\ \mathrm{constant})},$$

so that

$$\frac{\delta Q}{\mathrm{T}_1} = \Sigma \frac{f'(p)}{f(p)}\,\delta p + \delta \log \mathrm{T}_1 + \frac{\delta \mathrm{V}_{(p\ \mathrm{constant})}}{\mathrm{T}_1}. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Since T_1 is assumed to be proportional to the absolute temperature, and since the first two terms on the right-hand side of the equation are perfect differentials, we see that, in order that $\delta Q/\theta$ should be a perfect differential,

$$\frac{\delta \mathrm{V}_{(p\ \mathrm{constant})}}{\theta}$$

must be one too.

The state of the body is determined if we know the value of the p coordinates and the temperature, so that $\delta \mathrm{V}$, when p is constant, may be written as

$$\frac{d\mathrm{V}}{d\theta}\cdot\delta\theta,$$

where $d\mathrm{V}/d\theta$ is very large when the temperature is near the melting or the boiling points of the substance.

Making this substitution for δV in equation (10), we have

$$\delta Q = \Sigma \frac{dT_1}{dp} \delta p + \delta T_1 + \frac{dV}{d\theta} \cdot \delta\theta. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Now let us suppose that only one coordinate, p_1, changes, and that just as much heat is supplied or absorbed as is sufficient to prevent the temperature from changing; then, since the temperature is constant, δT_1 and $\delta\theta$ both vanish, and we have

$$\delta Q = \frac{dT_1}{dp_1} \delta p_1.$$

Now, if P_1 be the force which is required to keep p_1 constant when the system is in a steady state,

$$P_1 = \frac{dV}{dp_1} - \frac{dT_1}{dp_1} - \frac{dT_2}{dp_1}$$

$$= \frac{dV}{dp_1} - \frac{f'(p)}{f(p)} T_1 - \frac{dT}{dp_1}.$$

Now, since dV/dp_1 and dT_2/dp_1 do not explicitly involve θ, and since T_1 is proportional to θ, we have

$$\theta \left(\frac{dP_1}{d\theta}\right) = -\frac{f'(p)}{f(p)} T_1$$

$$= -\frac{dT_1}{dp_1},$$

where, in finding $\left(\frac{dP_1}{d\theta}\right)$, θ is the only quantity which is supposed to vary.

Thus equation (11) becomes

$$(\delta Q)_{\theta \text{ constant}} = -\theta \left(\frac{dP_1}{d\theta}\right) \delta p. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12).]$$

This result can be obtained from the Second Law of Thermodynamics; it was so obtained by VON HELMHOLTZ, and applied by him to the very important case of the heat produced in the voltaic cell in his paper "Die Thermodynamik chemischer Vorgänge" ('Wissenschaftliche Abhandlungen,' vol. 2, p. 962).

§ 4. It will be seen from the preceding work that the Second Law of Thermodynamics cannot be deduced from the principle of Least Action, unless we know a good deal about the distribution of energy among the molecules, and unless we make in addition a good many assumptions. For this reason, in discussing the applications of Dynamics to Physics, I prefer to apply the principle of Least Action directly to the various problems, and not to start from the Second Law as an intermediate stage. In the rest of the paper I shall endeavour to show how this can be done.

The Application of Dynamical Principles to Phenomena which are in a Steady State.

§ 5. The most convenient principle for this purpose is the Hamiltonian one, according to which, if i be constant,

$$\delta \int_0^i \mathrm{L}\, dt = \Sigma \left(\frac{d\mathrm{L}}{d\dot{q}}\delta q\right)_0^i, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12^*)$$

where q is one of the coordinates helping to fix the configuration of the system, and L the Lagrangian function or ROUTH's modification of it, according as it is or is not expressed entirely in terms of the velocities of the coordinates.

If

$$\int_0^i \mathrm{L}\, dt = \mathrm{S},$$

and if S be expressed in terms of i, and the coordinates at the times 0 and i, then, if q be a coordinate at the time i, we see from equation (12*) that

$$\frac{d\mathrm{T}}{d\dot{q}} = \frac{d\mathrm{S}}{dq},$$

and, by LAGRANGE's equation,

$$\frac{d}{dt}\frac{d\mathrm{T}}{d\dot{q}} = \frac{d}{dq}(\mathrm{T} - \mathrm{V});$$

hence we see that the momentum corresponding to any coordinate and the rate of change of the momentum can both be expressed as the differential coefficients of functions with respect to that coordinate.

We shall now proceed to show that for Steady Motion

$$\delta\bar{\mathrm{L}} = 0,$$

where $\bar{\mathrm{L}}$ is the mean value of L, and where δ is to be interpreted in the following way.

All, or nearly all, the systems we shall have to deal with are those which consist of a large number of molecules, and we may conveniently for our purpose divide the coordinates, fixing the configuration of such a system into two kinds:—

(a) Molar coordinates, which fix the configuration of the system as a whole, and whose value we may by various physical processes alter at our pleasure. When we say that the system is in a steady state, all that we mean is that the configuration as fixed by the molar coordinates is steady.

(b) Molecular coordinates, which fix the position of individual molecules. The values of these coordinates are quite beyond our control.

Now, if we consider the molar coordinates, we shall see that they are of two kinds: the first kind, which I called in my first paper kinosthenic coordinates, only enter into the expressions for the energy through their differential coefficients, and do not occur explicitly themselves; the molar coordinates of the second kind enter explicitly into the expressions for the energies, and do not occur merely as differential coefficients.

A good example of the two classes of coordinates is afforded by the coordinates required to fix the position of a rod suspended by one extremity. We may fix it by the angle θ which the rod makes with the vertical, and the azimuth ϕ of the plane through the rod and the vertical line through its fixed extremity. The expression for the kinetic energy of the rod in terms of these coordinates is of the form

$$\mathrm{A}\dot{\theta}^2 + \mathrm{B}\sin^2\theta\dot{\phi}^2\;;$$

the potential energy is of the form

$$\mathrm{C}\cos\theta,$$

where A, B, C, are constants. We see that ϕ is a coordinate of the first kind, since it only enters the expression for the kinetic energy through its differential coefficient, while θ is a coordinate of the second kind, as functions of θ occur in the expressions for the kinetic and potential energies. When the system is in a steady state the velocity of the first kind of coordinate is constant, while that of the second kind is zero. In the variations which we shall suppose $\overline{\mathrm{L}}$ to suffer we shall suppose that the velocities of the kinosthenic coordinates remain unaltered, while the coordinates of the second kind are varied. In calculating the mean value of L for a system in a steady state, we may suppose that all the terms in the kinetic energy which involve a differential coefficient of a coordinate of the second kind are omitted, since in the steady state these differential coefficients vanish. We may, therefore, for our purpose, without loss of generality, suppose that $d\mathrm{L}/d\dot{q}_2 = 0$, where q_2 is a molar coordinate of the second kind.

The equation

$$\delta\overline{\mathrm{L}} = \Sigma\left(\frac{d\mathrm{L}}{d\dot{q}}\,\delta q\right)_0^1$$

may conveniently be written

$$\delta\overline{\mathrm{L}} = \Sigma\left(\frac{d\mathrm{L}}{d\dot{q}_1}\,\delta q_1\right)_0^1 + \Sigma\left(\frac{d\mathrm{L}}{d\dot{q}_2}\,\delta q_2\right)_0^1 + \Sigma\left(\frac{d\mathrm{L}}{d\dot{q}_3}\,\delta q_3\right)_0^1;$$

where q_1 and q_2 are molar coordinates of the first and second kinds respectively, and q_3 is a molecular coordinate. We may disregard the last term by the reasoning, due to CLAUSIUS, which we have already given on page 474, and we have just seen that we may suppose $d\mathrm{L}/d\dot{q}_2 = 0$, so that the equation becomes

$$\delta\,\overline{\mathrm{L}} = \Sigma\left(\frac{d\mathrm{L}}{d\dot{q}_1}\,\delta q_1\right)_0^1;$$

but, since the motion is steady, $d\mathrm{L}/d\dot{q}_1$ is constant, so that this may be written

$$\delta\,\overline{\mathrm{L}} = \Sigma\,\frac{d\mathrm{L}}{d\dot{q}_1}\,(\delta q_1)_0^1.$$

Now we have supposed that the variation is of such a kind that q_1 remains unaltered; in this case δq_1 remains constant throughout the motion, and therefore $(\delta q_1)_0^1$ vanishes, so that we have

$$\delta\,\overline{\mathrm{L}} = 0, \qquad \qquad (13)$$

or $\overline{\mathrm{L}}$ has a stationary value for all changes which leave the velocities unchanged.

It is convenient to work with the mean values of L, because, as we shall see later on, it is possible in many cases involving the motion of great numbers of molecules to calculate $\overline{\mathrm{L}}$ from data given by experiment, when it would not be possible to calculate L.

The expression for the energy of a system consisting of a great number of molecules will contain terms of three kinds: (1) terms depending entirely on molar coordinates; (2) terms depending partly upon molar and partly upon molecular coordinates; and (3) terms depending entirely upon molecular coordinates. The energy expressed by the terms of the first kind can be entirely converted into mechanical work, while that expressed by the terms (2) and (3) can only be partially converted, the extent of the conversion depending on the distribution of kinetic energy throughout the system. VON HELMHOLTZ* calls the first kind of energy free energy, the other he calls bound energy.

Since the velocities are supposed to remain constant in the variations we contemplate in equation (13), it is evident that the only terms in the kinetic energy which are affected are those which involve the coordinates themselves. The energy expressed by such terms we may call the positional kinetic energy, and it is the only part of the kinetic energy which we need consider, or which has any influence on the way in which any transformation of energy takes place. We shall now go on to apply the principle that

$$\delta\,\overline{\mathrm{L}} = 0$$

to some special cases.

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* VON HELMHOLTZ, "Die Thermodynamik chemischer Vorgänge," 'Wissenschaftliche Abhandlungen,' vol. 2, p. 958.

Evaporation.

§ 6. The first case we shall take is that of evaporation. Let us suppose that we have a liquid and its vapour in a closed vessel, and endeavour to find an expression for the density of the vapour when it is in equilibrium with the liquid. We have here two systems for which we have to find expressions for $\overline{\mathrm{L}}$ when in a steady state, the first being the gas, the second the liquid.

The variation we shall consider is that which would be produced if a small quantity of the liquid were vaporised, keeping the velocities of the molecules the same as in the liquid condition, and thus keeping the temperature of the liquid and gas constant. We must find the effect of this change on the value of $\overline{\mathrm{L}}$ for the gas and the liquid. To do this for the gas, let us consider the case of a cylinder furnished with a piston and containing a given quantity of gas. Let x denote the distance of the piston from the base of the cylinder, and let us look on the gas as a dynamical system defined by the coordinate x.

We have, by LAGRANGE'S equations,

$$\frac{d}{dt}\frac{d\mathrm{L}}{d\dot{x}} - \frac{d\mathrm{L}}{dx} = \text{external force tending to increase } x\,;$$

or, when there is equilibrium,

$$-\int_0^1 \frac{d\mathrm{L}}{dx}\,dt = \text{average external force tending to increase } x.$$

Since x does not enter into the limits of integration,

$$\int_0^1 \frac{d\mathrm{L}}{dx}\,dt = \frac{d\overline{\mathrm{L}}}{dx}.$$

The average external force tending to increase x is $-p\mathrm{A}$, where p is the pressure per unit area, and A is the area of the piston.

Thus

$$\frac{d\overline{\mathrm{L}}}{dx} = p\mathrm{A}.$$

If the gas obeys BOYLE'S Law,

$$p = \mathrm{R}\rho\theta,$$

where ρ is the density of the gas and θ the absolute temperature. If v be the volume of the gas, and if its mass be unity, we have

$$\frac{dv}{dx} = \mathrm{A}, \quad \text{and} \quad \rho = \frac{1}{v},$$

so that

$$\frac{d\overline{\mathrm{L}}}{dx} = -\mathrm{R}\theta\frac{1}{\rho}\frac{d\rho}{dx}$$

$$= -\mathrm{R}\theta\frac{d}{dx}\log\rho.$$

Now, during the changes that we contemplate, θ remains constant; hence we see that the change in $\overline{\mathrm{L}}$ is the same as the change in

$$\mathrm{R}\theta\log\frac{\rho_0}{\rho},$$

where ρ_0 is some constant density, so that we may put for the positional part of the kinetic energy, and that part of $\overline{\mathrm{V}}$ which depends on the density,

$$\overline{\mathrm{L}} = \overline{\mathrm{L}}_0 + \mathrm{R}\theta\log\frac{\rho_0}{\rho},$$

where $\overline{\mathrm{L}}_0$ is the value of $\overline{\mathrm{L}}$ when the density is ρ_0. As the energy vanishes at the zero of absolute temperature, $\overline{\mathrm{L}}_0$ will contain θ as a factor, so that we may put for the mean kinetic energy, and that part of V which depends on the density,

$$\overline{\mathrm{L}} = \theta\left(\mathrm{A} + \mathrm{R}\log\frac{\rho_0}{\rho}\right), \quad \ldots\ldots\ldots \quad (14)$$

where A may be a function of θ, but not of ρ.

This is the value of the aforesaid part of $\overline{\mathrm{L}}$ for unit mass of the gas; if the mass of the gas were m, the value of this part of $\overline{\mathrm{L}}$ would be

$$m\theta\left(\mathrm{A} + \mathrm{R}\log\frac{\rho_0}{\rho}\right),$$

and we may treat the gas as if it were a dynamical system whose positional Lagrangian function contained the term

$$m\theta\left\{\mathrm{A} + \mathrm{R}\log\frac{\rho_0}{\rho}\right\},$$

all the variations being made at constant temperature.

We have next to consider the liquid. The expansion of solids and liquids by heat shows that there must be some terms in the expression for the energies of a solid or liquid which indicate the existence of a stress depending on the temperature. In order to find such terms, let us suppose that v is the volume of the solid or liquid at the absolute temperature θ. The dilatation per degree of temperature is

$$\frac{1}{v}\frac{dv}{d\theta}.$$

If the rate of dilatation be uniform and equal to β, the dilatation for θ degrees is $\beta\theta$, the stress required to produce this dilatation is $\kappa\beta\theta$, where κ is the bulk modulus. Now, we can show by HAMILTON'S principle that there will be a stress of this amount if, in the expression for the positional kinetic energy, there is the term

$$\int_{v_0}^{v} \kappa\beta\theta\, dv,$$

where v_0 is a constant volume.

Since

$$\beta = \left(\frac{1}{v}\frac{dv}{d\theta}\right)_{p \text{ constant}},$$

$$\kappa = -\left(v\frac{dp}{dv}\right)_{\theta \text{ constant}},$$

p being the pressure to which the surface of the solid or liquid is exposed,

$$\beta\kappa = -\frac{dv}{d\theta}\frac{dp}{dv} = \left(\frac{dp}{d\theta}\right)_{v \text{ constant}};$$

so that the term in the positional kinetic energy may be written

$$\int_{v_0}^{v} \theta\left(\frac{dp}{d\theta}\right)_{v \text{ constant}} dv. \quad \text{. . . . .} \quad (15)$$

Thus a dynamical system with this term in the expression for the positional kinetic energy will behave like the solid or liquid so far as expansion by heat goes.

We may add to this the term

$$\text{M}c_1\theta,$$

where M is the mass of the solid or liquid, and c_1 a constant, as this term will not give rise to any stresses tending to strain the body. Unless this term has different values for the different states in which the body can exist, the temperature being kept constant, it will disappear from the variation equation.

We can now solve the problem of finding the density of the saturated vapour of a liquid at any temperature.

Let us suppose that we have a mass N of the liquid and its vapour in a closed space: let ξ be the mass of the vapour, N $-$ ξ that of the liquid, w_1, w_2, the mean intrinsic potential energies of unit mass of the vapour and liquid respectively, Q the volume occupied by the vapour. Then, if there is no energy due to surface-tension, electrification, and so on, the value of $\bar{\text{L}}$ for the vapour, using the same notation as before, is

$$\xi\left(\text{A}\theta + \text{R}\theta\log\frac{\rho_0}{\rho}\right) - \xi w_1,$$

for the liquid

$$(\text{N} - \xi)\, c_1\theta + \int_{v_0}^{v} \theta\frac{dp}{d\theta}dv - (\text{N} - \xi)\, w_2.$$

If σ be the density of the liquid

$$v = \frac{\mathrm{N} - \xi}{\sigma};$$

we have also

$$\rho \mathrm{Q} = \xi;$$

hence the value of $\overline{\mathrm{L}}$ for the solid and liquid equals

$$\xi \left(\mathrm{A}\theta + \mathrm{R}\theta \log \frac{\rho_0 \mathrm{Q}}{\xi} \right) + (\mathrm{N} - \xi)\, c_1 \theta + \theta \int_{v_0}^{v} \frac{dp}{d\theta}\, dv - \xi w_1 - (\mathrm{N} - \xi)\, w_2.$$

Let us suppose that the mass of the vapour is increased by $\delta\xi$; then, since $\overline{\mathrm{L}}$ is stationary,

$$\frac{d\overline{\mathrm{L}}}{d\xi} = 0,$$

the temperature remaining constant. Hence we have

$$\mathrm{A}\theta + \mathrm{R}\theta \log \frac{\rho_0 \mathrm{Q}}{\xi} - \mathrm{R}\theta + \xi \mathrm{R}\, \theta \frac{1}{\mathrm{Q}} \frac{d\mathrm{Q}}{d\xi} - c_1 \theta - \frac{1}{\sigma} \frac{dp}{d\theta} - w_1 + w_2 = 0. \quad . \quad (16)$$

When the mass of the vapour increases by $\delta\xi$, the mass of the liquid diminishes by the same amount, so that the volume of the liquid diminishes by $\delta\xi/\sigma$, and therefore, since the liquid and vapour are supposed to be contained in a vessel of constant volume, the volume of the liquid increases by the same amount, so that

$$\frac{d\mathrm{Q}}{d\xi} = \frac{1}{\sigma},$$

and equation (16) becomes

$$\mathrm{A}\theta + \mathrm{R}\theta \log_\epsilon \frac{\rho_0}{\rho} - \mathrm{R}\theta \left(1 - \frac{\rho}{\sigma} \right) - c_1 \theta - \frac{1}{\sigma}\, \theta \frac{dp}{d\theta} - w_1 + w_2 = 0; \quad . \quad . \quad (17)$$

or if, for brevity, we write

$$s = - \frac{1}{\mathrm{R}\sigma} \frac{dp}{d\theta} + \frac{\mathrm{A}}{\mathrm{R}} - 1 - \frac{c_1}{\mathrm{R}},$$

$$\rho = \rho_0\, \epsilon^s\, \epsilon^{-\rho/\sigma}\, \epsilon^{w_2 - w_1/\mathrm{R}\theta}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

or, since ρ/σ is very small, we have approximately, writing $\rho_0{}'$ for $\rho_0\, \epsilon^s$,

$$\rho = \rho_0{}'\, \epsilon^{w_2 - w_1/\mathrm{R}\theta}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

[The quantity most closely related to $w_1 - w_2$ is the latent heat of evaporation, but the two quantities are not necessarily identical, for $w_1 - w_2$ is the excess of the intrinsic potential energy of unit mass of the vapour over that of unit mass of the liquid at the same temperature. The latent heat, however, at this temperature is the amount of work required to convert unit mass of liquid into vapour. If the kinetic energy of unit mass of the liquid is the same as that of unit mass of the gas at the same temperature, the latent heat will equal $w_1 - w_2$, but if the kinetic energies are different, then, since the latent heat equals the difference between the sum of the kinetic and potential energies, it will not equal $w_1 - w_2$.]*

In the above work we have assumed that the vapour obeys BOYLE'S Law. If we assume that the relation between pressure, density and temperature is that given by VAN DER WAALS' formula

$$p = \frac{R\theta}{v - b} - \frac{a}{v^2},$$

where v is the reciprocal of the density, and a and b constants, we may show, in a way similar to that by which we established equation (16), that, when the vapour is in equilibrium with the fluid,

$$R\theta \log \left(\frac{\frac{1}{\rho} - b}{\frac{1}{\rho_0} - b} \right) + a\rho \left(2 - \frac{\rho}{\sigma} \right) - \left(1 - \frac{\rho}{\sigma} \right) \frac{R\theta}{1 - b\rho} - c_1\theta - \frac{1}{\sigma}\theta \frac{dp}{d\theta} - w_1 + w_2 = 0\,;$$

or, since ρ/σ is very small, we may write this equation as

$$R\theta \log \left(\frac{\frac{1}{\rho} - b}{\frac{1}{\rho_0} - b} \right) + 2a\rho - R\theta\, b\rho - L\theta - (w_1 - w_2) = 0, \quad . \quad . \quad . \quad (20)$$

neglecting b^2, and writing L for a number of constant terms.

§ 7. The method just given enables us to calculate readily the effect of slight changes in the physical conditions on the vapour-pressure. Let us take, first, the effect of surface-tension. If the shape of the liquid is such that the area of its free surface changes when any of it evaporates, then we must take into account the energy due to the surface-tension. Let us suppose that the liquid is a spherical drop, whose radius is a; then we must add to the expression for the mean potential energy of the liquid the term $4\pi a^2 T$, where T is the surface-tension of the liquid. In this case, using the same notation as before, and assuming BOYLE'S Law, we have

$$\overline{L} = \xi \left(A\theta + R\theta \log \frac{\rho_0 Q}{\xi} \right) + (N - \xi)\, c_1\theta + \int_{v_0}^{v} \theta \frac{dp}{d\theta}\, dv - \xi w_1 - (N - \xi)\, w_2 - 4\pi a^2 T\,;$$

and the equation got by making the value of $\overline{L}$ stationary for a small change in ξ is

$$A\theta + R\theta \log \frac{\rho_0}{\rho} - R\theta + R\theta \frac{\rho}{\sigma} - c_1\theta - \frac{1}{\sigma}\theta \frac{dp}{d\theta} - w_1 + w_2 - 8\pi a T \frac{da}{d\xi} = 0\,; \quad (21)$$

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* Paragraph substituted October, 1887.

but

$$d\xi = -4\pi a^2 \sigma \, da,$$

so that

$$\frac{da}{d\xi} = -\frac{1}{4\pi a^2 \sigma},$$

and equation (21) becomes

$$A\theta + R\theta \log \frac{\rho_0}{\rho} - R\theta + R\theta \frac{\rho}{\sigma} - c_1\theta - \frac{1}{\sigma}\theta \frac{dp}{d\theta} - w_1 + w_2 + \frac{2T}{a\sigma} = 0. \quad . \quad (22)$$

Comparing this with equation (17), we see that, if $\delta\rho$ be the change in the vapour-pressure due to the curvature,

$$-R\theta \frac{\delta\rho}{\rho} + R\theta \frac{\delta\rho}{\sigma} + \frac{2T}{a\sigma} = 0,$$

or

$$R\theta \, \delta\rho = \frac{2\rho}{\sigma - \rho} \frac{T}{a}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

This coincides with the formula given by Sir WILLIAM THOMSON ('Proceedings of the Royal Society of Edinburgh,' Feb. 7, 1870; quoted in MAXWELL'S 'Theory of Heat,' p. 290).

We can also prove that the density of the saturated vapour will be altered by charging drops of the liquid with electricity. For suppose the drop to be spherical and charged with a quantity e of electricity. The potential energy due to the electrification of the drop is $\frac{1}{2}e^2/a$; subtracting this from the value previously given for $\bar{L}$, we may easily prove, in the same way as before, that the change $\delta\rho$ in the vapour-density, due to the electrification, is given by the equation

$$R\theta \, \delta\rho = -\frac{1}{8\pi} \frac{e^2}{a^4} \frac{\rho}{\sigma - \rho}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

assuming that as the drops evaporate the electricity remains behind on the drop. This seems to be proved by BLAKE'S experiments on the evaporation of electrified liquids (WIEDEMANN'S 'Lehre von der Elektricität,' vol. 4, p. 1212). We see from equation (24) that electrification diminishes the density of the saturated vapour, so that moisture might condense on a drop of water when electrified, though the same drop would evaporate if not charged with electricity. This would tend to make electrified drops of rain larger than unelectrified ones, and would probably tend to increase the size of the rain drops in a thunderstorm.

The maximum value of e/a^2 in air at atmospheric pressure is about 130 C.G.S. units in electrostatic measure, so that the maximum change in the density of the saturated vapour is given by the equation

$$R\theta\,\delta\rho = \frac{169 \times 10^2}{8\pi}\,\frac{\rho}{\sigma - \rho}\,.$$

$\rho/(\sigma - \rho)$ for water at atmospheric pressure is about $\frac{1}{800}$, so that δp, the alteration in pressure, which equals $R\theta\,\delta\rho$, is equal to

$$\frac{-169 \times 10^2}{8\pi \times 800}\,,$$

which is roughly about ·87, so that the maximum change in the vapour-pressure which can be produced by electrification is about $\frac{1}{14000}$ of the vapour-pressure of water at 15° C. In sulphuric acid the ratio would be very much greater.

We can calculate in a similar way the alteration in the vapour-pressure produced by any alteration in the state of the liquid. All we have to do is to calculate the change in the value of $\overline{L}$ due to this alteration. If this change be χ, then we may prove, just as before, that

$$R\theta\,\delta\rho = \frac{d\chi}{d\xi}\,\frac{\rho\sigma}{\sigma - \rho}\,. \qquad \qquad (25)$$

It should be noticed that $\delta\rho$ and $d\chi/d\xi$ are of the same sign, so that the presence of any kind of energy which causes $\overline{L}$ to increase as evaporation goes on will facilitate the evaporation. Thus, in the case of surface-tension, the potential energy due to the surface-tension diminishes as evaporation goes on: this corresponds to an increase in $\overline{L}$, so that the surface-tension will facilitate the evaporation; again, in the electrical case, the potential energy due to the electrification increases as evaporation goes on: this corresponds to a decrease in $\overline{L}$, so that the electrification will tend to stop the evaporation. These are only special cases of a general principle, of which we shall find frequent illustrations in the subsequent work.

Dissociation.

§ 8. Another problem to which the method can be applied is that of a gas partly dissociated into two components. Let us suppose that we have a quantity of gas contained in a vessel whose volume is V, and that part of it is in its normal condition, which we shall call A, while the molecules of the rest of the gas have been split up: we shall call this state of the gas B. Let ξ, η, be the masses of the gases in the states A and B respectively. Then the value of $\overline{L}$ for the gas in the state A is, by the investigation on p. 487,

$$\xi\left(A_1\theta + R_1\theta \log \frac{\rho_0}{\rho} - v_1\right),$$

where A_1 is a constant, ρ the density of the gas in the state A, θ the absolute temperature, v_1 the mean potential energy of unit mass of the gas; $R_1 = p/\rho\theta$, p being the pressure of the gas.

Since $\rho v = \xi$, we may write this as

$$\xi\left(A_1\theta + R_1\theta\log\frac{\rho_0 V}{\xi} - v_1\right). \qquad (26)$$

The value of $\overline{L}$ for the gas in state B is similarly

$$\eta\left(A_2\theta + R_2\theta\log\frac{\rho_0' V}{\eta} - v_2\right), \qquad (27)$$

where letters with the suffix 2 denote for gas in the state B quantities corresponding to those denoted by the same letters with the suffix 1 for gas in the state A. The value of $\overline{L}$ for the whole system equals the sum of (26) and (27).

Let us suppose that a mass $\delta\xi$ of the gas in the state A gets decomposed; then, if $\delta\eta$ be the increase in the mass of the gas in the state B, we have $\delta\eta = \delta\xi$. The change in the positional part of $\overline{L}$ for the system is

$$-\delta\xi\left(A_1\theta + R_1\theta\log\frac{\rho_0 V}{\xi} - R_1\theta - V_1\right) + \delta\eta\left(A_2\theta + R_2\theta\log\frac{\rho_0' V}{\eta} - R_2\theta - V_2\right);$$

but $\delta\eta = \delta\xi$, and when the system is in a steady state the variation of $\overline{L}$ vanishes, so that we have

$$\{A_1 - A_2 + (R_1 - R_2)\}\theta + R_1\theta\log\frac{\rho_0 V}{\xi} - R_2\theta\log\frac{\rho_0' V}{\eta} - (V_1 - V_2) = 0. \qquad (28)$$

If two of the molecules of the gas in the state B make up one of those in the state A, that is, if the gas on dissociation splits up into two components, we have

$$R_2 = 2R_1.$$

Making this substitution, equation (28) becomes

$$R_1\log\frac{\eta^2\alpha}{\xi V} + A_1 - A_2 + R_1 = \frac{V_1 - V_2}{\theta}, \qquad (29)$$

where α is a constant.

If the density of the mixture of normal and dissociated gas be δ, and the density of the normal gas at the same density and pressure d, then we have

$$\frac{\delta}{d} = \frac{\xi + \eta}{\xi + 2\eta},$$

so that

$$\frac{2\delta - d}{d - \delta} = \frac{\xi}{\eta},$$

and

$$\frac{2\delta - d}{\delta} = \frac{\xi}{\xi + \eta};$$

again

$$\mathrm{V}\delta = \xi + \eta;$$

so that

$$\xi = \mathrm{V}\,(2\delta - d),$$

$$\eta = \mathrm{V}\,(d - \delta).$$

Substituting these values for ξ and η in equation (29), we get

$$\mathrm{R}_1 \log \frac{\alpha\,(d-\delta)^2}{2\delta - d} + \mathrm{A}_1 - \mathrm{A}_2 + \mathrm{R}_1 = \frac{\mathrm{V}_1 - \mathrm{V}_2}{\theta}. \qquad \text{(30)}$$

This formula agrees substantially in form with one given by Professor Willard Gibbs in his paper on the "Equilibrium of Heterogeneous Substances" ('Transactions of the Connecticut Academy of Arts and Sciences,' vol. 3, 1874–8, p. 239). In his paper on the vapour-densities of nitrogen tetroxide, formic acid, acetic acid, and perchloride of phosphorus ('American Journal of Science and Arts,' vol. 18, 1879, p. 277), Professor Gibbs compares the density given by his formula with those found by various experimenters for the substances mentioned in the title of his paper, and he finds that the two sets of values agree very closely.

Liquefaction and Solution.

§ 9. We can apply the Hamiltonian principle to cases when a solid and liquid are in equilibrium in presence of each other, as, for example, when we have a mixture of ice and water, or a salt in a saturated solution of a liquid in which it can dissolve.

Let us first consider the case of liquefaction and take the case of the melting of ice as the typical one. We must first find the value of $\overline{\mathrm{L}}$ for a mixture of ice and water.

The positional part of $\overline{\mathrm{T}}$ for a solid or a liquid contains the term

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

where v is the volume of the solid or liquid, v_0 is a constant, and $\partial p/\partial\theta$ is obtained on the supposition that v is constant. Thus the positional part of $\overline{\mathrm{L}}$ for the mixture of ice and water equals

$$-\left(\theta\int_{v_0}^{v}\frac{\partial p}{\partial\theta}\,dv\right)_{\text{ice}}-\left(\theta\int_{v_0'}^{v'}\frac{\partial p}{\partial\theta}\,dv\right)_{\text{wa}}-\overline{\mathrm{V}}, \quad . \quad . \quad . \quad . \quad . \quad (31)$$

where $\overline{\mathrm{V}}$ is the mean potential energy of the mixture. By HAMILTON'S principle this expression must be stationary when there is equilibrium, the temperature remaining constant. Let us suppose unit mass of ice to melt: the change in the first terms is

$$\theta\int_{v_1'}^{v_1}\frac{\partial p}{\partial\theta}\,dv,$$

where v_1' is the volume of unit mass of water, and v_1 the volume of unit mass of ice. The increase in the potential energy is equal to the latent heat under the pressure p of water, so that HAMILTON'S principle gives

$$\theta\int_{v_1'}^{v_1}\frac{\partial p}{\partial\theta}\,dv=\lambda. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

Now PLANCK has shown* that

$$\int_{v_1'}^{v_1}\frac{\partial p}{\partial\theta}\,dv=\frac{d\mathrm{P}}{d\theta}(v_1-v_1'), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

where P, the pressure to which both the ice and water are subjected, is regarded as a function of the temperature alone.

Hence we have, by equation (32),

$$\theta\frac{d\mathrm{P}}{d\theta}(v_1-v_1')=\lambda, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

the well-known equation connecting the change in the melting point of ice with the change in the pressure to which it is subjected. In this equation λ is the increase in the potential energy when unit mass of the ice melts. It will depend to some extent upon external circumstances; thus, if the water is of such a shape that the area of its free surface changes when ice melts, then, on account of the energy due to surface-tension, λ will depend upon the change in the surface. As the volume diminishes as the ice melts, the surface will in general diminish, so that the energy due to this cause will be diminished by the liquefaction, and the effect of pressure upon the freezing-point increased. Since the volume changes, work is done by or against the external pressure: thus λ will be a function of the pressure. If λ_0 be the value of λ when the pressure is zero, λ the value when the pressure is p, we may easily prove that

$$\lambda=\lambda_0-p(v_1-v_1'),$$

so that λ diminishes as the pressure increases, and the effect on the freezing-point of a given increment of pressure will increase as the pressure increases.

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[*] 'WIEDEMANN'S Annalen,' vol. 13, p. 541.

Solution.

§ 10. The next case we shall consider is that of a saturated salt solution.

Let w be the mean value of $\partial p/\partial \theta$ (v constant) at the temperature θ for the salt, w' the value of the corresponding quantity for the solution; let v be the volume of the salt, v' that of the solution, q the mass of the salt, q' that of the solution; V_1 the mean potential energy of unit mass of the salt, V_2 that of unit mass of the solution. Then, if there is no energy due to strain, electrification, &c., the positional part of $\overline{\mathrm{L}}$ will be equal to

$$\theta w v + \theta w' v' - q\,\mathrm{V}_1 - q'\,\mathrm{V}_2. \quad \text{. . . . .} \quad (35)$$

When there is equilibrium this must be stationary, so that, if we suppose a small quantity $\delta q'$ of the salt to melt, the value of $\overline{\mathrm{L}}$ must remain unaltered.

If σ and ρ are the densities of the salt and the solution respectively, then when the mass $\delta q'$ of the salt melts the changes in the volume of the salt and the solution are given by

$$\left.\begin{aligned} \delta v &= -\,\delta q'/\sigma \\ \delta v' &= \delta q_1'/\rho + q'\frac{d}{dq_1}\left(\frac{1}{\rho}\right)\delta q' \end{aligned}\right\}. \quad \text{. . . . .} \quad (36)$$

As the properties of the fluid may alter with the amount of salt dissolved, we must regard w' and V_2 as functions of q. Remembering this, we see that the change in the value of $\overline{\mathrm{L}}$, when a mass $\delta q'$ of the salt dissolves, is

$$\delta q'\left\{-\,\theta\frac{w}{\sigma} + \theta\frac{w'}{\rho} + \theta w' q'\frac{d}{dq'}\left(\frac{1}{\rho}\right) + \theta v'\frac{dw'}{dq'} + \mathrm{V}_1 - \mathrm{V}_2 - q'\frac{d\mathrm{V}_2}{dq'}\right\},$$

and this, by the Hamiltonian principle, must vanish. Hence, equating the quantity inside the brackets to zero, we have

$$\frac{w'}{\rho} + w'q'\frac{d}{dq'}\frac{1}{\rho} + v'\frac{dw'}{dq'} = \frac{w}{\sigma} + \frac{1}{\theta}\left(\mathrm{V}_2 - \mathrm{V}_1 + q'\frac{d\mathrm{V}_2}{dq'}\right). \quad \text{. . . .} \quad (37)$$

This equation would determine ρ, the density of the saturated solution, if we knew how w', V_2, and ρ depended upon the amount of salt in unit volume of the solution; as, however, we have not this information, we cannot reduce this formula to numbers. We can, however, use it to calculate the effect upon the density of the solution of any change in the external circumstances. In the preceding investigation we have supposed that the energy possessed by the salt and the solution was all intrinsic as it were, and that none of it depended upon strain, electrification, magnetisation, and so on.

The methods of calculating the potential energy due to strain, &c., are, of course, well known. The corresponding terms in the kinetic energy can be calculated in the following way.

We saw, on p. 480, that if y is a coordinate of any type, and P a quantity such that, when y is increased by δy, the energy in the system is increased by $\mathrm{P}\delta y$, then

$$\frac{d\mathrm{T}}{dy} = -\theta\frac{d\mathrm{P}}{d\theta}.$$

P may be regarded as a force of the type y, so that, if this force depends upon the temperature, there will be a term in the mean kinetic energy equal to

$$-\theta\int\frac{d\mathrm{P}}{d\theta}dy,$$

so that the expression for the positional part of the kinetic energy equals

$$\theta\int\frac{dp}{d\theta}dv - \theta\Sigma\int\frac{d\mathrm{P}}{d\theta}dy\,;$$

the summation being extended over all the types of coordinates. The term in the potential energy corresponding to the coordinate of type y will be

$$\int\mathrm{P}_0\,dy,$$

where P_0 is the part of P which is independent of the temperature.

By the above equations we can calculate the term in the expressions for both the kinetic and potential energies involving the coordinates of any type. If, however, we only require to calculate the value of $\overline{\mathrm{L}}$, a much simpler process is applicable. For when the system is in a steady state

$$\overline{\mathrm{P}} = \frac{d\overline{\mathrm{L}}}{dy},$$

so that we have

$$\overline{\mathrm{L}} = \int\mathrm{P}\,dy. \qquad (38)$$

Let us now apply these equations to calculate the effect which any change in the external circumstances has upon the solubility of a salt. Let us, for example, consider the effect of capillarity. Then, if the process of solution alters the volume of the mixture of salt and water, it will in general alter the surface, and so alter the energy due to the surface-tension. If it increases the energy, the surface-tension will tend to stop the solution; if it diminishes the energy, the surface-tension will facilitate the solution. The energy due to the surface-tension will change even though the volume remains unaltered, if the surface-tension depends upon the quantity of salt dissolved in the liquid; if the surface-tension diminishes as the salt dissolves, then the surface-tension will facilitate the solution; if it increases, it will tend to prevent the salt dissolving. This result, as well as the preceding, follows from equation (37). We see, by that equation, that anything which makes $d(q'\mathrm{V}_2)/dq'$ increase will increase the difference between ω'/ρ for the solution, and the same quantity for the salt, and therefore probably diminish the quantity of salt in the solution; for it seems natural to expect that, the more salt we have dissolved in the solution, the more nearly will the properties of the solution approximate to those of the salt. Any additional energy which increases as solution goes on makes $d(q'V_2)/dq'$ positive, and therefore tends to stop the solution.

To calculate the magnitude of the effect due to capillarity, let us suppose that the mixture of salt and solution is in the form of a spray of spherical drops of radius a. The additional term in $q'V_2$ due to the surface-tension will be

$$4\pi a^2 T,$$

where T is the surface-tension. We have then, from (37),

$$\theta\delta\left(\frac{w'}{\rho} + w'q'\frac{d}{dq'}\frac{1}{\rho} + v'\frac{dw'}{dq'}\right) = 8\pi a T\frac{da}{dq'} + 4\pi a^2\frac{dT}{dq'};$$

but

$$\frac{4}{3}\pi a^3 = \frac{q}{\sigma} + \frac{q'}{\rho},$$

so that

$$4\pi a^2\frac{da}{dq'} = \frac{1}{\rho} - \frac{1}{\sigma} + q'\frac{d}{dq'}\left(\frac{1}{\rho}\right),$$

and therefore

$$\theta\delta\left(\frac{w'}{\rho} + w'q'\frac{d}{dq'}\frac{1}{\rho} + v'\frac{dw'}{dq'}\right) = \frac{2}{a}\left(\frac{1}{\rho} - \frac{1}{\sigma} + q'\frac{d}{dq'}\frac{1}{\rho}\right)T + \frac{3}{a}\left(\frac{q}{\sigma} + \frac{q'}{\rho}\right)\frac{dT}{dq'}. \qquad (39)$$

We can determine experimentally the value of all the quantities on the right-hand side of this equation, and, if we know the quantity in brackets on the left-hand side as a function of ρ, we can at once determine the change in the density of the solution. We can express this in a way which more readily admits of comparison with experiment. Suppose that the existence of the surface-tension causes as much salt to be absorbed at θ as would be absorbed if there were no surface-tension at $\theta + \delta\theta$; then, by comparing equations (37) and (39), we see that

$$\frac{\delta\theta}{\theta} = -\frac{\left\{\frac{2}{a}\left(\frac{1}{\rho} - \frac{1}{\sigma} + q'\frac{d}{dq'}\frac{1}{\rho}\right)T + \frac{3}{a}\left(\frac{q}{\sigma} + \frac{q'}{\rho}\right)\frac{dT}{dq'}\right\}}{V_2 - V_1 + q'\frac{dV_2}{dq'}}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (40)$$

but the denominator is the increase of potential energy when unit mass of the salt dissolves. We can measure this by the cooling. Let it be denoted by λ; then

$$\lambda\frac{\delta\theta}{\theta} = -\left\{\frac{2}{a}\left(\frac{1}{\rho} - \frac{1}{\sigma} + q'\frac{d}{dq'}\frac{1}{\rho}\right)T + \frac{3}{a}\left(\frac{q}{\sigma} + \frac{q'}{\rho}\right)\frac{dT}{dq'}\right\}. \quad . \quad . \quad . \qquad (41)$$

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,

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

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),

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

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

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

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

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

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

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

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 $36 \times 4{\cdot}2 \times 10^7$ 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

$$\delta\theta = \frac{288 \times 10^8 \times 10^{-1}}{36 \times 4{\cdot}2 \times 10^7}$$
$$= 2°.$$

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

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* 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 ·348 part in 10·9, which is about 3·2 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 $\frac{1}{12}$ of a part per degree Centigrade, so that for 1·6° the increase would be about ·13 in 34: this is ·40 per cent. The value found by Sorby was ·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

$$\{A\} + \{B\} = \{C\} + \{D\}.$$

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

$$H_2SO_4 + 2NaNO_3 = 2HNO_3 + Na_2SO_4\,;$$

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 $\overline{\mathrm{L}}$ equals

$$\theta\left[m_1 p\xi\left(c_1 + \mathrm{R}_1 \log\frac{\rho_0 \mathrm{Q}}{m_1 p\xi}\right) + m_2 q\eta\left(c_2 + \mathrm{R}_2 \log\frac{\rho_0{}' \mathrm{Q}}{m_2 q\eta}\right)\right.$$
$$\left. + m_3 r\zeta\left(c_3 + \mathrm{R}_3 \log\frac{\rho_0{}'' \mathrm{Q}}{m_3 r\zeta}\right) + m_4 s\epsilon\left(c_4 + \mathrm{R}_4 \log\frac{\rho_0{}''' \mathrm{Q}}{m_4 s\epsilon}\right)\right] - w, \quad . \quad . \quad (45)$$

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 ξ, η, ζ, ϵ, 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

$$\xi + \zeta = \text{a constant},$$
$$\xi + \epsilon = \;.\;.\;.\;.\;.\;.\;,$$
$$\eta + \zeta = \;.\;.\;.\;.\;.\;.\;,$$

so that

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

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

$$d\xi\left[\theta\left\{m_1 p\left(c_1 + \mathrm{R}_1 \log\frac{\rho_0 \mathrm{Q}}{m_1 p\xi} - \mathrm{R}_1\right) + m_2 q\left(c_2 + \mathrm{R}_2 \log\frac{\rho_0{}' \mathrm{Q}}{m_2 q\eta} - \mathrm{R}_2\right)\right.\right.$$
$$\left.\left. - m_3 r\left(c_3 + \mathrm{R}_3 \log\frac{\rho_0{}'' \mathrm{Q}}{m_3 r\epsilon} - \mathrm{R}_3\right) - m_4 s\left(c_4 + \mathrm{R}_4 \log\frac{\rho_0{}''' \mathrm{Q}}{m_4 s\epsilon} - \mathrm{R}_4\right)\right\} - \frac{dw}{d\xi}\right];$$

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)

$$\mathrm{R}_1 m_1 = \mathrm{R}_2 m_2 = \mathrm{R}_3 m_3 = \mathrm{R}_4 m_4. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

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

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

We see from this equation that anything which increases $d\omega/d\xi$ will increase $\log \rho_0 \mathrm{Q}/m_1 p\xi + \ldots$, 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

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

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

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

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

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

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 $\overline{\mathrm{L}}$ is

$$\theta\left\{m_1 p\xi\left(c_1 + \mathrm{R}_1 \log\frac{\rho_0 \mathrm{Q}}{m_1 p\xi}\right) + m_2 q\eta\left(c_2 + \mathrm{R}_2 \log\frac{\rho_0' \mathrm{Q}}{m_2 q\eta}\right) + m_3 r\zeta\left(c_3 + \mathrm{R}_3 \log\frac{\rho_0'' \mathrm{Q}}{m_3 r\zeta}\right)\right\} - w,$$

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 $\overline{\mathrm{L}}$ should be unaltered when ξ is increased by $d\xi$ gives

$$\theta\left\{m_1 p(c_1 - \mathrm{R}_1) + m_2 q(c_2 - \mathrm{R}_2) - m_3 r(c_3 - \mathrm{R}_3) + m_1 p \mathrm{R}_1 \log\frac{\rho_0 \mathrm{Q}}{m_1 p\xi} + m_2 q \mathrm{R}_2 \log\frac{\rho_0' \mathrm{Q}}{m_2 q\eta} - m_3 r \mathrm{R}_3 \log\frac{\rho_0'' \mathrm{Q}}{m_3 r\zeta}\right\} = \frac{dw}{d\xi}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (52)$$

For perfect gases

$$\mathrm{R}_1 m_1 = \mathrm{R}_2 m_2 = \mathrm{R}_3 m_3 = \mathrm{K}.$$

Making this substitution, the equation of equilibrium becomes

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

This equation may be written

$$\frac{\xi^p \eta^q}{\zeta^r} = \mathrm{CQ}^{p+q-r} e^{\frac{dw}{d\xi} \frac{1}{\mathrm{K}\theta}}. \quad \quad (54)$$

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

$$\omega = \mathrm{CQ}^{p+r-r} e^{-\frac{dw}{d\xi} \frac{1}{\mathrm{K}\theta}}; \quad \quad (55)$$

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

$$\frac{\delta\omega}{\omega} = -\frac{1}{\mathrm{K}\theta} \frac{d\,.\,\delta w}{d\xi}, \quad \quad (56)$$

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 $\overline{L}$ 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 produces 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

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

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

$$H_2SO_4 + 2NaNO_3 = 2HNO_3 + Na_2SO_4,$$

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 $Na_2N_2O_6$, $H_2N_2O_6$, 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.

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* 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 $H_2N_2O_6$; a similar conclusion applies to the molecule of sodium nitrate, the molecule of which in the solution has to be represented by $Na_2N_2O_6$. 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 $H_2N_2O_6$; 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 $H_2N_2O_6$ 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

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

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

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

Hence $\overline{\mathrm{L}}$ for the system equals

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

The condition that $\overline{\mathrm{L}}$ should be stationary is therefore

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

This equation may be written as

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

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

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

The Effect of Temperature on the Equilibrium.

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

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

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 $\mathrm{K}\theta$ is large, so that the term in ω which varies most rapidly with the temperature is $e^{\frac{dw}{d\xi}\frac{1}{\mathrm{K}\theta}}$,

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

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

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

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

$$\mathrm{H}' = \mathrm{N}c\frac{dw}{d\xi},$$

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,

$$\frac{1}{\mathrm{K}\theta}\frac{dw}{d\xi} = \frac{\mathrm{H}'}{\dfrac{\mathrm{N}m\,pc}{\rho}}$$

$$= \frac{\mathrm{H}'}{pc/\rho},$$

since

$$\mathrm{N}m = 1.$$

Since pc/ρ is the same for all gases, and since for Hydrogen it is about $10^{11}/4{\cdot}5$, we have

$$\frac{1}{\kappa\theta}\frac{dw}{d\xi} = \frac{4{\cdot}5\,\mathrm{H}'}{10^{11}},$$

and therefore, by equation (62),

$$\frac{\delta\omega}{\omega} = -\frac{4{\cdot}5\,\mathrm{H}'}{10^{11}}\frac{\delta\theta}{\theta}.$$

In the case of hydrochloric acid, sulphuric acid, sodium sulphate, and sodium chloride THOMSEN * found $\mathrm{H}' = 2 \times 10^3 \times 4{\cdot}2 \times 10^7$, 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

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

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

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* 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

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

so that, if $d\,.\,\delta w/d\xi$ 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

$$\delta w = \mathrm{TS},$$

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

Hence we have, from Equation (63),

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

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, $d\,.\,\delta w/d\xi$ 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

$$\frac{d\,.\,\delta\omega}{d\xi} = p\frac{d\mathrm{Q}}{d\xi} + \tfrac{1}{2}\frac{d}{d\xi}\left(\frac{\mathrm{Q}p^2}{\kappa}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (65)$$

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 versâ*, the change in the coefficient of reaction due to this case is given by the equation

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

or, approximately,

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

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

$$\frac{\delta\omega}{\omega} = \tfrac{1}{2}\frac{1}{\mathrm{K}\theta}\frac{d}{d\xi}\left(\frac{\mathrm{Q}p^2}{\kappa}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (67)$$

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 ξ, η, ζ, ϵ, ω, be the number of molecules of hydrogen, oxygen, carbonic oxide, carbonic acid, and water respectively; then the value of $\bar{\mathrm{L}}$ will be

$$\theta\left\{m_1\,\xi\,\mathrm{R}_1\log\frac{\rho_0\mathrm{Q}}{m_1\xi}+m_2\,\eta\,\mathrm{R}_2\log\frac{\rho_0{}'\mathrm{Q}}{m_2\eta}+m_3\,\zeta\,\mathrm{R}_3\log\frac{\rho_0{}''\mathrm{Q}}{m_3\zeta}\right.$$
$$\left.+\,m_4\,\epsilon\,\mathrm{R}_4\log\frac{\rho_0{}'''\mathrm{Q}}{m_4\epsilon}+m_5\,\omega\,\mathrm{R}_5\log\frac{\rho_0{}''''\mathrm{Q}}{m_5\omega}\right\}-w,$$

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, . . . 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,

$$\xi+\omega=\text{a constant};$$

and, since the quantity of oxygen remains constant,

$$\eta+\tfrac{1}{2}\zeta+\epsilon+\tfrac{1}{2}\omega=\text{a constant}; \quad \ldots\ldots\ldots \quad (68)$$

since the quantity of carbon remains constant,

$$\zeta+\epsilon=\text{a constant}.$$

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

$$\left.\begin{array}{lll}\dfrac{d\eta}{d\xi}=\ \ \tfrac{1}{2}, & \dfrac{d\zeta}{d\xi}=\ \ 0, & \dfrac{d\omega}{d\xi}=-1,\\[2ex] \dfrac{d\eta}{d\epsilon}=-\tfrac{1}{2}, & \dfrac{d\zeta}{d\epsilon}=-1, & \dfrac{d\omega}{d\epsilon}=\ \ 0.\end{array}\right\} \quad \ldots\ldots \quad (69)$$

By the Hamiltonian principle we have

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

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

so that

$$\theta\left\{m_1\,\mathrm{R}_1\log\frac{\rho_0\mathrm{Q}}{m_1\xi}-m_1\,\mathrm{R}_1+\tfrac{1}{2}\left(m_2\,\mathrm{R}_2\log\frac{\rho_0{}'\mathrm{Q}}{m_2\eta}-m_2\,\mathrm{R}_2\right)\right.$$
$$\left.-\left(m_5\,\mathrm{R}_5\log\frac{\rho_0{}''\mathrm{Q}}{m_5\omega}-m_5\,\mathrm{R}_5\right)\right\}=\left(\frac{dw}{d\xi}\right)_{\epsilon\ \text{constant.}} \quad \ldots \quad (70)$$

Since $m_1\,\mathrm{R}_1=m_2\,\mathrm{R}_2=m_3\,\mathrm{R}_3=m_4\,\mathrm{R}_4=m_5\,\mathrm{R}_5=\kappa$, we may write this equation as

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

or

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

where C_1 is a constant.

From the equation

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

we get, in a similar way,

$$\frac{\zeta^2\eta}{\epsilon^2}=Q\,C_2\,\epsilon^{\frac{2}{\kappa\theta}\left(\frac{dw}{d\epsilon}\right)}. \quad \ldots\ldots\ldots\ldots \quad (72)$$

Equations (71) and (72), along with the three equations (68), are sufficient to determine the five quantities ξ, η, ζ, ϵ, ω.

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

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

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 $\overline{L}$, viz.,

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

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[*] '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 ξ, η, ζ . . . be the number of equivalent molecules of the substances A, B, C . . . in the solution, then, since $\bar{\mathrm{L}}$ must be stationary when the system is in equilibrium, we have

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

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, . . . , the equations of the type (74) will enable us to find the values of ξ, η, . . . 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 ξ, η, ζ . . . be the number of equivalents of these substances: these will be connected by various equations; let us choose ξ, η . . . as independent variables. Then, since when there is equilibrium $d\bar{\mathrm{L}}/d\xi = 0$, $d\bar{\mathrm{L}}/d\eta = 0$, 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, &c., are absent from the equations of motion of the mixture, and we may assume, at any rate when $d\bar{\mathrm{L}}/d\xi$, $d\bar{\mathrm{L}}/d\eta$, are small, that

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

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 $\bar{\mathrm{L}}$ is increased by $\delta\mathrm{L}$; then, if $\delta\dot{\xi}$ denotes the change in the velocity of ξ, we have

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

so that

$$\frac{\delta\dot{\xi}}{\dot{\xi}} = \frac{\dfrac{d\delta\mathrm{L}}{d\xi}}{\dfrac{d\bar{\mathrm{L}}}{d\xi}}; \qquad \ldots\ldots\ldots\ldots \qquad (76)$$

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

$$\frac{\delta\dot{\xi}}{\dot{\xi}} = -\frac{\dfrac{d}{d\xi}(\mathrm{ST})}{\dfrac{d\bar{\mathrm{L}}}{d\xi}}. \qquad \ldots\ldots\ldots\ldots \qquad (77)$$

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

$$\frac{\delta\dot{\xi}}{\dot{\xi}} = -\frac{p\dfrac{dv}{d\xi} - \frac{1}{2}p^2\dfrac{d\frac{1}{\kappa}}{d\xi}}{\dfrac{d\bar{\mathrm{L}}}{d\xi}}, \qquad \ldots\ldots\ldots \qquad (78)$$

where V is the volume of the mixture and κ its coefficient of compressibility. The value of $d\,\bar{\mathrm{L}}/d\xi$ 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,

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

thus the term

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

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 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

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* '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

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

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

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

then LAGRANGE'S equations give

$$\frac{d\mathrm{L}}{dt} + \mathrm{Q}f = \text{external electromotive force tending to increase } f,$$
$$= \mathrm{X} \text{ say.}$$

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

$$\overline{\frac{d\mathrm{L}}{dt}} + \mathrm{Q}\int_0^1 f\,dt = \overline{\mathrm{X}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (79)$$

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),

$$\frac{d\mathrm{L}}{dt} + \frac{\mathrm{Q}u}{\alpha n} = \bar{\chi}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (80)$$

the ordinary electrical equation if the specific resistance of the substance equals $\mathrm{Q}/\alpha n$. 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

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

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

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

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 $4\pi/\mathrm{K}$, 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 $-\tfrac{1}{2}\mathrm{Q}\,(f^2 + g^2 + h^2)$ 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

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

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

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

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

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

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 $\sigma n a$ for Q, where σ is the specific resistance, we may write this term as

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

Now the experiments of Sir W. THOMSON and Mr. TOMLINSON show that the resistance of metals is affected by strain, so that $\sigma n a$ 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

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

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

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

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

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

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

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

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

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

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 $\overline{\mathrm{T}} - \overline{\mathrm{V}}$ due to this term is

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

or

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

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 $\overline{\mathrm{T}} - \overline{\mathrm{V}}$ 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 $\overline{\mathrm{T}} - \overline{\mathrm{V}}$, is given by the equation

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

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

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

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

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

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.