

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

$$P_1 dx_1 + P_2 dx_2 + \dots$$

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

$$2\delta \int_0^i T dt = i\delta(T + V) + \left[\sum \frac{dT}{dq} \delta q \right]_0^i, \quad \dots \dots \dots (1)$$

$$2\delta \int_0^i (T - V) dt = (T + V) \delta i + \left[\sum \frac{dT}{dq} \delta q \right]_0^i, \quad \dots \dots \dots (2)$$

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—

$$\delta (T + V) = \delta Q, \quad (3)$$

where δQ is a small quantity of work supplied to the system. The quantity $\delta (T + V)$ occurs on the right-hand side of equation (1) : let us now consider the term $[\sum \delta q dT/d\dot{q}]_0^i$, which also occurs on the same side of the equation. If the motion be oscillatory, and i a period of complete recurrence ; $\delta q dT/d\dot{q}$ 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 $[\sum \delta q dT/d\dot{q}]$, 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 $[\sum \delta q dT/d\dot{q}]_0^i$ 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—

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

or

$$2\delta (iT_m) = i \delta Q, \quad (4)$$

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

$$2\delta \log (iT_m) = \delta Q/T_m, \quad (5)$$

so that $\delta Q/T_m$ is a perfect differential.

One of the ways of stating the Second Law of Thermodynamics is that $\delta Q/\theta$ 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 *a 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 $d\phi = dQ/T_m$. 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, \dots, q_n and the corresponding momenta p_1, p_2, \dots, p_n between the limits $q_1, q_1 + \delta q_1, q_2, q_2 + \delta q_2, \dots, q_n, q_n + \delta q_n, p_1, p_1 + \delta p_1, \dots, p_n, p_n + \delta p_n$, is

$$C e^{-h(T+\chi)} dq_1 dq_2 \dots dq_n \cdot dp_1 dp_2 \dots dp_n,$$

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

* 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, \dots, 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 $\dot{x}_1, \dot{x}_2, \dots$ circulating through these conductors is of the form

$$\frac{1}{2}(L_{11}\dot{x}_1^2 + 2L_{12}\dot{x}_1\dot{x}_2 + \dots).$$

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

$$\frac{1}{2}(L_1\dot{y}_1^2 + L_2\dot{y}_2^2 + \dots).$$

The electrical equations are :—

$$\frac{d}{dt}(L_1\dot{y}_1) = \text{rate of diminution in the number of lines of force passing through the circuit corresponding to } y_1,$$

$$\frac{d}{dt}(L_2\dot{y}_2) = \text{the same thing for the circuit } y_2,$$

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

$$\frac{d}{dt}(L_1\dot{y}_1) = \lambda \frac{d}{dt}(L_2\dot{y}_2),$$

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

$$L_1\dot{y}_1 = \lambda L_2\dot{y}_2.$$

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

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

that corresponding to y_2 is

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

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, \dots 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 $\delta p_1, \delta p_2 \dots$. 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,

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

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,

$$\frac{d}{dt} \frac{dT}{dp_1} - \frac{dT}{dp} + \frac{dV}{dp} = P;$$

now

$$T = T_1 + T_2,$$

and by definition

$$\frac{dT_1}{dp_1} = 0,$$

we have also, by the Conservation of Energy,

$$\delta Q = \delta T_1 + \delta T_2 + \delta V - \sum P \delta p; \quad \dots \dots \dots (6^*)$$

now

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

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

$$2T_2 = \sum \dot{p} \frac{dT_2}{dp},$$

and therefore

$$2 \delta T_2 = \sum \left(\delta \dot{p} \frac{dT_2}{dp} + \dot{p} \delta \frac{dT_2}{dp} \right); \quad \dots \dots \dots (8)$$

subtracting (7) from (8), we have

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

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

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

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

so that equation (6) becomes

$$\delta Q = \Sigma \delta p \left(\frac{d}{dt} \frac{dT_2}{dp} - \frac{dT_2}{dp} + \frac{dV}{dp} - P \right) + \delta V_{p \text{ constant}} + \delta T_1 ;$$

substituting for P from (5), we have

$$\delta Q = \Sigma \frac{dT_1}{dp} \delta p + \delta T_1 + \delta V_{p \text{ constant}}. \quad \dots \quad (9)$$

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

$$f(p) T_3$$

when T_3 does not involve p .

Thus

$$\begin{aligned} \frac{dT_1}{dp} &= f'(p) T_3 \\ &= \frac{f'(p)}{f(p)} T_1, \end{aligned}$$

and therefore, by (9),

$$\delta Q = \Sigma \frac{f'(p)}{f(p)} T_1 \delta p + \delta T_1 + \delta V_{(p \text{ constant})},$$

so that

$$\frac{\delta Q}{T_1} = \Sigma \frac{f'(p)}{f(p)} \delta p + \delta \log T_1 + \frac{\delta V_{(p \text{ constant})}}{T_1}. \quad \dots \quad (10)$$

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,

$$\frac{\delta V_{(p \text{ constant})}}{\theta}$$

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 δV , when p is constant, may be written as

$$\frac{dV}{d\theta} \cdot \delta\theta,$$

where $dV/d\theta$ 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

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

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,

$$\begin{aligned} P_1 &= \frac{dV}{dp_1} - \frac{dT_1}{dp_1} - \frac{dT_2}{dp_1} \\ &= \frac{dV}{dp_1} - \frac{f'(p)}{f(p)} T_1 - \frac{dT_2}{dp_1}. \end{aligned}$$

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

$$\begin{aligned} \theta \left(\frac{dP_1}{d\theta} \right) &= - \frac{f'(p)}{f(p)} T_1 \\ &= - \frac{dT_1}{dp_1}, \end{aligned}$$

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

Thus equation (11) becomes

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

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,

$$\delta \int_0^i L dt = \Sigma \left(\frac{dL}{dq} \delta q \right)_0^i, \quad \dots \dots \dots (12^*)$$

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

$$\int_0^i L dt = S,$$

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

$$\frac{dT}{dq} = \frac{dS}{dq},$$

and, by LAGRANGE'S equation,

$$\frac{d}{dt} \frac{dT}{dq} = \frac{d}{dq} (T - V);$$

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

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

where \bar{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

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

the potential energy is of the form

$$C \cos \theta,$$

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 \bar{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 $dL/dq_2 = 0$, where q_2 is a molar coordinate of the second kind.

The equation

$$\delta \bar{L} = \sum \left(\frac{dL}{dq} \delta q \right)_0^1$$

may conveniently be written

$$\delta \bar{L} = \sum \left(\frac{dL}{dq_1} \delta q_1 \right)_0^1 + \sum \left(\frac{dL}{dq_2} \delta q_2 \right)_0^1 + \sum \left(\frac{dL}{dq_3} \delta q_3 \right)_0^1;$$

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 $dL/d\dot{q}_2 = 0$, so that the equation becomes

$$\delta \bar{L} = \Sigma \left(\frac{dL}{dq_1} \delta q_1 \right)_0^1;$$

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

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

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

$$\delta \bar{L} = 0, \quad (13)$$

or \bar{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 \bar{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

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

to some special cases.

* 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 \bar{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 \bar{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,

$$\frac{d}{dt} \frac{dL}{dx} - \frac{dL}{dx} = \text{external force tending to increase } x ;$$

or, when there is equilibrium,

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

Since x does not enter into the limits of integration,

$$\int_0^1 \frac{dL}{dx} dt = \frac{d\bar{L}}{dx}.$$

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

Thus

$$\frac{d\bar{L}}{dx} = pA.$$

If the gas obeys BOYLE'S Law,

$$p = R\rho\theta,$$

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

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

so that

$$\begin{aligned}\frac{d\bar{L}}{dx} &= -R\theta \frac{1}{\rho} \frac{d\rho}{dx} \\ &= -R\theta \frac{d}{dx} \log \rho.\end{aligned}$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$Mc_1\theta,$$

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, $N - \xi$ 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{L} for the vapour, using the same notation as before, is

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

for the liquid

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

If σ be the density of the liquid

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

we have also

$$\rho Q = \xi;$$

hence the value of \bar{L} for the solid and liquid equals

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

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

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

the temperature remaining constant. Hence we have

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

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

$$\frac{dQ}{d\xi} = \frac{1}{\sigma},$$

and equation (16) becomes

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

or if, for brevity, we write

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

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

or, since ρ/σ is very small, we have approximately, writing ρ_0' for $\rho_0 \epsilon^s$,

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

[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

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

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

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

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

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

* Paragraph substituted October, 1887.

but

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

so that

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

and equation (21) becomes

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

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

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

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

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

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 Elektrizität,' 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

$$R\theta \delta\rho = \frac{169 \times 10^3}{8\pi} \frac{\rho}{\sigma - \rho}.$$

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

$$\frac{-169 \times 10^3}{8\pi \times 800},$$

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 \bar{L} due to this alteration. If this change be χ , then we may prove, just as before, that

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

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 \bar{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 \bar{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 \bar{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 \bar{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

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

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

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

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 \bar{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 \bar{L} for the system is

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

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

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

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

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

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

$$V\delta = \xi + \eta;$$

so that

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

$$\eta = V(d - \delta).$$

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

$$R_1 \log \frac{\alpha(d - \delta)^2}{2\delta - d} + A_1 - A_2 + R_1 = \frac{V_1 - V_2}{\theta}. \quad \dots \dots (30)$$

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 \bar{L} for a mixture of ice and water.

The positional part of \bar{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 \bar{L} for the mixture of ice and water equals

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

where \bar{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

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

Now PLANCK has shown* that

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

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),

$$\theta \frac{dP}{d\theta} (v_1 - v_1') = \lambda, \quad \dots \dots \dots (34)$$

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.

* '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 \bar{L} will be equal to

$$\theta wv + \theta w'v' - qV_1 - q'V_2. \quad \dots \dots \dots (35)$$

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 \bar{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

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

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 \bar{L} , when a mass $\delta q'$ of the salt dissolves, is

$$\delta q' \left\{ -\theta \frac{w}{\sigma} + \theta \frac{w'}{\rho} + \theta w' q' \frac{d}{dq} \left(\frac{1}{\rho} \right) + \theta v' \frac{dw'}{dq} + V_1 - V_2 - q' \frac{dV_2}{dq} \right\},$$

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

$$\frac{w'}{\rho} + w' q' \frac{d}{dq} \frac{1}{\rho} + v' \frac{dw'}{dq} = \frac{w}{\sigma} + \frac{1}{\theta} \left(V_2 - V_1 + q' \frac{dV_2}{dq} \right). \quad \dots \dots (37)$$

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 $P\delta y$, then

$$\frac{dT}{dy} = -\theta \frac{dP}{d\theta}.$$

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

$$-\theta \int \frac{dP}{d\theta} dy,$$

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

$$\theta \int \frac{dp}{d\theta} dv - \theta \Sigma \int \frac{dP}{d\theta} dy;$$

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

$$\int P_0 dy,$$

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 \bar{L} , a much simpler process is applicable. For when the system is in a steady state

$$\bar{P} = \frac{d\bar{L}}{dy},$$

so that we have

$$\bar{L} = \int P dy. \quad (38)$$

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 $d(q'V_2)/dq'$ increase will increase

the difference between w'/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

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

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

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

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

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