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AN INTRODUCTION TO THERMODYNAMICS FOR CHEMISTS

To My
FATHER AND MOTHER

AN INTRODUCTION TO THERMODYNAMICS FOR CHEMISTS

BY

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PREFACE

The aim of the present book is, as the title implies, to provide an introduction to Thermodynamics and its applications to Chemistry. Whilst there are several works on the subject of Chemical Thermodynamics in English, it is felt that their treatment of the concepts of free energy and entropy is hardly adequate to their importance. They confine themselves to reactions at constant volume and apply the Criterion of Equilibrium $(dA)_{TV} = 0$, or the maximum work of the process at constant volume and temperature is zero. But whilst this is true enough, most of our measurements refer to reactions at constant pressure, and it therefore seems to me far better to employ the criterion of equilibrium $(dF)_T = 0$, or the free energy change at constant temperature (Gibbs's Thermodynamic Potential) is zero, since this is true in the case of any reaction whatsoever, and is not limited to the case of constant volume. I believe that a proper understanding of this fundamental subject is essential if thermodynamics is to be a part of the useful equipment of the chemist, and I am fully convinced that it should be treated in an elementary text-book on the subject.

The only book which differentiates clearly between free energy and maximum work is the classic work of G. N. Lewis and M. Randall, but this has several disadvantages as regards the student. In the first place it is much too advanced for the beginner, and secondly it is rather too full of practical details which, while making it excellent as a work of reference, rather detract from its value as an introductory text-book.

I have therefore attempted to satisfy the need for an introductory text-book which does treat this fundamental question, and which, at the same time, considers the more recent applications of Thermodynamics such as the theory of Debye and Hückel or the treatment of concentrated solutions. Moreover, the subject of entropy is approached in a manner different from that usually adopted, and it is hoped that this concept will thus be rendered less abstruse. No more mathematics has been assumed than is

required for the Higher School Certificate Examination of the various Boards.

While every effort has been made to eliminate errors, it is possible that some may have escaped detection, and I shall be grateful if readers will bring these to my notice.

I am very pleased to have this opportunity of expressing my gratitude and appreciation to Professor E. C. C. Baly, F.R.S., for his ready assistance and encouragement during the preparation of this book. I should also like to express my thanks to my mother for undertaking the labour of reading the proofs and to my sister for checking the index, and lastly to thank Mr. F. P. Dunn for his unfailing courtesy and assistance during the production of the book.

D. JOHNSTON MARTI

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Aug. 1933.

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AN INTRODUCTION TO THERMODYNAMICS FOR CHEMISTS

CHAPTER I

FUNDAMENTAL CONSIDERATIONS. THE FIRST LAW OF THERMODYNAMICS

Perhaps one of the greatest difficulties that confronts the student who specializes in any branch of knowledge is that of preserving a sense of proportion and the power of seeing a phenomenon in its true perspective. In our everyday relations with the world, Nature has solved the problem for us, by endowing us with two eyes instead of one, so that we see an object from two different points of view. And this is, in every case, the best method to adopt. A single aspect can at best be only partial, but several different partial views of the same object help us to form a more complete picture of the whole.

The chemist, whose function it is to investigate the relations between the various types of matter, has therefore elaborated for his use, two eyes which have proved to be of great range and adaptability. These two eyes or aspects are known as the Kinetic Theory and Thermodynamics. The first aspect, with which the reader will be familiar, regards matter as composed of very small, discrete particles, the motion of which corresponds to the heat energy of the system. From this basis a number of very important ideas are developed, such as Boyle's Law for gases, or the relation between the colligative properties of solutions. The second aspect, which is the one we propose to consider here, deals, not so much with the matter itself, as with the energy changes which occur in it. It does not formulate any concept of the matter which is undergoing the change, so that it is entirely immaterial whether we adopt the kinetic theory or a continuous theory of matter. But while this is a great advantage in some respects, as regards the generality of the results which we shall obtain, there is no

doubt that a mechanical model is a great gain to the investigator, since it enables him to visualize the process under consideration. For this reason it is usually best to superpose the two aspects by introducing concepts derived from the kinetic theory into our thermodynamical considerations, thereby gaining in completeness of description what is lost in generality.

The chief names which are associated with the earlier work in this field of thermodynamics are the physicists Black, Rumford, Hess, Carnot, Mayer, Joule, Clausius, Kelvin and Helmholtz. To these are due the realization and precise formulation of the First and Second Laws of Thermodynamics. The application of these laws to chemical problems, especially to the problem of Chemical Equilibrium, is the work of such men as van't Hoff, Planck, J. Willard Gibbs, etc., while with the practical applications are associated men like Haber, Nernst, G. N. Lewis and numerous others. To Nernst we also owe the more recent principle which has come to be regarded as a Third Law of Thermodynamics. This third law will be considered later. For the present we propose to consider the first two laws and their applications.

First Law of Thermodynamics.

Numerous attempts have been made, from time to time, to devise a source of perpetual motion which would drive our trains and our factories, without it being necessary to supply it with energy in any form. But these attempts have, in every case, failed to produce the desired result. No machine has yet been constructed which can manufacture energy from nothing, and these repeated failures have slowly borne in upon man the conviction that such a machine has never been constructed because it is an impossibility. This conviction, expressed in a formal manner, is the well-known principle of the conservation of energy and this principle constitutes the first fundamental law of thermodynamics.

Let us consider the matter a little more precisely. We are all familiar with the fact that energy can exist in various forms, heat energy, mechanical energy, electrical energy, etc. Rumford, and later Joule and others, showed that a given number of ergs of mechanical energy may be converted, for example by friction, into a certain definite number of calories of heat energy. In fact these two quantities of energy are equivalent to one another, or rather

we have the same quantity of energy present in two different forms and measured in terms of two different units. Again, if a ball be thrown upwards with an initial velocity v, its kinetic energy is $\frac{1}{2}mv^2$, where m is its mass. As it rises, however, its velocity falls until finally it comes to rest and its kinetic energy is zero. But it is now, unless suddenly arrested, capable of falling to its initial position and regaining exactly the same kinetic energy as it had when it commenced its upward journey, namely $\frac{1}{2}mv^2$. We therefore speak of this capacity to fall as being due to the presence of Potential Energy in the body. The potential energy at the point where the body comes momentarily to rest is equal to the initial kinetic energy and at any intermediate point of the path the sum of the kinetic and potential energy of the body is a constant and equal to $\frac{1}{2}mv^2$, where v is the initial velocity as before. Another interesting example is the case of fusion. Any liquid is said to possess latent heat or latent energy, as a result of the heat energy absorbed during the transformation from the solid to the liquid state, since it is known, that, if we reverse the process, the same quantity of heat is evolved. These are all cases of the transformation of energy from one form into another, and the First Law of Thermodynamics states in effect that, in all these changes, no change in the total amount of energy occurs; when one form of energy disappears exactly the same quantity of another form appears. To proceed further, however, it is necessary to state the law in a mathematical form.

When any portion of space or of matter is the subject of thermodynamic consideration, that portion is termed a *System*. It is evident that such a system will possess a certain total quantity of internal energy. This quantity will be denoted by the letter U. This energy may be present in several different forms, but this is entirely immaterial from the standpoint of thermodynamics. So long as the system is completely isolated from its surroundings this quantity U cannot change. But of course this is only a hypothetical case. It is impossible in practice to isolate any system completely.

We shall now consider a system which is capable of undergoing a change by doing a certain amount of work w. Thus, for instance, if we consider such a system as a gas enclosed in a vertical cylinder A fitted with a weighted piston. If the total mass of the piston and the weight is m, then the total downward force is mg, where

g is the acceleration of gravity. If the force exerted by the gas in the upward direction exceeds this quantity mg, the gas expands. Let the expansion in volume be ΔV, the height through which the piston is raised be h, and the area of the piston be a. Then the work done by the gas in expanding, and therefore in overcoming the force mg, is given by—

$$w = \text{Force} \times \text{Distance moved.}$$
$$= mg \times h.$$

Now mg/a, i.e. the force per unit area, is the pressure exerted vertically downwards by the weight and piston, and therefore opposing expansion. Let this pressure be denoted by P, then since $\Delta V = ah$, we have

$$w = mg/a \times a.h$$
$$= P\Delta V.$$

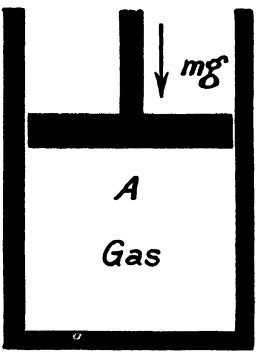

FIG. 1.

The gas system has thus done work, $w = mgh = P\Delta V$, upon its surroundings (the weight and piston).

In general, when such a change occurs, it is accompanied by the absorption or evolution of heat, from or to the surroundings. Let us denote the heat *absorbed* by the system by the symbol $+ q$. If the value of $+ q$ for any particular process is negative, the system is giving out heat to the surroundings, so that the heat evolved in any process will be represented, on our notation, by $- q$.

Since the system has not been regarded as isolated, in general, a change will also have occurred in the total internal energy of the system, namely in U. Let us denote an *increase* in the internal energy of the system by $+ \Delta U$. Then the First Law of Thermodynamics states that the increase in the total internal energy of the system, is equal to the heat absorbed from the surroundings minus the work done by the system upon the surroundings.

Expressed mathematically, this takes the form—

$$\Delta U = q - w \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Before proceeding further, it will be well to distinguish between two different kinds of properties, extensive and intensive. An **extensive property** of a substance is proportional to the quantity

of the substance present, thus mass, volume, heat capacity, etc., are extensive properties.

An **intensive property** is independent of the quantity of substance present, for example, pressure, temperature, density, specific heat, etc. This is usually the only kind of properties which are enumerated, when a list of the properties of a substance is given.

It will be evident that the internal energy, U, belongs to the first category, since, if we have two identical systems, the total internal energy of the two together is double that of each one separately.

We now propose to define another extensive property of any system, namely the heat content. Living, as we do, in an atmosphere of practically constant pressure, it is evident that the simplest method of carrying out calorimetric measurements is under constant pressure. Thus, for instance, our values of the latent heat of fusion and of vaporization, or of the heat of a chemical reaction, usually refer, unless the contrary is stated, to changes at constant pressure. Suppose, now, we consider a system of total internal energy U_A, and allow it to expand from its initial volume V_A to volume V_B, under constant pressure P. The internal energy at the end of the expansion will be denoted by U_B and the heat absorbed during the process by q. Then the work done by the system upon the surroundings in overcoming the pressure P is given by—

$$w = P\Delta V = P(V_B - V_A).$$

The increase in internal energy (which may of course be negative) is

$$\Delta U = U_B - U_A.$$

But by the First Law,

$$\Delta U = q - w$$

so that

$$U_B - U_A = q - PV_B + PV_A$$

or

$$q = (U_B + PV_B) - (U_A + PV_A) \quad . \quad . \quad . \quad (2)$$

Thus, for the case of expansion at constant pressure, q is seen to be the difference of two terms of the form $(U + PV)$. This expression is therefore called the *heat content* of the system defined by

$$H = U + PV \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If ΔH represents an *increase* in H, we have, for changes at constant pressure—

$$\Delta H = q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This equality by no means holds, however, for cases when the pressure changes. Thus, for instance, consider the case where the volume is kept constant, but the pressure of the system increases from P_A to P_B. Then since no volume change occurs and no other form of external work is accomplished, $w = 0$, so that we have—

$$\Delta U = q_v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

the suffix v denoting the fact that the volume is maintained constant. On the other hand we have

$$\begin{aligned} \Delta H &= (U_B + P_B V) - (U_A + P_A V) \\ &= \Delta U + V(P_B - P_A) \\ &= q_v + V(P_B - P_A) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6) \end{aligned}$$

It should be observed that for chemical reactions in the solid or liquid state the change in volume is usually small, so that the difference between the heat of reaction at constant pressure ΔH, and that at constant volume ΔU, is negligible. In the case of gaseous reactions, suppose we have n_1 moles of gas occupying volume V_1, reacting together to give n_2 moles of resultants occupying a volume V_2, and let us assume for the sake of simplicity that the gas law $PV = RT$ per mole may be applied. Then for the reactants we have $PV_1 = n_1 RT$, and for the resultants $PV_2 = n_2 RT$, so that

$$P(V_2 - V_1) = (n_2 - n_1)RT$$

and hence—

$$\Delta H = \Delta U + (n_2 - n_1)RT \quad . \quad . \quad . \quad . \quad . \quad (7)$$

It follows that if $n_1 = n_2$, i.e. if no change in the total number of molecules occurs, then

$$\Delta H = \Delta U \quad . \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

It will have been observed that we have only considered changes in the total internal energy, U, and in the heat content, H, of a system. The absolute values of U and H are not required for the purposes of thermodynamics. It should be noted, however, that these quantities are properties of the system, in the sense that, if we consider the system as undergoing any series of changes whatsoever, such that the final state of the system is completely identical with the initial state, then the initial and final values of the total internal energy, U, and of the heat content, H, of the system

are identical. Such a series of changes is termed a Cycle. That this identity of the initial and final values is true of the total internal energy is self-evident, and since P and V are the same at the beginning and end of the cycle, it follows that the heat content, $H = U + PV$, is also a property of the system. Moreover, we have seen that the internal energy, U, is an extensive property and the term PV being the product of an intensive and an extensive property will be, itself, an extensive property. Hence the heat content, H, is also an extensive property of the system.

We shall now turn our attention to a closer consideration of the work term, w. For simplicity, we shall consider the case of a gas, although it will be evident that, so long as we do not in any way introduce the nature of the gas, say by introducing the gas laws, the considerations are equally valid for solid or liquid systems. Suppose we have a gas enclosed in a cylinder which is fitted with a piston, and we allow the gas to expand against an external pressure P by an infinitesimal amount dV. Then the work done by the system is PdV and this is obviously greater the greater the value of the external pressure P. There is, however, a limit to the value of P, which is determined by the fact that it cannot exceed the pressure of the gas inside the cylinder, or expansion will not occur. If the gas pressure is $P + dP$, i.e. if it is greater than the external pressure P by an infinitesimal amount, then the work done by the system in expanding is the **maximum work** possible from the system when undergoing an expansion of amount dV. If, now, the expansion is continued from volume V_1 to volume V_2, the pressure of the gas inside the cylinder is continually decreasing, the initial and final values being $P_1 + dP$ and $P_2 + dP$, and in order that the expansion may still occur we must decrease the external pressure continually from P_1 to P_2 so that at any moment it differs from the internal pressure of the gas only by an infinitesimal amount. The total maximum work done by the system during the expansion, which will be denoted by w_{max} is given by—

$$w_{\text{max.}} = \int_{V_1}^{V_2} PdV.$$

Such a process is termed a **reversible process,** since, if at any point in the expansion we decrease the gas pressure by an infinitesimal amount, the direction of motion is reversed, that is

the gas contracts. The whole question of reversible processes will be more fully considered later, when we come to deal with the Second Law.

It appears, then, that any system has a certain maximum capacity for work and we, therefore, propose to introduce a new property of the system which will be termed the **work content** and will be denoted by the letter A. This work content will probably depend upon the temperature of the system and we will therefore find it convenient to restrict its use, for the present, to isothermal processes. When a system does positive work upon its surroundings, at constant temperature, we may speak of a decrease in the work content, and this will be denoted by $-\Delta A$, the negative sign being employed as usual to denote a decrease. $-\Delta A$ is thus the maximum work which a system can perform when undergoing any isothermal change. $+\Delta A$, which represents an increase in the work content of the system, is naturally the work done *upon* the system by the surroundings during the given changes. The work content A, itself, is a property of the system just as are U and H and it will be more completely defined later on, when the reasons for restricting ourselves to isothermal processes will become clear.

For the case of expansion just considered we may write—

$$-\Delta A = \int_{V_1}^{V_2} P dV \quad . \quad . \quad . \quad . \quad . \quad (8)$$

This expression is perfectly general and refers to the isothermal expansion of any system whatsoever. If now we confine our attention, for the moment, to the case of a perfect gas, we may introduce the gas law $PV = RT$ per mole and we are thus enabled to integrate this expression (8) for this particular case, provided the temperature is kept constant. We thus obtain for the maximum work of the process of isothermal expansion from V_1 to V_2 of one mole of gas—

$$-\Delta A = \int_{V_1}^{V_2} RT \frac{dV}{V}$$

$$= RT \, ln \, V_2/V_1 \, [1] \quad . \quad . \quad . \quad . \quad . \quad (9)$$

By means of a second application of the gas laws, equation (9) may also be written—

$$-\Delta A = RT \, ln \, P_1/P_2 \quad . \quad . \quad . \quad . \quad . \quad (10)$$

[1] *ln* is used throughout the book to indicate a natural logarithm.

As we shall see later, any process in which maximum work is done is a reversible process, so that we have, in general, for any reversible isothermal process

$$-\Delta A = w$$

so that the first law may, for such processes, be written—

$$\Delta U = q + \Delta A \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

We shall now consider one or two examples of the maximum work which may theoretically be obtained from various processes.

(i) **Osmotic Processes.** The process of isothermally diluting a solution is obviously one of increase in volume and work may therefore be obtained from it. In order to obtain the maximum work we must, as in the case of the expansion of a gas, conceive of the process being carried out in a truly reversible manner. This is accomplished by means of a device known as a semi-permeable membrane. This allows the pure solvent to pass through, but prevents the passage of the solute, so that the solute can exert its osmotic pressure against the membrane. In practice, we can, of course, only approximate to this ideal, although several very good semi-permeable membranes have been prepared. This is, however, immaterial to our purpose. All we require is to postulate the existence of such a membrane in order to obtain the maximum osmotic work possible. Suppose we have a cylinder containing two layers, one of a pure liquid solvent, the other of a solution in the same solvent, separated by a piston which consists of a semi-permeable membrane shown unshaded in Fig. 2. The piston is weighted, so that the downward pressure is less than the osmotic pressure of the solution by an infinitesimal amount. The piston will then rise, the solvent forcing its way through into the solution. The case is entirely analogous to that of the expansion of a gas and the maximum osmotic work done by the solution in expanding from volume V_1 to volume V_2 is

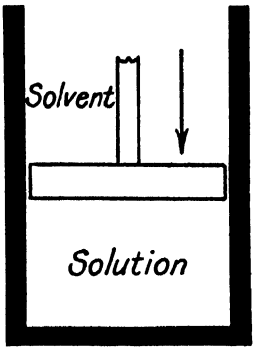

FIG. 2.

$$-\Delta A = \int_{V_1}^{V_2} P dV.$$

If we are dealing with a dilute, aqueous solution of a weak electrolyte, we may again apply the gas law, and obtain for the maximum osmotic work per gram-ion or per mole

$$-\Delta A = RT \ ln \ V_2/V_1 = RT \ ln \ P_1/P_2$$

where P_1 and P_2 are the osmotic pressures of the solution at volumes V_1 and V_2; or, expressed in terms of concentrations C_1 and C_2, we have—

$$-\Delta A = RT \ ln \ C_1/C_2 \quad . \quad . \quad . \quad . \quad (12)$$

(ii) **The Three-Stage Distillation Process.** The process, now about to be considered, is one of great utility in thermodynamic treatment. Suppose we have a pure liquid contained in a cylinder I

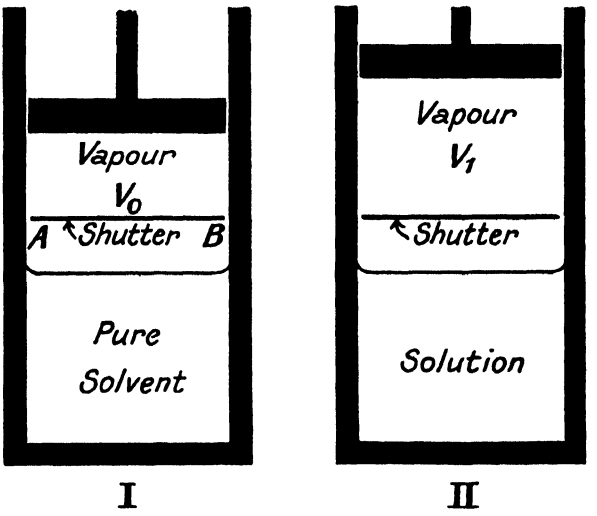

FIG. 3.

(see Fig. 3) the vapour pressure of which, at a temperature $T°$ is p_0. In cylinder II is a solution of a non-volatile solute, the solvent being identical with the pure liquid in I, and the vapour pressure of the solvent in the solution being p_1, where p_1 is less than p_0.

The quantity of solution in II is so great that the addition of one mole of solvent has no appreciable effect on the concentration. We require to find the maximum work involved in the process of transferring one mole of the liquid from I and adding it to the solution in II, the whole process being accomplished isothermally and reversibly by means of the following three-stage distillation process:

(*a*) One mole of solvent in I is vaporized isothermally and

reversibly at the vapour pressure p_0 which is constant, so that the maximum work done by the system is

$$(-\Delta A)_1 = p_0(V_0 - v_0)$$

where v_0 is the volume occupied by one mole of liquid, V_0 the volume of one mole of vapour.

(*b*) A frictionless weightless shutter AB is now slid across the cylinder to isolate the mole of vapour. This does not require the expenditure of any work. The vapour is now allowed to expand isothermally and reversibly until its pressure has fallen to $p_1 + dp$, i.e. practically to the vapour pressure of the solvent p_1, above the solution. Let the new volume be V_1. The maximum work done by the system is

$$(-\Delta A)_2 = \int_{V_0}^{V_1} p dV.$$

(*c*) The mole of vapour is now compressed isothermally and reversibly into the solution in II at the constant pressure p_1. The work done by the system is

$$(-\Delta A)_3 = p_1(v_1 - V_1)$$

where v_1 is the volume occupied by one mole of solvent in the solution.

The process is now complete and the total maximum work done by the system is

$$\begin{aligned} -\Delta A &= (-\Delta A)_1 + (-\Delta A)_2 + (-\Delta A)_3 \\ &= p_0(V_0 - v_0) + \int_{V_0}^{V_1} p dV + p_1(v_1 - V_1) \quad . \quad . \quad (13) \end{aligned}$$

Now v_0 and v_1 are very small compared with V_0 and V_1 and may therefore be neglected, so that expression (13) becomes

$$-\Delta A = p_0 V_0 + \int_{V_0}^{V_1} p dV - p_1 V_1 \quad . \quad . \quad . \quad (13a)$$

Now, integrating the second term on the right-hand side by parts we have—

$$\int_{V_0}^{V_1} p dV = p_1 V_1 - p_0 V_0 - \int_{p_0}^{p_1} V dp$$

so that

$$-\Delta A = p_0V_0 + p_1V_1 - p_0V_0 - \int_{p_0}^{p_1} Vdp - p_1V_1$$

or

$$-\Delta A = -\int_{p_0}^{p_1} Vdp \quad . \quad . \quad . \quad . \quad (14)$$

This expression is perfectly general, since the gas laws have not been assumed for the vapour. If, now, we assume the gas law $pV = RT$ per mole, we obtain—

$$-\Delta A = -\int_{p_0}^{p_1} RT\frac{dp}{p}$$

$$= RT\ ln\ p_0/p_1. \quad . \quad . \quad . \quad . \quad (15)$$

It will be observed that, according to equation (14) the total maximum work performed by the system in passing through the three-stage process, is of the form $\int Vdp$. For any single stage, however, the work term must be of the form $\int pdV$ and cannot, under any circumstances, be of the form $\int Vdp$. In the particular case when the vapour behaves as a perfect gas, however, the term pdV is numerically equal to $-Vdp$. This follows immediately from the following considerations. According to the gas law,

$$pV = RT = \text{Constant (at any given temperature).}$$

Hence $d(pV) = pdV + Vdp = 0$
so that $pdV = -Vdp$.

Hence expression (14) becomes, for the case of a perfect gas,

$$-\Delta A = \int_{V_0}^{V_1} pdV = RT\ ln\ V_1/V_0 = RT\ ln\ p_0/p_1$$

as before.

This may also be seen immediately from equation (13*a*), viz.

$$-\Delta A = p_0V_0 + \int_{V_0}^{V_1} pdV - p_1V_1$$

since, for a perfect gas we have, at constant temperature

$$p_0 V_0 = p_1 V_1$$

and we are left with

$$-\Delta A = \int_{V_0}^{V_1} p dV.$$

The work done by a system in expansion may be very conveniently determined by means of a pressure-volume diagram, since the integral $\int_{V_1}^{V_2} p dv$ is equal to the area below the curve. Thus in the figure shown (Fig. 4) BA represents the pressure-volume curve of the system at constant temperature T, i.e. BA is an isothermal line. The work done in expanding from volume V_1 to volume V_2 is represented by the area of the figure BAV_2V_1.

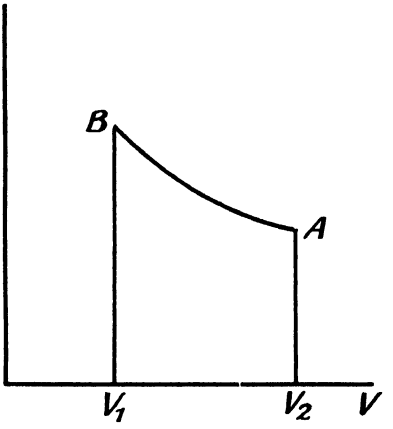

FIG. 4.

We have hitherto only considered expansion against a pressure as representing the maximum work term of any process ($-\Delta A$). But, as we know, mechanical work is of various types, and the maximum work term usually involved in a chemical or physical change is composed of several such types, as, for example, electrical energy, or energy of translatory motion of the system as a whole. The question of electrical energy will be considered in a later chapter.

A word of warning will perhaps not be out of place here. Some authors, following van't Hoff, have termed the maximum work term ($-\Delta A$) the "Change in free energy" of the system. It is better, however, to reserve this term for a quantity which will be defined later, since, by so doing, much confusion is avoided.

Heat Capacity and Molecular Heats. We now require to obtain a precise definition of another extensive property of any system, namely the Heat Capacity. This is measured by the amount of heat required to raise the temperature of the system

by one degree. If q calories are absorbed by the system for a temperature rise of ΔT, then the average heat capacity over the temperature range from T to $T + \Delta T$ is $q/\Delta T$. It is known, however, that the heat capacity varies with the temperature, so that at any particular temperature the heat capacity is the limit of the ratio $q/\Delta T$ as ΔT tends to zero. The heat capacity depends, however, also upon the volume changes which may occur during the absorption of heat and it is therefore convenient to distinguish between two heat capacities, that measured at constant volume, denoted by C_v, and the heat capacity at constant pressure, denoted by C_p.

Let us consider the heat capacity at constant volume first. We have already seen (expression 5) that

$$q_v = \Delta U$$

so that the heat capacity is given by

$$C_v = \left(\text{Limit}_{\Delta T \to 0} \frac{\Delta U}{\Delta T}\right)_v.$$

The suffix v is used to denote the fact that the volume is kept constant. But the limit of a ratio such as $\frac{\Delta U}{\Delta T}$ is the differential coefficient of U with respect to T, i.e. $\frac{dU}{dT}$. Since, however, the volume is kept constant, this is what is known as a partial differential coefficient and is denoted by $\frac{\partial U}{\partial T}$ or $\left(\frac{\partial U}{\partial T}\right)_v$ the suffix v indicating constant volume. Hence we may write

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

These partial differential coefficients will be more fully explained at the end of this section, for the benefit of those not already familiar with their use.

In the case of constant pressure measurements, we have seen that $q = \Delta H$ (expression 4) so that it will be evident, without further discussion that

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Partial Differentiation. Every system has three properties, pressure, temperature and volume, any one of which may change.

These properties are called the variables of the system. Now we know that if we arbitrarily assign values to any two of these variables, say the volume and the temperature, then the third variable is also automatically fixed. This is expressed mathematically by saying that pressure is a **function** of the volume and the temperature and we write, briefly,

$$P = f_1(T, V).$$

In the same way, we may regard the temperature as a function of the pressure and the volume so that

$$T = f_2(P, V),$$

or alternatively, we may express the relationship by writing

$$V = f_3(T, P).$$

Taking the first of these cases, namely $P = f_1(T, V)$, we notice that, if we fix one of the variables T or V, say the temperature, the other is still free to change. Consequently we may draw a plane graph of the relation between P and V for this particular value of the temperature. An example of this type of diagram has already been considered (Fig. 4). If, now, we differentiate the expression $f_1(T, V)$ regarding T simply as a constant, we obtain the slope of this pressure-volume curve for the particular value of the temperature, T, under consideration. The differential coefficient so obtained is termed a **partial differential coefficient,** since one of the variables is kept constant, and it is written

$$\left(\frac{\partial P}{\partial V}\right)_T \text{ or simply } \frac{\partial P}{\partial V},$$

the suffix T indicating the fact that the temperature is maintained constant. For example, consider the equation for the perfect gas as a function of this type. For one mole of gas we have

$$PV = RT$$

so that

$$P = \frac{RT}{V}.$$

Now regarding V as a constant and differentiating with respect to T we obtain

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}.$$

On the other hand, if we regard T as a constant and differentiate with respect to V we obtain

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{V^2}.$$

Now since it is only necessary to fix two of the variables, pressure, temperature or volume, in order to fix any *given* system completely, it follows that other properties of the system, such as the total internal energy, the heat content, etc., may be regarded as functions

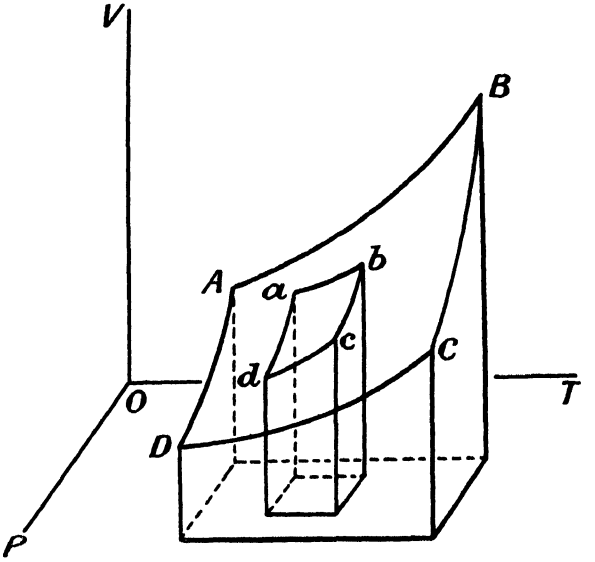

FIG. 5.

of any two of these variables. Thus, for instance, we may write

$$U = F_1(P, V) \text{ or } U = F_2(P, T)$$

and so on, and consequently we may obtain partial differential coefficients of the form $\left(\frac{\partial U}{\partial T}\right)_V$, etc.

The complete function may be represented by means of a solid figure, with reference to three rectangular co-ordinates. Thus, for example, the function $V = f_1(T, P)$ may be represented as in Fig. 5, the axes being volume, temperature and pressure. Consider the point d at which the co-ordinates are P, V, T. Suppose T is increased by an infinitesimally small amount to $T + dT$ and P is increased to $P + dP$. Then corresponding to these changes we have a small change in the volume from V to $V + dV$. The system is now represented by the point b whose co-ordinates are

$P + dP$, $V + dV$, $T + dT$. Now this change may be effected in two stages. We may pass from d to c by changing the temperature from T to $T + dT$ while the pressure is maintained constant, and then we may proceed from c to b by changing the pressure from P to $P + dP$ while the temperature is constant. In the first step the volume change is evidently

$$\left(\frac{\partial V}{\partial T}\right)_P dT \text{ since } \left(\frac{\partial V}{\partial T}\right)_P \text{ is the slope of } dc.$$

In the second step the volume change is $\left(\frac{\partial V}{\partial P}\right)_T dP$.

Hence the total increase in volume is given by

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT \quad . \quad . \quad . \quad (18)$$

This is a very important mathematical relation and holds for any three variables say x, y, z, connected by a relation of the form

$$x = \phi(y, z)$$

which merely expresses the fact that x is some function of y and z so that if we fix the values of y and z the value of x is automatically fixed.

Considering equation (18), as it stands, we may postulate that while P and T change, V must remain constant so that dV is zero and we obtain—

$$\left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT = 0$$

so that

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \Big/ \left(\frac{\partial V}{\partial P}\right)_T \quad . \quad . \quad . \quad . \quad (19)$$

the suffix V on the left-hand side expressing the constancy of the volume.

Since, as we have seen, U may also be regarded as a function of the temperature and the volume, equation (18) becomes

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV.$$

Dividing through by dT and imposing the condition that the pressure is maintained constant we obtain—

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad . \quad . \quad (20)$$

We are now in a position to deduce a relation between the two heat capacities C_p and C_v. We have seen that $\left(\frac{\partial U}{\partial T}\right)_V = C_v$, so that equation (20) becomes—

$$\left(\frac{\partial U}{\partial T}\right)_P = C_v + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad . \quad . \quad . \quad (21)$$

Now we know that

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial (U + PV)}{\partial T}\right)_P$$

$$= \left(\frac{\partial U}{\partial T}\right)_P + \left(\frac{\partial (PV)}{\partial T}\right)_P$$

and since in the last term on the right-hand side P is constant, this term becomes $P\left(\frac{\partial V}{\partial T}\right)_P$ so that we have

$$C_p = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \quad . \quad . \quad . \quad . \quad (22)$$

Combining (21) and (22) we obtain—

$$C_p - C_v = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P \quad . \quad . \quad . \quad (23)$$

In a similar manner, it may be shown that

$$C_p - C_v = \left[V + \left(\frac{\partial H}{\partial P}\right)_T\right]\left(\frac{\partial P}{\partial T}\right)_V \quad . \quad . \quad . \quad (24)$$

and the reader will find the deduction of this equation a useful example for practice.

Another important mathematical relation, which will not be proved here, but the proof of which will be found in text-books of mathematics, deals with partial differential coefficients of the second order. It may be stated as follows :

$$\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial^2 V}{\partial P \partial T} = \frac{\partial}{\partial T}\left(\frac{\partial V}{\partial P}\right)_T \quad . \quad . \quad . \quad (25)$$

Kirchhoff's Equation. Let us consider some change occurring in a system, such as a chemical reaction, the volume of the system being kept constant. At temperature T the change is accompanied by the absorption of a quantity of heat equal to q_v. At a slightly higher temperature $T + dT$ the heat absorbed is $q_v + dq_v$. Let s_1 be the heat capacity measured at constant volume of the system

before the change (the reactants), and s_2 the heat capacity at constant volume of the system after the change (the resultants). Suppose we start with the reactants at temperature T, and finish with the resultants at temperature $T + dT$. We may carry out the change by either of two methods which may be conveniently represented by the following diagram (Fig. 6).

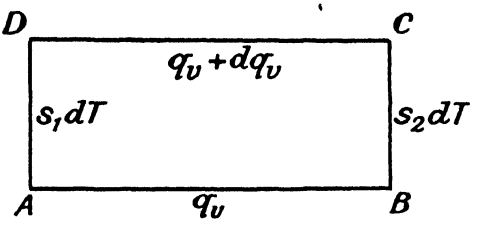

FIG. 6.

A represents the initial state and C the final state. We may proceed either (i) along AB and BC by first allowing the reaction to take place at constant temperature T, and then warming the resultants to $T + dT$, when the total heat absorbed is

$$q_v + s_2 dT$$

or (ii) along AD and DC, by first warming the reactants to the temperature $T + dT$ and then allowing the reaction to proceed isothermally at this temperature. The heat absorbed in this case is

$$q_v + dq_v + s_1 dT.$$

Now since the volume is kept constant during these changes, no external work is done, so that by the First Law of Thermodynamics the total heat absorbed by either path is equal to the difference in total internal energy between A and C and therefore the heat effect along either path is the same. That is

$$q_v + dq_v + s_1 dT = q_v + s_2 dT$$

or

$$\frac{dq_v}{dT} = s_2 - s_1.$$

Now for any reaction at constant volume we have by expression (5)

$$q_v = \Delta U$$

so that

$$\left(\frac{\partial(\Delta U)}{\partial T}\right)_v = s_2 - s_1 \quad . \quad . \quad . \quad . \quad . \quad (26)$$

This is Kirchhoff's Equation, which enables us to calculate the temperature coefficient of the heat of reaction at constant volume from a knowledge of the specific heats of the reactants and resultants. The temperature coefficient thus obtained is very much more accurate than would be obtained by direct measurements of q_v at various temperatures.

Application of the First Law of Thermodynamics to a Cyclic Process.

We have already seen that the internal energy of any system must be regarded as a property of the system, so that if we pass through any cycle of changes, the initial and final values of the total internal energy U are the same. In other words, for any completed cycle $\Delta U = 0$. But the first law imposes the condition that

$$U = q - w$$

and hence, for a completed cycle

$$q - w = 0$$

or

$$q = w \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

In words we may say that the total heat absorbed in any cyclic process is equal to the total work done by the system.

Isothermal Expansion of a Perfect Gas. We will now proceed to describe an experiment which was carried out by Joule. Two large, similar vessels, connected by means of a tap, were immersed in a bath, which was kept thoroughly mixed, so as to maintain a uniform temperature throughout. Apparatus for the accurate measurement of any change in the temperature of the bath was employed. Vessel I was filled with gas, vessel II evacuated. The tap was now turned on, so that gas passed from I to II until the pressure was the same in both vessels. In this experiment, since there is no change in the total volume of the system the work done by the system upon the surroundings is zero, i.e. $w = 0$. Moreover, if we are dealing with a perfect gas, there will be no force of cohesion to overcome, so that there will be no internal work done in expanding. It should be noted that the expanding gas from I does work against the pressure of the gas which has already passed into II, but this is counterbalanced by the fact that the same amount of work is required to compress the gas in II, so that the net work is zero. Since, then, neither

internal nor external work is done, it follows that the total internal energy of the system is unchanged, i.e. $\Delta U = 0$. Hence, by the first law, since

$$\Delta U = q - w$$

it follows that $q = 0$. In other words, there should be no heat effect observed in the expansion. When Joule performed the experiment outlined above he was unable to detect any change in the temperature of the bath with the apparatus at his disposal.

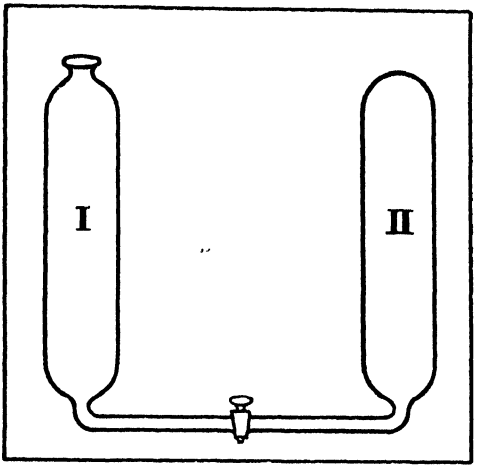

FIG. 7.

Actually a slight temperature change does occur, owing to the mutual attractive forces existing between the molecules, but the experimental technique was not sufficiently delicate to detect it. For the case of a perfect gas, however, these forces are non-existent and hence the internal energy is independent of the volume at any given temperature, or expressing the same idea in mathematical language, we write

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

This may, in fact, be employed as a partial definition of a perfect gas and may be expressed thus: A perfect gas is a substance, the total internal energy of which is a function of the temperature only. This definition is not, however, complete as we shall see later; other substances satisfy this condition which do not obey the gas law $PV = RT$.

We will now proceed to a consideration of the Second fundamental law of Thermodynamics.

CHAPTER II

THE SECOND LAW OF THERMODYNAMICS

The Law of Conservation of Energy or the First Law of Thermodynamics describes the quantitative relations which obtain when one type of energy is transformed into another. The Second Law, on the other hand, deals with the limits of the interconvertibility of the different forms of energy.

The First Law, as we have seen, was the result of the numerous unsuccessful attempts which had been made to produce a machine which would do work continually without requiring any expenditure of energy, the repeated failures leading men to the conclusion that the cause lay in some deep-rooted law of Nature. Mayer and Helmholtz thus formulated the law of conservation of energy. But there remained a possibility which was by no means precluded by this law. It is true that energy cannot be obtained from nowhere, but what of the vast stores of energy which are contained in the surroundings—the atmosphere, for example, or the ocean? If these stores of heat energy could be converted into mechanical energy, we should have at our command a practically unlimited source of energy, which would render dynamos, steam engines, etc., unnecessary.

But here again the efforts which would-be inventors have lavished upon the search for such a machine have met with repeated failure, and slowly the feeling gained ground that such an apparatus, which would convert the heat of the environment into mechanical work, must involve the contradiction of another law of Nature and is therefore an impossibility. We may tentatively express this conviction by saying that whereas, so far as we know, it is always possible to convert mechanical energy (work) into heat (e.g. by causing the energy to rotate the paddles in a Joule calorimeter containing water), the reverse process, namely the change from heat into work, is only possible under certain conditions.

To enable us to determine more precisely what these conditions are, let us consider the question of the transference of heat from

one body to another. Now we know that if two bodies at different temperatures are brought into contact, heat flows from the body at the higher to the body at the lower temperature. This process occurs spontaneously and is usually described as a "Natural Process." Moreover, we know that, by employing some mechanical contrivance, such, for example, as a steam engine, this process may be made to yield a certain amount of external work. The reverse process, on the other hand, namely the passage of heat from a body at a lower to one at a higher temperature, does not, to the best of our knowledge, occur naturally or spontaneously, but it may be made to occur by the application of external work, i.e. by causing the environment to do positive work upon the system. Clausius therefore put forward the following principle: "It is impossible for a self-acting machine working in a cycle, unaided by any external agency, to convey heat from a body at a low temperature to one at a higher temperature; or heat cannot *of itself* (i.e. without the performance of work by some external agency) pass from a cold to a less cold body."

A somewhat different statement of the same principle, due to Lord Kelvin (1851), is as follows:

"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 surrounding objects."

These may serve, for the present, as partial statements of the Second Law of Thermodynamics, but, as we shall see, the second law itself is much more general and far-reaching in its application.

We are now, however, in a position to derive a mathematical expression which is of great utility and which depends upon this partial aspect of the second law. Suppose we have one mole of a perfect gas enclosed in a cylinder, which is fitted with a movable piston. The cylinder and its contents are brought into contact with a large reservoir at the constant temperature T_1, and the gas is allowed to expand isothermally and reversibly from its initial volume V_1 to a volume V_2. The work done by the system, since the expansion is reversible, i.e. maximum work is done, is

$$-\Delta A_1 = RT_1 \ln V_2/V_1 \quad . \quad . \quad . \quad . \quad (1)$$

Since, as we have seen, the change in internal energy of a perfect gas during isothermal expansion or contraction is zero, i.e. $\Delta U = 0$, we have, by the first law,

$$-\Delta A = q$$

so that

$$q_1 = RT_1 \ ln \ V_2/V_1 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The reservoir is assumed to be of sufficient capacity that the loss of this quantity of heat does not affect the temperature. The system is now cooled from the temperature T_1 to the temperature T_2, the volume being maintained constant. The heat given out will be $C_v(T_1 - T_2)$, where C_v is the molecular heat of the gas at constant volume.

The third step in the process consists in causing the gas to contract isothermally and reversibly to its initial volume V_1, the system being in contact with another large reservoir of heat at the temperature T_2. Work will have to be performed upon the system by the surroundings by amount $RT_2 \ ln \ V_2/V_1$, so that the work done *by* the system is

$$-\Delta A_2 = -RT_2 \ ln \ V_2/V_1 \quad . \quad . \quad . \quad . \quad (3)$$

and since

$$-\Delta A_2 = q_2$$

we have

$$q_2 = -RT_2 \ ln \ V_2/V_1 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Finally we must warm the gas to its initial temperature T_1 at the constant volume V_1. The heat absorbed is $C_v(T_1 - T_2)$ which is exactly equal to the heat evolved in the second step of the process.

We have now completed the cycle, the system being again in its initial state. The total work performed by the gas over the whole cycle is, since the net temperature change is zero—

$$\begin{aligned} -\Delta A &= -\Delta A_1 - \Delta A_2 \\ &= RT_1 \ ln \ V_2/V_1 - RT_2 \ ln \ V_2/V_1 \\ &= R \ ln \ \frac{V_2}{V_1}.(T_1 - T_2) \quad . \quad . \quad . \quad . \quad (5) \end{aligned}$$

But by equation (2) we have

$$q_1/T_1 = R \ ln \ V_2/V_1$$

so that expression (5) becomes

$$-\Delta A = \frac{T_1 - T_2}{T_1}(q_1) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If, now, we decrease the difference between the temperatures T_1

and T_2 to an infinitesimally small quantity dT, this expression becomes—

$$d(-\Delta A) = q_1 \frac{dT}{T_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

It is now necessary to show that this expression, which has been deduced for the ideal case of a perfect gas, is, in reality, perfectly general and entirely independent of the system undergoing the cycle. The proof is known as Carnot's Theorem.

Before proceeding with the proof, however, we must consider, a little more closely, the nature of a reversible process, although a complete discussion will be deferred until we have considered the full significance of the second law. A reversible process is, strictly speaking, an impossibility, since it assumes that all the forces are exactly balanced. Thus, for example, we consider the expansion of a gas with the opposing external pressure exactly equal to the internal gas pressure, or the sinking of a solid when the upthrust due to the water is exactly equal to the gravitational force exerted upon the solid in the downward direction so that the body can just float. These processes are evidently impossible and in order that they may be considered at all feasible, we imagine that *an infinitesimal difference exists between the opposing forces.* This has been done, already, in the consideration of the case of an expanding gas, where we regarded the external pressure P, opposing expansion, as being smaller than the internal gas pressure by an infinitesimal amount dP. The work done by the system in expanding through an infinitely small volume dV is PdV. Now if we consider an infinitesimal change to occur in the pressures, so that the internal pressure is $P - dP$, the external pressure, as before, P, then the work done by the surroundings upon the system when it contracts through a volume dV is $(P - dP)dV$ or $PdV - dP.dV$.

Now $dP.dV$ is of the second order of differentials and may therefore be neglected in comparison with PdV which is of the first order. Hence the work done upon the system is PdV. This is equal to the work done by the system in the former case of expansion. Hence the reversal of the direction of motion requires that the same work factor is involved, only that, whereas in the one direction work is done by the system, in the reverse direction the same quantity of work must be done upon the system or in other words in one direction the work output of the system is

positive, in the opposite direction it is negative in sign but numerically identical. This is the fundamental property of the reversible process from which its name is derived.

The nearest approach to such a reversible process in actual practice is obtained in the measurement of the electromotive force of a cell by means of the Wheatstone bridge method. In this measurement the *P.D.* from the cell is just balanced by an opposing *P.D.* of a magnitude as nearly as possible the same. The current passing through the galvanometer (and therefore the current taken from the cell) is negligibly small, and the processes occurring in the cell are thus, as nearly as possible, proceeding reversibly, doing maximum work against the opposing *P.D.*

It will be obvious that, in every reversible process the force opposing the change is the maximum possible for the process to occur at all. If it be just greater by an infinitesimal amount the process cannot occur. Hence the work done in any reversible process is also a maximum, since the work done is the product of a force—the intensity factor, and a distance—the capacity factor which is obviously constant for any given process.

Carnot's Theorem. Suppose that, in addition to the perfect gas system already considered (which we shall call System I), we have another system (II), working reversibly in a cycle, which takes in the same quantity of heat q_1 at the higher temperature T_1 as does system I, but gives out less heat than system I at the lower temperature T_2. Suppose the amount given out at temperature T_2 is q_2' (where $q_2' < q_2$). Then, for the whole cycle, we have $\Delta U = 0$, so that the work done by the system $w = q_1 - q_2'$, where w is greater than $-\Delta A$, the maximum work of system I. We may now consider the two systems linked up together, system II working in the forward direction and performing positive work w, system I working in the reverse direction, i.e. taking in heat q_2 from the reservoir at T_2 and giving out heat q_1 to the reservoir at temperature T_1. The work required by system I is $-\Delta A$ and this may be done by system II when an amount of useful work $w - (-\Delta A)$ is left over and is available for any purpose we desire. Now system I takes more heat from the cold reservoir, namely q_2, than is replaced by system II, so that we are continuously converting heat from the coldest surrounding body, i.e. the reservoir at T_2, into useful work, and this contradicts the statement of Kelvin given above. If we cause this extra work

$(w - (-\Delta A))$ to be converted into heat and allow this heat to pass to the hot reservoir, we have a system which will cause heat to pass continuously from a cold to a hot body without requiring any work, i.e. the statement of Clausius is contradicted.

It follows from this theorem that the work done by any system, working in a reversible cycle between the same temperature limits, must perform the same amount of work. This work is the maximum work of the cycle. Of course, if heat losses occur through friction, etc., as in fact they do in all actual processes, the work performed will be less than this maximum, even if we have managed to approximate to reversible conditions. We thus obtain, for any reversible cyclic process, working between the two temperatures T_1 and T_2

$$-\Delta A = \frac{q_1}{T_1}(T_1 - T_2) \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where q_1 is the heat taken in by the system at the temperature T_1.

Now suppose the temperature difference $(T_1 - T_2)$ is infinitesimally small, so that the temperature limits may be denoted by T and $T - dT$, then

$$d(-\Delta A) = \frac{q}{T}.dT \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

We have thus arrived at a most important result which amounts to a mathematical formulation of the second law for a reversible cyclic process.

Let us now consider the following cycle. Suppose we have any reversible process whatsoever occurring in a system at the constant temperature T_1, such, for example, as a chemical reaction (conducted reversibly), and suppose that the work done by the process at this temperature is $(-\Delta A)_1$. This is the first stage of the cycle and involves the absorption of a quantity q_1 of heat. The next stage consists in cooling the system reversibly from the temperature T_1 to the temperature T_2, the volume being maintained constant. In the third stage the system is caused to undergo exactly the reverse process to that occurring in stage I, the final volume to be identical with the volume at the commencement of the cycle. The work which must be done upon the system is $(-\Delta A)_2$ and this is, since the process is reversible, the work which the system would perform if the process occurring at stage I were carried out at temperature T_2. Finally, the fourth stage consists in raising the

temperature of the system to T_1, the volume being maintained constant. The cycle is now complete and we may therefore write—

$$-\Delta A = \frac{q_1}{T_1}(T_1 - T_2).$$

Now $(-\Delta A) = (-\Delta A)_1 - (-\Delta A)_2$ is the difference between the work done by the system in undergoing the process at the two temperatures T_1 and T_2; hence the limit of the ratio $\frac{-\Delta A}{T_1 - T_2}$ as the temperature difference becomes infinitesimally small, namely $\frac{d(-\Delta A)}{dT}$, is the temperature coefficient of the maximum work done by the system when the process occurs reversibly and isothermally at the temperature T. Since, however, we have ensured that no volume change shall occur as a result of the change in the temperature from T_1 to T_2, we must express this fact by writing the coefficient, $\left(\frac{\partial(-\Delta A)}{\partial T}\right)_V$. We have, then, for any reversible, isothermal process whatsoever,

$$\frac{q}{T} = \left(\frac{\partial(-\Delta A)}{\partial T}\right)_V \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where q is the heat absorbed by the system during the process at temperature T.

Now the process itself is perfectly general. It may and often does involve a volume change in the system. Let us consider some process in which the only work done is in expansion against a pressure, i.e. no electrical work, etc., is performed. The work done by a system in expanding, against a pressure, P, through a volume dV is

$$-\Delta A = PdV \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Now we have assumed that the volume change is in no way dependent on the temperature and hence we may regard dV as a constant and differentiate the expression for $-\Delta A$ with respect to temperature. We thus obtain—

$$\left(\frac{\partial(-\Delta A)}{\partial T}\right)_V = \left(\frac{\partial P}{\partial T}\right)_V .dV$$

the suffix V referring to the fact that the volume in no sense depends upon the temperature. Hence, from expression (10),

$$q = T\left(\frac{\partial P}{\partial T}\right)_V .dV \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Now the heat absorbed when a system undergoes expansion through unit volume is often termed the latent heat of expansion of that system, so that, if we denote the latent heat by L we have $L = \frac{q}{dV}$ or

$$L = T\left(\frac{\partial P}{\partial T}\right)_V \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Let us now apply this very important relation to the case of vaporization of a liquid. Let λ be the latent heat of the process per mole of the liquid, V_1 and V_2 the volumes occupied by one mole of the liquid and vapour respectively. Then the latent heat per unit volume change is

$$L = \frac{\lambda}{V_2 - V_1}.$$

Hence equation (13) gives

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\lambda}{T(V_2 - V_1)} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where P is the vapour pressure of the liquid at the absolute temperature T. This is known as the Clapeyron equation. It applies equally to the case of fusion and connects the slope of the pressure-temperature diagram with the latent heat of the process, the absolute temperature and the volume change.

We may simplify the exact form of the equation (expression 14) by first of all neglecting V_1 the volume of the liquid in comparison with V_2 the volume of the vapour, and secondly by assuming that the vapour obeys the gas law $PV = RT$ per mole, so that $V_2 = \frac{RT}{P}$. The Clapeyron equation thus becomes—

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\lambda . P}{RT^2}$$

or

$$\frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V = \frac{\lambda}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

or

$$\left(\frac{\partial \ln P}{\partial T}\right)_V = \frac{\lambda}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad (15a)$$

Illustrations of the Application of the Clapeyron Equation.

I. At what height must the barometer stand in order that water may boil at 101° C. ?

Let the rise in the pressure be x cms. of mercury for a rise in the boiling-point of 1° C. That is $\left(\frac{\partial P}{\partial T}\right)_V = x$ cms.

so that $\left(\frac{\partial P}{\partial T}\right)_V = x \times 13{\cdot}6 \times 981$ dynes per degree.

$P = 1$ atmosphere $= 10^6$ dynes approximately.

Hence

$$\frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V = \frac{x \times 13{\cdot}6 \times 981}{10^6}$$

$\lambda = 536$ cals. per gram $= 536 \times 18$ cals. per mole at 100° C.

$$R = 2 \text{ cals.}$$

It follows that

$$\frac{x \times 13{\cdot}6 \times 981}{10^6} = \frac{536 \times 18}{2 \times (273 + 100)^2}$$

so that $$x = 2{\cdot}7 \text{ cms.}$$

i.e. the barometer must stand at 787 mms.

II. What will be the change in the freezing-point of water if the pressure be increased by 1 atmosphere ?

The Clapeyron Equation is for the case of fusion

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\lambda}{T(V_2 - V_1)}$$

where V_2 is the volume of 1 gm. of liquid water, V_1 is the volume of 1 gm. of solid ice. Experiment gives $V_2 = 1$ c.c. ; $V_1 = 1{\cdot}1$ c.c. Hence $V_2 - V_1 = 1 - 1{\cdot}1 = -0{\cdot}1$ c.c.

The latent heat of fusion per gram is 80 calories. If we measure the pressure in dynes this must be expressed in ergs, so that

$$\lambda = 80 \times 4{\cdot}2 \times 10^7 \text{ ergs per gram.}$$

Hence

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{80 \times 4{\cdot}2 \times 10^7}{273 \times (-0{\cdot}1)}$$

$$= -1{\cdot}2 \times 10^8 \text{ dynes per degree.}$$

The negative sign indicates that as the pressure increases the temperature of fusion falls. This is a consequence of the fact

that the volume of the liquid is less than that of the solid. If we express this coefficient in atmospheres per degree, since 1 atmosphere is equal to 10^6 dynes, we have—

$$\left(\frac{\partial P}{\partial T}\right)_V = -1{\cdot}2 \times 10^2 \text{ atmospheres per degree.}$$

The reciprocal of this gives the rise in temperature for an increase in pressure of 1 atmosphere, that is

$$-1/(1{\cdot}2 \times 10^2) = -0{\cdot}0083 \text{ degrees per atmosphere,}$$

i.e. the temperature of fusion falls 0·0083° for one atmosphere increase in pressure. It will be evident that this effect is extremely minute, as would be expected from the small volume change accompanying the fusion process. Note that for a substance such as benzene, for example, $\left(\frac{\partial P}{\partial T}\right)_V$ is not negative as in the case of water.

Another extremely important relation, which we are now in a position to derive, is the *Gibbs-Helmholtz Equation*. This is obtained by substituting the value of q for any reversible process given by equation (10) namely

$$q = T\left(\frac{\partial(-\Delta A)}{\partial T}\right)_V$$

in the expression, for a reversible process, of the First Law of Thermodynamics, viz.

$$\Delta U = q + \Delta A.$$

We thus obtain

$$\Delta U - \Delta A = T\left(\frac{\partial(-\Delta A)}{\partial T}\right)_V \quad . \quad . \quad . \quad . \quad (16)$$

The importance of this equation will be more manifest later. It is, as we have seen, a result of the combination of the First and Second Laws of Thermodynamics.

We must now consider the Second Law of Thermodynamics in greater detail and attempt to arrive at a more complete conception of its meaning and applicability. In the case of the passage of heat from one body to another, we saw that the Second Law differentiated between the "Natural" or spontaneous process—heat passing from a warm to a colder body, and the "impossible" process, i.e. the process which does not occur naturally, namely

the passage of heat from a cold to a warm body. Now we saw that the difference between these two types of process, in the case of heat transfer, is that whereas the former is always capable of yielding a certain finite amount of work, the latter process cannot be made to occur unless a finite amount of work is performed upon the system. It therefore seems not unnatural to extend these ideas to the case of any process whatsoever, and say that: All natural processes are, when properly applied, capable of yielding a finite quantity of mechanical work, and all unnatural processes, namely the reversal of natural processes, require for their accomplishment that a finite amount of work be performed upon the system. If the external conditions are such that the natural process yields the maximum work, i.e. if the process is reversible, then in order to reverse the process the same quantity of mechanical work is required by the system. Repeated efforts have been made to test the validity of this idea of the natural process and no single experimental exception has been observed. This, then, is one of the ways in which the Second Law may be stated.

Now, if we have a natural process occurring in some system, we know that the process will eventually stop and the system will no longer undergo any change. The system is then incapable of doing any external work and we say that it has arrived at a condition of *Equilibrium*. We may therefore say that every system which is not already in a condition of equilibrium, tends to change in such a manner as to attain to that state, and is, in virtue of this tendency, capable of performing a certain finite quantity of external work. This process of change towards a condition of equilibrium is sometimes spoken of as a "degradation of the system as a whole," since the quantity of external work which the system is capable of performing is gradually decreasing, and in fact the maximum work which the system is capable of producing will give us some measure of how far the system is from the equilibrium state. We shall employ this fact when we come to discuss equilibrium in greater detail. For the present, however, we propose to consider a more complete measure of the "tendency to change" of a system. This is the extremely important, though somewhat abstruse conception of **entropy.**

We have already seen that a reversible process is, strictly speaking, an impossibility. All actual, natural processes are therefore irreversible, and the reversible process is, in fact, the limiting case—

the point at which the natural process passes into the unnatural process. This will perhaps be made clearer by considering once more the process of expansion against a pressure. Consider a substance enclosed in a cylinder which is fitted with a piston. The piston, in moving outwards and allowing the substance inside the cylinder to expand, has to do work against an external pressure P.

If the pressure of the substance inside the cylinder is P_1 then so long as P is less than P_1 the system tends to expand naturally. This process is irreversible and the work done by the system is less than the maximum. As the external pressure is increased to approach the value of the internal pressure P_1, the process becomes more and more nearly reversible, and the tendency for it to occur becomes smaller, since there is greater resistance to overcome. In the limit, when P is equal to P_1, the process is reversible and cannot,

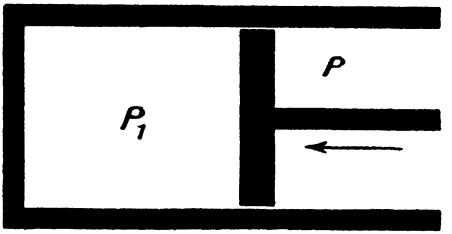

FIG. 8.

in actual fact, occur at all. If, however, P is still further increased, the natural process is no longer expansion but contraction and work must be performed upon the system to enable expansion to occur. We thus see that the measure of the " tendency to change " of a system is, in effect, a measure of the degree of irreversibility of the natural process which the system is undergoing at the moment of consideration.

Now, in order to find a suitable measure of the degree of irreversibility of a given process, we compare it with some standard irreversible process, and we here propose to adopt the simple standard process employed by Lewis and Randall in their introduction to the subject of entropy (*Thermodynamics and Free Energy of Chemical Substances*). This standard system consists of a coiled spring which naturally and therefore irreversibly tends to uncoil itself and thereby to perform a certain quantity of mechanical work. This work, we shall suppose to be converted, by friction,

into heat, and the heat to pass to a heat reservoir which is supposed to be of sufficient size that the heat absorbed does not alter the temperature T. Denote the quantity of heat which passes to the reservoir by q, then this quantity q gives us a partial measure of the degree of irreversibility of the process of uncoiling of the spring, since it is evident that the further the spring is coiled the more work it can do and consequently the more heat will be given up to the reservoir. This, however, is not quite complete. We must also consider the temperature of the reservoir. For suppose we have a system consisting of the spring and two reservoirs, the one at a temperature T, the other at the lower temperature T'. Then when the spring uncoils itself, heat q passes irreversibly to the reservoir at T. But we may now allow this same quantity of heat to pass from the warmer to the cooler reservoir, and this is a natural and therefore irreversible process. The net result is, however, the same as if the heat q had passed immediately into the second reservoir at T' and therefore the lower the temperature of the reservoir the greater the irreversibility of the process. Moreover, it is reasonable to say that if heat q passes from a reservoir at temperature T to one at absolute zero then the process is twice as irreversible as the passage of the same quantity of heat from a reservoir at temperature $\frac{T}{2}$ to one at absolute zero.

We thus see that the most complete measure of the degree of irreversibility of the process under consideration will be obtained by regarding it as directly proportional to the quantity of heat q which passes to the reservoir and inversely proportional to the absolute temperature of the reservoir, T, and it may therefore be defined as the ratio q/T. As the spring uncoils, the system approaches more nearly to the condition of equilibrium. It thus gains somewhat more of those properties which characterize the equilibrium state. We express this by saying that the system **gains in entropy**, and we equate the gain in entropy for the spring-reservoir system to q/T. Thus if S_1 be the initial and S_2 the final value of the entropy, then

$$S_2 - S_1 = \frac{q}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

We may note that entropy has the same dimensions as heat capacity and may therefore be expressed in calories per degree.

If, as usual, we denote an increase in entropy by ΔS, equation (17) becomes

$$\Delta S = \frac{q}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

for the spring-reservoir system which we have considered.

Having now defined our standard process, the next point is to consider how we may employ it to determine the degree of irreversibility of any other natural process occurring in some system, or, in other words, to determine the increase which occurs in the entropy of the system as a result of the process.

Suppose we consider some irreversible change, such, for instance, as a chemical reaction, occurring in a system A. Now we can imagine some mechanism by means of which this process may be completely reversed, provided mechanical work be done upon the system. This is not always easy in practice ; thus, for instance, if a complex material such as wood or paper be burned, there is no known method of reversing the process so that the products of combustion are transformed into the initial substances again. But this does not affect the thermodynamical argument. It is sufficient for our purpose that the process should theoretically be possible, and, in fact, is possible in certain simpler cases. Thus, for instance, when hydrogen and oxygen combine with explosive violence to form water the process is irreversible, but, by means of mechanical work, we can produce electrical energy and electrolyse the water formed, the original gases being reformed.

We now propose to supply the mechanical work necessary to restore the system completely to its initial state, by means of the energy of the coiled spring, and to effect the restoration, in such a manner, that every single step in the process is reversible. The temperature of the reservoir is regarded as equal to that of the system under consideration. The work which must be done upon the system by the spring is obviously, under these conditions, a minimum, being equal to the maximum work which the forward process was capable of performing if it had been conducted reversibly instead of irreversibly. The system (Spring + System A) has therefore gained in entropy by the amount ΔS, say. Suppose the work done by the spring is equivalent to heat q. Then the spring has lost this amount of energy. Suppose instead of causing this energy to do work upon system A, we had allowed it to pass to the reservoir at temperature T, then the increase of entropy of

the spring-reservoir system would be $\frac{q}{T}$. But the system A is now completely in its initial state, so that the entropy of the system is now restored to the value it had before the process occurred. Hence the forward change, which we are considering, corresponds to an increase in entropy of system A equal to

$$\Delta S = \frac{q}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

It will be evident that we have regarded Entropy as another property of the system, being completely determined by the present state of the system and in no way dependent upon its history. As in the case of Total Internal Energy U and Heat Content H, we are concerned only with changes in entropy and not with the actual value of the entropy of a system. It follows, from the definition of entropy change, that if we double the quantity of substance undergoing the change the heat term q will be doubled and hence the entropy change is doubled. Entropy is thus an extensive property of the system. It follows, also, that the entropy of any system is equal to the sum of the entropies of all the separate portions of that system.

We may, as in the case of Internal Energy U, state this fact, that the Entropy is a property of the system, in a somewhat different way by saying that the total change in entropy when a system passes through any cycle of changes, such that the initial and final states are identical, is zero, or, for a completed cycle

$$\Delta S = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

This is a very important and useful point of view.

We have thus obtained a method of determining the increase in entropy which occurs when any irreversible change takes place in a system, although the method may appear somewhat arbitrary and not always easy of application. The question of entropy presents, however, many difficulties to the student and it will be well to consider the matter a little more closely.

Suppose we have a **completely isolated system,** i.e. a system which is wholly segregated from its surroundings. We have seen that the total internal energy of such a system necessarily remains constant, since no energy can pass to or from the system. This is not, however, the case with the total entropy S of the system. Unless all the separate parts of the system are in equilibrium,

internal changes will occur. Thus, for instance, if our system consists of dilute brine in contact with sodium chloride, more salt dissolves in the solution. Again, if the system consists of a gas at high pressure in contact with the same gas at a lower pressure, the pressure tends to equalize itself by the diffusion of the gas from the region of higher to that of lower pressure. All such natural processes involve an increase in the entropy of the system as a whole and this increase may be determined by allowing the process to occur naturally and then bringing the isolated system into contact with the spring-reservoir system and causing the spring to do work reversibly upon the isolated system in such a manner that the system is completely restored to its initial state.

Suppose, however, that a reversible change occurs in this isolated system. Now we may cause such a process to go in the opposite direction, without requiring to perform any work upon the system *from outside*, that is without our having recourse to the spring-reservoir system at all. Hence it follows that when a reversible process occurs in an isolated system the entropy of the system remains constant. This follows immediately from our definition of entropy change as degree of irreversibility, since obviously, the degree of irreversibility of a reversible process is zero.

We are now in a position to make what is, in effect, the most general and complete statement of the Second Law of Thermodynamics.

In any **completely isolated system** the entropy tends to increase to a maximum value, unless it has already attained to that maximum value, that is, unless the system has already arrived at a condition of equilibrium.

It should, however, be carefully noted that this definition only applies to a completely isolated system. Now, in actual practice, we can never deal with such a system, although we sometimes approximate to one, and it is by no means true that the entropy of every part of an isolated system or the entropy of a non-isolated system always tends to increase when the system is not in equilibrium. Thus, for instance, suppose we have a body at a temperature $T + dT$ in contact with a large reservoir of heat at temperature T. Heat will pass from the body to the reservoir. Let the amount of heat which so passes be q. Now since the difference in temperature is infinitesimally small, the process will be, in effect, reversible. Nevertheless, heat has passed from the body and we propose to

inquire what change, if any, has occurred in the entropy of the body itself irrespective of the reservoir. Now we cannot simply employ the spring-reservoir system to reverse the process, for that involves bringing in the reservoir again, or some other reservoir of the same temperature, and we have already seen that for the total system Body + Reservoir there has been, since the passage of heat was effected reversibly, no change in entropy. The reverse change could therefore be accomplished without requiring the spring at all and we have not arrived at a solution of the problem of the entropy change in the body itself. Let us, however, consider what happened to the reservoir during the initial process of the passage of heat q from the body. This heat q was absorbed by the reservoir and it could have been obtained by the uncoiling of a spring, in connection, as before, with the reservoir. The spring-reservoir system would thus have suffered a **degradation** and therefore an **increase in entropy** of amount $\frac{q}{T}$. Hence the body must have undergone a *decrease* in entropy of $\frac{q}{T}$.

In general, therefore, if a body absorbs heat **reversibly,** from the surroundings, of amount q calories, then there is an **increase** in the entropy of the body ΔS, where

$$\Delta S = \frac{q}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

T being the temperature of the body.

This very important relation is the usual definition of entropy change and is that employed originally by Clausius. It is, however, far more difficult to comprehend its meaning from this point of view since it is essentially as a measure of the irreversibility of a process that we require the concept of entropy.

It may be useful here to summarize our ideas of entropy changes as follows:

(i) In any completely isolated system the entropy tends to increase towards a maximum unless the system has already attained a condition of equilibrium. The entropy increase is a measure of the degree of irreversibility of the process occurring in the system. If the process is reversible the change in entropy is zero.

(ii) For a non-isolated system, we can postulate no such general law. If, however, the process occurring is reversible and involves

the absorption of heat q from the surroundings there is an increase in entropy of $\frac{q}{T}$ where T is the temperature of the system. If the system absorbs heat q reversibly and converts this into work there is a decrease in the work content but an *increase* in the entropy of $\frac{q}{T}$, or, since $q = -\Delta A$, the increase in entropy is $\frac{-\Delta A}{T}$. It will be evident that in the very familiar process of the radiation of heat from a warm to a cold body, there is a **decrease** in the entropy of the warm body. Since, however, the process of radiation is irreversible the decrease is less than the increase in entropy of the cooler body, so that the total entropy of the two bodies together increases.

CHAPTER III

SOME CONSEQUENCES OF THE FIRST AND SECOND LAWS

We have now considered, in some detail, the two fundamental laws, upon which the whole of the classical structure of Thermodynamics was built. Before proceeding, however, to apply these laws to the specific problems of physical chemistry, we shall find it of great advantage to develop our ideas by tracing some of the more important consequences of these laws. For this purpose, the language of mathematics is undoubtedly the simplest to employ, although the student may not find it always the easiest to understand. It will therefore be found advantageous, wherever possible, to translate the results obtained by means of mathematical reasoning into the ordinary language of the physical chemist.

In the first place, we know that the heat dq which is absorbed when any system is warmed through an infinitesimally small interval of temperature dT is

$$dq = CdT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where C is the heat capacity of the system. If, now, the volume is maintained constant, the heat capacity C becomes C_v so that

$$dq' = C_v dT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Suppose now that the volume is changed by an infinitesimal amount dV while the temperature is kept constant. Then since L is the latent heat of expansion of the system per unit increase in volume, the heat dq'' absorbed is LdV. The net result is the same as if the volume change and the temperature change had occurred simultaneously so that the total heat absorbed over the whole process is $dq = dq' + dq''$, that is

$$dq = C_v dT + LdV \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This is a perfectly general equation and refers to any change which takes place in a system. The expansion is effected against the pressure P of the surroundings, so that the work done by the

system is PdV. In general this process will be accompanied by a change in the total internal energy U of the system. Let us suppose that the internal energy is increased by an infinitesimal amount dU, then the First Law for the system takes the form—

$$dU = dq - PdV \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Substituting the value of dq given by equation (3) we obtain—

$$dU = C_v dT + (L - P)dV \quad . \quad . \quad . \quad . \quad (5)$$

Let us now apply this equation to the particular case of a perfect gas. We have seen, in our consideration of Joule's experiment, that the internal energy of a perfect gas is a function of the temperature alone, being independent of the volume occupied. Hence the term containing the volume element dV must be zero, that is, for a perfect gas—

$$(L - P)dV = 0$$

or $$L = P \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and $$dU = C_v dT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

We may therefore substitute P for L in equation (3) and obtain, for the case of a perfect gas—

$$dq = C_v dT + PdV \quad . \quad . \quad . \quad . \quad . \quad (8)$$

We have, in the previous chapter, defined the entropy as an extensive property of any system, and we have shown that for any completed cycle of changes there is no change in the total entropy, or $\Delta S = 0$. It will, however, be instructive to consider a cyclic change performed upon a perfect gas and to follow the entropy changes which occur.

We have seen that when a perfect gas undergoes any change whatsoever, the following relation between the heat absorbed and the changes in volume and temperature, must be satisfied at every step in the process:

$$dq = C_v dT + PdV.$$

If the process is conducted reversibly P is equal to the pressure of the gas itself and moreover we may, for such a process, obtain the entropy change, simply by dividing this expression through by the temperature T. Thus

$$dS = \frac{dq}{T} = C_v \frac{dT}{T} + P\frac{dV}{T} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

If we are dealing with one mole of a perfect gas we may apply the gas law in the form $PV = RT$, so that equation (9) becomes—

$$dS = \frac{dq}{T} = C_v \frac{dT}{T} + R\frac{dV}{V}$$
$$= C_v d\ ln\ T + Rd\ ln\ V \quad . \quad . \quad (10)$$

Now since we may assume that the molecular heat of a perfect gas at constant volume C_v is a constant, we may integrate equation (10) and obtain—

$$S = C_v\ ln\ T + R\ ln\ V + S' \quad . \quad . \quad . \quad . \quad (11)$$

where S' is an integration constant.

This is an equation of great importance and is the so-called entropy equation of a perfect gas. The constant S' is evidently the value of the entropy of one mole of a perfect gas at one degree absolute when it occupies unit volume (that is the entropy it would have if it could exist as a gas under these conditions). Its value is not determinable on the basis of elementary thermodynamics.

If, now, we allow the volume of the mole of gas which we are considering to change from V_1 to V_2, while the temperature changes from T_1 to T_2, then the entropy changes from S_1 to S_2, where

$$S_2 - S_1 = C_v\ ln \frac{T_2}{T_1} + R\ ln \frac{V_2}{V_1} \quad . \quad . \quad . \quad . \quad (12)$$

Now it is evident that if we consider the gas to undergo any complete cycle of changes so that the initial and final states are identical, i.e. $V_1 = V_2$ and $T_1 = T_2$, then equation (12) becomes—

$$S_2 - S_1 = C_v\ ln \frac{T_1}{T_1} + R\ ln \frac{V_1}{V_1} = 0 \quad . \quad . \quad . \quad (13)$$

or the initial and final values of the entropy are the same. Thus we see that for the case of a perfect gas the total entropy change over a complete cycle is zero so that entropy is a true property of the system.

Dependence of Entropy upon the Variables of a System. We now propose to consider the variation of the entropy of any system whatsoever with the other variables Pressure, Volume and Temperature. According to equation (1), we have—

$$dq = CdT$$

so that

$$dS = \frac{dq}{T} = C\frac{dT}{T} = Cd\ ln\ T \quad . \quad . \quad . \quad . \quad (14)$$

This is the most general equation for the entropy change, but its use is restricted, since we do not ordinarily measure the heat capacity except for changes either at constant volume or constant pressure. Suppose the volume of the system to be maintained constant, then equation (14) becomes

$$dS = \frac{dq}{T} = C_v dT/T$$

or expressed with greater mathematical precision, since the volume is not allowed to vary,

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

This equation shows us that for any system undergoing a change at constant volume the entropy-temperature coefficient or the slope of the entropy-temperature diagram is equal to the ratio of the heat capacity at constant volume to the absolute temperature.

Again, if we keep the pressure constant we obtain—

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

This is perhaps an even more important equation than expression (15), since, as we have already remarked, most of our experimental work is performed at constant pressure. It enables us to calculate the entropy change occurring in any system as a result of an increase in the temperature.

But we have already seen that $C_v = \left(\frac{\partial U}{\partial T}\right)_V$, so that equation (15) becomes—

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

and $C_p = \left(\frac{\partial H}{\partial T}\right)_P$, so that equation (16) becomes—

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

We may now perform the purely mathematical operation of differentiating equation (17) with respect to volume keeping the temperature constant. We thus obtain

$$\frac{1}{T}\left(\frac{\partial C_v}{\partial V}\right)_T = \frac{\partial^2 S}{\partial T \partial V} = \frac{1}{T}\frac{\partial^2 U}{\partial T \partial V} \quad . \quad . \quad . \quad . \quad (19)$$

Similarly, from equation (18) we obtain

$$\frac{1}{T}\left(\frac{\partial C_p}{\partial P}\right)_T = \frac{\partial^2 S}{\partial T \partial P} = \frac{1}{T}\frac{\partial^2 H}{\partial T \partial P} \quad . \quad . \quad . \quad . \quad (20)$$

Now according to equation (4), we have, for any system—

$$dU = dq - PdV$$

and since $dS = \frac{dq}{T}$, we may write—

$$dU = TdS - PdV \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Let us confine our attention to an isothermal process and divide the equation through by dV. We obtain

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P. \quad . \quad . \quad . \quad . \quad (22)$$

Differentiate equation (22) with respect to the temperature keeping the volume constant, then

$$\frac{\partial^2 U}{\partial V \partial T} = T\frac{\partial^2 S}{\partial T \partial V} + \left(\frac{\partial S}{\partial V}\right)_T - \left(\frac{\partial P}{\partial T}\right)_V \quad . \quad . \quad . \quad (23)$$

But by equation (20)

$$\frac{\partial^2 U}{\partial V \partial T} = T\frac{\partial^2 S}{\partial T \partial V}$$

so that equation (23) becomes

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad . \quad . \quad . \quad . \quad . \quad (24)$$

This equation tells us that for any system at a given temperature, pressure and volume, the entropy-volume coefficient for a reversible isothermal change is equal to the slope of the pressure temperature diagram, or the pressure-temperature coefficient for a reversible change at constant volume. We are thus enabled to calculate the change in the entropy of a system corresponding to a change in volume, at constant temperature.

This equation involves, however, a coefficient $\left(\frac{\partial P}{\partial T}\right)_V$ which is rarely measured in practice, so that it is usual to transform it by means of equation I (19), which states that

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \Big/ \left(\frac{\partial V}{\partial P}\right)_T$$

so that

$$\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \Big/ \left(\frac{\partial V}{\partial P}\right)_T \quad . \quad . \quad . \quad . \quad (25)$$

Now the coefficient of cubical expansion of a system is always measured at constant pressure and is therefore $\left(\frac{\partial V}{\partial T}\right)_P \cdot \frac{1}{V}$. Let us denote this by α. Again $-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ is the so-called coefficient of compressibility so that, denoting this by β, equation (25) becomes

$$\left(\frac{\partial S}{\partial V}\right)_T = \alpha/\beta \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

Again, we have defined the heat content of a system, H by

$$H = U + PV.$$

Hence $$dH = dU + PdV + VdP$$

which, by equation (4) becomes

$$dH = TdS + VdP \quad . \quad . \quad . \quad . \quad . \quad (27)$$

In precisely the same manner as before, we obtain

$$V = -T\left(\frac{\partial S}{\partial P}\right)_T + \left(\frac{\partial H}{\partial P}\right)_T \quad . \quad . \quad . \quad . \quad . \quad (28)$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad . \quad . \quad . \quad . \quad . \quad (29)$$

or substituting again the value for the coefficient of cubical expansion α, we obtain

$$\left(\frac{\partial S}{\partial P}\right)_T = -\alpha V \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

This equation tells us that the entropy-pressure coefficient for an isothermal process is opposite in sign but numerically equal to the product of the volume and the coefficient of cubical expansion of the system. We have thus shown how the entropy changes with volume and pressure in the case of an isothermal process.

Let us now substitute the value of $\left(\frac{\partial S}{\partial V}\right)_T$ given by equation (24) in equation (22). The resulting equation is

$$P = T\left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial U}{\partial V}\right)_T \quad . \quad . \quad . \quad . \quad . \quad (31)$$

In a similar manner from equations (28) and (29) we obtain

$$V = T\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial H}{\partial P}\right)_T \quad . \quad . \quad . \quad . \quad . \quad (32)$$

These equations are of great importance since they amount to

thermodynamical equations of state which must be satisfied by any system whatever.

Now, in our consideration of the first law, we obtained the relation (equation I (23))—

$$C_p - C_v = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P.$$

Substitute the value of P given by equation (31) and we arrive at the important relation—

$$C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P \quad . \quad . \quad . \quad . \quad (33)$$

which again on introducing the expression given by equation I (19) becomes

$$C_p - C_v = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \Big/ \left(\frac{\partial V}{\partial P}\right)_T \quad . \quad . \quad . \quad (34)$$

Substituting the value of the coefficient of expansion $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ and the coefficient of compressibility $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ we obtain

$$C_p - C_v = \frac{\alpha^2 VT}{\beta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

This equation is of great practical utility, since the values of the coefficients on the right-hand side are all easily obtainable and we are thus enabled to calculate C_v, which is difficult to determine directly, from the known values of C_p. The equation is, as we have seen, perfectly general and is applicable to any system whatsoever.

It may be of interest as an example of the mathematical manipulation of these quantities, to deduce, from a consideration of entropy change, a relation already obtained (equation II (13)) for the latent heat of expansion of a system, namely $L = T\left(\frac{\partial P}{\partial T}\right)_V$.

We may start with equation (3),

$$dq = C_v dT + L dV$$

from which we obtain, by dividing through by T, the entropy equation for any system—

$$dS = \frac{dq}{T} = \frac{C_v dT}{T} + \frac{L dV}{T} \quad . \quad . \quad . \quad . \quad . \quad (36)$$

Now we know, that since S is a property of the system, or in other words, since dS is a complete differential, so that over a complete cycle $\int dS = 0$, we can apply equation I (25) and obtain—

$$\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right).$$

From equation (35) for a change at constant volume, since $dV = 0$ we obtain $\left(\frac{\partial S}{\partial T}\right)_V = C_v/T$ an equation which we have already derived earlier in this chapter (equation 15). We obtain—

$$\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right) = \frac{1}{T}\left(\frac{\partial C_v}{\partial V}\right).$$

Similarly, we have

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{L}{T}$$

$$\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right) = \frac{1}{T}\cdot\frac{\partial L}{\partial T} - \frac{L}{T^2}.$$

Hence we obtain

$$\frac{1}{T}\left(\frac{\partial C_v}{\partial V}\right) = \frac{1}{T}\cdot\frac{\partial L}{\partial T} - \frac{L}{T^2}$$

or

$$\frac{\partial C_v}{\partial V} = \frac{\partial L}{\partial T} - \frac{L}{T} \quad \ldots\ldots\ldots \quad (37)$$

Now we have also seen, that according to equation (5)

$$dU = C_v dT + (L - P)dV$$

so that, applying equation I (25) again, since for a cycle $\int dU = 0$, we have

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right).$$

Now $\left(\frac{\partial U}{\partial T}\right)_V = C_v$, so that

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right) = \frac{\partial C_v}{\partial V}$$

again $\frac{\partial U}{\partial V} = L - P$, so that

$$\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right) = \frac{\partial L}{\partial T} - \frac{\partial P}{\partial T}$$

Hence, combining these two equations, we obtain

$$\frac{\partial C_v}{\partial V} = \frac{\partial L}{\partial T} - \frac{\partial P}{\partial T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

Equating the two values of $\frac{\partial C_v}{\partial V}$ given by equations (37) and (38) results in

$$\frac{\partial L}{\partial T} - \frac{L}{T} = \frac{\partial L}{\partial T} - \frac{\partial P}{\partial T}$$

or

$$L = T\left(\frac{\partial P}{\partial T}\right)_V \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

which is the expression we proposed to derive.

A very useful expression may be obtained from equation (39) as follows: Let us differentiate the equation with respect to temperature, the volume being kept constant. We obtain—

$$\left(\frac{\partial L}{\partial T}\right)_V = \left(\frac{\partial P}{\partial T}\right)_V + T\left(\frac{\partial^2 P}{\partial T^2}\right)_V.$$

Now equation (37) gives

$$\left(\frac{\partial C_v}{\partial V}\right)_T = \left(\frac{\partial L}{\partial T}\right)_V - \left(\frac{\partial P}{\partial T}\right)_V$$

so that combining the two

$$\left(\frac{\partial C_v}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right) \quad . \quad . \quad . \quad . \quad . \quad (40)$$

We have hitherto regarded the heat term dq as made up of two portions $C_v dT$ and $L dV$ representing the heat involved in the changes in temperature and volume accompanying the process. We may, however, consider it from the slightly different point of view of the changes which occur in the pressure and temperature. Thus suppose the increase in temperature is dT, and the increase in pressure is dP, then the heat absorbed during the process may be regarded as the sum of two terms, (*a*) the amount of heat required to raise the temperature through an interval dT while the pressure is kept constant, namely $C_p dT$; and (*b*) the amount of heat absorbed when the pressure changes by dP. If we let L' be the latent heat of the pressure change, that is the heat required to keep the temperature constant when the pressure is changed

by one unit, then the heat absorbed, as a result of pressure change dP, is $L'dP$, so that

$$dq = C_p dT + L'dP \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

and dividing through by T

$$dS = \frac{dq}{T} = \frac{C_p dT}{T} + L'\frac{dP}{T} \quad . \quad . \quad . \quad . \quad . \quad (42)$$

We may now follow the same method as that employed in the deduction of equation (39), and obtain

$$\frac{\partial}{\partial P}\left(\frac{\partial S}{\partial T}\right) = \frac{\partial}{\partial P}\left(\frac{C_p}{T}\right)$$

$$\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial P}\right) = \frac{\partial}{\partial T}\left(\frac{L'}{T}\right).$$

These are equal, so that

$$\frac{1}{T}\frac{\partial C_p}{\partial T} = \frac{1}{T}\cdot\frac{\partial L'}{\partial T} - \frac{L'}{T^2}$$

or

$$\frac{\partial C_p}{\partial T} = \frac{\partial L'}{\partial T} - \frac{L'}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

Now we have by equation (4)

$$dU = dq - PdV$$

so that $dH = d(U + PV) = dU + PdV + VdP$

becomes $dH = dq + VdP \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$

Now H is a property of the system, so that as before—

$$\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right).$$

Hence, since we have

$$\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial T}\right) = \frac{\partial C_p}{\partial P} \text{ and } \frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right) = \frac{\partial(L' + V)}{\partial T}$$

therefore

$$\frac{\partial C_p}{\partial P} = \left(\frac{\partial L'}{\partial T}\right)_P + \left(\frac{\partial V}{\partial T}\right)_P \quad . \quad . \quad . \quad . \quad . \quad (45)$$

Combining equations (43) and (45) we obtain—

$$L' = -T\left(\frac{\partial V}{\partial T}\right)_P \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

Substituting the value of the coefficient of cubical expansion this expression becomes—

$$L' = -TV\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

Differentiate equation (46) with respect to temperature keeping the pressure constant. We obtain

$$\left(\frac{\partial L'}{\partial T}\right)_P = -\left(\frac{\partial V}{\partial T}\right)_P - T\left(\frac{\partial^2 V}{\partial T^2}\right)_P \quad . \quad . \quad . \quad (48)$$

Combining this with equation (45) we obtain

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T\frac{\partial^2 V}{\partial T^2} \quad . \quad . \quad . \quad . \quad . \quad (49)$$

Equations (40) and (49) are important since they show us how the specific heat of a system varies with the volume and the pressure while the temperature is maintained constant. We shall deal with these variations later when we come to consider the equations of state.

Changes in Entropy accompanying various Processes

A consideration of great value, which will, no doubt, render the concept of entropy much clearer, is the question of its practical application. We therefore propose to calculate the entropy changes occurring in some of the more important processes with which the physical chemist has to deal.

We have seen that for any reversible process, occurring in a non-isolated system, and involving the absorption of heat q at a temperature T, the increase in entropy ΔS is given by—

$$\Delta S = \frac{q}{T}.$$

Let us now apply this equation to the case of the vaporization of water under the pressure of its own vapour at 100° C. The water and its vapour are in equilibrium and we may therefore imagine the process accomplished reversibly as follows. Suppose we have a cylinder A (Fig. 9), containing water at 100° C. above which is the water vapour at the equilibrium vapour pressure of one atmosphere. The cylinder is closed by means of a piston ab which is weighted so that the downward pressure is smaller than one atmosphere by an infinitesimal amount. Heat q is supplied to the system and one mole of water is vaporized at the constant pressure of the atmosphere, the piston rising to the position $a'b'$.

The entropy increase in this mole of water is q/T where T is the absolute temperature. But the heat absorbed per gram, i.e. the latent heat of vaporization per gram, is 536 calories, so that the heat q absorbed per mole is 536×18 cals. Hence the increase in entropy is

$$\Delta S = \frac{536 \times 18}{(273 + 100)} \text{ cals. per degree.}$$

$$= 25{\cdot}87 \text{ cals. per degree.}$$

This may best be expressed by means of an equation such as

$$H_2O \text{ (liquid ; 1 atmosphere)} = H_2O \text{ (vapour ; 1 atmosphere)}$$
$$\Delta S^* = 25{\cdot}87 \text{ cals. per degree.}$$

The case of fusion may be treated in exactly the same manner provided we are considering equilibrium conditions.

In general, however, we are not considering a reversible process and the question arises as to how we are to calculate the change in entropy of a non-isolated system when an irreversible process takes place. It should be carefully noted that we cannot equate the entropy increase to the ratio of the heat absorbed during the process and the absolute temperature, since the relation (50) only holds for reversible processes. The entropy change is usually very different from the ratio $\frac{q}{T}$.

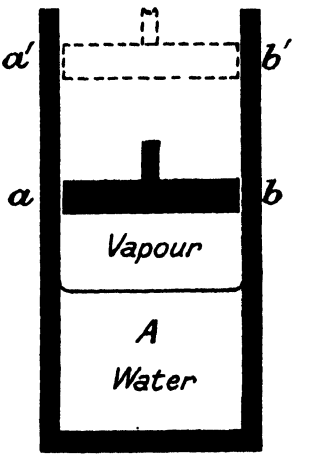

Fig. 9.

Now we have shown that the entropy is a property of any system so that if, by any series of processes whatsoever, we cause a system to pass from a state A to another state B, the entropy difference between A and B is entirely independent of the path traversed. We may therefore imagine some particular path which is reversible at every step in the process, and by calculating the entropy changes which occur in this reversible process, we arrive at the entropy difference between the system in the two states A and B.

When the process occurring is simply one of expansion or of a change in pressure while the temperature is maintained constant

we may employ the equations already deduced (equations 25 and 26; and equations 29 and 30).

$$\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \Big/ \left(\frac{\partial V}{\partial P}\right)_T = \alpha/\beta \quad (25 \text{ and } 26)$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -\alpha V \quad (29 \text{ and } 30)$$

Thus, for example, we may employ the second equation, in the form

$$\int dS = -\int (\alpha V).\, dP \quad . \quad . \quad . \quad . \quad . \quad (51)$$

to calculate the difference in entropy between water in equilibrium with its own vapour at 25° (vapour pressure 0·0313 atmospheres) and at 100° C. (vapour pressure 1 atmosphere) as a result solely of the change in pressure, i.e. disregarding the temperature change. We shall take the coefficient of cubical expansion of water per mole (i.e. αV) at 25° C. as 0·00465 and regard this as constant, independent of pressure. Hence

$$\int dS = -0{\cdot}00465 \int_{P=0{\cdot}0313 \text{ atm.}}^{P=1 \text{ atm.}} dP$$

or $\Delta S = -0{\cdot}00465 \times 0{\cdot}97$ c.c. atmospheres per degree.

that is $-0{\cdot}0045$ c.c. atmospheres per degree.

Now 1 atmosphere $= 10^6$ dynes and 1 calorie $= 4{\cdot}2 \times 10^7$ ergs, so that ΔS becomes

$$-\frac{0{\cdot}0045 \times 10^6}{4{\cdot}2 \times 10^7} = -0{\cdot}00011 \text{ cals. per degree.}$$

This is evidently a very small quantity, far smaller than the change in entropy as a result of the temperature change.

In order to measure the change in entropy accompanying a change in temperature of the system we may employ equations (15) and (16) namely,

$$\left(\frac{\partial S}{\partial T}\right)_V = C_v/T; \quad \left(\frac{\partial S}{\partial T}\right)_P = C_p/T.$$

These equations may be integrated most simply if the specific heat be regarded as a constant. This, however, is not always permissible and the specific heat must therefore be expressed as a function of the temperature. Thus, for instance, the heat capacity at constant

pressure of water vapour per mole may be expressed, within the limits of experimental error for any temperature between 0° C. and 2000° C., by the empirical relation

$$C_p = 8{\cdot}81 - 0{\cdot}0019T + 0{\cdot}00000222T^2$$

Hence $$C_p/T = \frac{8{\cdot}81}{T} - 0{\cdot}0019 + 0{\cdot}00000222T$$

from which we obtain on integrating—

$$\int dS = 8{\cdot}81 \; ln \; T - 0{\cdot}0019T + 0{\cdot}00000111T^2 + \text{Constant.}$$

If now we substitute the limits of the temperature change we are considering, we obtain the entropy change of the process. Thus if the limits are T_1 and T_2, then, neglecting the last term

$$S_2 - S_1 = 8{\cdot}81 \; ln\frac{T_2}{T_1} - 0{\cdot}0019(T_2 - T_1).$$

The entropy change occurring in a chemical reaction will be considered later. The change is very far from being reversible, so that the relation $\Delta S = q/T$, does not hold.

A type of process which is of considerable interest and importance, and which has not yet received our attention, is the so-called adiabatic process. This is the name given to any process in which no heat is either gained or lost by the system. The system is not completely isolated since it is capable of performing work upon the surroundings, but no heat is able to pass to or from the system.

Let us consider one mole of a perfect gas expanding adiabatically by the amount dV against an external pressure P. Then the work done is PdV. Now by the first law

$$dU = dq - PdV$$

and since $dq = 0$, it follows that

$$dU = -PdV \quad . \quad . \quad . \quad . \quad . \quad . \quad (52)$$

But we have seen that for a perfect gas (equation 7)

$$dU = C_v dT.$$

Hence it follows that

$$PdV = -C_v dT$$

or, since for one mole of gas, we may write $PV = RT$, we obtain—

$$\frac{RT}{V}dV = -C_v dT$$

which is the same as

$$R.d\ ln\ V = -\ C_v d\ ln\ T \quad . \quad . \quad . \quad . \quad (53)$$

Now, for a perfect gas we may regard C_v as a constant and integrate this equation

$$R.ln\ V = -\ C_v\ ln\ T + \text{Constant} \quad . \quad . \quad . \quad (54)$$

or, since again C_v is a constant we may divide through by it and obtain

$$\frac{R}{C_v}\ ln\ V = -\ ln\ T + \text{Constant}$$

which is equivalent to

$$T.V^{R/C_v} = \text{Constant} \quad . \quad . \quad . \quad . \quad . \quad (55)$$

Now we have seen that for any substance whatever equation I (23) gives

$$C_p - C_v = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P.$$

But in the case of a perfect gas we have shown that the total internal energy is independent of the volume, i.e. $\left(\frac{\partial U}{V}\right)_T = 0$ and, since by the gas law, $PV = RT$ for one mole we have $V = RT/P$. We may now differentiate this expression with respect to T, keeping the pressure constant and obtain—

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}.$$

Hence equation I (23) becomes

$$C_p - C_v = (P)\frac{R}{P} = R.$$

We may therefore transform equation (55) as follows:

$$T.V^{R/C_v} = T.V^{(C_p - C_v)/C_v} = \text{Constant}.$$

That is $$\frac{T.V^{C_p/C_v}}{V} = \text{Constant}.$$

Now $T/V = P/R$ so that the equation becomes

$$\frac{P}{R}.V^{C_p/C_v} = \text{Constant}$$

or putting $C_p/C_v = \gamma$ and including R in the constant

$$PV^{\gamma} = \text{Constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad (56)$$

This is the well-known equation governing adiabatic changes. If we consider the pressure volume diagram for the case of a simple compression from volume V_1 to volume V_2, it shows us at once that the curve for the adiabatic compression is steeper than the corresponding curve for the isothermal process. The latter, of course, obeys the simple law of Boyle $PV = \text{Constant}$. In the diagram (Fig. 10) AB represents the adiabatic compression, while AC represents the isothermal compression between the same volume limits. The work required in the adiabatic compression is obviously greater than that required in the isothermal by an amount represented by the area ABC.

As regards the entropy change which accompanies an adiabatic change it is evident that, if the process which occurs is reversible, since no heat is either gained or lost by the system, the entropy change $\Delta S = \frac{q}{T}$ will be zero. Such a process is frequently termed **isentropic.**

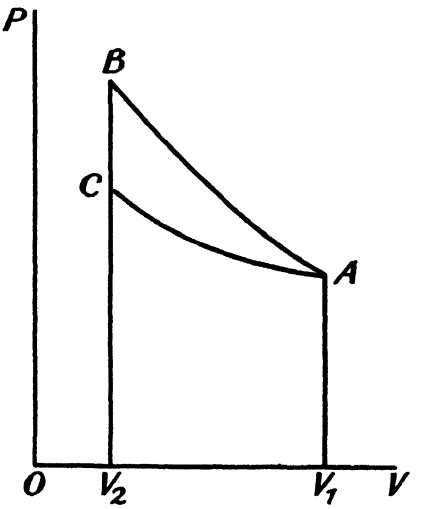

FIG. 10.

When such a process as we have just considered occurs it is accompanied by a change in the temperature. This temperature change may be obtained by means of the following equations which are valid for any system and are not restricted to the case of a perfect gas.

Since the entropy is a property of the system we may apply the equation I (19) and obtain equations of the form

$$\left(\frac{\partial T}{\partial P}\right)_S = -\left(\frac{\partial S}{\partial P}\right)_T \Big/ \left(\frac{\partial S}{\partial T}\right)_P \quad . \quad . \quad . \quad (57)$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial S}{\partial V}\right)_T \Big/ \left(\frac{\partial S}{\partial T}\right)_V \quad . \quad . \quad . \quad (58)$$

Now we have seen that according to equations (15) and (16)

$$\left(\frac{\partial S}{\partial T}\right)_P = C_p/T\,; \quad \left(\frac{\partial S}{\partial T}\right)_V = C_v/T$$

and by equations (26) and (30) we have

$$\left(\frac{\partial S}{\partial V}\right)_T = \alpha/\beta\,; \quad \left(\frac{\partial S}{\partial P}\right)_T = -\alpha V$$

so that equations (57) and (58) become

$$\left(\frac{\partial T}{\partial P}\right)_S = +\alpha V.T/C_p \quad . \quad . \quad . \quad . \quad (59)$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\alpha T/\beta C_v \quad . \quad . \quad . \quad . \quad . \quad (60)$$

If the adiabatic process under consideration is not reversible, however, the system is no longer isentropic and the entropy change can, as usual, be determined by effecting the change from initial to final states by means of a series of reversible processes. These processes will not, however, be adiabatic since the entropy as a whole has changed and some heat will therefore be evolved or absorbed by the system in the reversible changes.

These calculations will suffice for the present in giving the student an indication of the methods adopted in the application of entropy considerations. For a more complete account the reader is referred to Lewis and Randall's book already mentioned.

Entropy in Terms of the Molecular Hypothesis.

Before leaving the subject of entropy, however, we may very profitably spend some time considering it from a somewhat different point of view, namely that of the Kinetic Theory. According to this theory, matter consists of a very large number of extremely small " particles " in various types of motion—translatory, vibratory, rotatory. In the simple case of a monatomic gas only translatory motion is possible and the kinetic energy of the molecules corresponds to the heat energy of the system (and the Total Internal Energy U). From a consideration of this energy, several useful laws have been deduced, such, for example, as Boyle's or Charles's laws. Now in the elementary treatment of this case it is often expedient to simplify the mathematical calculation by attributing to each individual molecule, the same velocity. But this is by no means what actually obtains in practice. The molecular velocity varies within wide limits, although it is true that certain velocities are more favoured than others, and in order to arrive at a meaning for the term entropy it is necessary to take account of this fact

Now, it is manifestly impossible to deal individually with each molecule in turn. Some method of averaging must be adopted if the mathematics is to be feasible at all and the method which is employed is that known as Statistical Mechanics. This method depends essentially, as its name implies, upon the application of the laws of Statistics or Probability to the system under consideration and their combination with the ordinary laws of mechanics. Suppose we are considering some property P possessed in varying amounts by all the molecules of the system, then Statistical Mechanics attempts to determine the distribution of that property, that is, it attempts to find a specification of the number N_1 of molecules for which the amount of the property P lies between P_1 and $P_1 + \delta P_1$; the number N_2 having the value of P between P_2 and $P_2 + \delta P_2$ and so on. Such a specification is known as a statistical statement of the system with respect to the property P and from it we may obtain the distribution of the property P.

The laws of Probability, which form the basis of the calculation may be stated simply as follows:

I. If an event may occur in any one of a ways and fail in any one of b ways then the mathematical probability of its occurrence ϕ is given by—

$$\phi = \frac{a}{a+b} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (61)$$

II. The probability of the simultaneous occurrence of two or more independent events is the product of the probabilities of each individual. Thus if we have three events the probabilities of which are respectively ϕ_1, ϕ_2, ϕ_3, then the mathematical probability of their simultaneous occurrence is

$$\phi = \phi_1.\phi_2.\phi_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (62)$$

Suppose we have a system of gas molecules and we require to find the distribution of some property P such as the kinetic energy, or molecular velocity, then a complete statistical statement of the system would, as we have seen, take the form—

N_1 molecules have value of P between P_1 and $P_1 + \delta P_1$
N_2 molecules have value of P between P_2 and $P_2 + \delta P_2$
N_3 molecules have value of P between P_3 and $P_3 + \delta P_3$.

On the other hand, if we could consider each molecule in turn A, B, C, D, etc., we should obtain a still more complete statement which would take the form:

The N_1 molecules between P_1 and $P_1 + \delta P_1$ comprise A, B, E, etc.
The N_2 molecules between P_2 and $P_2 + \delta P_2$ comprise C, D, G, etc.,

and so on, each individual molecule being assigned a place in the scheme. Such a complete specification is termed a microscopic statement of the system. Now, it is evident, that for any given statistical state there are a very large number of possible microscopic states and the number of such possible microscopic states is, in effect, the number of ways in which that particular statistical state may exist.

The mathematical probability ϕ of any particular statistical state is therefore given by the total number of microscopic states, W, corresponding to this statistical state, divided by the total number M of microscopic states for all possible statistical states. We may express this mathematically thus—

$$\phi = W/M \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (63)$$

It will at once be evident that W is less than M so that ϕ cannot be greater than unity and, moreover, if we sum the values of the mathematical probability for all the possible statistical states the result is unity, that is

$$\Sigma\phi = \frac{\Sigma W}{M} = M/M = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (64)$$

For any given system, however, the denominator M representing the total number of microscopic states in which the system can exist must be a constant, independent of the particular statistical state under consideration. Hence we may ignore this quantity and regard the numerator W as a measure of the probability of the given statistical state. W is known as the **thermodynamical probability** for reasons which will appear as we proceed, and we may therefore define the thermodynamical probability of any statistical state as the total number of ways in which the statistical state may be realized or the total number of microscopic states corresponding to that statistical state. Now it is well known that if N is the total number of molecules and we have N_1 in one class, N_2 in another, N_3 in a third and so on, then the total number of ways in which this arrangement may obtain is given by

$$W = \frac{N!}{N_1!\ N_2!\ N_3!\ \ldots} \quad . \quad . \quad . \quad . \quad . \quad . \quad (65)$$

This, then, is a definition of the thermodynamic probability of any

given statistical state. It is evident that W cannot be less than unity and is usually much greater than unity.

Let us now consider some special statistical state a little more closely. There are two such states which are unique and therefore deserve our attention.

I. The first of these is that state for which all the molecules have exactly the same value of the given property P. Thus, for instance, if we are considering velocities, all the molecules have the same velocity. This is the simplifying assumption which is usually made in the elementary treatment of the kinetic theory of gases. Since all the velocities have the same value the molecules must all be included in one category so that the thermodynamical probability is given by

$$W = \frac{N!}{N!} = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (66)$$

Now we have seen that unity is the lowest possible value of the thermodynamical probability, i.e. W is a minimum, so that, as we should expect, this state is extremely unstable and is never encountered in actual practice. The system tends to change so as to give the normal or equilibrium distribution.

II. The second unique state is the equilibrium state which corresponds to complete chaos in the distribution of the property P, e.g. of position and velocity. The value of the thermodynamical probability W is a maximum, that is to say the equilibrium state is the most probable state, the state to which the maximum number of microscopic states correspond.

Now let us consider any intermediate statistical state for which the thermodynamical probability W is less than the maximum. Such a state is less probable than the equilibrium state towards which it is tending so that we may say that the **thermodynamical probability W of the statistical state of a system tends to increase towards a maximum value,** unless the system has already attained that maximum value, i.e. unless the system has already arrived at a condition of equilibrium.

Our consideration of entropy has shown us that, for any isolated system, not in equilibrium, the entropy also tends to increase towards a maximum value. There is consequently some relationship between these two quantities entropy and thermodynamical probability, and we may express this relationship by saying that

the entropy of a system is a function of the thermodynamic probability of the statistical state of the system, or expressed in symbols—

$$S = f(W) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (67)$$

In adopting this relation we are implying that the entropy is entirely dependent upon the thermodynamical probability of the state. This assumption, which was originally due to Boltzmann, has been vindicated rather by subsequent practical utility than by *a priori* likelihood.

We may proceed further than this, however, and endeavour to determine the nature of the function. Suppose we have two systems for which the values of the entropy and thermodynamic probability are respectively S_1, W_1, and S_2, W_2. Let S and W be the values of the total entropy and thermodynamical probability of the statistical state of the combined system. Now, since the entropy is an extensive property of any system, we have seen that the total entropy of the combined system is equal to the sum of the entropies of the two individual systems, so that we may write

$$S = S_1 + S_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (68)$$

But, by the second law of probability, the probability of the combined system is equal to the product of the probabilities of the two individual systems, or expressed mathematically,

$$W = W_1.W_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (69)$$

If now we substitute these values for S and W in equation (67) we obtain

$$S = f(W_1W_2) = f(W_1) + f(W_2) \quad . \quad . \quad . \quad . \quad (70)$$

It is evident from this equation that the function we require is of a logarithmic nature, so that we may write the expression (70) in the form—

$$S = k\,ln\,W + \text{Constant} \quad . \quad . \quad . \quad . \quad (71)$$

where k is a constant the same for all systems.

This equation does not depend upon any specific assumptions in regard to the nature of the system and is therefore perfectly general and applies not only for any system but for any statistical state of that system. The constant which must be added to $k\,ln\,W$ to give the entropy may depend upon the particular system under consideration, but it is entirely independent of the statistical state in which the system happens to exist at the moment.

Boltzmann applied this equation to the case of a statistical

investigation of the distribution of velocities in a system of monatomic gas molecules. Each molecule in the system is defined by six co-ordinates, the three space co-ordinates, x, y, z, and the resolved velocities along those co-ordinates, u, v, w. The absolute velocity of any molecule is evidently given by

$$c = \sqrt{u^2 + v^2 + w^2}.$$

The internal energy U of the system is regarded as entirely due to the translatory motion of the gas molecules, so that we have

$$U = \Sigma \tfrac{1}{2} m(u^2 + v^2 + w^2).$$

We imagine some statistical statement to be made of the form

N_1 molecules have velocities between u_1 and $u_1 + du_1$
v_1 and $v_1 + dv_1$
w_1 and $w_1 + dw_1$
and positions between x_1 and $x_1 + dx_1$
y_1 and $y_1 + dy_1$
z_1 and $z_1 + dz_1$
N_2 molecules have velocities between u_2 and $u_2 + du_2$, etc.

The sum of all these terms $N_1 + N_2 + \ldots$ is N the total number of molecules present. $N = \Sigma N_1$. If we put

$$\tfrac{1}{2} m({u_1}^2 + {v_1}^2 + {w_1}^2) = \varepsilon_1.$$

Then the total internal energy U is given by

$$U = \Sigma N_1 \varepsilon_1.$$

Boltzmann then applied the equilibrium conditions, viz. W is a maximum so that $dW = 0$; $dN = 0$ so that $\Sigma dN_1 = 0$; $dU = \Sigma \varepsilon_1 dN_1 = 0$. By an involved process of mathematical reasoning he obtained

$$N_1 = A\, e^{-\beta({u_1}^2 + {v_1}^2 + {w_1}^2)}\, du_1 . dv_1 . dw_1 . dx_1 . dy_1 . dz_1$$

where $A = \dfrac{N}{V} (\beta/\pi)^{3/2}$; $\beta = 3Nm/4U$.

From this expression he calculated the probability W and hence from equation (71) he obtained the following equation for the entropy

$$S = \frac{3}{2} kN \ln U + kN \ln V + \text{Constant} \quad . \quad . \quad (72)$$

We may now compare this expression with equation III (17), namely

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V.$$

Differentiate equation (72) with respect to temperature.

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{3}{2}kN\,\frac{1}{U}\cdot\left(\frac{\partial U}{\partial T}\right)_V \quad . \quad . \quad . \quad . \quad (73)$$

Hence we have $$\frac{3}{2}kN\,\frac{1}{U} = \frac{1}{T}$$

or $$U = \frac{3}{2}kNT.$$

Now k is the gas constant per molecule, so that if N is the number of molecules in one gram-mole, i.e. if the system contains one mole of gas, then $kN = R$ the gas-constant per mole. Hence

$$U = \frac{3}{2}RT.$$

Substituting this value in Boltzmann's expression we obtain

$$S = \frac{3}{2}R\ ln\left(\frac{3}{2}RT\right) + R\ ln\ V + \text{Constant}.$$

But for the case of a perfect gas, if C_v is the specific heat per mole at constant volume, then $C_v = \frac{3}{2}R$. Hence if we include $ln\ \frac{3}{2}R$ under the constant term, we obtain

$$S = C_v\ ln\ T + R\ ln\ V + \text{Constant} \quad . \quad . \quad . \quad (74)$$

which is identical with the entropy equation for the perfect gas which we obtained by integrating equation (10), on the assumption that C_v is a constant. It is evident that we cannot evaluate the constant S' either on the basis of pure thermodynamics or by the aid of statistical mechanics. To determine S' we require to employ the Nernst Heat Theorem. An excellent account of the relation between thermodynamic and statistico-mechanical considerations is to be found in Rice, *Statistical Mechanics* (Constable, 1930).

CHAPTER IV

APPLICATIONS TO THE PROBLEM OF THE CONTINUITY OF STATE

Our consideration of Joule's experiment taught us that the total internal energy of a given mass of a perfect gas at constant temperature is independent of the volume occupied, or $\left(\frac{\partial U}{\partial V}\right)_T = 0$, and as a consequence of this fact we saw (equation III (6)) that if L is the latent heat of isothermal expansion and P is the pressure of the gas, then

$$L = P.$$

But by equation II (13) we have

$$L = T\left(\frac{\partial P}{\partial T}\right)_V$$

so that, for a perfect gas we may write—

$$P = T\left(\frac{\partial P}{\partial T}\right)_V \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Neglecting, for the moment, the variable V, since the volume is regarded as a constant, we may write this equation in the form

$$\frac{dP}{P} = \frac{dT}{T}$$

and on integrating this expression we obtain

$$ln\ P = ln\ T + \text{Constant}$$

or

$$P = T \times \text{Constant}.$$

Now this constant may be written $f_1(V)$ since the volume is constant so that the general solution of equation (1) for any volume is

$$P = T\,.f_1(V) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This relation must be satisfied by a perfect gas. It is not, however, a complete definition; substances other than a perfect gas may obey equation (2), and we now propose to consider what further

criteria are necessary in order that our definition of a perfect gas shall not be ambiguous.

The experiment which gives us the clue to this missing factor was first performed by Joule and Thomson (Lord Kelvin, *Collected Papers*, vol. I, p. 333 *et seq.*). They allowed a gas to pass through a porous plug from a vessel containing the gas at high pressure to one at low pressure. The essential difference between this experiment and the Joule experiment, already considered, is the porous plug which sets up sufficient resistance to the passage of the gas that we may regard the pressure on either side as practically constant, and we are consequently considering the sudden transfer of gas from a region of high to one of low pressure. The whole apparatus was rendered, as far as possible, impermeable to heat, and thermometers placed on either side of the plug indicated any

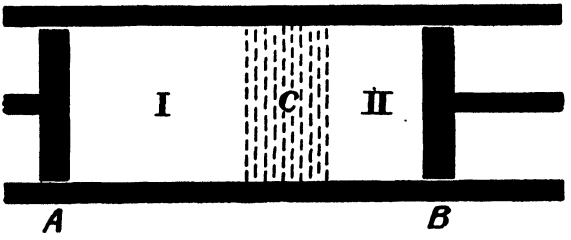

FIG. 11.

change in the temperature of the gas after passing through the plug.

At ordinary temperatures and pressures, it was found that, in the case of all gases except hydrogen and helium, a cooling effect accompanies the expansion, the cooling being greater the more the gas under investigation diverged from the ideal. Hydrogen and helium exhibit a heating effect at ordinary temperatures, but at low temperatures they too have been found to show a cooling effect.

We may, first of all, calculate this thermal effect in terms of other properties of the system by means of the following thermodynamic method. In Fig. 11, suppose C is the plug separating gas in the two portions I and II in which the pressures are P_1 and P_2 respectively. The pistons are so adjusted that these pressures are maintained constant. The whole apparatus is regarded as impermeable to heat, so that any processes occurring in the system must be adiabatic.

We now allow one mole of gas to pass through the plug by moving piston A inwards and simultaneously moving piston B outwards. If this process is accomplished reversibly then the work done by the system will be $P_2V_2 - P_1V_1$, where V_1 and V_2 are the volumes occupied by the mole of gas before and after the expansion. Since the process is adiabatic, i.e. $q = 0$, it follows from the first law that if U_1 and U_2 are the initial and final values of the total internal energy of the mole of gas, then

$$U_2 - U_1 = -(P_2V_2 - P_1V_1)$$

or

$$U_1 + P_1V_1 = U_2 + P_2V_2 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

But, by our definition of the heat content, we have

$$U + PV = H$$

so that the heat content of the system must be constant throughout the process, or

$$\Delta H = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Now in order to find the change in the temperature of the gas for unit pressure difference between the two sides of the plug, i.e. to determine $\frac{\partial T}{\partial P}$, we may apply the condition that H is constant and obtain by making use of the method of equation I (19) the following equation:

$$\left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial H}{\partial P}\right)_T \Big/ \left(\frac{\partial H}{\partial T}\right)_P \quad . \quad . \quad . \quad . \quad (5)$$

Now $\left(\frac{\partial H}{\partial T}\right)_P = C_p$, by equation I (17) so that

$$\left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial H}{\partial P}\right)_T \Big/ C_p \quad . \quad . \quad . \quad . \quad (6)$$

The thermodynamic equations just deduced are perfectly general so that the phenomenon which we are discussing is characteristic of matter in any fluid state, and not merely of substances in the gaseous state, although the latter is the only state which has been properly investigated.

According to Joule and Thomson, the cooling effect satisfies the following equation

$$-\Delta T = k(P_1 - P_2) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where P_1 is the high pressure on one side of the plug, P_2 the low pressure on the other side and k is a constant which is characteristic

of the particular gas considered and measures the depression in temperature for unit pressure difference. The following are the values of k given by Joule and Thomson calculated for a pressure difference of one atmosphere and ordinary temperatures:

$$k_{air} = 0{\cdot}262\,; \quad k_{CO_2} = 1{\cdot}225.$$

Natanson records a dependence of k upon the absolute pressure of the experiment and Joule and Thomson also found a variation with temperature. They considered that this latter variation could be represented by a formula of the type

$$k = a/T^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where a is a constant. Rose-Innes (*Phil. Mag.*, 1898, **45**, p. 227) considers that the variation of the thermal effect with temperature may be better represented by the following equation—

$$k = \alpha - \frac{\beta}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where α and β are both constants. His results are expressed in degrees per unit of pressure where the unit taken is the pound per square foot, not, as above, the atmosphere. In these units he gives the following values for the constants α and β:

	α	β
Air	441·5	0·697
Carbon dioxide . . .	2615	4·98
Hydrogen	64·1	0·331

A comparison of the values of k calculated from the two expressions (8) and (9) with the experimental results is given in the table on opposite page (Rose-Innes, *loc. cit.*).

The units of pressure are the pound per square foot.

The chief merit of the Rose-Innes formula, as compared with that of Lord Kelvin, is the fact that it predicts an inversion temperature at which the thermal effect is zero. Thus, when $\alpha = \beta/T$ or $T = \beta/\alpha$ the value of $k = \alpha - \beta/T$ is zero, that is the temperature neither rises nor falls on passing through the plug. The simple formula of Kelvin, $k = a/T^2$ does not give an inversion point and it is known that, in the case of hydrogen, which gives a heating effect at ordinary temperatures, the effect decreases as the temperature is lowered finally passing through zero and becoming a cooling effect. It is probable, therefore, that an inversion point is characteristic of all gases at sufficiently high temperatures.

Name of Gas.	Temp.	Actual Cooling Effect.	Calculated Cooling Effect.	
			I. Kelvin's Formula.	II. Rose-Innes Formula.
Air	0° C.	0·92° C.	0·92°	0·920°
	7·1	0·88	0·87	0·879
	39·5	0·75	0·70	0·716
	92·8	0·51	0·51	0·510
Carbon-dioxide .	0	4·64	4·64	4·60
	7·4	4·37	4·40	4·35
	35·6	3·41	3·63	3·49
	54·0	2·95	3·23	3·02
	93·5	2·16	2·57	2·16
	97·5	2·14	2·52	2·08
Hydrogen . .	4·5	− 0·100	—	− 0·100
	91·0	− 0·155	—	− 0·155

Now this thermal effect, which is exhibited by all actual gases is due to their non-ideal nature. We have already seen that owing to the cohesive forces between the molecules, the condition $\left(\frac{\partial U}{\partial V}\right)_T = 0$, breaks down for actual gases and the investigations of Amagat and others have shown that Boyle's law for a perfect gas, viz. $(PV)_T =$ Constant, also breaks down for real gases. For a perfect gas, however, these two laws apply, so that for any isothermal change in such a gas

$$\Delta U = 0\,; \quad \Delta(PV) = 0.$$

Hence
$$\Delta H = \Delta(U + PV) = 0 \quad . \quad . \quad . \quad . \quad . \quad (10)$$

But, we have seen that, in the Joule Thomson experiment for any substance whatever, there is no change in the heat content, i.e. $\Delta H = 0$, and hence, since actual gases are known **not** to be perfect and variations occur in both U and in PV on expansion, it follows that there must be a change in temperature in order to maintain the constancy of the heat content, unless it happens that ΔU is just equal to $-\Delta(PV)$. This last relation is, of course, the condition for an inversion point, namely

$$\left(\frac{\partial U}{\partial P}\right)_T = -\left(\frac{\partial (PV)}{\partial P}\right)_T \text{ or } \left(\frac{\partial H}{\partial P}\right)_T = 0 \quad . \quad . \quad (11)$$

This equation follows immediately from equation (6) if we put the condition that the thermal effect is zero, i.e. $\left(\frac{\partial T}{\partial P}\right)_H = 0$.

The thermal effect is therefore due to the breakdown of both Joule's law and Boyle's law. Now the deviations from Boyle's law are given by Amagat's curves in which the values of PV are plotted against P for a series of temperatures. A study of his data, with which the student is assumed to be familiar, shows that at ordinary temperatures $\left(\frac{\partial(PV)}{\partial P}\right)_T$ is positive at all pressures for hydrogen and helium and negative for all other gases at ordinary pressures becoming positive at much higher pressures. Now, if $\left(\frac{\partial(PV)}{\partial P}\right)_T$ is positive, it follows that a decrease in pressure is accompanied by a decrease in the product (PV). But for the Joule-Thomson experiment, we have seen that the condition, $dH = d(U + PV) = 0$, must be satisfied, and if, for the moment, we regard the gas as obeying Joule's law, i.e. $dU = 0$, it follows that $d(PV)$ must be zero or the product (PV) is a constant. Hence in order to ensure that PV shall not decrease on expansion, but remain constant, it is necessary to increase the temperature, i.e. the decrease in pressure is accompanied by an *increase* in temperature. On the other hand, if $\frac{\partial(PV)}{\partial P}$ is negative a similar process of reasoning will show that a decrease in pressure is accompanied by a cooling effect, so that the result of the breakdown of Boyle's law may be either a heating or a cooling effect according to the slope of the $(PV).P$ diagram under the conditions of pressure and temperature which obtain in the gas.

The deviations from Joule's law are directly due to the cohesive forces between the molecules. These always tend to oppose expansion so that a decrease in pressure must be accompanied by an increase in the total internal energy of the gas, i.e. $\frac{\partial U}{\partial P}$ is negative, or $\frac{\partial U}{\partial V}$ is positive and the expansion which necessitates a constant value of U (if we neglect the deviations due to Boyle's law) must therefore be accompanied by a decrease in temperature. The Joule-Thomson effect is thus the sum of these two temperature changes due to deviations from—

(*a*) Boyle's law—Heating or cooling effect according to the conditions.

(*b*) Joule's law—Cooling effect in every case.

We are now in a position to obtain the second criterion for a perfect gas. According to equations III (41) and (44), we have

$$dq = C_p dT + L' dP$$
$$dH = dq \quad + V.dP,$$

Combining these two expressions we obtain

$$dH = C_p dT + (L' + V)dP \quad . \quad . \quad . \quad . \quad (12)$$

Now, we have seen, that for the Joule-Thomson experiment, the following condition must hold—

$$dH = d(U + PV) = 0$$

so that

$$C_p dT + (L' + V)dP = 0 \quad . \quad . \quad . \quad . \quad . \quad (13)$$

This equation is perfectly general, since we have introduced no limiting conditions. We may now, however, put the condition that the thermal effect is zero, that is $dT = 0$, and obtain

$$(L' + V)dP = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

But equation III (46) gives for L'

$$L' = -T\left(\frac{\partial V}{\partial T}\right)_P$$

and since dP is necessarily a finite quantity,

$$V = T\left(\frac{\partial V}{\partial T}\right)_P \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

This is the criterion of an inversion point for any substance whatever. We may vary the notation, somewhat, by introducing the value for the coefficient of expansion $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ when we get

$$\alpha = 1/T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

or the inversion temperature is equal, on the absolute scale, to the reciprocal of the coefficient of expansion of the gas.

For the perfect gas, however, every temperature must satisfy the condition that the thermal effect is zero, that is equation (15) must hold for every value of the temperature, pressure and volume. This is, indeed, the missing criterion for the perfect gas, which we desired to determine. The solution may be obtained in the same manner as for equation (1), and is of the form

$$V = T.f_2(P) \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where $f_2(P)$ is, as before, an integration constant, so that the two criteria are equations (2) and (17)

$$P = T.f_1(V)$$
$$V = T.f_2(P).$$

Dividing one by the other we obtain

$$\frac{P}{V} = \frac{f_1(V)}{f_2(P)}.$$

From this relation it is evident that the function $f_1(V)$ must be of the form k/V, while $f_2(P)$ must be of the form k/P, where k is the same constant in both cases; hence the two criteria become

$$P = \frac{kT}{V}; \quad V = \frac{kT}{P}$$

which are both identical and may be expressed in the usual form

$$PV = kT$$

which is the complete equation of state for a perfect gas.

We now propose to examine some of the more important equations of state which have been put forward to describe the experimental results, in the light of the general thermodynamic relations, obtained in the last chapter. We saw that the most general equations of state which must be satisfied by any system, and which must therefore be in agreement with the experimental equations, are equations III (31) and (32)

$$P = T\left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial U}{\partial V}\right)_T \quad . \quad . \quad . \quad . \quad (18)$$

$$V = T\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial H}{\partial P}\right)_T \quad . \quad . \quad . \quad . \quad (19)$$

In addition we deduced the following relations

$$L = T\left(\frac{\partial P}{\partial T}\right)_V \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

$$\left(\frac{\partial C_v}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V \quad . \quad . \quad . \quad . \quad . \quad (21)$$

and

$$C_p - C_v = T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V \quad . \quad . \quad . \quad . \quad (22)$$

which are all perfectly general in their application.

Finally, we have deduced the condition for an inversion point (equations 15, 16)

$$V = T\left(\frac{\partial V}{\partial T}\right)_P \text{ or } \alpha = 1/T.$$

I. **Equation for the Perfect Gas.** We may begin by considering the well-known equation for the perfect gas, namely $PV = RT$. Let us differentiate the equation with respect to temperature, keeping the volume constant. We thus obtain

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Hence by equation (18)

$$P = \frac{R}{V}T - \left(\frac{\partial U}{\partial V}\right)_T \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

But $RT/V = P$, so that

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

an expression which has already been considered in connexion with Joule's experiment.

Similarly, from equation (19) we obtain

$$\left(\frac{\partial H}{\partial P}\right)_T = 0 \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

This expression follows immediately from the standpoint of Boyle's law, $PV = \text{Constant}$ at constant temperature. For since $H = U + PV$ and U and PV are both independent of volume and pressure when the temperature is constant, it is evident that H is also constant. Again equation (20) gives

$$L = T\left(\frac{\partial P}{\partial T}\right)_V = \frac{RT}{V} = P \quad . \quad . \quad . \quad . \quad . \quad (27)$$

another expression deduced in the last chapter. If we differentiate equation (23) again with respect to temperature, keeping the volume constant, we obtain

$$\left(\frac{\partial^2 P}{\partial T^2}\right) = 0 \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

Hence it follows by equation (21) that

$$\left(\frac{\partial C_v}{\partial V}\right)_T = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28a)$$

or the specific heat at constant volume is independent of the abso-

lute volume occupied for any given temperature. We have already seen that equation (22) leads to the relation

$$C_p - C_v = R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

and also that equation (15) for the inversion point is satisfied for any value of the pressure, temperature and volume, being, in fact, a criterion of the perfect gas.

II. **Van der Waals' Equation.** We now pass on to investigate the equation of van der Waals, namely

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT.$$

Differentiate with respect to temperature keeping the volume constant.

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - b} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

Hence by equation (18)

$$P = \frac{RT}{V - b} - \left(\frac{\partial U}{\partial V}\right)_T$$

$$= P + \frac{a}{V^2} - \left(\frac{\partial U}{\partial V}\right)_T$$

or

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

Thus, as we should expect, the change in internal energy with unit volume change at constant temperature is equal to the factor introduced into the equation to allow for cohesive forces between the molecules, i.e. the forces, opposing the expansion, which decrease as the volume increases.

Again, by equation (19)

$$V = T\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial H}{\partial P}\right)_T.$$

Let us differentiate the van der Waals equation with respect to temperature keeping the pressure constant. We obtain

$$\left(P + \frac{a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_P + (V - b)\frac{-2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_P = R$$

or

$$\left(P - \frac{a}{V^2} + \frac{2ab}{V^3}\right)\left(\frac{\partial V}{\partial T}\right)_P = R \quad . \quad . \quad . \quad . \quad (31a)$$

so that

$$\left(\frac{\partial H}{\partial P}\right)_T = V - \frac{RT}{\left(P - \frac{a}{V^2} + \frac{2ab}{V^3}\right)}.$$

Now $RT = (P + a/V^2)(V - b)$, hence we obtain

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{PV - a/V + 2ab/V^2 - PV - a/V + Pb + ab/V^2}{P - a/V^2 + 2ab/V^3}$$

$$= \frac{b(P - a/V^2) - \frac{2a}{V}\left(1 - \frac{2b}{V}\right)}{P - a/V^2 + 2ab/V^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

This equation shows the variation in the heat content with pressure at constant temperature. It will be seen to be somewhat smaller than the constant b, the difference depending upon the cohesive forces between the molecules. That this is what we should expect will be evident, if we neglect for the moment the cohesive forces and consider a to be zero. Then equation (32) gives $\left(\frac{\partial H}{\partial P}\right)_T = 0$, and the van der Waals equation becomes $P(V - b) = RT$. Now, since the cohesive forces are neglected we may regard U as a constant at any temperature, and hence for any temperature

$$U + P(V - b) = \text{Constant} = K \text{ say}$$

But $$U + PV = H = K + Pb$$

so that the increase in heat content for unit pressure change, i.e. $\left(\frac{\partial H}{\partial P}\right)_T$ is equal to the constant b.

Equations (20) and (30) combined give

$$L = \frac{RT}{V - b} = P + a/V^2 \quad . \quad . \quad . \quad . \quad (33)$$

or the latent heat of expansion is greater than the pressure by an amount equal to the cohesive factor a/V^2 of the van der Waals equation. On differentiating equation (30) we again obtain

$$\left(\frac{\partial C_v}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right) = 0 \quad . \quad . \quad . \quad . \quad . \quad (34)$$

By comparing equations (34) and (28) we see that van der Waals' equation is similar to that for a perfect gas in that both equations require the specific heat at constant volume to be independent of the volume occupied, for any given temperature. This is not, however, borne out in practice. The general behaviour of gases seems to be that as the volume occupied per gram decreases from large values the specific heat at constant volume C_v increases,

passing, in some cases, through a maximum in the neighbourhood of the critical volume and then falling again as the contraction is increased beyond this point. Thus for CO_2 Dieterici (*Ann. der Physik.*, (4) 1903, **12**, 173) obtained the following results : When the volume occupied per gram was very small (1·1–1·125 c.c.) the value of C_v per gram was found to be 0·24. In the neighbourhood of the critical volume the maximum value 0·34 was obtained; beyond this point the specific heat decreases again. The equation of van der Waals is thus at fault in this particular.

Let us now apply equation (22) to van der Waals' equation, namely—

$$C_p - C_v = T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V$$

By equation (30) we have

$$T\left(\frac{\partial P}{\partial T}\right)_V = \frac{RT}{V-b} = P + a/V^2 \quad . \quad . \quad . \quad (35)$$

and from equation (31*a*):

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P - \frac{a}{V^2} + \frac{2ab}{V^3}}.$$

Multiplying these two equations together we obtain

$$C_p - C_v = \frac{R(P + a/V^2)}{(P + a/V^2) + \frac{2ab}{V^3} - \frac{2a}{V^2}}$$

$$= \frac{R}{1 - \frac{2a(V-b)^2}{RTV^3}}.$$

The denominator in this expression is evidently less than unity, so that $C_p - C_v$ is greater than R, the value obtained from the simple gas law $PV = RT$. This is borne out in practice at least in a qualitative manner as the following results show :

Gas.	C_v per gram.	C_p per gram.	$\frac{C_p - C_v}{R}$ per mole.	
Perfect gas . . .	—	—	1·985	
Hydrogen	2·4211	3·4090	1·976	1·985
Oxygen	0·1556	0·2175	1·981	
Ammonia	0·3951	0·5205	2·108	
Carbon dioxide . .	0·1669	0·2169	2·20	

III. **Clausius' Equation.** This equation may be written in the form

$$P = \frac{RT}{V-b} - \frac{a}{T(V+c)V} \quad . \quad . \quad . \quad . \quad (36)$$

Differentiate with respect to temperature keeping the volume constant.

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} + \frac{a}{T^2(V+c)V} \quad . \quad . \quad . \quad (37)$$

Hence by equation (18) we have

$$P = \frac{RT}{V-b} + \frac{a}{T(V+c)V} - \left(\frac{\partial U}{\partial V}\right)_T \quad . \quad . \quad . \quad (38)$$

Equating (36) and (38) we obtain

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{2a}{T(V+c)V} \quad . \quad . \quad . \quad . \quad (39)$$

The Clausius equation therefore differs from that of van der Waals, in that the change in internal energy per unit volume change at constant temperature is **twice** the factor introduced to allow for the cohesive forces between the molecules.

We may now differentiate the equation with respect to temperature keeping the pressure constant. Doing this we obtain

$$0 = \frac{R}{V-b} - \frac{RT}{(V-b)^2}\left(\frac{\partial V}{\partial T}\right)_P + \frac{a}{T^2(V+c)V} + \frac{a(2V+c)}{T(V+c)^2V^2}\left(\frac{\partial V}{\partial T}\right)_P \quad (40)$$

Hence

$$T\left(\frac{\partial V}{\partial T}\right)_P = \frac{\left(\frac{RT}{V-b} + \frac{a}{T(V+c)V}\right)}{\frac{RT}{(V-b)^2} - \frac{a(2V+c)}{T(V+c)^2V^2}} \quad . \quad . \quad . \quad (41)$$

The second term in both the numerator and denominator is a small fraction, so that this expression is evidently slightly greater than the ratio of the first terms, namely than $V-b$. Suppose we equate the expression to $V-kb$, where k is a factor slightly less than unity. Then we may write

$$T\left(\frac{\partial V}{\partial T}\right)_P = V - kb \quad . \quad . \quad . \quad . \quad . \quad (42)$$

Hence, by equation (19) we obtain

$$V = V - kb + \left(\frac{\partial H}{\partial P}\right)_T$$

or

$$\left(\frac{\partial H}{\partial P}\right)_T = kb \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

The change in the heat content with unit change of pressure at constant temperature is thus slightly less than the constant b, as in the case of the van der Waals equation. The difference is due to the cohesive forces.

Substituting the value of $\left(\frac{\partial P}{\partial T}\right)_V$ given by equation (37) in equation (20) we obtain the expression

$$L = \frac{RT}{V-b} + \frac{a}{T(V+c)V} \quad . \quad . \quad . \quad . \quad . \quad (44)$$

$$= P - \frac{2a}{T(V+c)V} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

The difference between the latent heat and the pressure is thus, on the basis of Clausius' equation, twice the cohesive factor, not equal to that factor as in the case of van der Waals' equation.

On differentiating equation (37) with respect to temperature at constant volume we have, by equation (21)

$$\left(\frac{\partial C_v}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V = -\frac{2a}{T^2(V+c)V} \quad . \quad . \quad (46)$$

This equation represents the behaviour of gases above the critical volume, as we have already seen, but there is no evidence of a maximum. The Clausius equation is therefore, in this particular, only valid for gases which are above the critical conditions.

As regards the difference between the specific heats at constant volume and constant pressure, we may apply equation (22)

$$C_p - C_v = T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

$$= (V-kb) \cdot \left\{\frac{R}{(V-b)} + \frac{a}{T^2(V+c)V}\right\} \quad . \quad (48)$$

This expression is evidently greater than R, so that

$$C_p - C_v > R.$$

In this instance the Clausius equation is therefore in qualitative agreement with the van der Waals equation and with experiment.

IV. **Dieterici Equation.** The following is one of the equations of state suggested by Dieterici:

$$P = \frac{RT}{V-b} \cdot e^{-a/TnV} \quad . \quad . \quad . \quad . \quad . \quad . \quad (49)$$

where a, b and n are constants. Taking logarithms we have

$$ln\ P = ln\ T + ln\frac{R}{V-b} - \frac{a}{T^n.V}.$$

Differentiate with respect to temperature keeping the volume constant.

$$d\ ln\ P = d\ ln\ T + \frac{na}{T^{n+1}.V}dT \quad . \quad . \quad . \quad . \quad (50)$$

or

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{T} + \frac{naP}{T^{n+1}V} \quad . \quad . \quad . \quad . \quad . \quad (51)$$

Hence equation (18) becomes

$$P = P + \frac{naP}{T^n.V} - \left(\frac{\partial U}{\partial V}\right)_T$$

so that

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{naP}{T^n.V} \quad . \quad . \quad . \quad . \quad . \quad (52)$$

It is, of course, difficult to attach any physical meaning to this expression. Equation (20) gives for the value of the latent heat,

$$L = P + \frac{naP}{T^n.V}. \quad . \quad . \quad . \quad . \quad . \quad (53)$$

The determination of the volume temperature coefficient $\left(\frac{\partial V}{\partial T}\right)_P$ results in a somewhat unwieldy expression and we do not propose to proceed any further with the Dieterici equation from the point of view of the equations (18) to (22).

Equations of State and Inversion Points.

We now intend to consider the various equations of state in the light of the porous plug experiment of Joule and Thomson and the existence of inversion points. We shall follow the procedure adopted by A. W. Porter (*Phil. Mag.*, series (6), 1906, xi, 554; ib., (6), 1910, xix, 888).

Van der Waals' Equation. It is preferable to employ this equation in the reduced form, viz.

$$\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta \quad . \quad . \quad . \quad . \quad . \quad (53)$$

The condition for the inversion point is given by

$$T\left(\frac{\partial V}{\partial T}\right)_P - V = 0$$

or in the reduced form

$$\theta\left(\frac{\partial \phi}{\partial \theta}\right)_\pi - \phi = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (54)$$

Differentiate equation (53) with respect to θ keeping π constant.

$$\left(\pi + \frac{3}{\phi^2}\right)3.\left(\frac{\partial \phi}{\partial \theta}\right) + (3\phi - 1)\,(-6/\phi^3)\left(\frac{\partial \phi}{\partial \theta}\right) = 8.$$

Putting $\left(\pi + \frac{3}{\phi^2}\right)$ equal to $8\theta/(3\phi - 1)$ and dividing through by $\frac{\partial \phi}{\partial \theta}$, which by equation (54) is equal to ϕ/θ, we obtain

$$\frac{8\theta}{(3\phi - 1)}.3 - \frac{6(3\phi - 1)}{\phi^3} = \frac{8\theta}{\phi}$$

so that

$$8\theta\left(\frac{3\phi - 3\phi + 1}{\phi(3\phi - 1)}\right) - \frac{6(3\phi - 1)}{\phi^3} = 0$$

or

$$\theta = \frac{3(3\phi - 1)^2}{4\phi^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (55)$$

From this equation we may calculate the inversion temperature corresponding to a series of values of the volume, by substituting the values of ϕ and obtaining those of θ. It is evident that for any one value of the inversion temperature θ we obtain a quadratic equation in ϕ so that there are two values of the volume corresponding to this temperature. Above a certain value of θ, however, the roots of the quadratic are imaginary, so that no inversion occurs for any value of the volume at such a temperature. This existence of a series of inversion points is borne out qualitatively by actual gases as will be shown in Fig. 12. The agreement is only qualitative, however. Dieterici's equation, which we shall now consider, is found to show better agreement as regards the numerical results.

Porter considered Dieterici's equation in the form

$$P(V - b) = RT\, e^{-A/RT^{3/2}V}$$

or the corresponding reduced equation

$$\pi(2\phi - 1) = \theta.e^{2\left(1 - \frac{1}{\phi\theta^{3/2}}\right)} \quad . \quad . \quad . \quad . \quad (56)$$

He determined the inversion points on the basis of this equation and found them to be represented by the equation

$$\pi\theta^{\frac{1}{3}} = (10 - \theta^{\frac{1}{3}})e^{2\left[1.2-\frac{2}{\phi\theta^{3/2}}\right]} \quad . \quad . \quad . \quad . \quad (57)$$

The curve given by this equation is represented by the full line in Fig. 12 while the curve corresponding to van der Waals' equation is represented by the dotted line. Several experimental points are also given, those for nitrogen being represented by ×, while those for carbon dioxide are represented by °. These values are calculated from Amagat's data. The agreement with Dieterici's equation is remarkably good. It will be observed that the Dieterici curve is not a true parabola, since it is not symmetrical and approaches the origin very rapidly, instead of cutting the axis at the point $\phi = 1$ as does the curve obtained for van der Waals' equation. The range over which the experimental curve is known is however too small to permit us to draw the complete curve.

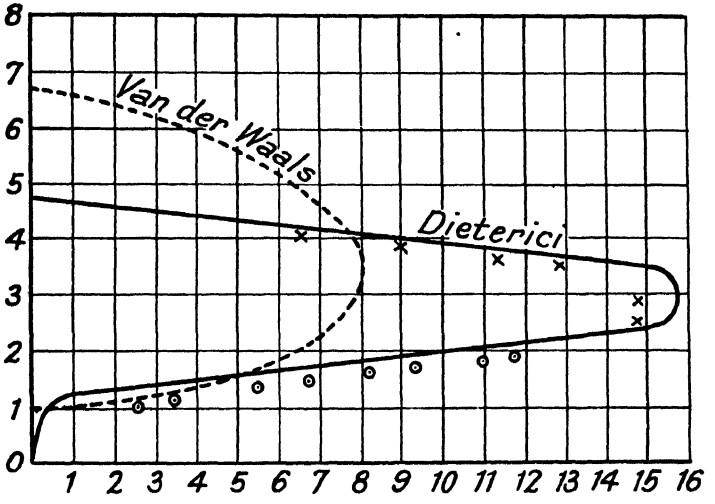

FIG. 12.

Porter finds that a still closer agreement with experiment is obtained if we modify the index of T in the exponential term, from 3/2 to about 1·65.

The above diagram (Fig. 12) is the plot of the inversion points, the ordinates representing the reduced temperature of the inversion points, the abscissæ the reduced pressures.

Further Consideration of the Clapeyron Equation. Equation II (14) gives the general form of the Clapeyron Equation for the vaporization of a liquid, viz.

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\lambda}{V_2 - V_1}.$$

The latent heat of vaporization λ may, however, be divided into two parts, namely the internal latent heat λ_i which is expended in overcoming the cohesive forces between the liquid molecules, and the external latent heat of expansion λ_{ex}. The work done in expansion is evidently $P(V_2 - V_1)$ where V_2 is the volume of the vapour, V_1 the volume of the liquid. As an approximation we may neglect V_1 in comparison with V_2 and put the work equal to PV_2. Assuming that the gas laws may be applied to the vapour, we obtain :

$$\lambda_{ex} = PV_2 = RT.$$

For a temperature of 100° C., i.e. 373° K., the latent heat of expansion λ_{ex} per gram of water is

$$\lambda_{ex} = RT/18 = \frac{2 \times 373}{18} = 41 \text{ calories.}$$

But $\lambda = 536$ calories, so that $\lambda_i = 495$ calories.

The following table gives some of the values obtained by Zeuner for the vaporization of water (Chwolson, *Lehrbuch der Physik*, vol. III, 654).

t° C.	$T = t + 273$.	Vap. Press. in mm.	$\lambda_{obs.}$	$\lambda_{ex.}$	λ_i.
− 20	253	0·927	620·39	29·57	590·82
− 10	263	2·093	613·45	30·30	583·15
0	273	4·600	606·50	31·07	575·43
25	298	25·55	589·11	33·20	555·91
50	323	91·98	571·66	35·54	536·12
75	348	288·5	554·14	37·96	516·18
100	373	760·0	536·50	40·20	496·30
125	398	1,743·9	518·73	42·25	476·48
150	423	3,581·2	500·79	44·09	456·70
175	448	6,717·4	482·65	45·71	436·94
200	473	11,689·0	464·30	47·13	417·17

It is evident that by far the greater portion of the latent heat is required to overcome the forces of cohesion, which is as we should expect, since in a liquid these forces become very great.

We have seen that the external latent heat is given by

$$\lambda_{ex} = P(V_2 - V_1)$$

and we know that $\lambda = \lambda_{ex} + \lambda_i$

so that $\lambda = \lambda_i + P(V_2 - V_1)$.

Substitute this value in the Clapeyron equation. We obtain

$$T\left(\frac{\partial P}{\partial T}\right)_V = \frac{\lambda_i + P(V_2 - V_1)}{V_2 - V_1}$$

or

$$\lambda_i = \left(T\frac{\partial P}{\partial T} - P\right)(V_2 - V_1) \quad . \quad . \quad . \quad . \quad (58)$$

Neglecting V_1 in comparison with V_2 and assuming the gas laws this expression becomes

$$T\left(\frac{\partial P}{\partial T}\right).\frac{RT}{P} - RT = \lambda_i$$

so that

$$\lambda_i = RT\left(T\frac{\partial\ ln\ P}{\partial T} - 1\right) \quad . \quad . \quad . \quad . \quad . \quad (59)$$

We shall now attempt to integrate the Clapeyron equation. To do this we must know how the latent heat depends upon temperature. If we denote by λ_m the total latent heat of vaporization per mole, then experiment shows that we may express λ_m as a function of temperature as follows:

$$\lambda_i = \lambda_m - RT = \lambda_0 + \alpha_0 T + \beta_0 T^2 + \gamma_0 T^3 + \ldots \quad . \quad (60)$$

Now by equation (59)

$$\lambda_m = \lambda_i + RT = RT^2\frac{d\ ln\ P}{dT} \quad . \quad . \quad . \quad . \quad (61)$$

$$= RT + RT^2\frac{d\ ln\ C}{dT} \quad . \quad . \quad . \quad (62)$$

Comparing equations (60) and (62) we obtain

$$\lambda_i = RT^2\frac{d\ ln\ C}{dT} = \lambda_0 + \alpha_0 T + \beta_0 T^2 + \gamma_0 T^3 + \ldots \quad . \quad (63)$$

Dividing through by RT^2 and integrating we obtain

$$ln\ C = -\frac{\lambda_0}{RT} + \frac{\alpha_0}{R}\ ln\ T + \frac{\beta_0}{R}T + \frac{\gamma_0}{2R}T^2 + \ldots + i \quad . \quad (64)$$

where i is an integration constant. Since $P = RTC$, then

$$ln\ P = ln\ R + ln\ T + ln\ C,$$

so that we may write

$$ln\ P = -\frac{\lambda_0}{RT} + \frac{(\alpha_0 + R)}{R} . ln\ T + \frac{\beta_0}{R}T + \frac{\gamma_0}{2R}T^2 + \ldots + i + ln\ R \quad . \quad (65)$$

The last two terms reduced to ordinary logarithms, viz. $\frac{ln\ R + i}{2{\cdot}303}$ form what Nernst called the "conventional chemical constant," C_0 of the substance under consideration. We have followed this method, which is now little used, in order to point out a fallacy which escaped the notice of chemists for a time. Equation (60) is at best only an empirical expression representing the heat of vaporization over a limited range of temperature. Hence the integration constant i partakes of the same empirical nature and does **not** represent the value of $ln\ C$ at absolute zero. In fact the value of i will only be a constant for the limited range over which the expression holds. This will be evident when we remember that the integral represents the area under the λ, T curve. Now if equation (60) does not represent this curve at low temperatures, neither will the integral represent the area under the curve. Nernst, unfortunately, fell into this error at first and determined a series of values of C_0 by extrapolation to low temperatures. These quantities are evidently valueless. The constant C_0 can, however, be determined from vapour pressure measurements for some one value of the temperature and this will be useful in determining the value of the vapour pressure at some other temperature. This warning in regard to the integration of empirical expressions will need to be borne in mind when we deal with the integration of the van't Hoff isochore in Chapter VI. When we come to consider the third law of thermodynamics the accurate integration of the Clapeyron equation will be considered and also the significance of the "true" chemical constant, which may be determined from measurements at low temperatures.

Trouton's Rule. An interesting and useful empirical principle is that known as Trouton's rule, according to which the molecular latent heat of vaporization divided by the boiling-point on the absolute scale is a constant for all normal or non-polar liquids. In other words, the entropy increase per mole $\frac{q}{T}$ is the same for

all such substances, on vaporization at the boiling-point. The following table indicates the accuracy of the rule. Non-polar substances are given first, after which are given a few values for alcohols and acids which are known to be polymerized.

Substance.	Boiling-Point.		$\Delta S = \lambda/T$ per Mole.
	° C.	° K.	
Methyl-ethyl acetone	78·68	351·68	21·25
Diethyl acetone	101·08	374·08	20·90
Dipropyl acetone	143·52	416·52	20·73
Acetal	102·91	375·91	20·78
Octane	125·3	398·3	20·28
Aniline	184·24	457·24	21·22
O. toluidine	198·92	471·92	21·55
Nitrobenzene	210·6	483·6	20·70
Aceto-nitrile	81·54	354·54	19·74
Pyridine	115·51	388·51	20·12
Ethyl alcohol	78·20	351·20	26·39
n. Propyl alcohol	96·1	369·1	26·59
Iso-butyl alcohol	107·53	380·53	26·12
Acetic acid	119·2	392·2	13·74
Propionic acid	141·05	414·05	16·34

The theoretical justification for this empirical expression depends upon the conception that the boiling-points may be regarded as corresponding temperatures. We employ the Clapeyron equation

$$\lambda = T\frac{\partial P}{\partial T}(V_2 - V_1)$$

and substitute the reduced terms $\pi = P/P_c$, $\phi = V/V_c$, $\theta = T/T_c$. We obtain

$$\frac{\lambda}{T} = \frac{P_c V_c}{T_c}\frac{\partial \pi}{\partial \theta}(\phi_2 - \phi_1).$$

Now according to the theory of corresponding states, π, ϕ and θ are the same for all substances, if we assume the boiling points to be corresponding temperatures, and moreover $\frac{P_c V_c}{T_c}$ is a constant. Hence λ/T must be a constant for all substances.

The table given above does not give values of λ/T for substances having very high boiling-points, but when these values are obtained

it is found that there is a marked trend in the "constant." Thus for liquids boiling at about 1000° C. the value of λ/T is about 50 per cent. greater than the value obtained for low boiling liquids like oxygen and nitrogen. Several attempts have been made to devise a more accurate statement of the rule, the most simple being that of Hildebrand (*J. Amer. Chem. Soc.*, 1915, **37**, 970). His rule takes the form: "The entropy change of vaporization is the same for different liquids, not at the boiling-points which are the temperatures where the several liquids have unit vapour pressure, but rather at temperatures where the liquids give the same vapour **concentration.**" Choosing arbitrarily temperatures at which the concentration of vapour is 0·005 moles per litre, he gives the following table for the entropy change in vaporization.

Substance.	ΔS.	Substance.	ΔS.
Nitrogen	27·6	Fluorbenzene . . .	27·4
Oxygen	27·6	Stannic chloride . .	27·2
Chlorine.	27·8	Octane	27·6
Pentane	27·0	Bromnaphthalene . .	27·6
Hexane	27·2	Mercury	26·2
Carbon tetrachloride .	27·0	Cadmium	26·4
Benzene.	27·4	Zinc	26·4

These values are certainly remarkably good, especially when we consider the variation in the boiling-points of the substances. The values for polar substances are larger, e.g., NH_3 32·4; water 32·0; EtOH 33·4.

Maxwell's Rule. It is well known that if we plot a pressure volume curve for any gas the form of the curve is *ABCD* in Fig. 13. If, however, we plot the curve represented by, say van der Waals' equation, we obtain a smooth curve of the form *ABFGECD*, without the sharp breaks at *B* and *C* exhibited by the experimental curve. Now it has been found that with care it is possible to realize experimentally points on the portions *BF* and *EC* of the curve, so that we have a certain amount of justification for assuming that the smooth curve would actually represent the pressure volume relations, even in the region where the system is normally heterogeneous, if we could ensure that the system would be homogeneous throughout this range. Now Maxwell's rule states that

the area *BFG* is equal to the area *GEC* and we can demonstrate the truth of this rule by considering the work terms involved in passing from *B* to *C*. The work done is, on the basis of our consideration, independent of the path traversed. We shall therefore consider the passage (*a*) along the experimental line *BC* and (*b*) along the theoretical line *BFGEC*. In the first case the work done upon the gas is evidently equal to the product of the vapour

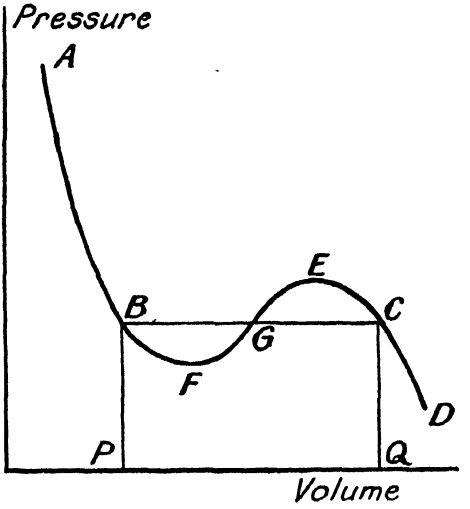

FIG. 13.

pressure P and the difference in volume $V_2 - V_1$, where V_2 is the volume of the vapour, V_1 the volume of the liquid.

$$\text{Work done} = P(V_2 - V_1).$$

If we follow the theoretical line the work done upon the gas is

$$\text{Work done} = \int_{V_1}^{V_2} PdV.$$

These two quantities are equal, that is

$$P(V_2 - V_1) = \int_{V_1}^{V_2} PdV \quad . \quad . \quad . \quad . \quad . \quad (66)$$

But $P(V_2 - V_1)$ is equal to the area *PBCQ*, and $\int_{V_1}^{V_2} PdV$ is equal to the area *PBFGECQ* below the curve. Hence it follows that

the area *GEC* must be equal to the area *BFG*, which is Maxwell's rule.

Let us now assume the validity of the van der Waals equation to enable us to integrate the expression obtained by following the theoretical path. We have

$$P = \frac{RT}{V - b} - \frac{a}{V^2}.$$

Hence

$$\int_{V_1}^{V_2} P dV = RT \ ln \frac{V_2 - b}{V_1 - b} + \frac{a}{V_2} - \frac{a}{V_1}.$$

Equating this expression to $P(V_2 - V_1)$ we obtain

$$P(V_2 - V_1) = RT \ ln \frac{V_2 - b}{V_1 - b} - \frac{a}{V_1 V_2}(V_2 - V_1)$$

or

$$\left(P + \frac{a}{V_1 V_2}\right)(V_2 - V_1) = RT \ ln \frac{V_2 - b}{V_1 - b} \quad . \quad . \quad (67)$$

The points B and C are on the curve, so that for these points the van der Waals equation must hold. Hence

$$\left(P + \frac{a}{V_2^2}\right)(V_2 - b) = RT \quad . \quad . \quad . \quad . \quad (68)$$

$$\left(P + \frac{a}{V_1^2}\right)(V_1 - b) = RT \quad . \quad . \quad . \quad . \quad (69)$$

From these three equations, we can for any given temperature calculate the value of the vapour pressure P or of the volumes V_1 and V_2 occupied by one mole of liquid and of saturated vapour respectively.

Dieterici's Equation for Latent Heat of Vaporization. An interesting though empirical expression has been suggested by Dieterici connecting the internal latent heat λ_i with the specific volumes of liquid and saturated vapour V_1 and V_2. The expression is

$$\lambda_i = k.RT \ ln \ V_2/V_1$$

where k is a constant. (*Ann. der. Physik.*, 1908, **25**, 269; ib., 1911, **35**, 220). The following table gives the values of this constant for the case of Iso-pentane. They are based upon Young's data.

$T°$ K.	Pressure of Saturated Vapour.	V_1 per Gram.	V_2 per Gram.	λ, Cals.	$RT \ln \frac{V_2}{V_1}$.	k.
283·0	390·5	1·5885	607·5	78·64	46·15	1·704
293·0	572·6	1·6141	424·0	75·97	44·76	1·697
303·0	815·3	1·6413	303·0	73·52	43·35	1·696
323·0	1,533·0	1·7005	167·6	68·95	40·66	1·696
343·0	2,653·0	1·7679	98·9	64·18	37·86	1·695
363·0	4,296·0	1·8475	61·85	59·49	34·94	1·703
383·0	6,596·0	1·9455	39·80	53·78	31·71	1·696
403·0	9,707·0	2·0720	26·10	47·65	27·99	1·702
423·0	13,804·0	2·2500	17·14	40·18	23·56	1·705
443·0	19,094·0	2·5550	10·71	29·53	17·40	1·697
458·0	23,992·0	3·1830	6·355	14·17	8·68	1·632
460·0	25,010·0	4·266	4·266	—	0	—

It will be seen that in the range of temperature considered, namely from 10° C. up to the critical point 187·8° C. (= 460·8° K.) the constant k is remarkably good, being well within the limits of experimental error. Not only so but the value of the constant, obtained for all normal non-polar liquids, is found to be the same. The total variation is said to be less than 2 per cent. The following table gives the values for a few such substances:

Substance.	k.	Substance.	k.
n.Pentane	1·707	Zinc Chloride	1·741
n.Hexane	1·752	Ethyl ether	1·724
n.Heptane	1·814	Methyl formate	1·706
n.Octane	1·858	Ethyl formate	1·747
2 : 3 dimethyl n.Butane	1·725	Methyl acetate	1·784
di-iso-butyl or		Propyl formate	1·774
2 : 5 dimethyl n.Hexane	1·813	Ethyl acetate	1·812
Hexamethylene	1·694	Methyl propionate	1·803
Benzene	1·690	Propyl acetate	1·850
Fluor-benzene	1·711	Ethyl propionate	1·837
Chlor-benzene	1·714	Methyl butyrate	1·824
Brom-benzene	1·691	Methyl iso-butyrate	1·810
Iodo-benzene	1·687	Carbon dioxide	1·717
Carbon tetrachloride	1·667	Sulphur dioxide	1·730

CHAPTER V

CRITERIA OF EQUILIBRIUM

Our consideration of the subject of entropy led us to the conclusion that, for any completely isolated system, the value of this property tends to increase towards a maximum value which is characteristic of the equilibrium state. Hence it is evident that we have at once a criterion of equilibrium for any isolated system, namely that the entropy is a maximum, or expressed mathematically, $dS = 0$.

We have also traced a certain equivalence between this statement and the fact that the equilibrium state is the state of maximum thermodynamic probability, so that for a completely isolated system we may also write, as our criterion of equilibrium $dW = 0$.

These criteria are perfectly general and are applicable to any system which is completely isolated. But, as we have seen, the systems which have to be investigated in the laboratory are usually very far from being isolated, in fact a completely isolated system is never quite realized in practice, so that these criteria are somewhat difficult to apply to actual cases. Moreover, the entropy is not always the simplest function to calculate, in the case of complex systems. We therefore seek for some criterion which, although it may be theoretically less general in scope, is nevertheless capable of much wider application to ordinary chemical problems.

Now we have seen that any natural process occurs in virtue of the fact that the system, when properly employed, is capable of yielding a certain maximum amount of external work. Hence the quantity of this external work gives us an indication of how far the system is from the equilibrium state. In other words, a criterion of equilibrium is that the maximum work of which the system is capable, in undergoing any change whatever must be zero, or $w_{max} = 0$. Thus suppose we are considering some change occurring in a system such as the diffusion of an electrolyte throughout a solution. In the diagram (Fig. 14) let c_1 and c_2 represent

the concentrations in two contiguous sections, A and B, of a solution. Then if c_1 is greater than c_2 experiment shows that solute will pass from A to B. Suppose an infinitely small number dn of moles so pass, then the maximum work which could be done by the system as a result of this transfer is, if the gas laws are assumed for the solution and the temperature is regarded as constant—

$$dn.RT \ln c_1/c_2.$$

This is positive, as we should expect for a natural or spontaneous process. As the diffusion proceeds, however, this work gradually decreases, finally becoming zero when c_1 is equal to c_2, i.e. when the concentration of the solution is uniform throughout. In order, then, to test whether the system has arrived at a condition of equilibrium, in regard to some process, we imagine the process to proceed by an infinitesimal amount and calculate the maximum work which the system is capable of performing in virtue of this change, if the process is properly applied. If this maximum work quantity is zero the system is in a state of equilibrium.

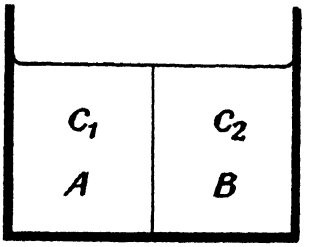

FIG. 14.

This is not, however, quite sufficient. In order to employ this criterion to practical problems, we must be a little more specific as regards the conditions of experiment. Now, as a rule, our measurements are carried out either at constant volume or, more generally under the constant pressure of the surroundings, usually the atmosphere. The example which we have just considered occurs at constant volume, but if the process under consideration involves an expansion while the external pressure is maintained constant, then the system will have to perform work upon the surroundings. This work is not available for external use, but is compulsory work; the pressure of the atmosphere is, in fact, tending to drive the process in the backward direction, and the system, to be in equilibrium, must overcome this tendency. This work must be done, if we imagine an infinitesimal change, even when the system has attained equilibrium. In addition to this work, however, if the system is undergoing any natural process, it is capable, if properly applied, of yielding a certain definite amount of external work which may be applied to drive some external machine. The

criterion of equilibrium for this case is thus, not that the value of w_{max} for an infinitesimally small change is zero, but that the available external work is zero.

This will probably become clearer if we consider an actual case, such as a chemical reaction occurring in a system, which we shall denote by the letter A. Suppose the reaction is accompanied by an increase in volume, and let the pressure of the atmosphere be P. Let us consider the reaction to proceed by an infinitesimal amount, the corresponding increase in the volume being dV. Then compulsory work of amount PdV must be done by the system upon the surroundings. But this gives us no indication as to whether the system has arrived at the equilibrium state. What we require to determine is whether the system is also **capable of performing any other external work** in virtue of the change, or, in mathematical language, we desire to find the value of the difference $(w_{max} - PdV)$. If this quantity is zero, the system is in a state of equilibrium.

Another way of regarding the problem is to consider the combined system (A + Atmosphere). We allow the process to proceed by an infinitesimal amount and calculate the maximum work which the combined system can, if properly applied, perform upon the surroundings of this combined system (which will not, of course, include the atmosphere). If this work is positive, we are dealing with a natural process occurring in the combined system; if the value is zero then the system is in equilibrium. Now it is immaterial whether or not any work changes have occurred in the combined system itself during this infinitesimal process, it is only the work done by the system as a whole upon some suitable machine that is of use in determining the equilibrium state. It should be carefully noted, however, that although this point of view of the combined system may serve as a useful guide in helping us to form our conception of the meaning of these criteria of equilibrium, the former aspect, of the system A by itself, is the one which is invariably employed in practice.

We must now attempt to formulate this criterion a little more precisely and we shall consider, first of all, the case of a system in which a process is occurring at constant volume. No external work is done upon the atmosphere during the process and if we restrict ourselves, for convenience, to an isothermal process, we have

$$w_{max} = -dA.$$

Hence the criterion of equilibrium for this case is $dA = 0$, or, if we wish to express the fact that the volume and temperature are regarded as constant, the criterion becomes—

$$(dA)_{TV} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or the maximum work of any isothermal process occurring in a system at constant volume is zero at the equilibrium point.

We are now in a position to define a quantity which has hitherto only been vaguely described as a property of the system, differences in which could be measured. This property has been called the **work content** and has been denoted by A. The first law of thermodynamics for an isothermal reversible process takes the form

$$dA = dU - q$$

or, since $q = TdS$, we have

$$dA = dU - TdS.$$

Now, since the temperature is constant we may integrate this expression and obtain

$$A = U - TS + \text{Constant.}$$

It is usual to regard the constant as zero and define the work content by the equation

$$A = U - TS \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Having obtained a complete definition of the criterion of equilibrium in systems the volume of which is constant, we now propose to turn our attention, once more, to the more important case of processes which occur at constant pressure. Suppose this pressure is denoted by P and that the volume change accompanying the process is dV (for an infinitesimal change). Then the maximum work which the system could perform and which would be available for external use is $w_{max} - PdV$ since we must deduct from w_{max} the compulsory work performed against the atmosphere. If we confine ourselves once again to an isothermal process we may replace w_{max} by $-dA$, so that the available work is $-dA - PdV$.

Now it is evident that if any system, such for instance as a crystal, is in contact with the atmosphere, and **not undergoing any change**, then the system must be in equilibrium with the atmosphere, that is the pressure of the crystal outwards must be equal to the pressure of the atmosphere. Now suppose an expansion occurs in the system of amount dV. Since the pressure of

the atmosphere which is opposing the expansion is equal to the pressure of the crystal, we may regard the expansion as reversible. The work done in expansion is PdV where P is now the pressure of the system itself as well as that of the surroundings. Now for such an isothermal reversible process the available energy is usually known as the **decrease in free energy** of the system. If we denote the free energy of the system by the letter F, then on the usual notation $-dF$ will denote an infinitesimally small decrease in the free energy, so that we may write

$$-dF = -dA - PdV \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and the condition of equilibrium which we have obtained is

$$(dF)_{TP} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

or the free energy change accompanying any isothermal process in a system in the equilibrium state and under constant pressure is zero.

Now since $dA = dU - TdS$, we may write equation (3) in the form

$$dF = dU - TdS + PdV \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and if we integrate this expression and neglect the integration constant we obtain, since pressure and temperature are both constants—

$$F = U - TS + PV \quad . \quad . \quad . \quad . \quad . \quad (6)$$

But since $U + PV = H$ where H is the heat content of the system it follows that

$$F = H - TS \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

It will be evident from this definition of the free energy of a system that F is an extensive property of the system, since we have seen that both H and S are such, while Temperature is an intensive property. In other words, for any completed cycle of changes we have $\int dF = 0$.

Equations (2) and (7) are very important, constituting, as they do, definitions of the work content and the free energy of any system.

The latter term, especially, has often been used very loosely and different authors have attached different meanings to it. But the meaning we have here adopted is that most usually employed

at the present day and is the one which seems to be at once the most logical and the most practical.

A little consideration will show that it is by no means necessary to limit this free energy criterion to the case where the pressure of the system is maintained constant. For, take the case of an isothermal change occurring in a system at constant volume. The system does not perform any work upon the surroundings so that the decrease in the free energy of the system is exactly equal to the maximum work which the system could have performed if suitable apparatus had been employed. In other words, we have for such a change

$$-\Delta F = -\Delta A.$$

These two cases, namely processes which occur at constant volume or at constant pressure are the most important practically, but it is evident that for any reversible isothermal process whatsoever, the decrease in the free energy of the system, i.e. the amount of available external work which the system was capable of performing if suitably employed, is equal to the total maximum work of the process $-\Delta A$, minus the work which actually is done by the system. Now it is just this available work, i.e. work which is **not** done but which could be done by the system (although its performance would upset the equilibrium) which really measures how far the system is from equilibrium, and when this quantity is zero we know that the system is already in the equilibrium state. Now for any isothermal process, this available energy is given by $-\Delta F$. Hence for any such process the criterion of equilibrium is that for an infinitesimal change $dF = 0$. To apply this criterion we imagine that the process can proceed reversibly by an infinitesimal amount and thus we calculate the maximum work performed in this imaginary process, and from this we subtract the maximum work which had to be performed by the system as a whole as a result of *external opposing* forces, i.e. we subtract the integral $\int PdV$ where P represents a pressure equivalent to the total opposing forces.

The criteria of equilibria which we propose to employ are thus

$$dS = 0\,; \quad (dA)_{TV} = 0\,; \quad (dF)_T = 0.$$

Before proceeding to their application to the problems of physical chemistry, however, it will be well to consider these functions

A and F a little more closely in relation to the variables of a system pressure, volume, and temperature.

We have defined these functions as follows:

$$A = U - TS$$
$$F = H - TS.$$

Let us differentiate them with respect to volume keeping the temperature constant. We obtain

$$\left(\frac{\partial A}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T - T\left(\frac{\partial S}{\partial V}\right)_T \quad . \quad . \quad . \quad . \quad (8)$$

$$\left(\frac{\partial F}{\partial V}\right)_T = \left(\frac{\partial H}{\partial V}\right)_T - T\left(\frac{\partial S}{\partial V}\right)_T \quad . \quad . \quad . \quad . \quad (9)$$

But by equation III (22) we have

$$P = T\left(\frac{\partial S}{\partial V}\right)_T - \left(\frac{\partial U}{\partial V}\right)_T$$

so that, for an isothermal process of expansion, we have

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

or

$$dA = -PdV$$

or the maximum work done by the system in expanding from V_1 to V_2 is

$$-\Delta A = -\int dA = \int_{V_1}^{V_2} PdV \quad . \quad . \quad . \quad . \quad (10)$$

which corresponds with our previous definition of $-\Delta A$.

On the other hand, if we differentiate A and F with respect to pressure keeping the temperature constant, we obtain—

$$\left(\frac{\partial A}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T - T\left(\frac{\partial S}{\partial P}\right)_T \quad . \quad . \quad . \quad . \quad (11)$$

$$\left(\frac{\partial F}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - T\left(\frac{\partial S}{\partial P}\right)_T \quad . \quad . \quad . \quad . \quad (12)$$

But by equation III (28) we have

$$V = \left(\frac{\partial H}{\partial P}\right)_T - T\left(\frac{\partial S}{\partial P}\right)_T \quad . \quad . \quad .$$

so that equation (12) becomes

$$\left(\frac{\partial F}{\partial P}\right)_T = V \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

or for an isothermal reversible process we may write

$$\int dF = \int V dP \quad . \quad . \quad . \quad . \quad . \quad . \quad (13a)$$

Now in Chapter I we considered a process known as the Three Stage Distillation Process, in which one mole of pure solvent was transferred isothermally and reversibly, via the vapour state into a solution. The maximum work done was found to be (equation I (13))

$$-\Delta A = p_0(V_0 - v_0) + \int_{V_0}^{V_1} p dV + p_1(v_1 - V_1)$$

where p_0 is the vapour pressure of the solvent, p_1 the vapour pressure of the solution, V_0 and V_1 are the volumes occupied by one mole of vapour at pressures p_0 and p_1 respectively and v_0 and v_1 the volume occupied by one mole of solvent in the pure solvent and in the solution respectively. We saw, however, that if we neglect v_0 and v_1 in comparison with V_0 and V_1, as we legitimately may in practice, then this expression reduces to

$$-\Delta A = \int V dp.$$

Now what we have actually done in neglecting these small volumes is to regard the volume of the whole system as constant, i.e. to neglect the change in volume of the mole of solvent on transferring it from the solvent to the solution. Since, then, the volume change is zero, we should expect the value obtained for the maximum work, or the decrease in the work content, to be equal to the decrease in the **free energy** of the system. But this is actually what we have obtained since we have just shown that $\int V dP = \int dF$ for an isothermal reversible process. The decrease in the work content is, strictly speaking, slightly different from this quantity although the error in regarding the two as identical is not very large, in this particular case. As a result of this close agreement between the values of ΔA and ΔF, much unfortunate confusion has arisen between them in the literature and it will therefore be well to distinguish carefully between the two quantities even in such a case. If the volume change involved is not negligible as, for instance, in the case of a gaseous reaction, the free energy

change is by no means equal to the change in the work content and the two may even be of opposite signs.

Let us now differentiate F with respect to the temperature, the pressure being maintained constant. We obtain

$$\left(\frac{\partial F}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P - T\left(\frac{\partial S}{\partial T}\right)_P - S \quad . \quad . \quad . \quad (14)$$

But, by equation III (18) the first two terms on the right-hand side are identical, so that equation (14) becomes

$$\left(\frac{\partial F}{\partial T}\right)_P = -S \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

or since $F = H - TS$, we have $-S = (F - H)/T$ so that

$$T\left(\frac{\partial F}{\partial T}\right)_P = F - H \quad . \quad . \quad . \quad . \quad . \quad (15)$$

If, now, instead of the integrals F and H, we consider change in these functions $-\Delta F$ and $-\Delta H$ we obtain

$$T\left(\frac{\partial(-\Delta F)}{\partial T}\right)_P = \Delta H - \Delta F \quad . \quad . \quad . \quad . \quad (16)$$

which will be seen to be of the same form as the Gibbs-Helmholtz equation

$$T\left(\frac{\partial(-\Delta A)}{\partial T}\right)_V = \Delta U - \Delta A \quad . \quad . \quad . \quad . \quad (17)$$

except that F and H are replaced by U and A and that whereas equation (16) refers to reactions at constant volume, equation (17) refers to processes at constant pressure.

There is one point in our discussion which has as yet only received a passing reference and which must now be considered a little more completely. This is the fact that we have entirely disregarded the integration constant in our derivation of the expressions for the free energy F and the work content A. Now we shall see in a later chapter that at absolute zero any change ΔF in the free energy is accompanied by an equal change in the heat content, i.e. at absolute zero $\Delta F = \Delta H$. Moreover, there is at this temperature no tendency for the system to lose free energy by a fall in the temperature, so that it seems reasonable to assume that at this temperature the free energy is equal to the heat content, or $F = H$. But if we substitute the condition $T = 0$ in the expression for the free energy which we have given, namely $F = H - TS$, we obtain $F = H$. Hence it appears that we are

justified in equating the integration constant to zero. Similar considerations apply to the definition of the work content A. When we come to deal with the Nernst Heat theorem in Chapter XII, the procedure will become clearer.

Before closing this chapter, however, we propose to give a table which will be found to be of great assistance in solving what will already have appeared to the student a somewhat laborious problem. We have introduced, one by one, quite an array of properties of a system, denoted by P, T, V, H, U, A, S, F, and we have derived a number of mathematical relations between these properties. However, it will be perfectly obvious that we have not nearly exhausted all the possible relations which could exist between these functions, and in order to facilitate the calculation of these expressions, Bridgman (*Phys. Rev.*, (2), 1914, **3**, 273) has elaborated the following method.

A series of expressions of the form $(\partial x)_z$ are given in the table where x and z are any of the above properties. By dividing one of these expressions by another, say $(\partial x)_z$ by $(\partial y)_z$, we obtain the value of the differential coefficient $\left(\frac{\partial x}{\partial y}\right)_z$. The theory of the method is given in the paper cited, and it will be seen from the table that the following general expression holds between the values in the table:

$$(\partial x)_z = -(\partial z)_x.$$

The following example will suffice to indicate the application of the method to specific cases. From the table we obtain $(\partial F)_T = -V$ and $(\partial P)_T = -1$, so that dividing one by the other we get

$$\left(\frac{\partial F}{\partial P}\right)_T = \frac{(\partial F)_T}{(\partial P)_T} = +V$$

which is the value given in expression (13).

Bridgman has had to employ three derivatives of the above properties in terms of which the others are expressed. He has therefore chosen three which are readily measureable, namely $\left(\frac{\partial V}{\partial T}\right)_P$, $\left(\frac{\partial V}{\partial P}\right)_T$ and $C_p = \left(\frac{\partial H}{\partial T}\right)_P$.

The following is the table:

$$(\partial T)_P = -(\partial P)_T = 1$$
$$(\partial V)_P = -(\partial P)_V = (\partial V/\partial T)_P$$
$$(\partial S)_P = -(\partial P)_S = C_p/T$$
$$(\partial U)_P = -(\partial P)_U = C_p - P(\partial V/\partial T)_P$$
$$(\partial H)_P = -(\partial P)_H = C_p$$
$$(\partial F)_P = -(\partial P)_F = -S$$
$$(\partial A)_P = -(\partial P)_A = -(S + P(\partial V/\partial T)_P)$$
$$(\partial V)_T = -(\partial T)_V = -(\partial V/\partial P)_T$$
$$(\partial S)_T = -(\partial T)_S = (\partial V/\partial T)_P$$
$$(\partial U)_T = -(\partial T)_U = T(\partial V/\partial T)_P + P(\partial V/\partial P)_T$$
$$(\partial H)_T = -(\partial T)_H = -V + T(\partial V/\partial T)_P$$
$$(\partial F)_T = -(\partial T)_F = -V$$
$$(\partial A)_T = -(\partial T)_A = P(\partial V/\partial P)_T$$
$$(\partial S)_V = -(\partial V)_S = \frac{1}{T}[C_p(\partial V/\partial P)_T + T(\partial V/\partial T)^2_P]$$
$$(\partial U)_V = -(\partial V)_U = C_p(\partial V/\partial P)_T + T(\partial V/\partial T)^2_P$$
$$(\partial H)_V = -(\partial V)_H = C_p(\partial V/\partial P)_T + T(\partial V/\partial T)^2_P - V(\partial V/\partial T)_P$$
$$(\partial F)_V = -(\partial V)_F = -[V(\partial V/\partial T)_P + S(\partial V/\partial P)_T]$$
$$(\partial A)_V = -(\partial V)_A = -S(\partial V/\partial P)_T$$
$$(\partial U)_S = -(\partial S)_U = \frac{P}{T}[C_p(\partial V/\partial P)_T + T(\partial V/\partial T)^2_P]$$
$$(\partial H)_S = -(\partial S)_H = -VC_p/T$$
$$(\partial F)_S = -(\partial S)_F = -\frac{1}{T}[VC_p - ST(\partial V/\partial T)_P]$$
$$(\partial A)_S = -(\partial S)_A = \frac{1}{T}[P\{C_p(\partial V/\partial P)_T + T(\partial V/\partial T)^2_P\} + ST(\partial V/\partial T)_P]$$
$$(\partial H)_U = -(\partial U)_H = -V[C_p - P(\partial V/\partial T)_P] - P[C_p(\partial V/\partial P)_T + T(\partial V/\partial T)^2_P]$$
$$(\partial F)_U = -(\partial U)_F = -V[C_p - P(\partial V/\partial T)_P] + S[T(\partial V/\partial T)_P + P(\partial V/\partial P)_T]$$
$$(\partial A)_U = -(\partial U)_A = P[C_p(\partial V/\partial P)_T + T(\partial V/\partial T)^2_P]$$
$$(\partial F)_H = -(\partial H)_F = -V(C_p + S) + TS(\partial V/\partial T)_P$$
$$(\partial A)_H = -(\partial H)_A = -[S + P(\partial V/\partial T)_P][V - T(\partial V/\partial T)_P] + P(\partial V/\partial P)_T$$
$$(\partial A)_F = -(\partial F)_A = -S[V + P(\partial V/\partial P)_T] - PV(\partial V/\partial T)_P$$

CHAPTER VI

APPLICATIONS OF THE CRITERIA OF EQUILIBRIA TO HOMOGENEOUS SYSTEMS

We shall consider, first of all, the case of a gaseous reaction which is carried out at constant temperature and volume, and we may evidently employ either the criterion $(dA)_{TV} = 0$, or the more general one $(dF)_T = 0$. In order to do this we must introduce a conception, due originally to van't Hoff, which is known as the "Equilibrium Box." Such a box is supposed to be of constant volume and to have sides, each of which is permeable to one only of the reacting species. Let us consider a reaction occurring at constant temperature of the form

$$A + B = C + D.$$

Such a reaction, as we know, will proceed until the equilibrium state is attained. Let us suppose that the four substances are all present in the box and that equilibrium already exists between them. The concentrations in the box will be denoted by C_A, C_B, C_C, C_D.

Now suppose an infinitely small number dn moles of A are introduced reversibly (that is at the equilibrium concentration and pressure) through one of the semi-permeable sides, into the box. The osmotic work done upon the system will be $P_A V_A$ where P_A is the partial pressure of A in the equilibrium box, V_A is the volume occupied by dn moles at this pressure. At the same time, suppose dn moles of B are also introduced isothermally and reversibly through another wall of the box. The osmotic work performed upon the system is $-P_B V_B$. Hence the total osmotic work performed *by* the system is $-P_A V_A - P_B V_B$. It will be evident that these quantities are too small to affect the concentrations of A and B in the box appreciably and the two species react immediately at constant volume and temperature forming dn moles of C and dn moles of D. These are immediately removed through two of the remaining walls, the opposing pressures being equal to

the partial pressures of C and D in the box, so that the removal is reversible. The work done by the system is $P_C V_C + P_D V_D$. Now since the substances in the box are in equilibrium and since equilibrium also obtains between the gases inside and outside the box, the maximum work done by the system over the whole of this imaginary process must be zero, the constancy of the volume ensuring that no external work is required. In symbols—

$$-\Delta A = -\Delta F = -P_A V_A - P_B V_B + P_C V_C + P_D V_D = 0.$$

This, of course, is only true provided the gases enter and leave the box in a reversible manner, i.e. at the equilibrium concentrations and pressures.

We may now imagine this process continued until 1 mole of A and 1 mole of B have reacted and been transformed to 1 mole of C and 1 mole of D, the whole process being carried out by infinitely small amounts and the net work over the whole process being zero.

Deduction of the Law of Mass Action for a Homogeneous Gaseous System.

We now consider two equilibrium boxes I and II, of the type already described. The gaseous reaction, which we shall consider, is as before $A + B = C + D$, and we regard the equilibrium concentrations as different in the two boxes. Let us denote them as follows :

	Concentrations.	Partial Pressures.	Vol. of dn moles.
In box I	C_A, C_B, C_C, C_D.	P_A, P_B, P_C, P_D.	v_A, v_B, v_C, v_D.
In box II	C'_A, C'_B, C'_C, C'_D.	P'_A, P'_B, P'_C, P'_D.	v'_A, v'_B, v'_C, v'_D.

We perform the following isothermal reversible cycle upon the system :

(*a*) Isothermally and reversibly withdraw dn moles of A from box I. The work done by the system is $P_A v_A$. The volume of this portion of substance A is now changed reversibly from v_A to v'_A, by means of the cylinder and piston denoted III in the diagram (Fig. 15), when the work done by the system is $\int_{v_A}^{v'_A} P dv$. It is then compressed isothermally and reversibly into box II, when the work done by the system is $-P'_A v'_A$. The total work done by the system in this three-stage process is

$$P_A v_A + \int_{v_A}^{v'_A} P dv - P'_A v'_A.$$

These three terms add mathematically to give $\int_{P'A}^{P_A} vdP$. That this happens to equal the free energy decrease $-\Delta F$ of the system is due to the fact that we have not altered the total volume of the two boxes.

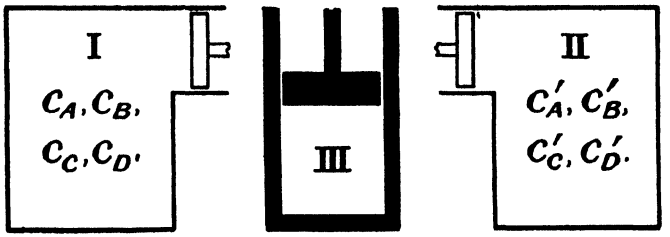

FIG. 15.

(*b*) Simultaneously we withdraw dn moles of B from I and transfer it isothermally and reversibly to the second box in a precisely similar manner. The work done, or since the volume is constant, the free energy decrease is $\int_{P'B}^{P_B} vdP$. These substances now react in box II, no work whatever being performed since the system is in equilibrium. The dn moles of C and D thus formed are then transferred isothermally and reversibly from box II to box I. The work of transfer is $\int_{P_C}^{P'_C} vdP + \int_{P_D}^{P'_D} vdP$.

The moles now react in box I forming dn moles of A and dn moles of B so that the whole system is now in its original state and since the contents of box I are in equilibrium it is evident that this last reaction is not accompanied by any work. The total work done by the system over the whole series of changes is—

$$-\Delta A = \int_{P'A}^{P_A} vdP + \int_{P'B}^{P_B} vdP + \int_{P_C}^{P'_C} vdP + \int_{P_D}^{P'_D} vdP \quad . \quad (1)$$

But since we have carried out the whole cycle isothermally and reversibly the total maximum work of the process must be zero, i.e. $-\Delta A = 0$. As we have already pointed out, we have in this cycle also determined the free energy decrease, since for any system at constant volume $-\Delta A = -\Delta F$.

Let us now assume that we can apply the gas laws to the system under consideration. If we do this we obtain

$$-\Delta A = -\Delta F = dnRT\ ln\frac{P_A}{P'_A} + dn.RT\ ln\frac{P_B}{P'_B} + dn.RT\ ln\frac{P'_C}{P_C} + dnRT\ ln\frac{P'_D}{P_D} = 0.$$

Dividing through by $dn.RT$ we obtain

$$ln\frac{P_A}{P'_A} + ln\frac{P_B}{P'_B} - ln\frac{P_C}{P'_C} - ln\frac{P_D}{P'_D} = 0$$

or

$$\frac{P_A \times P_B}{P_C \times P_D} = \frac{P'_A \times P'_B}{P'_C \times P'_D} = \text{Constant} = K_p \text{ (say)} \quad . \quad (2)$$

If, now we substitute $P = RTC$, we obtain the similar equation—

$$\frac{C_A \times C_B}{C_C \times C_D} = \frac{C'_A \times C'_B}{C'_C \times C'_D} = \text{Constant} = K_c \quad . \quad . \quad (3)$$

This is the well-known law of mass action as enunciated by Guldberg and Waage. It refers, as we have seen, to a homogeneous gaseous reaction at constant temperature. Moreover, its deduction from thermodynamical principles depends upon the assumption that the system behaves like a perfect gas, and hence the applicability of the law is limited to those cases for which this assumption is valid.

We now pass on to a very important consideration which is known from its originator as the van't Hoff Isotherm.

Van't Hoff Isotherm. Let us consider a reaction such as the following:

$$n_1A + n_2B + n_3C + \ldots = n_1'A' + n_2'B' + n_3'C' + \ldots$$

and suppose we have a series of large reservoirs containing respectively A, B, C, ..., A', B', C', ..., all at arbitrary concentrations which we shall represent by C_A, C_B, C_C, ..., $C_{A'}$, $C_{B'}$, $C_{C'}$, ... These reservoirs are supposed to be of sufficient capacity that the loss of say n_1 moles of A from the reservoir containing that substance will not have any appreciable effect upon the concentration of A in that reservoir. In addition to these reservoirs, we have an equilibrium box one side of which is permeable to each of the substances A, B, C, ..., A', B', C', ..., respectively. In this box the substances are all at the equilibrium concentrations, which

we shall denote by (A), (B), (C), ..., (A'), (B'), (C'), ... The whole system is maintained at a constant temperature.

The following process is accomplished isothermally and reversibly, each part of the process occurring simultaneously with the other parts. Let us denote the reservoirs by the symbols R_A, R_B, ... $R_{A'}$, etc.

We transfer n_1 moles of A from R_A to the equilibrium box
n_2 ,, ,, B ,, R_B ,, ,, ,,
n_3 ,, ,, C ,, R_C ,, ,, ,,
etc., etc., etc.

If this process is carried on proportionately but in infinitesimal quantities at a time the substances react as soon as they enter the box forming the resultants A', B', C', etc., which may immediately be removed and transferred to the respective reservoirs. In this way the total concentration of each of the substances in the equilibrium box will remain unaltered throughout the whole process of transfer. Eventually we shall have transferred from the equilibrium box—

n_1' moles of A' to reservoir $R_{A'}$
n_2' moles of B' to reservoir $R_{B'}$
n_3' moles of C' to reservoir $R_{C'}$
etc., etc., etc.

The process is now complete and we propose to determine the decrease in free energy of the whole system as a result of the change. This may be accomplished by either of two methods. The first consists simply in calculating the decrease in free energy accompanying the transfer of each of the species, A, B, ..., A', B', etc., by means of the relation obtained in the last chapter (equation 13a), namely

$$\Delta F = \int dF = \int V dP.$$

The other method which is the one originally employed by van't Hoff is to regard the reservoirs as being of sufficient size that the change in concentration is negligible if **the volume is kept constant.** Van't Hoff thus calculates the maximum work accompanying this reversible, imaginary, process, and hence he determines the decrease in the work content which occurs when n_1 moles of A at concentration C_A plus n_2 moles of B at concentration C_B

plus, etc., react to give n'_1 moles of A' at concentration $C_{A'}$, plus n'_2 moles of B' at concentration $C_{B'}$ plus, etc., the volume of the whole system being constant. His formulæ therefore refer to $-\Delta A$, for a system at constant volume, although it is evident that what he really obtained is $-\Delta F$ for any reaction whatsoever which occurs at constant temperature.

Now let us consider the transfer of one of the substances, say A; n_1 moles of this substance are transferred to the equilibrium box from the reservoir R_A. The free energy decrease is therefore given by

$$-\Delta F = \int_{P_{\epsilon A}}^{P_A} v dP$$

where $P_{\epsilon A}$ is the partial pressure of A in the equilibrium box and P_A is the pressure of the gas in the reservoir R_A. It is evident, from our previous considerations, that this is equal to the maximum work done by the system, during the process of transfer, if the volume is regarded as constant.

Let us now assume, as before, that the gas laws may be applied to the system. The decrease in the free energy of the system due to the transfer thus becomes

$$-\Delta F_1 = n_1 . RT \ ln \frac{P_A}{P_{\epsilon A}}$$

since we are dealing with n_1 moles of the substance.

On the other hand, if we consider the transfer of n'_1 moles of A', since the direction is from the equilibrium box to the reservoir, the free energy decrease must be

$$-\Delta F_1' = -n'_1 . RT \ ln \frac{P_{A'}}{P_{\epsilon A'}}.$$

We must now sum all these terms in order to obtain the total decrease in the free energy. We thus obtain

$$-\Delta F = \Sigma n . RT \ ln \frac{P}{P_\epsilon} - \Sigma n' . RT \ ln \frac{P'}{P_\epsilon'} \quad . \quad . \quad (4)$$

Since we have assumed the applicability of the gas laws we may replace P by RTC in this equation and obtain

$$-\Delta F = \Sigma n . RT \ ln \frac{C}{C_\epsilon} - \Sigma n' . RT \ ln \frac{C'}{C_\epsilon'} \quad . \quad . \quad (4a)$$

Now it is usual to express the equilibrium constant of the reaction in the following manner

$$K_c = \frac{(A')^{n'_1}.(B')^{n'_2}.(C')^{n'_3}\ \ldots}{(A)^{n_1}.(B)^{n_2}.(C)^{n_3}\ \ldots}$$

so that we may write

$$ln\ K_c = \Sigma n'\ ln\ C_c' \ldots \Sigma n\ ln\ C_c.$$

Hence equation (4*a*) becomes

$$-\Delta F = RT\ ln\ K_c - RT.\Sigma n'\ ln\ C' + RT.\Sigma n\ ln\ C.$$

The last two terms of this expression are of the form

$$-RT\ ln \frac{C'_{A'}.C'_{B'}.C'_{C'}.C'_{D'}\ \ldots\ldots}{C_A.C_B.C_C.C_D\ \ldots\ldots}$$

that is, it has the same form as the equilibrium constant term $RT\ ln\ K_c$ except that it is negative in sign and that the concentrations are the arbitrary values instead of the equilibrium concentrations. This term is usually expressed by the symbols $-RT\Sigma n.ln\ C$, so that we may write

$$-\Delta F = RT.ln\ K_c - RT\Sigma n.ln\ C \quad . \quad . \quad . \quad (5)$$

This equation is known as the van't Hoff Isotherm and is of great practical importance.

It will be evident from equation (3) that if we express the equilibrium constant in terms of the partial pressures of the reacting substances, instead of concentrations, i.e. if we put

$$K_p = \frac{P_{eA'} \times P_{eB'} \times P_{eC'}\ \ldots}{P_{eA} \times P_{eB} \times P_{eC}\ \ldots\ldots}$$

then we may equally well express the isotherm as follows:

$$-\Delta F = RT\ ln\ K_p - RT\Sigma n.ln\ P \quad . \quad . \quad . \quad (6)$$

where $\Sigma n.ln\ P$ is of the same form as the equilibrium constant K_p, but contains the arbitrary pressures instead of the equilibrium values.

If the reaction which we are considering occurs at constant volume, i.e. if, in the deduction of the isotherm, the total volume is regarded as constant, then $-\Delta F = -\Delta A$, so that

$$-\Delta A = RT.\ ln\ K_c - RT\Sigma n.\ ln\ C \quad . \quad . \quad . \quad (7)$$

We now propose to determine the manner in which the equilibrium constant of a reaction varies with the temperature, and we shall consider two important cases, namely reactions at constant

volume and reactions at constant pressure. In the first case, that of constant volume, we have seen that the isotherm takes the form—

$$-\Delta A = RT\ ln\ K_c - RT\Sigma n.ln\ C.$$

Let us differentiate this expression with respect to temperature, then since the volume is constant

$$\left(\frac{\partial(-\Delta A)}{\partial T}\right)_V = R\ ln\ K_c + RT\left(\frac{\partial\ ln\ K_c}{\partial T}\right)_V - R\Sigma n\ ln\ C - RT\left(\frac{\partial(\Sigma n\ ln\ C)}{\partial T}\right)_V.$$

But, by equation (7), we have

$$R\ ln\ K_c - R\Sigma n.ln\ C = \frac{-\Delta A}{T}$$

and since the concentrations C are arbitrary and in no way dependent upon the temperature, it follows that

$$\frac{\partial(\Sigma n.\ ln\ C)}{\partial T} = 0.$$

Hence we obtain, on multiplying the expression through by T,

$$T\left(\frac{\partial(-\Delta A)}{\partial T}\right)_V = RT^2\frac{\partial\ ln\ Kc}{\partial T} - \Delta A \quad . \quad . \quad . \quad (8)$$

Now the Gibbs-Helmholtz equation gives (equation V (17))

$$T\left(\frac{\partial(-\Delta A)}{\partial T}\right)_V = \Delta U - \Delta A.$$

Hence, by comparing the two equations, we obtain

$$\left(\frac{\partial\ ln.\ K_c}{\partial T}\right)_V = \frac{\Delta U}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

But we are considering a reaction which occurs at constant volume and we have seen that for such a reaction by equation I (5)

$$\Delta U = q_v$$

where q_v is the heat absorbed by the system during the reaction. Moreover, since the equilibrium constant K_c is itself independent of the volume, it is unnecessary to write the differential coefficient of $ln\ K_c$ as a partial coefficient. Hence equation (9) may be written

$$\frac{d\ ln\ Kc}{dT} = \frac{q_v}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

This expression is known as the van't Hoff Isochore and is of great

practical utility. It follows, as an immediate consequence of this equation that if we are dealing with a reaction of the form

$$n_1A + n_2B + \ldots\ldots = n_1'A' + n_2'B' + \ldots\ldots$$

which involves the absorption of heat, i.e. q_v is positive, and if, in the usual way, we write

$$K_c = \frac{(A')^{n_1'}(B')^{n_2'} \ldots\ldots}{(A)^{n_1}(B)^{n_2} \ldots\ldots}$$

then an increase in temperature is followed by an increase in the value of the equilibrium constant K_c, that is the forward reaction is favoured (i.e. from left to right).

We shall now turn our attention to the case of a reaction at constant pressure. For this case it will be found convenient to employ the isotherm in the form

$$-\Delta F = RT \ln K_p - RT\Sigma n \ln P$$

since if the total pressure is kept constant, the concentrations of the various reacting substances, C_A, C_B, $C_{A'}$, etc., must vary with the temperature, and we can therefore no longer write $\frac{\partial(\Sigma n . \ln C)}{\partial T} = 0$, whereas the constancy of the total pressure requires the constancy of the partial pressures of these substances and hence we have

$$\frac{\partial(\Sigma n . \ln P)}{\partial T} = 0.$$

Let us now differentiate $-\Delta F$ with respect to temperature,

$$\left(\frac{\partial(-\Delta F)}{\partial T}\right)_P = R \ln K_p + RT\frac{d \ln K_p}{dT} - R\Sigma n \ln P - RT\frac{\partial(\Sigma n \ln P)}{\partial T}$$

$$= \frac{-\Delta F}{T} + RT\, d \ln K_p/dT$$

so that we have

$$T\left(\frac{\partial(-\Delta F)}{\partial T}\right)_P = -\Delta F + RT^2\frac{d \ln K_p}{dT} \quad . \quad . \quad (11)$$

But by equation V (16)

$$T\left(\frac{\partial(-\Delta F)}{\partial T}\right)_P = -\Delta F + \Delta H$$

so that, comparing the two equations, we obtain

$$\frac{d\ ln\ K_p}{dT} = \frac{\Delta H}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

But equation I (7*a*) gives $\Delta H = q_p$, where q_p is the heat of reaction at constant pressure (heat absorbed). Hence

$$\frac{d\ ln\ K_p}{dT} = \frac{q_p}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

This relation follows also from the fact that if the expansion is represented at constant pressure by the increase in the number of moles, i.e. Σn, then assuming the gas laws

$$q_p = q_v + P\Delta V = q_v + \Sigma n.RT.$$

Moreover, since $P = RTC$, we have $K_p = K_c \times (RT)^{\Sigma n}$ so that

$$ln\ K_p = ln\ K_c + \Sigma n.\ ln\ RT.$$

Hence we have, on differentiating with respect to T

$$\begin{aligned}\frac{d\ ln\ K_p}{dT} &= \frac{d\ ln\ K_c}{dT} + \Sigma n.\frac{1}{T} \\ &= \frac{q_v}{RT^2} + \frac{\Sigma n.\ RT}{RT^2} \\ &= \frac{q_p}{RT^2}\end{aligned}$$

which is identical with equation (13).

In actual practice it is usual to employ the integrated form of these equations. Now as an approximation, for a small temperature range, we may regard the heat of reaction at constant volume, q_v as constant and integrate the isochore between the limits T_1 and T_2 at which the equilibrium constants are K_1 and K_2. We obtain

$$\log K_1 - \log K_2 = 0{\cdot}4343\frac{q_v}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad . \quad . \quad (14)$$

the constant 0·4343 merely converting the logarithms from the natural to the Briggsian type.

The following example will illustrate the use of this formula (Knox, *Physico-Chemical Calculations*, Problem 166).

At a temperature 27° C. and 1 atmosphere pressure the equilibrium constant of the reaction $N_2O_4 = 2NO_2$, namely

$$K_c = C^2_{NO_2}/C_{N_2O_4}$$

is 0·0017. At 111° C. the constant is 0·204. What is the heat of dissociation per mole at constant volume ?

$$q_v = R \ln \frac{K_2}{K_1}\left(\frac{T_1 T_2}{T_2 - T_1}\right)$$

$R = 2$ calories per mole

$T_1 = 27°$ C. $= 300°$ K. ; $T_2 = 111°$ C. $= 384°$ K.

Hence
$$q_v = 2 \times 2{\cdot}313 \log \frac{0{\cdot}204}{0{\cdot}0017} \times \frac{300 \times 384}{84}$$
$$= 13{,}110 \text{ calories.}$$

The assumption that the heat of reaction at constant volume, or the increase ΔU in the internal energy of the system, is independent of the temperature, is at best only an approximation, however, and we must express this quantity as a function of the temperature, if we are to integrate the isochore. This is done in the following manner.

The direct measurement of the heats of reaction q_v at various temperatures is not, in general, sufficiently accurate for our purpose. However, we have, by Kirchhoff's equation (expression I (26))

$$\left(\frac{\partial(\Delta U)}{\partial T}\right)_V = s_2 - s_1$$

where s_1 and s_2 are the total heat capacities of the reactants and resultants respectively at constant volume. Now $s_1 = \Sigma C_{v\ \text{Reactants}}$ and $s_2 = \Sigma C_{v\ \text{Resultants}}$. Hence $s_2 - s_1$ is the total change in the heat capacity at constant volume and equal to

$$\Sigma C_{v\ \text{Resultants}} - \Sigma C_{v\ \text{Reactants}} = \Delta C_v, \text{ say.}$$

Now experiment shows that we may write C_v for one mole of each substance as a function of the temperature as follows :

$$C_v = \alpha + \beta T + \gamma T^2 + \ldots \quad . \quad . \quad . \quad . \quad (15)$$

where α, β, γ, are constants for the particular substance, which may be determined experimentally. Usually the constants decrease so rapidly in magnitude that only the first three or four terms are needed. Hence we may write

$$\Delta C_v = \Delta\alpha + \Delta\beta T + \Delta\gamma T^2 + \ldots \quad . \quad . \quad . \quad (16)$$

where $\Delta\alpha$, etc., represent the algebraic sum of all the terms α for all the species multiplied by the number of moles of that sub-

stance represented in the stoicheioimetric equation, i.e. $\Delta\alpha = \Sigma n\alpha$. Hence by the Kirchhoff equation

$$\frac{\partial(\Delta U)}{\partial T} = \Delta\alpha + \Delta\beta T + \Delta\gamma T^2 + \ldots \quad . \quad . \quad . \quad (17)$$

On integrating this expression we obtain

$$\Delta U = \Delta U_0 + \Delta\alpha T + \frac{\Delta\beta}{2}T^2 + \frac{\Delta\gamma}{3}T^3 + \ldots \quad . \quad . \quad (18)$$

where ΔU_0 is a constant of integration which can be calculated from one experimental value of the heat of reaction at constant volume q_v. It is **not**, as might be thought, equal to the heat of reaction at absolute zero, since as we have shown in an earlier chapter, the empirical expression (15) is only valid over a limited temperature range.

If, now, we employ equation (18) to integrate the van't Hoff Isochore, we have

$$\frac{d\ ln\ K_c}{dT} = \frac{\Delta U}{RT^2} = \frac{\Delta U_0}{RT^2} + \frac{\Delta\alpha}{RT} + \frac{\Delta\beta}{2R} + \frac{\Delta\gamma T}{3R} + \ldots$$

so that on integrating we obtain—

$$ln\ K_c = \frac{-\Delta U_0}{RT^2} + \frac{\Delta\alpha}{R}\ ln\ T + \frac{\Delta\beta}{2R}T + \frac{\Delta\gamma}{6R}T^2 + \ldots + I \quad (19)$$

where I is an integration constant. It will be evident that this equation is only useful over a limited temperature range and that the integration constant I has no fundamental significance as it was once thought to have. The equation is best used, either by calculating I for some value of the temperature in the range within which the equation is valid, and hence calculating the value of K_c at some other temperature in the range, or by considering only differences between the values of $ln\ K_c$, when the integration constant vanishes.

The expression just deduced is of great practical utility, however, within the temperature range for which it is valid, since for many reactions the volume change is either zero or negligibly small. It enables us to calculate K_c from specific heat data provided the heat of reaction for one particular temperature is known and also the value of K_c for some one temperature.

More important still, however, is the integration of the other similar expression which we deduced for the case of a reaction at

constant pressure, and involving the equilibrium constant K_p. The expression is

$$\frac{d\ ln\ K_p}{dT} = \frac{q_p}{RT^2} = \frac{\Delta H}{RT^2}.$$

Now we have seen by equation I (17) that for any substance

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P.$$

Hence if, in any reaction, ΔC_p is the total change in the heat capacity at constant pressure, then in the same notation as before

$$\Delta C_p = \left(\frac{\partial \Delta H}{\partial T}\right)_P \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

This is, as we should expect, of the same form as Kirchhoff's equation, except that as usual for the case of constant pressure H replaces U. Now, as before, we may express the specific heat of any substance as a function of the temperature by means of the series

$$C_p = \alpha' + \beta' T + \gamma' T^2 + \ldots \quad . \quad . \quad . \quad . \quad . \quad (21)$$

where α', β', γ', are constants characteristic of each substance. Hence for the algebraic sum, we have

$$\Delta C_p = \Delta\alpha' + \Delta\beta' T + \Delta\gamma' T^2 + \ldots \quad . \quad . \quad . \quad . \quad (22)$$

On integration we obtain—

$$\Delta H = \Delta H_0 + \Delta\alpha' T + \frac{\Delta\beta'}{2} T^2 + \frac{\Delta\gamma'}{3} T^3 + \ldots \quad . \quad . \quad (23)$$

Hence

$$\frac{d\ ln\ K_p}{dT} = \frac{\Delta H_0}{RT^2} + \frac{\Delta\alpha'}{RT} + \frac{\Delta\beta'}{2R} + \frac{\Delta\gamma'}{3R} T + \ldots \quad . \quad . \quad (24)$$

Integrating we obtain—

$$ln\ K_p = \frac{-\Delta H_0}{RT} + \frac{\Delta\alpha'}{R}\ ln\ T + \frac{\Delta\beta'}{2R} T + \frac{\Delta\gamma'}{6R} T^2 + \ldots + I' \quad . \quad (25)$$

where I' again cannot be determined on the basis of classical thermodynamics and has the same limitations as the constant I. Of course, if we are considering the integration between two temperature limits this constant cancels out and we are thus enabled to calculate the value of K_p for any temperature whatever, provided we know the value for some one given temperature and the values of the constants ΔH_0, $\Delta\alpha'$, $\Delta\beta'$, $\Delta\gamma'$, which may be deter-

mined very simply from the experimental values of ΔH_0, α', β', γ', for the individual substances.

Application of the Entropy Criterion to Homogeneous Systems.

It will be both interesting and instructive to attempt the deduction of some of these formulæ by means of the criterion that the entropy of a completely isolated system is a maximum at the equilibrium point, or $dS = 0$. Suppose we have such a system at the constant temperature T and that the following reaction is taking place in that system

$$n_1A + n_2B + n_3C + \ldots = n_1'A' + n_2'B' + n_3'C' + \ldots$$

Let us assume that the equilibrium state has been attained and imagine the process to proceed by an infinitesimal amount. Changes will occur in the entropy values of each of the substances of infinitesimal amount; in the case of the reactants which are disappearing we have a decrease of the form $-dS_A$, $-dS_B$, etc., while for the reactants we have an increase of amount $+dS_{A'}$, $+dS_{B'}$, etc. Now since the entropy is an extensive property of any system it follows that the total entropy change over the whole system is equal to the algebraic sum of the changes in the entropy of all the individual substances. That is

$$dS = dS_{A'} + dS_{B'} + \ldots - dS_A - dS_B - \ldots\ldots$$

We must now, as before, introduce the assumption that the substances taking part in the reaction may all be regarded as perfect gases and we may then write (by equation III (10))

$$dS_A = C_v d\ ln\ T + Rd\ ln\ V_A \text{ for 1 mole}$$

and so on for all the other substances. Now since $V = 1/C$, it follows that $ln\ V = -ln\ C$, so that

$$dS_A = C_v d\ ln\ T - Rd\ ln\ C_A \quad . \quad . \quad . \quad . \quad (26)$$

But, since T is a constant it is evident that $d\ ln\ T = 0$, so that we have

$$dS_A = -Rd\ ln\ C_A \text{ for 1 mole.}$$

But there are n_1 moles of A taking part in the reaction, hence

$$dS_A = -Rn_1 d\ ln\ C_A = -R.d\ ln\ C_A^{n_1}.$$

Hence for the whole reaction

$$dS = Rd\ ln\ C_{A'}^{n_1'} + Rd\ ln\ C_{B'}^{n_2'} + \ldots - Rd\ ln\ C_A^{n_1} - Rd\ ln\ C_B^{n_2} - \ldots$$

Now the criterion of equilibrium is that $dS = 0$ and therefore if we divide the above expression through by R we have

$$d \ln C_{A'}^{n_1'} + d \ln C_{B'}^{n_2'} + \ldots - d \ln C_A^{n_1} - d \ln C_B^{n_2} - \ldots = 0.$$

On integrating this expression we obtain

$$\ln C_{A'}^{n_1'} + \ln C_{B'}^{n_2'} + \ldots - \ln C_A^{n_1} - \ln C_B^{n_2} - \ldots = \text{Constant}$$

or
$$\frac{C_{A'}^{n_1'} . C_{B'}^{n_2'} . \ldots}{C_A^{n_1} . C_B^{n_2} . \ldots} = \text{Constant} = K_c$$

which is the law of mass action. Hence by the application of the criterion $dS = 0$ for an infinitesimal change in an isolated system at the equilibrium state, together with the law for a perfect gas, we may arrive at the Guldberg and Waage expression and we have thus obtained the law by two independent thermodynamic methods.

We have up to this point been dealing with an infinitesimal change in a completely isolated system. We now propose to consider a different type of system, however. Suppose we have an equilibrium box in which the reaction just considered has proceeded to the equilibrium point. The sides are permeable, each to one only of the substances A, B, .. A', B' .... The temperature is maintained constant. In addition to the box, we have at the same temperature reservoirs of each of these substances at the equilibrium concentrations. The reaction is carried out in infinitesimal amounts just as in the case of the deduction of the van't Hoff isotherm until n_1 moles of A, n_2 moles of B, etc., have passed into the box, and n_1' moles of A', n_2' moles of B', etc., have passed out of the box to their respective reservoirs. It is proposed to find the total change in the entropy of the whole system. It will be assumed that the total pressure of the system is maintained constant, the volume changing in the general case by an amount equivalent to the change in the number of moles as a result of the reaction. Now the change in the entropy of the equilibrium box and its contents is evidently zero, since its initial and final states are identical. Let us now consider the change which has occurred in the entropy of the substance A. Now all that has happened to the reservoir containing this substance is that it has, at constant pressure, lost n_1 moles of A. No change in the volume of the remaining quantity of A has occurred. But for 1 mole of A,

if we again assume we are dealing with a perfect gas, the entropy S_A is given by

$$S_A = C_v \ln T + R \ln V_A + S'_A \text{ where } S'_A \text{ is a constant}$$
$$= C_v \ln T - R \ln C_A + S'_A$$

Similarly $S_{A'} = C_v \ln T - R \ln C_{A'} + S'_{A'}$

Hence the total change in entropy over the whole process is given by

$$\Delta S = n_1' S_{A'} + n_2' S_{B'} + \ldots - n_1 S_A - n_2 S_B \ldots$$

where ΔS as usual denotes an increase.

The system is, naturally, not isolated, since if it were the process could not take place. Actually it has absorbed heat q_p from the surroundings, since we are postulating constant pressure, and hence the increase in entropy of the system is equal to q_p/T where T is the absolute temperature of the system, every part of the process having been accomplished reversibly. We may therefore write

$$q_p/T = \Sigma n C_v \ln T - \Sigma R.n \ln C + \Sigma n S'.$$

But since we have postulated that the concentrations C in the reservoirs are the equilibrium concentrations, we may replace $\Sigma n \ln C$ by the equilibrium constant K_c and obtain

$$\ln K_c = \frac{1}{R} \Sigma n C_v \ln T - \frac{q_p}{RT} + \frac{\Sigma n S'}{R}.$$

It will be observed that this expression gives K_c as a function of the temperature alone and indicates the fact that it is independent of the volume and pressure, as indeed it should be. We will now transform this expression by replacing K_c by K_p. We know that $K_p = K_c(RT)^{\Sigma n}$ and hence

$$\ln K_p = \ln K_c + \Sigma n \ln RT$$

so that we have

$$\ln K_p = \frac{1}{R} \Sigma n C_v \ln T + \Sigma n \ln RT - \frac{q_p}{RT} + \frac{\Sigma n S'}{R}.$$

Let us now differentiate this expression with respect to temperature. Since we are dealing with a perfect gas C_v may be regarded as a constant and moreover $\Sigma n S'$ is a constant, so that

$$\frac{d \ln K_p}{dT} = \frac{\Sigma n C_v}{RT} + \frac{\Sigma n R}{RT} + \frac{q_p}{RT^2} - \frac{1}{RT} \frac{\partial q_p}{\partial T}.$$

But we know that for a perfect gas $C_p - C_v = R$, so that

$$\frac{\Sigma n C_v}{RT} + \frac{\Sigma n R}{RT} = \frac{\Sigma n C_p}{RT}$$

and moreover, by equation (20) we have $\frac{\partial q_p}{\partial T} = \Sigma n C_p$ so that the terms on the right-hand side all cancel except q_p/RT^2 and we are left with the relation

$$\frac{d \ln K_p}{dT} = \frac{q_p}{RT^2}$$

which is the equation deduced before from considerations of the free energy changes accompanying the reaction.

Application of Thermodynamics to Radiation.

We have now discussed the application of the principles of thermodynamics to homogeneous equilibria in gaseous systems. Before closing this chapter, however, it will be of interest to consider an application to a somewhat different homogeneous system. Imagine a completely enclosed space which is entirely empty of all matter, but contains a quantity of radiant energy. At any given temperature, radiation will pass from the walls to the enclosed space, and in the reverse direction, at different rates until a condition of dynamic equilibrium is attained, when the velocities become identical. Such an enclosed space is known as "Hohlraum." When equilibrium has once been established, there will be, at any instant, the same quantity of radiant energy present in the Hohlraum.

Now let us suppose that, by means of a sliding partition it is possible to change the nature of the walls of the Hohlraum. The partition is assumed to be frictionless and weightless, so that its motion does not involve any change in the free energy of the system. If the quantity of radiation in the Hohlraum is changed as a result of the change in the nature of the walls, this process, being spontaneous, must be accompanied by an increase ΔS_1 in the entropy of the system. The partition is now restored to its initial state, and there must be a spontaneous process in the system by which the quantity of radiation in the Hohlraum is brought back to its initial value. This involves a second increase in the entropy, ΔS_2. But, the entropy is an extensive property of the system, so that the total change in the entropy is zero, i.e.

$$\Delta S_1 + \Delta S_2 = 0.$$

Now, ΔS_1 and ΔS_2 are both positive, for spontaneous processes, so that

$$\Delta S_1 - \Delta S_2 = 0.$$

In other words, no spontaneous change occurs when the material of the walls of the Hohlraum is changed, or the equilibrium quantity of radiation present in the Hohlraum is independent of the material of which the walls are composed.

Again if we consider the Hohlraum to consist of a series of small cells, the spatial configuration of which may be changed, it may be shown by similar reasoning that the quantity of radiant energy present is independent of the shape of the walls. The quantity of radiant energy present is evidently proportional to the volume, for if we bring two such enclosures into contact, no change in the quantity occurs as a result of change in shape and the total quantity of radiation in the combined Hohlraum will be the sum of the two quantities initially present in the separate enclosures.

Let us now imagine a Hohlraum of volume V in which a small isothermal expansion takes place. We may regard the system as analogous to that of a liquid in contact with its saturated vapour. The quantity of radiation present is proportional to the volume and expansion therefore involves the emission of a greater quantity of radiation by the walls of the enclosure. This will involve an absorption of heat from the surroundings. But if a system absorbs heat reversibly at constant temperature, the entropy of the system must increase. Now equation III (24) gives for any system

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

Bartoli (1876) pointed out that according to this equation, which is obtained on the basis of purely thermodynamical considerations, radiant energy must exert a pressure upon the walls of the containing vessel in which it is confined and that this pressure must increase with temperature, since, as we have seen $\left(\frac{\partial S}{\partial V}\right)_T$ is a positive quantity.

It was shown by Maxwell, on the basis of his electromagnetic theory of light, that this radiation pressure should have the value

$$P = \tfrac{1}{3}\frac{U}{V} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

where U is the total internal energy of the Hohlraum. This value has been confirmed by experiment. For a process occurring at constant temperature it is evident that

$$\frac{U}{V} = \left(\frac{\partial U}{\partial V}\right)_T$$

so that equation (28) takes the form

$$\left(\frac{\partial U}{\partial V}\right)_T = 3P \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

But by equation III (31) we have for any system

$$P = T\left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial U}{\partial V}\right)_T \quad . \quad . \quad . \quad . \quad . \quad (30)$$

Hence we obtain

$$T\left(\frac{\partial P}{\partial T}\right)_V = 4P \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

or integrating at constant volume

$$ln\ P = 4\ ln\ T + \text{Constant}$$

or

$$P = \text{Constant} \times T^4 \quad . \quad . \quad . \quad . \quad . \quad (32)$$

This important relation is known as Stefan's law, since it was first obtained as an empirical relation by him in 1879. The first deduction from Thermodynamic principles was made by Boltzmann (*Ann. Physik.*, 1884 (2), **22**, 291, 616). The ratio of U/V is known as the energy density of the radiation and a comparison of equations (28) and (32) shows that

$$u = \frac{U}{V} = \text{Const.} \times T^4$$

or the radiation density is proportional to the fourth power of the absolute temperature for equilibrium temperature radiation. Such equilibrium temperature radiation has exactly the same characteristics as " black body radiation," i.e. radiation from a perfectly emissive or absorbing surface. Hence the amount of radiation evolved from a perfectly " black " body is proportional to the fourth power of the absolute temperature.

It will be observed that in the actual proof of the Stefan-Boltzmann law we have not confined ourselves to purely thermodynamical reasoning. We have employed thermodynamic principles coupled with ideas derived from the electromagnetic theory of light. Our conclusions are therefore limited by the applicability of this theory.

CHAPTER VII

DILUTE SOLUTIONS

Matter can exist in several different forms, but none of these is capable of being applied to such a multitudinous variety of purposes as is the state of solution. It is scarcely surprising, therefore, that solutions should have been given a prominent place in scientific investigations. Moreover, the phenomenon of solution has, from its very strangeness, always attracted attention. Men have come to regard a solid as something hard and concrete, something, if not quite, at least bordering upon the " real." What more lasting and capable of endurance, for example, than a bar of steel ? Liquids, on the other hand, give the impression of instability, in fact, the expression " unstable as water " has become proverbial. And yet, if we take, say a few crystals of common salt, and bring them into contact with water, they slowly disappear and we are left with a perfectly clear, homogeneous liquid which, on a superficial examination, is very similar to the water which we added originally. Even the bar of steel may be " dissolved " if we employ a substance such as hydrochloric acid as the liquid.

To the chemist the problem of interest is the actual state in which the solid which has disappeared is present in the solution, but a complete answer to this question is not yet forthcoming. Experiment shows that the dissolved substance is uniformly distributed throughout the bulk of the liquid, and it is found that, in general, there is a certain limiting concentration, termed the saturation point, beyond which it is impossible to go. Various phenomena exhibited by solutions, such as osmotic pressure and the lowering of the vapour pressure, the elevation of the boiling-point and the depression of the freezing-point of a liquid when another substance is dissolved in it, were investigated experimentally and were found to bear a close relation one to the others. These properties are, in view of this relationship, usually known

as the colligative properties of the solution and the student will already be familiar with them.

The development of a theory of solutions really begins, however, with the work of van't Hoff (*Zeit. phys. Chem.*, 1887, **1**, 181; Ostwald's *Klassiker*, No. 110; J. H. van't Hoff, *Sein Leiben und Werken*, Leipzig (1912); Ber., 1894, **27**, 1), who pointed out that there is a marked analogy between the laws governing solutions and those of gases. The existence of this analogy led to the conception of a kinetic basis for the treatment of solutions, and van't Hoff was thus enabled to predict some of the relationships between the various colligative properties. Actually van't Hoff himself merely indicated the kinetic origin of the osmotic pressure, but the kinetic theory has been exhaustively applied to solutions by later investigators, among whom may be mentioned: L. Boltzmann, *Zeit. phys. Chem.*, 1890, **6**, 474; 1891, **7**, 88; E. Riecke, ib., 1890, **6**, 564; H. A. Lorentz, ib., 1891, **7**, 36; L. Natanson, ib., 1899, **30**, 681; M. Reinganum, *Boltzmannfestschrift*, Leipzig, 1904; G. Jaeger, *Wein. Ber.*, (iia) 1913, **22**, 979; P. Langevin, *J. Chim. Phys.*, 1912, **10**, 524.

The relationship between the various colligative properties can, however, as van't Hoff showed, be obtained even more precisely by means of thermodynamical reasoning. It is only necessary to assume some one experimental fact as to the nature of solutions such, for instance, as the fact that the solute obeys the gas laws, in order to obtain an exact formulation of each of the other related properties. The experimental basis with which we propose to start is the well-known law of Henry.

Henry's Law. According to this law, the solubility of a gas in a solvent is proportional to the pressure of the gas in the gas phase above the solution and in equilibrium with it. It is, in fact, a special case of the Nernst Distribution Law. Expressed mathematically we may write $p \propto C$, where p is the pressure of the gas in the gas phase and C is the concentration of the gas in the liquid phase. Bunsen (*Ann.*, 1855, **93**, 1), Khanikow and Luganin (*Ann. Chim. Phys.*, (4), 1867, **11**, 412), and others (see Ostwald, *Lehrbuch*, 1867, I, 620), have subjected the law to a fairly rigorous experimental test and have established that, for moderate pressures, the law holds with only a slight variation at most. As with the Nernst Distribution Law, however, it will be evident that the law of Henry is only valid for cases where the molecular state of the gas

in the solution is the same as that in the gaseous phase. Thus the law is by no means true for such gases as hydrochloric acid gas or sulphur dioxide. More recently the law has been investigated as regards its applicability over a wider range of pressure. Thus Sander (*Zeit. phys. Chem.*, 1912, **78**, 513) and Sackur and Stern (*Zeit. Electrochem.*, 1912, **18**, 641) have investigated the case of the solubility of carbon dioxide in various organic solvents. The distribution coefficient has been expressed in two ways:

I. Bunsen's Coefficient, k', denoting the quantity of gas measured at the pressure of the experiment in cubic centimetres at 0° C. which are absorbed by 1 gm. of the liquid.

II. Ostwald's Coefficient, k, is the ratio of the concentrations of the gas in the solution and in the gaseous phase.

In the latter definition the concentration is measured in grams of gas dissolved in a given volume of solution, not as in the former case in a given weight of solvent. The Ostwald definition is thus the one which seems the more natural, when we remember that we are dealing with a special case of the Distribution law. Actually, as the following results of Sackur and Stern (*loc. cit.*) show, the Ostwald definition gives the better constants over a wider range of pressure. (See Table on opposite page).

The values of k given in these tables show but slight variation whereas the values of the Bunsen Coefficient k' are by no means constant. It should be noted that, at the low temperatures employed, the solubility of carbon dioxide in the various solvents is very high, while the gas pressure is comparatively small. Thus for acetone the value of the concentration ratio is about 200 at − 78° C., and it is evident that, even when the concentration in the liquid phase is so high, the deviations from Henry's law are very slight, and the gaseous phase, since the pressure is small, also obeys the gas law. Now we are about to show that if a solution obeys Henry's law, it follows as a thermodynamical consequence that the solution must obey the gas law. Hence it follows that for such high concentrations of the solution the gas laws are still applicable. If, however, we are dealing with a gas at the same concentration, the experiments of Amagat and others have shown that the gas laws break down completely so that the law holds for much greater concentrations in solution than it does for the gaseous phase.

ABSORPTION COEFFICIENT OF CO_2 IN VARIOUS SOLVENTS

I. Temperature — 78° C.

Solvents.	Methyl Alcohol.		Acetone.	
Pressure of Gas in Mm. of Mercury.	k'.	k.	k'.	k.
50	194·0	120·5	311·0	196·6
100	195·0	119·6	322·0	198·1
200	202·9	120·1	344·5	201·5
400	221·5	122·2	400·0	208·8
640	—	—	487·0	215·7
700	260·0	126·8	—	—

II. Temperature — 59° C.

Solvents.	Ethyl Alcohol.		Acetone.		Methyl Acetate.	
Press. of Gas in mm. Hg.	k'.	k.	k'.	k.	k'.	k.
100	40·85	27·3	97·8	67·2	94·3	75·8
200	41·00	27·2	101·2	68·0	98·45	77·1
400	42·35	27·65	106·6	69·2	103·6	77·6
700	44·15	28·1	118·8	72·8	112·9	79·0

In the case of non-volatile solutes so-called (i.e. solutes having an extremely small vapour pressure) it is manifestly impossible, with our present methods, to verify Henry's law directly, although we may assume that it still applies, since the gas laws are found, by experiment, to describe the behaviour of dilute solutions of such solutes with sufficient accuracy. For such solutes, the limits of concentration are much lower and we may regard the gas law as applicable only to solutions below $0{\cdot}1N$.

We may, however, regard Henry's law as having sufficient experimental justification, for the case of solutions of gases, to warrant our making it the starting-point for our thermodynamical reasoning, and we propose to deduce from it the result that for such a solution, the solute obeys the gas law $PV = RT$, where P is the osmotic pressure, V is the volume occupied by 1 mole and R is the gas constant per mole.

Deduction of the Gas Law PV = RT for a Solution Obeying Henry's Law.

We consider a cylinder (Fig. 16) containing a quantity of the gas in equilibrium with its saturated solution. The solution is separated from the gas by a semi-permeable membrane which allows the passage of the gas, but not that of the solvent, either as liquid or vapour. This membrane is denoted by *cd* in the figure. The sides of the cylinder are assumed to be permeable only to the pure solvent, in which the cylinder is immersed. Two

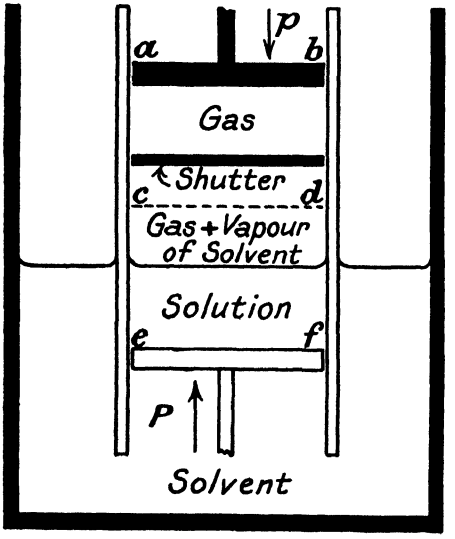

Fig. 16.

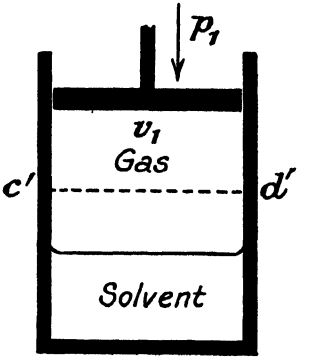

Fig. 17.

weighted pistons, *ab* and *ef*, are arranged so as to ensure equilibrium, the upper one, *ab*, being weighted so that it exerts a downward pressure equal to the pressure of the gas in the gas phase, the lower one, *ef*, exerting an upward pressure equal to the osmotic pressure of the solution. Let the pressure of the undissolved gas in the gas phase be p, its molecular volume be v, and let the osmotic pressure of the solution be P, the volume occupied by 1 mole of solute be V where $V = 1/C$, C being the concentration in moles per litre. Then *ab* exerts a downward pressure p, while *ef* exerts an upward pressure P. We consider the following isothermal reversible cycle.

(*a*) Transfer 1 mole of the gas from the solution to the gas phase

by raising the upper piston reversibly through a volume v and simultaneously allowing the lower piston, *ef*, to rise reversibly through volume V. The work done by the gas in causing piston, *ab*, to rise is pv, while the work done by the surroundings upon the solution in causing piston, *ef*, to rise is PV. Hence the net work done by the gas-solution system in the process of transfer is $-\Delta A_1 = pv - PV$. The level of the liquid is of course constant.

(*b*) The mole of gas is now isolated without the performance of any work by sliding across the cylinder a frictionless weightless shutter. The piston is then raised reversibly, the gas expanding to a practically infinite volume v_∞. The work done by the system is $\int_v^{v_\infty} pdv$. If, now, we assume the gas laws for the gaseous system, this expression becomes

$$-\Delta A_2 = RT \ln v_\infty/v.$$

(*c*) The cylinder containing the gas is placed over a volume V of the pure solvent in a vessel (Fig. 17) which is separated from the cylinder by a semi-permeable membrane, *c'd'*, which is similar to *cd*. Now since the pressure of the gas is infinitely small the tendency for the gas to be absorbed is also infinitely small. We may therefore allow the piston to descend reversibly so that the whole of the mole of gas is eventually absorbed by the liquid. Let the pressure at any instant in the gaseous phase be p_1, the volume occupied v_1. Then at any moment we know, by Henry's law, that the concentration C_1 in the solution is directly proportional to the pressure p_1. Now when all the gas has dissolved the pressure in the gas phase will be p, so that if the pressure of the gas is p_1 it follows that a fraction p_1/p of the mole must have gone into solution. Hence there are $1 - p_1/p$ moles of gas left in the gaseous phase, so that, applying the gas law, we obtain

$$p_1 v_1 = (1 - p_1/p)RT = RT - \frac{RTp_1}{p}.$$

But since $RT/p = v$ it follows that

$$p_1 = \frac{RT}{v + v_1}.$$

Now the work done by the system during the process of absorption is evidently given by

$$-\Delta A_3 = \int_{v_\infty}^{v_0} p_1 dv_1 = RT \int_{v_\infty}^{v_0} \frac{dv_1}{v + v_1}$$

$$= -RT \ln \frac{v_\infty + v}{v}$$

or neglecting v in comparison with v_∞, we have

$$-\Delta A_3 = -RT \ln v_\infty / v.$$

We may now add this volume V of solution to the original bulk, and since the concentrations are identical, no work will be done. The system is now in its initial state and the cycle is complete. Now, as we have seen, the work done in an isothermal reversible cycle is zero, so that we have

$$-\Delta A = (-\Delta A_1) + (-\Delta A_2) + (-\Delta A_3) = 0$$

or $$pv - PV + RT \ln v_\infty / v - RT \ln v_\infty / v = 0.$$

The last two terms evidently cancel so that we are left with

$$pv - PV = 0.$$

But, we have assumed that the gas law holds for the gaseous phase, so that $pv = RT$. Hence we have

$$PV = RT.$$

Thus we have shown that if we assume Henry's law, and the concentration of the gas in the gaseous phase is not too great to allow of the application of the gas law, then the gas law must hold for the solution. It may be mentioned that this analogy between gases and solutions allows us to give a partial definition of an ideal solution as follows. It is evident that, since the gas law is obeyed, Joule's law must also be satisfied. Hence if we dilute such a solution the heat effect will be zero.

Having deduced the gas law for a solution, we now proceed to determine, by means of thermodynamics, the relation between the osmotic pressure and the other colligative properties of a solution.

I. **Lowering of the Vapour Pressure.** We have already mentioned the fact that the pressure of the solvent vapour in equilibrium with a solution at any given temperature is less than the pressure of the vapour in equilibrium with the pure liquid solvent. To determine the relation between the osmotic pressure

of the solution and the lowering of the vapour pressure of the solvent due to the presence of the solute, we again employ an isothermal reversible cycle.

Consider two vessels I and II (Fig. 18) of cylindrical shape and fitted with pistons *ab*, *cd*, *ef*. The piston, *ef*, is assumed to be permeable only to solvent, the other pistons are completely impermeable. In vessel I we have a quantity of solvent in equilibrium with its vapour at pressure p_0. In vessel II is solvent separated from a quantity of solution of concentration C and osmotic pressure P, by the semi-permeable membrane, *ef*. The temperature

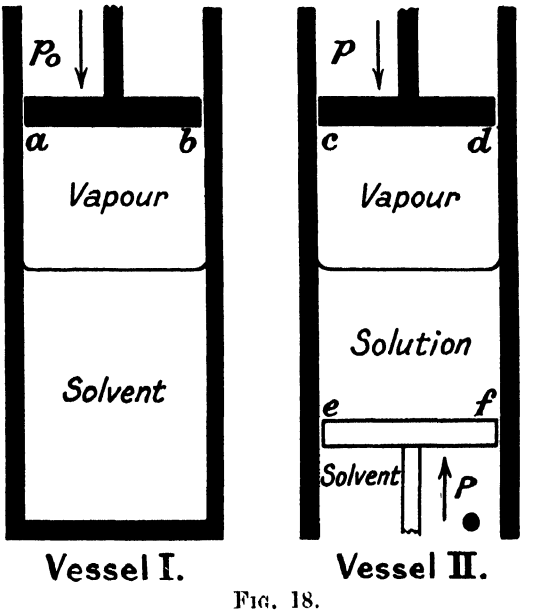

FIG. 18.

in both vessels is the same. Now we know that for a completely isothermal reversible cycle, since the free energy is an extensive property of the system, the total change in free energy over the whole cycle must be zero. We therefore propose, in this case, to follow the change in the free energy of the system instead of considering the maximum work performed by the system during the process. The following is the cycle:

(*a*) An infinitesimally small quantity dx moles of solvent are evaporated isothermally and reversibly by raising the piston *ab* in vessel I; the pressure of this quantity of vapour is then changed isothermally and reversibly from p_0 to p and the vapour is condensed at this pressure into the solution in vessel II. This is the

familiar three-stage distillation process and we have seen that the increase in the free energy accompanying it is given by—

$$\Delta F = \int_{p_0}^{p} v dp.$$

(*b*) The piston, *ef*, is then raised through a volume dV, where dV is the volume occupied by dx moles of solvent in the solution. The dx moles of solvent are thus squeezed out of the solution through the membrane into the pure solvent. The change in the free energy may be obtained by neglecting any change in the total volume of the system Solvent + Solution, i.e. by assuming that the volume of the dx moles of solvent does not change on passing from the solution to the solvent. This is an approximation. We may then regard the matter from two points of view. Since no change in the volume occurs the increase in free energy of the system is equal to the maximum work performed upon the system, namely PdV. On the other hand, we may regard the change from the point of view of the hydrostatic pressure. In the solution the (partial) hydrostatic pressure **due to the solvent** is evidently less than that in the pure solvent by an amount equal to the osmotic pressure of the solution P. Let P' be the hydrostatic pressure in the pure solvent, then $P' - P$ is the pressure in the solution, so that the free energy change is given by

$$\Delta F = \int_{P'-P}^{P'} dVdP \quad (dV \text{ is the volume transferred})$$

and since the volume dV is constant this integral merely becomes PdV.

The dx moles of solvent may now be added to the pure solvent in vessel I, without any further change in the free energy of the whole system. Hence the total increase in the free energy over the whole cycle is given by

$$\Delta F = \Delta F_1 + \Delta F_2$$
$$= \int_{p_0}^{p} v dp + PdV.$$

It will be evident that the error involved in regarding this as equal to the maximum work done over the whole process is negligi-

ble, and we could thus have considered ΔA instead of ΔF for the cycle. However, it is better to consider the free energy changes occurring, since the proof is then free from the limitation already considered in dealing with the three-stage distillation process.

Now let us assume that the gas laws are valid for the solvent vapour. Then equating ΔF to zero, we obtain—

$$dx.RT\ ln\ p/p_0 + PdV = 0 \quad . \quad . \quad . \quad . \quad (1)$$

Let m be the molecular weight of the solvent in the vapour phase, then $m\frac{dx}{dV} = \rho'$ the density of the solvent **as present in the solution.** Hence equation (1) becomes

$$ln\frac{p_0}{p} = \frac{Pm}{\rho' RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This relation, which is the accurate form of Raoult's law, does not require that the gas laws shall be obeyed by the solution. The only assumption we have made is that the vapour obeys the gas laws. Actually, however, we may, for a dilute solution, make the further assumptions: (i) that the density ρ' of the solvent in the solution is equal to the density, ρ, of the pure solvent itself; and (ii) that the gas laws are obeyed by the solution. Making this last assumption we obtain, $P = RTC$, so that equation (2) becomes—

$$ln\frac{p_0}{p} = \frac{C.m}{\rho} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now, we may write

$$ln\frac{p_0}{p} = ln\left(1 + \frac{p_0 - p}{p}\right)$$

and if the difference between p_0 and p is small, it is evident that $\frac{p_0 - p}{p}$ is still smaller. But we know that if we expand $ln\ (1 + x)$ when x is very small the expansion reduces simply to x itself. Hence $ln\left(1 - \frac{p_0 - p}{p}\right)$ may be equated to $\frac{p_0 - p}{p}$, and finally since p_0 is very nearly equal to p, we may substitute p_0 for p in the denominator of the expression and obtain

$$ln\frac{p_0}{p} = \frac{p_0 - p}{p_0}.$$

Hence we obtain the approximate form of Raoult's law, with

which the student will already be familiar, from kinetic considerations, namely

$$\frac{p_0 - p}{p_0} = \frac{m.P}{\rho RT} = \frac{m.C}{\rho} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

II. **Elevation of the Boiling-point.** We now come to consider the experimental fact that the boiling-point of a solution is higher than that of the pure solvent in the light of thermodynamical considerations. Consider two vessels I and II as in Fig. 19. Vessel I contains pure liquid solvent at its boiling-point $T°$ K (K is the

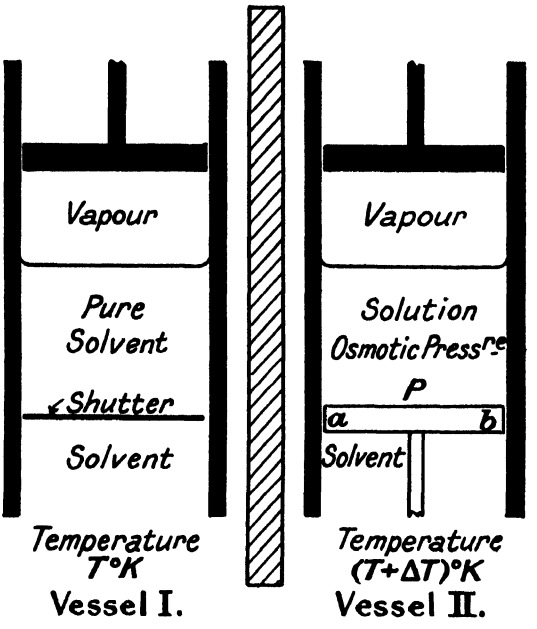

Fig. 19.

absolute scale). The pressure is, of course, equal to that of the atmosphere, namely P'. Vessel II contains solution also at the boiling-point which in this case is $(T + \Delta T)°$ K. Let the concentration of the solution be C, and its osmotic pressure P. We propose to consider the following cyclic process, which is not, as in the previous case, an isothermal one.

(*a*) Allow dx grams (not moles) of solvent to evaporate from the solution in II, isothermally and reversibly. A quantity of heat, $L'dx$, will be absorbed by the system where L' is the latent heat of vaporization per gram of the solvent at the temperature $T + \Delta T$. The only work done by the system is equal to $P'dV$ where P' is

the pressure of the atmosphere and dV is the volume increase on vaporization. This, however, is compulsory work done upon the surroundings at constant pressure. Hence the free energy change in the process is zero.

(*b*) Cool the dx grams of vapour from the temperature $T + \Delta T$ to the temperature T reversibly, the pressure being maintained constant. If C_p is the specific heat per gram the heat given out is $C_p dx \Delta T$. The change in free energy is easily obtained from the table on page 98. Here we find that $\left(\frac{\partial F}{\partial T}\right)_P = -S$, where S is the entropy of the system. If we let S be the entropy of one gram of the vapour, then the entropy of dx grams will be $S.dx$. Hence assuming that the entropy is constant over the range of temperature ΔT, it follows that the increase in free energy as a result of the temperature change will be $\Delta F_1 = S.dx.\Delta T$. It is evident that we may neglect the small amount of heat absorbed in comparison with $L'dx$, since $C_p.dx.\Delta T$, is of the second order of small quantities whereas $L'dx$ is of the first order.

(*c*) Condense the dx grams of vapour into the pure solvent in I. The heat given out will be Ldx where L is the latent heat of the solvent at temperature T. This is only slightly different from $L'dx$. The system contracts by an amount dV' which is almost equal to dV, and the maximum work done upon the system is $P'dV'$, but once again the free energy change is zero.

(*d*) Separate the quantity dx of solvent from the main bulk by sliding a frictionless, weightless shutter across the cylinder. This process is not accompanied by any change in the free energy of the system. The liquid thus isolated is now raised to the temperature $T + \Delta T$. Heat will be absorbed of amount $C'_p dx.\Delta T$, where C'_p is the specific heat of the liquid solvent per gram. The increase in free energy as a result of the increase in temperature will be $-S'dx\Delta T$ where S' is the entropy of the liquid solvent per gram. Denote this by ΔF_2, then

$$\Delta F_2 = -S'.dx.\Delta T.$$

(*e*) The last stage in the process consists in adding the mass dx of solvent isothermally and reversibly at the temperature $T + \Delta T$ to the solution, by means of the piston, *ab*, which is permeable only to the solvent. The work done by the system is PdV and since this does not represent an increase in volume of the system

Solution + Solvent as a whole it is equal to the free energy decrease of the system. Hence the increase in free energy ΔF_3 is $-PdV$. The cycle is now complete and the total increase in free energy is given by

$$\begin{aligned}\delta(\Delta F) &= \Delta F_1 + \Delta F_2 + \Delta F_3 \\ &= S.dx\Delta T - S'dx.\Delta T - PdV \quad . \quad . \quad . \quad (5)\end{aligned}$$

But it is evident that the first two terms are of the second order of small quantities and may therefore be neglected in comparison with PdV which is of the first order. Hence equation (5) becomes

$$\delta(-\Delta F) = PdV \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The free energy decrease over the whole cycle has been represented by $\delta(-\Delta F)$, because the temperature range ΔT is a small quantity.

Now we have for any cyclic process at constant pressure

$$T\frac{d(-\Delta F)}{dT} = q_p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where q_p is the heat absorbed at constant pressure at the higher temperature, in this case $T + \Delta T = T'$ say. This equation is evident by comparison with equation II (9), or it may be deduced directly from the fact, just mentioned, that $\left(\frac{\partial F}{\partial T}\right)_P = -S$, from which it follows that

$$\left(\frac{\partial(-\Delta F)}{\partial T}\right)_P = +\Delta S = +\frac{q_p}{T}$$

which is the same as equation (7). Now the heat absorbed in the first stage of the cyclic process under consideration at the temperature T' is $L'dx$. Hence we have

$$L'dx = T'\frac{d(-\Delta F)}{dT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The temperature difference ΔT is usually small, however, and the error involved in replacing dT by ΔT in the above equation is consequently negligible. Moreover $d(-\Delta F)$ is put equal to PdV. Hence

$$L'dx = T'\frac{PdV}{\Delta T}.$$

The ratio dx/dV is, however, equal to the density ρ of the solvent.

We therefore obtain

$$P = \frac{L'\rho\Delta T}{T'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

This is the accurate form of the expression for the elevation of the boiling-point. If now we assume that the solution obeys the gas laws we may replace P by RTC and obtain

$$C = \frac{L'\rho\Delta T}{RT'^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

This is usually written in the form

$$C = K.\Delta T$$

where $K = L'\rho/RT'^2$. Tables of K are compiled, for different solvents, and in these tables it is usual to employ the boiling-point T of the pure solvent and the latent heat of vaporization L at this temperature. The error thus involved is small.

The value of R is 2 calories and since it is usual to work in terms of 100 grams of solvent, tables of the constant in the form

$$E' = \frac{2T^2}{100L} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

are usually given, the density of the liquid not being included. The following table gives a series of values of E' for different substances, the observed values being compared with those calculated from equation (11) (see Young, *Stoichiometry*).

Solvent.	E' Calculated.	E' Observed.
Water	18·9	18·5 to 19
Acetic acid	38·8	39·0
Benzene	51·0	49·0
Phenol	76·0	74·0
Formic acid	28·4	27·7
Nitrobenzene	76·3	71·0

The elevation of the boiling-point of a solvent when a substance is dissolved in it is the basis of the ebullioscopic method for the determination of the molecular weight of substances in solution, which is more frequently employed in practice than the cryoscopic method as it has several advantages over the latter. For references to the recent work on the practical aspects of the subject see Menzies and Wright, *J. Amer. Chem. Soc.*, 1921, **43**, 2314.

III. **Depression of the Freezing-point.** Analogous to the phenomenon just considered is the depression of the freezing-point of a solvent when some substance is dissolved in it. This constitutes the basis of the cryoscopic method of molecular weight determination. Its mathematical relation to the osmotic pressure of the solution may be determined by a similar cycle to that employed in the case of the boiling-point.

We have two cylinders, I and II, separated by a non-conducting substance *AB*. Vessel I (Fig. 20) contains the pure liquid solvent in equilibrium with the pure solid solvent at the freezing-point

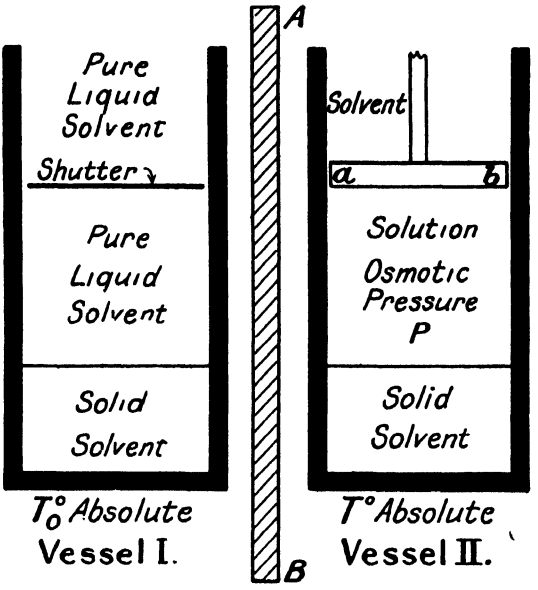

FIG. 20.

$T_0°$ K. Vessel II contains a solution of some substance in the solvent, the concentration being C and the osmotic pressure P. This is in equilibrium with the pure solid solvent at the freezing-point of the solution $T°$ K. Suppose the difference between the freezing-points, $T_0 - T = \Delta T$. The following is the cycle:

(*a*) Suppose a small quantity dx grams of solid solvent in vessel I is melted. The heat absorbed is Ldx where L is the latent heat of fusion per gram of the solvent at the temperature T_0. The work done will be $P'dv$ where P' is the pressure of the atmosphere and dv is the increase in volume (in the case of water dv is negative). This is the only work done, however, and since this is the com-

pulsory work of expansion or contraction it follows that the change in the free energy of the system is zero.

(*b*) This quantity dx of liquid solvent is now separated from the bulk of the liquid in vessel I by means of a frictionless, weightless shutter, no free energy change being involved. Suppose the volume occupied by this mass of liquid at temperature T_0 is dV. We now cool the liquid at constant pressure to the temperature T, assuming that it does not freeze *en route*. The heat evolved is $C_p.dx.\Delta T$, where C_p is the specific heat per gram of the liquid at constant pressure. Since ΔT is small it follows that the heat evolved is of the second order of small quantities and may therefore be neglected in comparison with Ldx. The change in free energy in cooling through ΔT is given by

$$d(-\Delta F)_1 = -S_1.dx.\Delta T$$

where S_1 is the entropy of 1 gram of liquid solvent.

(*c*) The small mass of liquid is now added reversibly to the solution in II at the temperature T, by means of the semi-permeable piston *ab*. The decrease in free energy or the available work done by the system is $+PdV$, where P is the osmotic pressure of the solution. This expression neglects any change in volume of the system as a whole. We thus have

$$d(-\Delta F)_2 = PdV.$$

(*d*) Freeze out a mass of solvent equal to dx from the solution in II. The heat evolved is $L'dx$ where L' is the latent heat of vaporization per gram of solvent at temperature $T°$ K, and the work done upon the system is $P'dv'$, where dv' is the new volume change, but, once again, the change in the free energy is zero. The mass dx of solid is now isolated from the bulk of solid solvent in vessel II, no work being done and no change in the free energy occurring.

(*e*) Warm this mass of solid to the temperature T_0. The heat absorbed by the system is $C'_p.dx.\Delta T$, where C'_p is the specific heat per gram of the solid solvent at constant pressure. This again is negligible in comparison with Ldx. The change in the free energy accompanying this fall in temperature is given by

$$d(-\Delta F)_3 = S_2.dx.\Delta T$$

where S_2 is the entropy of 1 gram of the solid solvent. The total

change in the free energy of the system over the whole cycle is

$$\begin{aligned} d(-\Delta F) &= d(-\Delta F)_1 + d(-\Delta F)_2 + d(-\Delta F)_3 \\ &= -S_1.dx\Delta T + PdV + S_2.dx\Delta T \end{aligned}$$

The first and last terms may be neglected in comparison with PdV and we are therefore left with

$$d(-\Delta F) = PdV.$$

Now we know that

$$d(-\Delta F) = q_p\frac{\Delta T}{T_0}$$

where q_p is the heat absorbed at the temperature T_0, i.e. we have

$$PdV = Ldx.\frac{\Delta T}{T_0}$$

and since $\frac{dx}{dV} = \rho$, the density of the liquid solvent, we obtain on substituting

$$P = \frac{L\rho\Delta T}{T_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

This equation does not involve any assumption as to the nature of the solution itself. If now we assume that the solute obeys the gas laws, we may write $P = RTC$ and obtain—

$$C = \frac{L\rho\Delta T}{RT_0^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

This equation is the precise form of the Raoult expression connecting the concentration of a solution with the depression of the freezing-point of the solvent. As we should expect, it is of the same form as the expression for the elevation of the boiling-point.

IV. **Depression of the Solubility.** Another interesting colligative property is the depression of the solubility of one liquid in another as a result of the presence of a solute in one of the liquids. Suppose we take the case of two partially miscible liquids, such as water and ether. Then if the pure liquids be mixed the solubility of the ether in water will be a certain definite quantity say s_0. If, now, some solute is added to the ether, its vapour pressure will be decreased and consequently, by Henry's law, the concentration of the ether in the water, i.e. the solubility, will be decreased in the same ratio. Hence if s is the new solubility and p_0, p, are

the vapour pressures of pure ether and of ether containing the solute respectively, we have, by equation (2)

$$ln \frac{s_0}{s} = ln \frac{p_0}{p} = \frac{Pm}{\rho RT} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

If, now, we assume the gas laws for the solution we obtain—

$$ln \frac{s_0}{s} = \frac{Cm}{\rho} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Again, since the difference between s and s_0 is usually small, we may write this equation in the approximate form—

$$\frac{s_0 - s}{s_0} = \frac{Cm}{\rho} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

It is evident that this phenomenon could also be employed to determine the molecular weight of substances in solution, but the practical application is neither so simple, nor so accurate as the boiling-point method, or the recent vapour pressure method of Menzies.

We have now determined, on the basis of thermodynamics, the relations which exist between the various colligative properties of a solution. Experiment has in many cases been found to yield results in excellent agreement with the theory. A large class of substances, termed electrolytes on account of their power of carrying an electric current, were found, however, to behave in an anomalous manner. This behaviour remained unexplained until Arrhenius brought forward his famous theory of electrolytic dissociation into positive and negative ions. The student will already be familiar with this theory in its original, simple form, but we shall have occasion, later, to discuss some of the more recent developments of the theory and their relation to thermodynamics.

Thermodynamics is, however, capable of teaching us several other very important and useful facts about solutions, which do not require the introduction of the ionic theory. Thus, for example, let us attempt to determine the effect of temperature upon the solubility of a substance in a given solvent.

We consider two cylinders I and II containing a quantity of solution in equilibrium with the pure solute and surrounded by the pure solvent from which the solution is separated by a semi-permeable membrane (see Fig. 21). Vessel I is at temperature $T°$ Absolute, vessel II at temperature $T - dT$. The two vessels

are separated by a screen which is impermeable to heat. We imagine the following cycle:

(*a*) By moving the piston in vessel I a volume V of solvent is drawn into the solution reversibly, where V is the volume occupied by 1 mole of solute in vessel I. As the solvent enters the cylinder, in order to maintain equilibrium, a quantity of solute dissolves. Eventually, when the whole volume V has been absorbed 1 mole of solute has been dissolved. The heat absorbed may be represented by q. The whole process is accomplished isothermally, at temperature T. The free energy change is equal to the osmotic work done by the system, namely PV where P is the osmotic

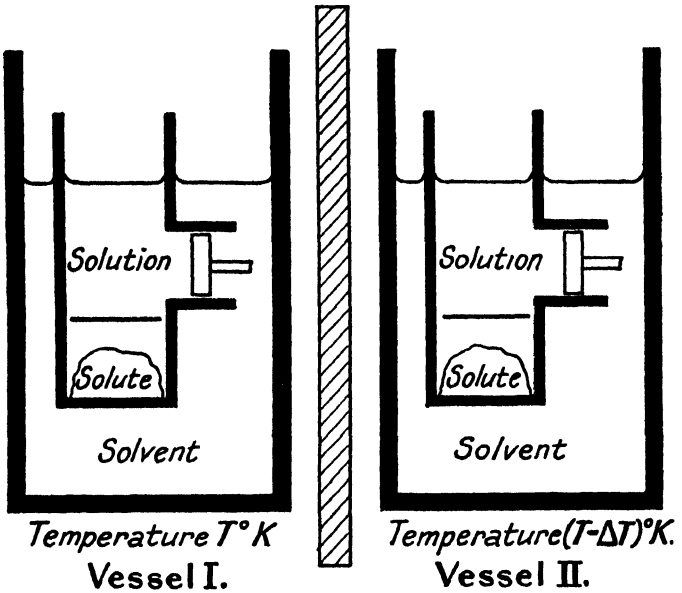

FIG. 21.

pressure of the solution. The concentration of the solution is, of course, the solubility at temperature T, and is equal to $1/V$, i.e. $s = 1/V$.

(*b*) Isolate the volume of solution thus formed by means of a frictionless, weightless shutter, thereby eliminating any change in the free energy. Dilute the isolated portion to the volume $V + dV$ which is the volume occupied by 1 mole of the solute at the lower temperature $T - dT°$. This requires osmotic work PdV and this is again the decrease in the free energy of the system. Simultaneously

(*c*) Cool this isolated portion to the lower temperature $T - dT$. The heat evolved is $C_p \times \text{mass} \times dT$, where C_p is the average

heat capacity of the solution per gram. This is a quantity of the first order of small quantities, since it contains the differential dT and is therefore negligible in comparison with q, which is of zero order. The free energy change in this cooling is also negligible. This may be seen on comparison with the cycles employed for the freezing-point and boiling-point. Suppose the osmotic pressure is now $P - dP$.

(*d*) The isolated portion may now be added, without any free energy change, to the bulk of the solution in vessel II. Now expel this volume $V - dV$ of solvent via the semi-permeable membrane; the osmotic work required and therefore the increase in free energy is

$$(P - dP)(V + dV) = PV + PdV - VdP - dP.dV.$$

As a consequence of this expulsion a quantity of solute exactly equal to 1 mole will be precipitated and the heat q' will be evolved.

(*e*) Separate this quantity of solvent and solute without causing any change in the free energy of the system and then warm each to the initial temperature T. The heat absorbed may be neglected, as also the change in the free energy of the system. These may now be added to the bulk of solute and solvent in I, without any further free energy change and the cycle is now complete.

The total decrease in the free energy is thus

$$\begin{aligned} d(-\Delta F) &= PV + PdV - (PV + PdV - VdP - dV.dP) \\ &= VdP + dV.dP. \end{aligned}$$

The second term may, however, be neglected in comparison with the first so that we have

$$d(-\Delta F) = VdP.$$

Now we know that

$$d(-\Delta F) = q'\frac{dT}{T}$$

so that we obtain—

$$VdP = q'\frac{dT}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

This equation is perfectly general, since the gas laws are not assumed. It therefore applies to any solution, whether concentrated or dilute. V may be replaced by $1/s$ where s is the solubility so that

$$\frac{dP}{dT} = \frac{q'.s}{T}$$

Let us now assume that the solution is a dilute one, that is to say the solute is only sparingly soluble, so that the gas law may be applied. Then $P = RTC = RTs$. Hence $\frac{dP}{dT} = Rs + RT\frac{ds}{dT}$.

Now the term q', which is the heat absorbed in the first stage in the cycle, is really the sum of two terms. It comprises the heat absorbed when 1 mole of solute is dissolved together with the heat absorbed to provide the osmotic work of expansion through volume V. Hence if we put q equal to the heat of solution per mole, then

$$q' = q + PV$$

or if we have assumed the gas laws $q' = q + RT$.

Hence equation (17) becomes

$$Rs + RT\frac{ds}{dT} = (q + RT)\frac{s}{T}.$$

This equation reduces to

$$q = RT^2\frac{d\ ln\ s}{dT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

which is evidently of a similar form to the van't Hoff Isochore. It should be noted that although we have regarded the solubility s as measured in moles per unit volume, this is by no means necessary for the validity of equation (18). This will be made evident by the following reasoning: Suppose we measure the solubility in grams per unit volume of solvent, then if the value obtained is s' and m is the molecular weight of the solute in solution, we have

$$s = s'.m$$

so that

$$ln\ s = ln\ s' + ln\ m.$$

But m is a constant so that $ln\ m$ is a constant for any given solute. Hence on differentiating we obtain

$$d\ ln\ s = d\ ln\ s'$$

so that equation (18) still holds if s' be substituted for s.

An interesting application of equation (18), in the form in which it is given above, is the calculation of the molecular weight of a substance in solution from measurements of the solubility and the heat of solution. We require the solubility of the substance at two temperatures not too far apart, and also the heat of solution per gram over the range of temperature considered, which may

be taken as a constant and equal to the value at the average of these two temperatures. The solubilities may be measured in grams per 100 grams of solvent.

The following data are given by van't Hoff—

100 grams of water dissolve 2·88 grams of succinic acid at 0° C.
100 ,, ,, ,, 4·22 ,, ,, ,, ,, 8·5° C.

The average temperature is 4·25° C. and the heat of solution at this temperature is 55 cals. We apply the equation in the form—

$$q = RT^2 . \frac{1}{s} \frac{ds}{dT}$$

and we replace the differentials by the differences Δs and ΔT between the solubilities and the temperatures respectively.

$$\Delta s = 4{\cdot}22 - 2{\cdot}88 = 1{\cdot}34$$
$$\Delta T = 8{\cdot}5.$$

The value of s employed will be the average value namely

$$s = \tfrac{1}{2}(2{\cdot}88 + 4{\cdot}22) = 3{\cdot}55.$$

T is the average temperature in degrees absolute, namely 273 + 4·25 or 277·25° K. Hence we obtain on substituting these values—

$$q = \frac{2 \times (277{\cdot}25)^2 \times 1{\cdot}34}{8{\cdot}5 \times 3{\cdot}55} = 6{,}830 \text{ calories.}$$

The heat of solution per gram is 55 calories so that the value of the molecular weight in solution must be 6830/55 or 124. The calculated molecular weight from the formula is 118.

Equation (18) may be integrated in a similar manner to that adopted in integrating the isochore. The simplest method is to regard the heat of solution q as independent of the temperature over the range of temperature considered. Making this assumption we obtain—

$$ln\ s = -\frac{q}{RT} + \text{Constant},$$

or if we consider the integration between the temperature limits T_1 and T_2, at which the solubilities are s_1 and s_2, we obtain—

$$ln\ s_2 - ln\ s_1 = \frac{q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

If, however, the assumption that q is constant over the temperature range under consideration is not justified we proceed as follows :

Let c_1, c_2, c represent the specific heats of the solute, solvent and solution respectively and assume that, for the temperature range under consideration, these magnitudes are constant. If q' is the heat absorbed when 1 gram of solute passes into the solution and s is the solubility in grams per 100 grams of solvent, then by Kirchhoff's law—

$$\frac{dq'}{dT} = \frac{c}{s}(100 + s) - \frac{1}{s}(100c_2 + sc_1) \quad . \quad . \quad . \quad (19)$$

$$= (c - c_1) + 100\frac{(c - c_2)}{s} \quad . \quad . \quad . \quad . \quad . \quad (19a)$$

Now experiment has shown that the difference of the specific heats of the solution and the pure solvent is proportional to the concentration, in the case of aqueous solutions. Hence we may write

$$c = c_2 + ks \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where k is a constant. Substituting this in equation (19a) we obtain

$$\frac{dq'}{dT} = (c - c_1) + 100\frac{(c_2 + ks - c_2)}{s}$$

$$= (c - c_1) + 100k \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Now the right-hand side of this equation is a constant, independent of the temperature, hence we may integrate the expression and obtain the relation

$$q' = q'_0 + (c - c_1)T + 100kT \quad . \quad . \quad . \quad . \quad (22)$$

Hence the heat of solution per mole, $q = mq'$, where m is the molecular weight of the solute in solution, so that

$$q = mq'_0 + m(c - c_1)T + 100mkT$$

$$= q_0 + \alpha_T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

α being a constant characteristic of the substance.

We may now substitute this value of q in the equation (18) obtaining

$$\frac{d\ ln\ s}{dT} = \frac{q_0 + \alpha T}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Let us integrate this expression to obtain $ln\ s$. We obtain—

$$ln\ s = -\frac{q_0}{RT} + \frac{\alpha}{R}\ ln\ T + \text{Constant} \quad . \quad . \quad . \quad (25)$$

or transforming to ordinary logs, putting the integration constant

equal to A and representing $2{\cdot}3026\frac{q_0}{R}$ by $-B$, $2{\cdot}3026\,\frac{\alpha}{R}$ by C we have—

$$\log s = A + \frac{B}{T} + C \log T \quad . \quad . \quad . \quad . \quad (26)$$

Partington and Hardman have investigated this equation for the case of aqueous solutions of cane sugar and obtained the following results (Partington, *Thermodynamics*, 1913, 307).

$$A = -32{\cdot}235\,; \quad B = +1283{\cdot}65\,; \quad C = +12{\cdot}2267.$$

$T°$ K.	s observed.	s calculated.	$s_{calc.} - s_{obs.}$
273	179·2	179·2	—
283	190·5	189·8	− 0·7
293	203·9	203·2	− 0·7
303	219·5	219·5	—
313	238·1	238·9	+ 1·7
323	260·4	262·0	+ 1·6
333	287·3	288·4	+ 1·1
343	320·5	320·5	—

It is evident that equation (26) is applicable up to high concentrations beyond those for which equation (18) is strictly applicable.

Law of Mass Action applied to Solutions. Suppose, now, we have the following reaction occurring in a solution—

$$n_1A + n_2B + n_3C + \ldots\ldots = n_1'A' + n_2'B' + n_3'C' + \ldots\ldots$$

Consider two equilibrium boxes containing these reacting substances in solution at different partial concentrations and assume that the equilibrium point has been attained in both boxes.

If, now, we transfer n_1 moles of A from box I to box II, the free energy change, provided no change in concentration occurs in either box, is given by

$$-\Delta F_A = \int_{P'_A}^{P_A} V dP$$

where P_A and P'_A are the partial osmotic pressures exerted by A in boxes I and II respectively. If we assume that the solution is dilute so that we may apply the gas laws we obtain—

$$-\Delta F = n_1 RT \ln \frac{P_A}{P'_A}.$$

Let us assume that only an infinitesimally small fraction has actually been transferred and that we have simultaneously and in the stoichiometric proportion transferred quantities of B, C, etc., from box I to box II. Here they react immediately to give A', B', C', etc., in the proportions represented by the equation. The free energy change accompanying the reaction is zero since the system is in a state of equilibrium. The resultants are then transferred back to box I, where they again react without any change in the free energy occurring, and the system is now in its initial condition. In this manner the concentrations in the boxes are maintained constant and we proceed until n_1 moles of A, n_2 moles of B, n_3 moles of C, etc., have passed from I to II, when n_1' moles of A', n_2' moles of B', n_3' moles of C', etc., will have passed in the reverse direction. The total change in the free energy is given by

$$-\Delta F = n_1 RT \ ln \frac{P_A}{P'_A} + n_2 RT \ ln \frac{P_B}{P'_B} + \ \ldots \ - n_1' RT \ ln \frac{P_{A'}}{P'_{A'}} - \ \ldots$$

and since the cycle is now complete, and it has been carried out isothermally and reversibly, it follows that the free energy change is zero. Equating the above expression to zero we obtain

$$\Sigma n \ ln \ P_A - \Sigma n \ ln \ P'_A = 0$$

or

$$\frac{P_A^{n_1} \times P_B^{n_2} \times P_C^{n_3} \ \ldots}{P_{A'}^{n_1'} \times P_{B'}^{n_2'} \times P_{C'}^{n_3'} \ \ldots} = \frac{P'_A{}^{n_1} \times P'_B{}^{n_2} \times \ \ldots}{P'_{A'}{}^{n_1'} \times P'_{B'}{}^{n_2'} \times \ \ldots}$$

$$= \text{Constant} = 1/K_p.$$

Thus the law of mass action has been proved for the case of a solution.

It is evident that, since we have assumed the gas law for the solution, we may replace P by RTC in the above expression and obtain the law of mass action in terms of concentrations.

Let us now suppose we have a system consisting of an equilibrium box and a series of reservoirs. In the box the following reaction, which is occurring in solution in some solvent, is assumed to have arrived at the equilibrium point—

$$n_1 A + n_2 B + n_3 C + \ldots . = n_1' A' + n_2' B' + n_3' C' + \ldots .$$

In the reservoirs we have solutions of A, B, C, . . . A', B', etc., in the given solvent at certain arbitrary concentrations. The system is similar to the one considered in Chapter VI, except that the solvent

is present. The solvent is also assumed to surround the cylinders and equilibrium box completely, and this constitutes the whole system.

We propose to carry out an exactly similar process to that considered in deducing the van't Hoff Isotherm for the case of a gaseous reaction. In order to calculate the free energy change accompanying the process it is necessary to consider the transfer of the various molecular species from the reservoirs to the equilibrium box, or in the reverse direction. Let us focus our attention upon the transfer of n_1 moles of A from the reservoir to the box. The concentration of A in the box is maintained constant, by the device, already explained, of allowing the whole process to occur simultaneously in infinitesimal steps. The free energy change accompanying the actual transfer of A is, if the concentration of A in the reservoir is constant, $-\Delta F = \int_{P_{\epsilon A}}^{P_A} V dP$, or if we assume the gas law for the solution

$$\Delta F = n_1 RT \ln \frac{P_{\epsilon A}}{P_A}$$

where P_A is the osmotic pressure in the reservoir and $P_{\epsilon A}$ is the partial osmotic pressure of A in the equilibrium box.

This, however, is not the only change which occurs in the free energy of the system as a result of the transfer of A, for it is necessary that the concentration of A in the reservoir be maintained constant. This is done by the device of simultaneously squeezing out of the reservoir, through a semi-permeable membrane, an amount of solvent equivalent to the quantity of A which has been transferred. The expelled solvent, of course, is still part of our system, and we must regard the work done upon the system in expelling it as equal to the free energy increase of the system due to the process. The solvent passes from the solution where its hydrostatic pressure is $P' - P_A$ to the pure solvent where its hydrostatic pressure is P' and the change in free energy is given by

$$\Delta F = \int_{P'-P_A}^{P'} V dP.$$

Actually we may, with but slight error, regard the volume of the expelled solvent as the same as that which it occupied in the solu-

tion. This is what we have done in all previous calculations. The volume will be $n_1 V_A$ where V_A is the volume occupied by 1 mole in the solution, since we have transferred n_1 moles. The free energy change thus becomes

$$\Delta F = n_1 . V_A . P_A,$$

which is equal to the osmotic work done upon the system in the change. Now if we assume the gas laws for the solution we have $P_A V_A = RT$, and we may therefore write the total decrease in free energy accompanying the transfer

$$-\Delta F = n_1 RT \ln \frac{P_A}{P_{eA}} - n_1 . V_A . P_A$$

$$= n_1 RT \ln \frac{C_A}{C_{eA}} - n_1 . RT.$$

This is similar to the expression obtained in the case of a perfect gas except for the last term. In order to obtain the total decrease in free energy over the whole reaction we must add these terms for all the molecules. Remembering that K_c is expressed thus

$$K_c = \frac{C_{A'}^{n_1'} \times C_{B'}^{n_2'} \times C_{C'}^{n_3'} \times \ldots}{C_A^{n_1} \times C_B^{n_2} \times C_C^{n_3} \times \ldots}$$

and expressing the arbitrary concentrations in a similar expression denoted by $RT\Sigma n \ln C$, as we did in the case of a gaseous reaction, we obtain the important relation

$$-\Delta F = RT \ln K_c - RT\Sigma n \ln C + \Sigma n . RT \quad . \quad . \quad (27)$$

Now we have assumed that the volume of the whole system is constant. Actually, as we have already mentioned, this is only approximately true, but we shall continue to make the assumption for the moment, and proceed to differentiate the expression with respect to temperature. Since the volume is constant, we may write $\Delta F = \Delta A$. We therefore obtain—

$$\frac{d(-\Delta F)}{dT} = \frac{d(-\Delta A)}{dT} = R \ln K_c + R \frac{d \ln K_c}{dT} - R\Sigma n \ln C + \Sigma n . R$$

But by equation (27) we know that

$$R \ln K_c - R\Sigma n \ln C + R\Sigma n = \frac{-\Delta A}{T}$$

so that we have

$$\frac{d(-\Delta A)}{dT} = \frac{-\Delta A}{T} + R \frac{d \ln K_c}{dT}$$

and since by equation V (17)

$$T\frac{d(-\Delta A)}{dT} = \Delta U - \Delta A = q_v - \Delta A$$

it follows that

$$\frac{d\ ln\ K_c}{dT} = \frac{q_v}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

In other words, we have shown that although the free energy change in the case of a reaction in solution differs from that in a gas, yet the van't Hoff Isochore still applies. This is an extremely important result.

As a matter of fact, the solubility s of any solute is in the form of an equilibrium constant since it expresses the ratio of the concentrations of solute to solvent in the solution. We may therefore substitute s for K_c in equation (28) and obtain

$$\frac{d\ ln\ s}{dT} = \frac{q}{RT^2}$$

which is equation (18) already deduced by means of a cycle.

We have hitherto made an assumption which is very nearly true, especially for the case of dilute solutions, that the volume occupied by the solvent in the solution is the same as the volume occupied in the pure solvent; in other words, that the addition of a solute to the solvent is not accompanied by any change in the volume of the solvent. We will now, however, attempt to allow for the slight volume change which does actually occur in practice. It is evident that it will only affect the last term of the expression for the free energy change of transfer. Thus in the case of transfer of n_1 moles of A the last term is strictly $-\int_{P_A}^{P'} VdP$. Now we know that $-\frac{1}{V}\frac{dV}{dP}$ is the coefficient of compressibility β, so that we have

$$VdP = -\frac{dV}{\beta}$$

and the free energy change accompanying the transfer of A from the reservoir to the box thus becomes

$$-\Delta F = n_1 RT\ ln\frac{P_A}{P_{eA}} + \int\frac{dV}{\beta}.$$

Now we may regard the coefficient of compressibility of a liquid as constant over the small range of pressure considered, so that the last term reduces to $\frac{\Delta V_A}{\beta}$ where ΔV_A is the increase in volume over the transfer of n_1 moles of A.

We thus have for the free energy change accompanying the whole process, for all the reacting substances

$$-\Delta F = RT \ln K_p - \Sigma RTn \ln P + \frac{\Delta V}{\beta} \quad . \quad . \quad (29)$$

where ΔV is the total increase in volume over the process.

The last term is the ratio of two small quantities ΔV and β and is consequently by no means negligible. It will be evident that we might equally well have written the equation in the form

$$-\Delta F = RT \ln K_c - RT \Sigma n \ln C + \frac{\Delta V}{\beta} \quad . \quad . \quad (30)$$

but since we are dealing with a volume change, while the pressure of the system is constant the former equation will be found to be of greater utility.

Since the reaction is accompanied by a change in the total volume of the system, it is evident that a change in the total pressure of the system will affect the equilibrium concentrations and therefore the equilibrium constant of the reaction. This is in marked contrast to the case of a gaseous reaction where K_c and K_p are both entirely independent of the total pressure.

To determine the relation between the equilibrium constant and the pressure of the system we may consider the following isothermal cycle:

(*a*) Carry out the reaction in the manner described above under the total hydrostatic pressure P'. The free energy change is given by

$$-\Delta F = RT \ln K_p - RT \Sigma n \ln P + \frac{\Delta V}{\beta}.$$

(*b*) The pressure of the system is now increased to $P' + dP'$ and the accompanying change in the free energy is given by

$$\Delta F = (V + \Delta V)dP$$

where V is the total volume of the whole system at the beginning of the cycle.

(*c*) Carry out the reaction at this pressure in the reverse direc-

tion and assume that the volume change is $\Delta V + d(\Delta V)$, this time being a decrease in volume. The change in the free energy accompanying the process is given by

$$+\Delta F = RT\ ln(K_p + dK_p) - RT\ \Sigma\ n\ ln\ P + \frac{1}{\beta}(\Delta V + d(\Delta V)).$$

(*d*) The final stage in the cycle consists in changing the pressure back to the original value, namely P'. This is accompanied by a decrease in the free energy of amount

$$-\Delta F = (V - d(\Delta V))dP.$$

It is evident that we may neglect $d(\Delta V)$ in comparison with V, so that this expression becomes

$$-\Delta F = VdP.$$

The cycle is now complete and the total change in the free energy must be zero, since we have assumed that the process is carried out isothermally and reversibly. Hence it follows that

$$-\Delta F = RT\ ln\ K_p - RT\ \Sigma\ n\ ln\ P + \frac{\Delta V}{\beta} - (V + \Delta V)dP$$

$$-RT\ ln(K_p + dK_p) + RT\ \Sigma\ n\ ln\ P - \frac{1}{\beta}(\Delta V + d(\Delta V)) + VdP = 0.$$

Now $d(\Delta V)$ may be neglected in comparison with ΔV, so that the third and seventh terms cancel and we are left with

$$RT\ ln(K_p + dK_p) - RT\ ln\ K_p = -\Delta V.dP \quad . \quad . \quad (31)$$

But

$$ln(K_p + dK_p) - ln\ K_p = ln\ (K_p + dK_p)/K_p$$

$$= ln\left(1 + \frac{dK_p}{K_p}\right)$$

and we know that the expansion of $ln\ (1 + x)$ when x is very small becomes equal to x itself, so that

$$ln\left(1 + \frac{dK_p}{K_p}\right) = \frac{dK_p}{K_p} = d\ ln\ K_p$$

so that equation (31) becomes—

$$\frac{d\ ln\ K_p}{dP} = -\frac{\Delta V}{RT}$$

where ΔV is the total increase in volume accompanying the reaction.

It should thus be possible, by measuring the value of K_p at two

different pressures to determine the contraction in volume which should occur as a result of ionization. The expression has been investigated by Fanjung, for the case of the constant K_c. It is evident that for any given temperature $d\ ln\ K_c/dP = d\ ln\ K_p/dP$.

The reaction considered was that of the ionization of certain acids and he obtained the actual contraction from measurements of the volume changes accompanying the neutralization of the acids by a strong base. The calculated contractions were obtained as follows:

For acetic acid at 18° C. Fanjung found that

$$\log K_1 = \bar{5}{\cdot}254 \text{ at } 1 \text{ atmosphere pressure.}$$
$$\log K_2 = \bar{5}{\cdot}305 \text{ ,, } 260 \text{ ,, ,,}$$

We may employ the above equation in its differential form and obtain

$$\frac{d\ ln\ K}{dP} = 2{\cdot}302\frac{\bar{5}{\cdot}305 - \bar{5}{\cdot}254}{(260 - 1)} = -\frac{-\Delta V}{RT}.$$

R must be measured in litre-atmospheres, the value being 0·0821 and the contraction will then be expressed in litres. Substituting $R = 0{\cdot}0821$ and $T = 291$ in the above expression we obtain for the contraction

$$-\Delta V = 0{\cdot}0108.$$

The following table gives the results obtained for some acids (*Zeit. phys. Chem.*, 1894, **14**, 673).

Acid	Contraction observed.	Contraction calculated.
	c.c.	c.c.
Formic	7·7	8·7
Acetic	10·5	10·8
Propionic	12·2	12·4
Butyric	13·1	13·4
Iso-butyric	13·8	13·3
Lactic	11·8	12·1
Succinic	11·8	11·2
Maleic	11·4	10·3

CHAPTER VIII

ELECTROCHEMISTRY OF DILUTE SOLUTIONS

Our discussion of the problem of equilibrium has shown us that, when any process occurs in a system, it does so in virtue of its power to yield a definite quantity of available work, that is to say, the process is accompanied by a decrease in the free energy of the system. Now there are several methods of harnessing this free energy change and obtaining useful external work from the system, but the simplest of these, and the one which most readily affords a method of measuring the free energy change, consists in the construction of a galvanic cell, where the process occurs with production of electrical work.

These galvanic cells are of various types. In the simple cell, prepared by Volta, we have an electrode of zinc and one of copper immersed in a dilute solution of sulphuric acid—

$$Zn \mid H_2SO_4 \mid Cu.$$

The zinc, which is the negative electrode, goes into solution and hydrogen is liberated at the positive electrode, copper. The reaction which is represented by the cell is thus

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

Another familiar cell is that known as the Daniell cell, which consists of solutions of copper sulphate and zinc sulphate in contact, the electrodes being of copper and zinc

$$Zn \mid ZnSO_4 \mid CuSO_4 \mid Cu.$$

The reaction which takes place in the cell is

$$Zn + CuSO_4 = ZnSO_4 + Cu.$$

The process which gives rise to the electric current need not, however, be a chemical one. Thus, for example, the following type of cell is familiar and will be found to be of great utility from a theoretical point of view. Two electrodes of silver dip respectively into two solutions of silver nitrate of different concentrations, e.g.

$$Ag \mid AgNO_3\ N/10. \mid AgNO_3\ N/100 \mid Ag.$$

In this cell the process is one of equalization of the concentrations of the solutions, a process which is ordinarily brought about by the simple process of diffusion, but is here effected by the silver dissolving off the electrode in the weaker solution, the negative pole, and a corresponding amount being deposited on the positive pole in the stronger solution, while the excess NO_3' ions in the stronger solution migrate to the weaker solution, so that the current inside the cell flows in the reverse direction, namely from the weak to the strong solution.

Reversible Cells. Volta's cell is of little use in the thermodynamic consideration of galvanic cells, since the cell reaction will continue to proceed when the electrodes are disconnected so that no current is passing through the cell. It is evident, however, that this must be avoided. The ideal cell for our purpose is one in which the reaction can only proceed when the poles are connected so that the maximum amount of electrical work is obtained from the process. If the process continues when no current is flowing through the cell, no electrical work is done. An ideal cell is usually known as a **reversible cell** and is characterized by the fact that if unit quantity of electricity passes through the cell first in one direction and then in the opposite direction the final state is identical with the initial state. The Daniell cell and the concentration cell already mentioned are reversible.

Now the chief advantage of the reversible cell lies in the fact that it provides a means of measuring the change in the free energy of the system which accompanies the reaction. When the electrodes are disconnected, no current flows through the cell so that the system is in equilibrium. There is, however, a certain difference of potential between the electrodes and this is equal to the electromotive force of the cell when the external resistance is infinitely great, that is when no current is being taken from the cell. In order to measure the value of this E.M.F. the method employed in practice is to oppose it by another electromotive force of exactly equal magnitude (or only differing from it by an infinitesimal amount), so that the system is in equilibrium. This is ideally the state of affairs which we postulated for the existence of a reversible process, and hence any process which we imagine to occur in the cell under these conditions will be, to all intents and purposes, strictly reversible and the free energy change accompanying the process will be equal to the electrical work done by

the system, i.e. to the product of the electromotive force and the algebraic sum of the quantity of electricity transferred. Thus if Q coulombs of positive electricity are transferred in the process from the negative to the positive electrode then the work done upon the system or the increase in the free energy of the system is given by

$$\Delta F = Q \times E$$

where E is the E.M.F. of the cell.

The experimental method of determining the maximum value of the electromotive force of a cell is that known as the Poggendorf Compensation Method, and depends upon the principle mentioned above. The apparatus is represented in the diagram (Fig. 22). A is a source of electricity such as an accumulator, which should

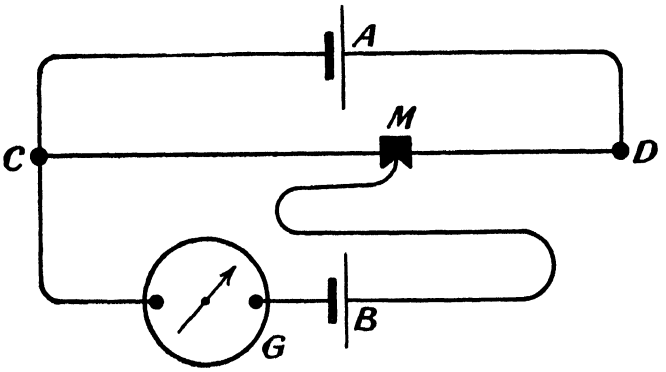

FIG. 22.

give a practically constant E.M.F. It is connected to the two ends of the uniform wire CD, so that there will be a constant potential gradient throughout its length. B is the cell, the E.M.F. of which it is desired to measure, and it is connected so that the currents from A and B are opposed. G is a galvanometer, usually of the moving-coil type having a high resistance and being used with a shunt until the balance point is nearly obtained. The sliding contact M is moved about until a position is found such that no current passes through the galvanometer. When this is so the E.M.F. of the cell B must be equal to the fall of potential along the wire CM. Since no current passes through the cell it is the maximum E.M.F. which is thus obtained. Now we require to find the potential fall along a unit length of the wire CD and hence the potential fall along CM. It is not sufficiently accurate to

regard this as simply the E.M.F. of the cell A divided by the length CD, and it is usual to calibrate the wire by substituting a standard cell, the E.M.F. of which is accurately known, in the place of B. Then if M' is the new position of the sliding contact and E' is the electromotive force of the standard cell,

$$E = \frac{CM}{CM'} . E'.$$

This apparatus is capable of an accuracy of only about one millivolt.

For more accurate work the following more elaborate potentiometer is employed. AB is a uniform wire 110 cms. in length which is stretched over a millimetre scale and connected at the end A with 15 resistance coils which are all accurately made equal to

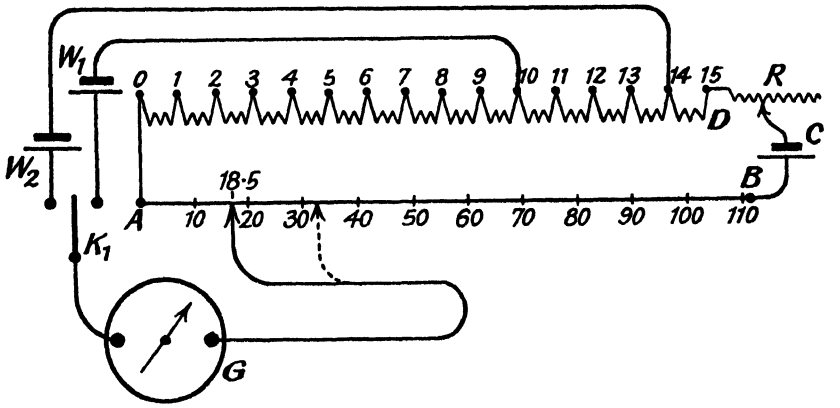

FIG. 23.

one another and to 100 cms. of the wire AB. The total resistance from plug 15 to the end of B will therefore be equivalent to 1,610 centimetres of the wire; and if the E.M.F. across DB is 1·610 volts then each metre of wire will be equivalent to 0·1 volt. Hence 1 cm. of the wire is equivalent to 1 millivolt.

In using this potentiometer the positive pole of the working cell C is connected with the plug 15 and the negative pole with the end B of the resistance wire. R is a variable resistance. The positive pole of a standard cadmium cell W_1 (E.M.F. 1·0185 volts) is connected with the plug 10 and the sliding contact is placed at the point 18·5 cms. on the wire. The resistance R is varied until no current passes through the galvanometer on closing the key K. The potential fall per centimetre is then 1 millivolt and the E.M.F.

of any other cell may be read off directly. Thus if the balance point obtained, when cell W_2 is connected instead of W_1, is when positive pole of cell is connected to plug 14 and the sliding contact is at 32·5 cms., then E.M.F. of W_2 is 1·4325 volts. Usually the 15 coils are arranged around a circle and the bridge wire is also wound on a cylinder and moves against a sliding contact. The position of the contact is read off by means of a vernier. In this

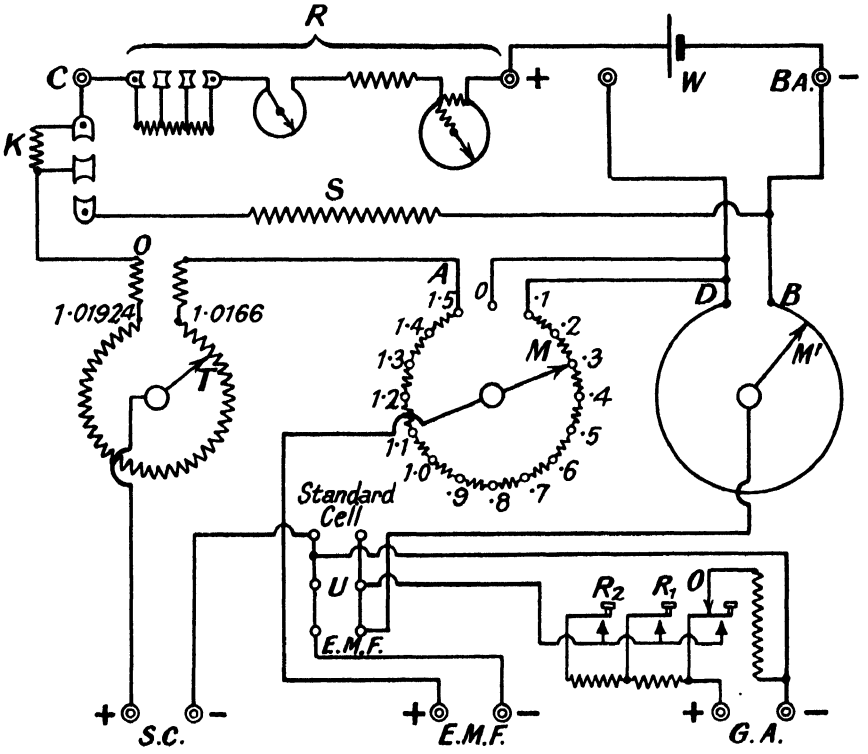

FIG. 24.
Leeds and Northrup Potentiometer.

way the apparatus is rendered more compact. The above diagram (Fig. 24) shows the construction of this apparatus.

Single Electrode Potentials. We have seen that it is possible, by means of a suitable mechanism, known as a galvanic cell, to conduct a reaction electrically in such a manner that the decrease in the free energy of the system reappears as electrical work but, before attempting the application of thermodynamic considerations to such cells, it will be of considerable advantage to inquire a little more closely into the mechanism by means of which the electric current is produced.

It has been found that if two substances, or indeed two different forms or phases of the same substance, are brought into contact, there is set up an electrical difference in potential between the two. The origin of these electrical effects is very obscure and depends upon many factors, such as the physical state of the phases and their composition, the temperature, the surface tension, etc. We do not propose to concern ourselves, however, with the origin of these differences of potential. Confining ourselves to the case of the electrical effects produced in dilute solutions, our object will be to see how far the theory of thermodynamics has been successfully applied to the more simple types of contact.

Let us consider, first of all, the case of a solid dipping into a liquid. Thus, for instance, we have electrical potential differences if a rod of zinc be immersed in any of the following solutions, $ZnSO_4$, $ZnCl_2$, H_2SO_4, etc. Such a system is known as an electrical element. Now the galvanic cell is so constructed that two such elements are combined, an electrical potential difference existing between the two. If, now, by combining the two elements and connecting the electrodes it is possible to cause some change to occur, such as a chemical reaction, then a current flows between the electrodes.

Reversible Electrodes. It will be evident, if the examples just mentioned are considered, that there are two types of such electrical elements, namely those in which a reaction is taking place, such as a rod of zinc or iron in a solution of one of the mineral acids, where the metal dissolves in the acid; and secondly, those elements where no chemical reaction can possibly occur, for example zinc immersed in a solution of zinc sulphate, or silver in contact with a solution of silver nitrate. In the former case the potential difference is continually changing until the reaction is complete; in the case of elements where no reaction occurs the potential difference will be a constant under the given conditions. This latter type of element is known as a **reversible** element or a reversible electrode, since it is characterized by the fact that the system is in equilibrium. Two such reversible elements when combined will form a reversible cell, which, as we have already seen, is such that no reaction occurs except when the two metal electrodes are electrically connected so that a current flows between them.

The potential difference set up in such reversible electrodes was

found to be dependent to some extent upon the physical state of the surface of the metal. If, however, two rods of zinc, for example, are placed in a solution of zinc sulphate and electrically connected outside the solution, a current is found to flow between the two rods, and this current gradually decreases until, after a longer or shorter interval, it has diminished to zero. Now this current is evidently due to the difference in the physical state of the surfaces of the two rods and if we proceed as above until the current between the rods is zero, we have obtained two rods which are electrically similar and which if immersed in any solution will give the same contact potential difference. We have, therefore, eliminated the effect of the surface completely, and it is then found, experimentally, that for a reversible electrode the contact potential difference at any given temperature is a simple function of the concentration of the metal ions in the solution. The function is of the form $\pi = \pi_0 + K \ln C$ where π_0 and K are constants, C is the concentration.

The first reasonable explanation of this phenomenon was given by Nernst (*Zeit. phys. Chem.*, 1889, **2**, 613; **4**, 129) and was remarkable for its extreme simplicity. In spite of many difficulties, which will be considered in due course, the theory is still worthy of presentation. Nernst considered that we may regard every substance as possessing a certain tendency to pass into solution in any solvent, the tendency varying with the substance and the solvent considered. Consequently, when a solid, such as a strip of silver, is brought into contact with a solution, say of silver nitrate, the solid may be said to exert a certain "Solution Pressure" which we shall denote by P. This pressure is analogous to the vapour pressure exerted by the solid which may be regarded as a measure of the tendency of the solid to pass into the vapour state. The solution pressure is thus of the same form as an osmotic pressure. Now in the bulk of the solution the ions of the metal are also exerting their partial osmotic pressure which we shall denote by p. The case under consideration, namely the electrode $Ag \mid AgNO_3$ is one which is reversible with respect to the monovalent cation Ag^+. The system is in equilibrium and it is evident that any infinitesimal process which we may imagine to occur will involve no change in the free energy so long as equilibrium is maintained. Let us consider the reversible transfer of dx gram-ions of silver from the solution to the metal electrode. This pro-

cess requires that positive electrical work be done upon the system and this work causes an increase to occur in the free energy of amount $\pi \times dQ$ where π is the potential difference between the metal and the solution, the metal being considered positive, and dQ is the quantity of electricity transferred.

In addition to this, however, we have to consider the free energy change occurring as a result of the transfer of the metal ions to a region of pressure P, the solution pressure of the metal, from a region of pressure p the partial osmotic pressure of the metal ions in the solution. This transfer involves an increase in the free energy of $\int_p^P V dp$. Hence the total change in the free energy is given by

$$\Delta F = \pi \times dQ + \int_p^P V dp \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and this must be equated to zero. Now if the solution is sufficiently dilute we may consider that it obeys the gas laws and we may then integrate the free energy change of transfer and obtain

$$\Delta F = \pi dQ + dx.RT \ ln \frac{P}{p} = 0$$

since we are dealing with dx moles. But $dQ/dx = Q$ the quantity of electricity associated with 1 gram ion of a monovalent substance, so that we obtain

$$\pi = -\frac{RT}{Q} ln \frac{P}{p} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or for a metal of valence n we should have

$$\pi = -\frac{RT}{nQ} ln \frac{P}{p} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Since for any particular electrode the solution pressure is a constant for a given solution we may transform this expression into

$$\pi = \frac{RT}{nQ} ln \ p + \text{Constant} \quad . \quad . \quad . \quad . \quad (4)$$

or transforming equation (3) to concentrations instead of pressures, by means of the gas law $PV = RT$ the expression takes the form

$$\pi = \frac{RT}{nQ} ln \ C + \pi_0 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where π_0 is a constant for any given temperature, C is the con-

centration of the solution. It thus follows that the electrode potential difference is a simple function of the concentration of the solution and the constant π_0 is evidently the value of the contact potential difference when the concentration is unity (i.e. when $ln\, C = 0$). This may be transformed to an expression involving logarithms to the base 10, and if we desire the potential difference to be in volts, we measure energy in volt-coulombs and obtain for the value of $(RT/nQ) \times 2{\cdot}303$—

$$\frac{2{\cdot}303\ RT}{nQ} = \frac{0{\cdot}058}{n} \text{ at } 18^\circ \text{ C.}$$

$$\frac{2{\cdot}303\ RT}{nQ} = \frac{0{\cdot}059}{n} \text{ at } 25^\circ \text{ C.}$$

As we have already foreshadowed, however, this mode of calculating the electrode potential difference has been subjected to much adverse criticism. This is due to the fact that it is difficult to ascribe a real physical significance to the solution pressure P. The nature of the criticism which has been brought forward may perhaps best be illustrated by quoting from Lehfeldt (*Phil. Mag.*, 1899 (v), **48**, 430).

"The values of the solution pressure P are easy to calculate from the observed values of the electromotive force. According to Le Blanc (*Elektrochemie*, p. 185), we have

	P	
Zinc	$9{\cdot}9 \times 10^{18}$	atmospheres
Nickel	$1{\cdot}3 \times 10^{0}$	,,
Palladium	$1{\cdot}5 \times 10^{-36}$	,,

"There are certain obvious difficulties in the way of accepting these numbers as representing a physical reality. The first of them is startlingly large; that, however, may not be a true difficulty. The third is so small as to involve the rejection of the entire molecular theory of fluids. If it is true that fluids consist of molecules with a diameter of the order of magnitude 10^{-8} cms., then the production of a pressure so low is impossible; for pressure is a statistical effect due to the impact of numerous molecules, and in order to give such a pressure the solution would need to contain only one or two molecules of palladium in a space the size of the earth. Hence P can have a real meaning only if the metal is very greatly more divisible than the ordinary molecular theory assumes."

This criticism is not, however, nearly so serious as it appears at first sight. Lehfeldt does not appear to have grasped the real significance which Nernst attached to the constant P. As Krüger pointed out (*Zeit. phys. Chem.*, 1900, **35**, 18) the solution pressure does not represent a static condition in the solution but rather the

tendency of the ions to pass into solution. It is really a probability factor and is analogous to the small dissociation " pressure " of say, water vapour which is given by v. Helmholtz (*Zur Thermodynamik chem. Vorgange*; Wissenschaftliche Abhandlungen III, 109) as $0{\cdot}2938 \times 10^{-38}$ an even smaller quantity. Such quantities really indicate the number of molecules or ions which pass from one state to another in a given time, thus when we obtain a small value for the solution pressure it is really no contradiction of the kinetic theory but an indication that the number of ions leaving the metal per second is a very small number (probably a small fraction).

Nevertheless, considerable discredit was thrown upon Nernst's theory and it was certainly a marked advance when Butler published his paper on " The Kinetic Interpretation of the Nernst Theory of Electromotive Force " (*Trans. Farad. Soc.*, 1924, **19**, Part III, 729). This paper should undoubtedly be read by the student, but we propose here to give a summary of the method employed.

The kinetic treatment involves the introduction of the methods of statistical mechanics, but, as this is beyond the scope of the present book, we shall take the results obtained, by its means, for granted. We may assume, on the basis of the lattice theory of crystal structure, that the surface of the metal consists of a lattice of metal ions and electrons. The electromotive process is concerned with the metal ions in the surface layer and those in the solution. Equilibrium is attained when equal numbers of ions are dissolved and deposited at the surface in any interval of time. If the concentration of metal ions in the solution is less than corresponds to equilibrium, that is, if the rate of deposition is less than the rate of solution, metal ions will leave the surface of the metal and pass into solution, thereby leaving the surface of the metal with an excess of negative electrons. The effect of this negative charge is to retard the passage of positive ions away from the surface and to assist their deposition from solution. The rate of deposition will be increased and the rate of solution decreased; consequently the charge will accumulate until the two processes occur at equal rates.

As in the general case of a crystalline solid, we suppose that the metal exerts a force of attraction on metal ions in the vicinity of the surface, and since the metal ions are fixed in definite positions

so as to continue the crystal lattice, the force of attraction is highly localized, that is, it falls off rapidly with the distance. Secondly, we have to take into consideration the attraction of the liquid for the metal ions. This is greatest at the surface and falls off on entering the liquid. The resultant of these two forces gives rise to a balance point at a certain distance from the surface, the distance being of the order of molecular magnitudes. Actually, however, we have, in addition to these forces, an electric field set up as a consequence of the potential difference. We must therefore inquire how the electric charge is distributed near the surface.

There is no reason for supposing that the positive ions that have passed into solution and the negative electrons left in the metal constitute a rigid electrical double layer. Undoubtedly the positive ions in solution will tend to arrange themselves as near as possible to the negatively charged surface, but the amount of metal ion passing into solution in the attainment of the equilibrium potential is so small that the concentration of metal ions even in the vicinity of the surface will not be appreciably affected. The lines of force emanating from the excess electrons in the surface may anchor themselves on any positive ions near the surface and owing to thermal agitation these will be at varying distances. Therefore the electrical attraction on a positive ion will be greatest at the surface and will gradually fall off as we penetrate into the zone of excess positive ions in the solution. This electrical attraction causes a shift in the balance point.

Now the work required to bring one gram-ion from the surface to the balance point is made up of two parts (*a*) the mechanical work W'_1 against the combined attractive forces of the surface and the solution, and (*b*) the electrical work $-nQE'$, where Q is the quantity of electricity associated with one gram-ion of a monovalent substance, n is the valency of the metal and E' is the potential difference between the surface and the balance point. This latter work is negative since the field does work upon the ion in moving. The total work required is thus $W'_1 - nQE'$ and this is the energy acquired by the ions in reaching the balance point. Now Butler shows that the number of ions acquiring this energy, and thus reaching the balance point in one second is given by

$$\theta_1 = N_1 T^{\frac{1}{2}} A' e^{-(W'_1 - nQE')/RT}$$

where N_1 is the number of ions per unit area of metal surface and A' is a constant.

Similarly, the number of gram-ions reaching the balance point from the solution is given by

$$\theta_2 = N_s T^{\frac{1}{2}} A'' e^{-(W'_2 + nQE'')/RT}$$

where N_s is the number of ions per c.c. in the solution; the electrical field in this case opposing the motion. For equilibrium it is evident that these two quantities must be equal, so that

$$N_1 T^{\frac{1}{2}} A' e^{-(W'_1 - nQE')/RT} = N_s T^{\frac{1}{2}} A'' e^{-(W'_2 + nQE'')/RT}.$$

Taking logs. we have

$$\frac{W'_2 - W'_1}{RT} = ln \frac{N_s A''}{N_1 A'} - \frac{nQ(E' + E'')}{RT}.$$

Now $W'_2 - W'_1 = W_2 - W_1$, where W_1 and W_2 are the values of the work terms when the electrical field is zero and the difference $W_2 - W_1$ is evidently equal to q, the heat absorbed in the passage of one gram-ion into solution. Moreover, $E' + E'' = E$, the total potential difference. Hence we obtain

$$E = \frac{q}{nQ} + \frac{RT}{nQ} ln \frac{A''N_0}{1000A'N_1} + \frac{RT}{nQ} ln\, C \quad . \quad . \quad (6)$$

where C is the concentration. Comparing this with the Nernst formula which may be written in the form

$$E = E_0 + \frac{RT}{nQ} ln\, C$$

we see that we may put

$$E_0 = \frac{q}{nQ} + \frac{RT}{nQ} ln \frac{A''N_0}{1000A'N_1} \quad . \quad . \quad . \quad . \quad (7)$$

Butler has evaluated the two terms on the left-hand side and has compared his values with those of E_0. The calculated values obtained were satisfactory at least as regards the order of magnitude. Butler showed that the former term q/nQ is by far the predominant one. The following table compares the experimental values of E_0 with those calculated for q/nQ.

Process.	E_0.	q/nQ.
Ag–Ag$^{\cdot}$	+ 0·799	+ 1·097
Zn–Zn$^{\cdot\cdot}$	− 0·758	− 0·760
Cu–Cu$^{\cdot\cdot}$	+ 0·345	+ 0·347
Na–Na$^{\cdot}$	− 2·71	− 2·486
Fe–Fe$^{\cdot\cdot}$	− 0·441	− 0·481

We may thus take it for granted that the Nernst Equation in the form

$$E = E_0 + \frac{RT}{nQ} ln\ C$$

does, in fact, represent the variation of the contact potential difference with the concentration of the ion with respect to which the electrode is reversible. We therefore propose to apply this expression to enable us to calculate the electromotive force of various cells.

I. **Concentration Cells with Transport.** This is the simple type of concentration cell already considered, of which the following is a typical example:

$$Ag \;\Big|\; \begin{matrix} AgNO_3 \\ c_1 \end{matrix} \;\Big\vdots\; \begin{matrix} AgNO_3 \\ c_2 \end{matrix} \;\Big|\; Ag$$

In this cell we have three surfaces of separation and therefore three contact potential differences, namely—

E_1 at boundary $Ag \mid AgNO_3\ (c_1)$
E_2 at boundary $AgNO_3\ (c_1) \vdots AgNO_3\ (c_2)$
E_3 at boundary $AgNO_3\ (c_2) \mid Ag.$

We have not as yet calculated the potential difference which is set up between two solutions of an electrolyte at different concentrations when contact is established between them, and it is convenient, for many purposes, to be able to neglect this quantity. Fortunately, it is often possible, in practice, to eliminate this liquid-liquid P.D. One very simple device which may be employed for the purpose is due to Nernst, and consists in having some strong electrolyte present in uniform concentration throughout the solutions. Thus for cells containing *HCl* at different concentrations Nernst employed saturated *KCl* throughout. The current inside the cell is thus carried practically entirely by the added electrolyte, instead of the *HCl*. The mechanism underlying its action will appear somewhat clearer when we come to consider the liquid-liquid P.D. in greater detail. It is, of course, essential that the added electrolyte shall have no effect on the original solutions. Thus *KCl* would obviously be useless for silver nitrate concentration cells since it would cause the precipitation of *AgCl*.

Another method, which is not always applicable and which is less easy to understand, consists in separating the solutions by a

concentrated solution of ammonium nitrate or potassium chloride. The apparatus usually employed is diagrammatically represented in Fig. 25.

Now we know that in the $Ag \mid AgNO_3$ element the silver metal is positive with respect to the solution and if we suppose c_2 to be greater than c_1, it follows that the electrode dipping into solution c_2 has a higher positive charge than the electrode dipping into solution c_1. The difference $E_3 - E_1$ is thus the potential difference between the electrodes (measured in the positive direction),

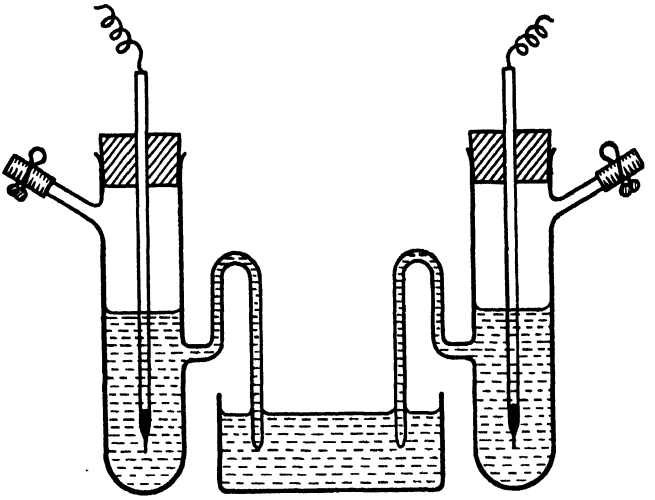

FIG. 25.

in other words $E_3 - E_1$ is the electromotive force E of the cell. Now we know

$$E_1 = E_0 + \frac{RT}{nQ} ln\, c_1$$

$$E_3 = E_0 + \frac{RT}{nQ} ln\, c_2.$$

Hence it follows that—

$$E = E_3 - E_1 = \frac{RT}{nQ} ln \frac{c_2}{c_1} \quad , \quad . \quad . \quad . \quad (8)$$

This is the simple expression for the electromotive force of a concentration cell with transport, in terms of the concentrations of the ions with respect to which the cell is reversible. This expression has been investigated in the case of silver nitrate cells by Abegg and Cumming (*Zeit. Elektrochem.*, 1907, **13**, 18).

The following are their results:

Concentration of $AgNO_3$	Ratio of Ionic Concentrations c_2/c_1.	$\frac{RT}{nQ} ln \frac{c_2}{c_1}$.	Observed $E.M.F.$
$\frac{N}{10} : \frac{N}{100}$	9·0	0·0563 volts	0·0556
$\frac{N}{100} : \frac{N}{1000}$	9·6	0·0580 ,,	0·0579

We must now proceed to determine the magnitude of the potential difference which exists between two solutions in contact, and we will, first of all, consider the simple case where the two solutions contain the same electrolyte at different concentrations. Thus, for instance, in the cell already mentioned we have two solutions of silver nitrate at concentrations c_1 and c_2.

$$Ag \mid AgNO_3\,(c_1) \vdots AgNO_3\,(c_2) \mid Ag.$$

Now, in the absence of the silver electrodes, it is evident that the electrolyte will diffuse from the stronger to the weaker solution until the concentration is the same throughout the cell. This, in fact, is the natural or spontaneous process which corresponds to the E.M.F. of the cell. Let us consider this process of diffusion a little more closely.

In general the anions do not travel with the same velocity as the cations and consequently a greater number of the faster-moving ions will, at first, cross the boundary in a given time. This results in a slight excess of one type of ion on one side of the boundary, so that an electrical potential difference is set up between the two solutions. This P.D. has the effect of slowing down the faster-moving ion, so that eventually the two ions move at the same rate across the boundary and no further accumulation of electricity occurs. In practice, this steady state is attained practically instantaneously and the potential difference existing at the boundary is the liquid-liquid P.D. which we have denoted by E_2.

Let us assume, then, that we have two such solutions in contact. We imagine some arrangement by means of which the liquid-liquid potential difference E_2 is just balanced by an opposing P.D. so that the system is in equilibrium. In the case of silver nitrate solutions the velocity v of the anion is greater than the velocity

u of the cation. The dilute solution naturally assumes the charge of the faster-moving anion, so that the more concentrated solution has the higher potential.

Since the system is in equilibrium the free energy change accompanying any infinitesimal change will be zero. Let us consider the transfer of a small quantity dQ of electricity from the weaker to the stronger solution. This requires the performance of electrical work upon the system of amount $E_2 dQ$, so that we write for the increase in the free energy, due to this electrical work

$$\Delta F_1 = E_2 . dQ.$$

The fraction of the total charge carried by the positive ions is $dQ\left(\frac{u}{u+v}\right)$, that carried by the negative ions $dQ\left(\frac{v}{u+v}\right)$. Now each gram-ion carries a charge nQ where n is the valency, so that the number of positive ions passing from the weak to the strong solution is $\left(\frac{dQ}{nQ}\frac{u}{u+v}\right)$. If we denote the osmotic pressures of the two solutions, as before, by p_1 and p_2 and the concentrations by c_1 and c_2 ($c_2 > c_1$), then the increase in the free energy, accompanying this transfer, is given by

$$\left(\frac{u}{u+v}\right)\frac{dQ}{nQ}\int_{p_1}^{p_2} v dp = \Delta F_2$$

or, assuming the applicability of the gas laws to solutions,

$$\Delta F_2 = \frac{dQ}{nQ}\left(\frac{u}{u+v}\right) RT \ ln \ p_2/p_1.$$

Similarly, the free energy increase attending the transfer of $\frac{dQ}{nQ}\left(\frac{v}{u+v}\right)$ negative ions from the strong to the weak solution is

$$\Delta F_3 = \frac{dQ}{nQ}\left(\frac{v}{u+v}\right) RT \ ln \ p_1/p_2.$$

The total increase in the free energy of the system is thus the sum of these three quantities,

$$\Delta F = \Delta F_1 + \Delta F_2 + \Delta F_3 = 0$$

$$= E_2 dQ + \frac{dQ}{nQ}\left(\frac{u}{u+v}\right) RT \ ln \ p_2/p_1 + \frac{dQ}{nQ}\left(\frac{v}{u+v}\right) RT \ ln \ p_1/p_2$$

Hence we obtain—

$$E_2 = \frac{RT}{nQ}\frac{v-u}{u+v} ln\, p_2/p_1.$$

It is evident that if we employ the mobilities instead of ionic velocities, the fraction $\left(\frac{v-u}{u+v}\right)$ becomes $\left(\frac{V-U}{U+V}\right)$. Replacing the ratio p_2/p_1 by the equivalent concentration expression, since we have assumed the gas laws, we obtain

$$E_2 = \frac{RT}{nQ}\left(\frac{V-U}{U+V}\right) ln\, c_2/c_1.$$

The value just obtained enables us to calculate the total E.M.F. of a concentration cell with transport. The following diagram

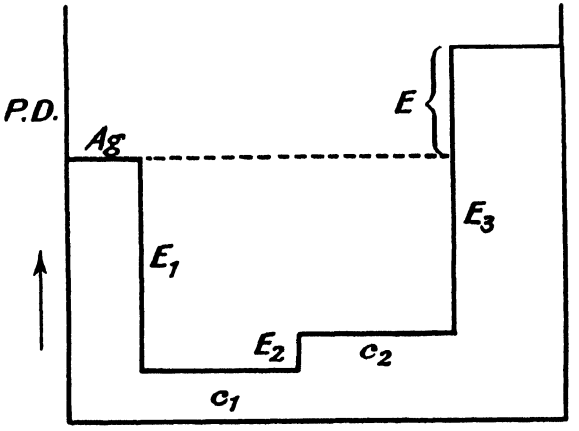

FIG. 26.

represents the potential differences for such a cell as the silver nitrate cell already considered.

$$E = E_3 + E_2 - E_1.$$

Now we have already seen that

$$E_3 - E_1 = \frac{RT}{nQ} ln\, c_2/c_1$$

and

$$E_2 = \frac{RT}{nQ}\left(\frac{V-U}{U+V}\right) ln\, c_2/c_1$$

so that

$$E = \frac{RT}{nQ}\left(\frac{2V}{U+V}\right) ln\, c_2/c_1 \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Of course if the potential difference E_2 acts in the reverse direction we have

$$E = \frac{RT}{nQ}\left(\frac{2U}{U+V}\right) ln\, c_2/c_1 \quad . \quad . \quad . \quad . \quad (11)$$

If we compare this expression with equation (8) we see that the effect of the liquid-liquid potential difference is represented by the factors $\left(\frac{2U}{U+V}\right)$ or $\left(\frac{2V}{U+V}\right)$ which are twice the transport numbers of the cation and anion respectively. The following table gives the transport numbers of several anions in different salts and at varying concentrations:

Salt.	Concentrations of Salt in Equivalents/Litre.					
	0·01.	0·02.	0·05.	0·1.	0·2.	0·5.
	Transport Number of Anions.					
Potassium chloride, ,, bromide, ,, iodide	0·503	0·503	0·503	—	—	—
Ammonium chloride, Sodium bromide	0·604	0·604	0·604	—	—	—
Lithium chloride	0·670	0·670	0·680	0·687	0·697	—
Potassium nitrate	—	—	—	0·497	0·496	0·492
Silver nitrate	0·528	0·528	0·528	0·528	0·527	0·519
Potassium hydroxide	—	—	—	0·735	0·736	0·738
Hydrochloric acid	0·174	0·174	0·174	—	—	—

It is evident that for such salts as potassium halides or nitrate the transport number is very nearly 0·5 so that the factor $\frac{2V}{U+V}$ is very nearly unity. Hence for such salts the liquid-liquid P.D. is negligible. For substances containing OH' or H^+ ions, however, this is very far from being the case. This is indicated by the following values:

	E_2
0·01 *N.KCl* : 0·1 *N.KCl*	0·0008 volts.
0·01 *N.HCl* : 0·1 *N.HCl*	0·0370 volts.

The student may possibly have observed that in our deduction of equation (9) we made two assumptions. The first of these is that the ratio of the concentrations c_2/c_1 is the same for the anions

as for the cations. Evidently this is only true for solutions of single electrolytes. The addition of another electrolyte which upsets the ionization, so that there are no longer equivalent quantities of the two ions, renders the equation invalid.

The second assumption is that the valency of anion and cation are the same. This is not necessarily the case, however. Let us denote the valency of the anion and cation by n_1 and n_2 respectively. Then the expression for E_2 becomes

$$E_2 = \frac{RT}{n_1 Q}\left(\frac{V}{U+V}\right) ln\ c_2/c_1 - \frac{RT}{n_2 Q}\left(\frac{U}{U+V}\right) ln\ c_2/c_1 . \quad (12)$$

If, for example, the electrolyte is zinc chloride, then n_1 is one, n_2 is two, so that

$$E_2 = \frac{RT}{Q}\left(\frac{V}{U+V}\right) ln\ c_2/c_1 - \frac{RT}{2Q}\left(\frac{U}{U+V}\right) ln\ c_2/c_1$$

$$= \frac{RT}{2Q}\left(\frac{2V-U}{U+V}\right) ln\ c_2/c_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The total E.M.F. of a concentration cell with transport having zinc chloride as electrolyte will be

$$E = \frac{RT}{2Q} ln\ c_2/c_1 + \frac{RT}{2Q}\left(\frac{2V-U}{U+V}\right) ln\ c_2/c_1$$

$$= \frac{RT}{2Q}\left(\frac{3V}{U+V}\right) ln\ c_2/c_1.$$

As regards the experimental measurement of the liquid-liquid potential difference, Cohen and Tombrock employed the following ingenious method (*Zeit. Elektrochem.*, 1907, **13**, 612):
The E.M.F. of the cell

$$Zn \mid ZnSO_4\ (c_1) \vdots ZnSO_4\ (c_2) \mid Zn$$

was measured. Let the value be E. Then we have

$$E = \frac{RT}{2Q} ln\ c_2/c_1 + E_2 \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where E_2 is, as before, the liquid-liquid P.D.

The following cell was then constructed

$$Hg \mid \begin{matrix} Hg_2SO_4 \text{ saturated in} \\ ZnSO_4 \text{ solution } (c_1) \end{matrix} \vdots \begin{matrix} Hg_2SO_4 \text{ saturated in} \\ ZnSO_4 \text{ solution } (c_2) \end{matrix} \mid Hg.$$

The mercury electrodes are surrounded by a saturated solution of mercurous sulphate, in a solution of zinc sulphate. Now the elec-

trode potential difference at one of these electrodes, say the left-hand one, is of the form

$$E_1' = E_0 + \frac{RT}{Q} ln\,[Hg^+]_1$$

where $[Hg^+]_1$ is the concentration of the mercurous ion in the solution. Since the solution of mercurous sulphate is saturated, however, it follows that the product $[Hg^+]^2[SO_4'']$, which is known as the solubility product, must be constant. Let this product be K^2, then we have

$$[Hg^+] = K/[SO_4'']^{\frac{1}{2}}$$

or

$$ln\,[Hg^+] = ln\,K - \tfrac{1}{2}\,ln\,[SO_4''] \quad . \quad . \quad . \quad . \quad (15)$$

At the right-hand electrode we have

$$E_2' = E_0 + \frac{RT}{Q} ln\,[Hg^+]_2.$$

Hence

$$E_2' - E_1' = \frac{RT}{Q} ln\,[Hg^+]_2 - \frac{RT}{Q} ln\,[Hg^+]_1$$

which, by equation (15), becomes

$$E_2' - E_1' = -\frac{RT}{2Q} ln\,[SO_4'']_2 + \frac{RT}{2Q} ln\,[SO_4'']_1.$$

The cell is thus reversible with respect to the anion SO_4'' and since we may neglect the change in the concentration of these ions due to the addition of the mercurous sulphate, we may regard them all as due to the ionization of the zinc sulphate. Now the concentrations of these ions are c_1 and c_2 respectively, since they must be equal to the concentrations of the zinc ions. Hence

$$E_2' - E_1' = -\frac{RT}{2Q} ln\,c_2/c_1.$$

The total electromotive force of the cell is therefore

$$E' = -\frac{RT}{2Q} ln\,c_2/c_1 + E_2 \quad . \quad . \quad . \quad . \quad (16)$$

This may be measured experimentally and on adding this value to that of E we obtain, as may be seen from equations (14) and (16),

$$E + E' = 2E_2.$$

Thus the liquid-liquid potential difference is obtained.

It will now be evident why Nernst's device of adding a strong electrolyte to the solutions eliminates the effect of the liquid-

liquid potential difference, since, under these circumstances, the majority of the current is conveyed through the cell by the added electrolyte which is at the same concentration throughout the cell.

Concentration Cells without Transport. We have hitherto been concerned with cells in which the current is transferred by the passage of ions through the solution. Thus in the familiar silver nitrate concentration cell $\frac{V}{U+V}$ gram-anions are transported per faraday from the strong to the weak solution while $\frac{U}{U+V}$ gram-cations move in the reverse direction. Actually one gram-ion of silver is dissolved off the electrode in the weaker solution, but owing to the transport a fraction of only $\frac{V}{U+V}$ gram-ions remains. These are equivalent to the NO_3' ions which have arrived in the same compartment, so that the net effect is the transfer of $\frac{V}{U+V}$ gram-ions of silver nitrate from the strong to the weak solution.

In the following cell, which was investigated by MacInnes and Parker (*Journ. Amer. Chem. Soc.*, 1915, **37**, 1445) no transport of the ions occurs:

$$\underset{E_4}{Ag \mid AgCl \text{ saturated in } KCl \text{ solution } (c_1)} \;\Big|\; \underset{E_3}{K_xHg} \;\Big|\; \underset{E_2}{AgCl \text{ saturated in } KCl \text{ solution } (c_2)} \;\Big|\; \underset{E_1}{Ag}$$

c_1 and c_2 denote the concentrations of the chloride ions ($c_1 > c_2$). The potassium amalgam may be employed as a potassium electrode reversible with respect to the *KCl*, as was shown by G. N. Lewis.

We may calculate the E.M.F. of the cell E as follows:

There are four surfaces of separation and hence four electrode potentials E_1, E_2, E_3, E_4, as indicated in the diagram.

$$E = E_1 - E_2 + E_3 - E_4$$

Now

$$E_1 = E_{Ag} + \frac{RT}{Q} ln\,[Ag^+]_2$$

$$E_2 = E_K + \frac{RT}{Q} ln\,[K^+]_2$$

$$E_3 = E_K + \frac{RT}{Q} ln\,[K^+]_1$$

$$E_4 = E_{Ag} + \frac{RT}{Q} ln\,[Ag^+]_1$$

where E_{Ag} and E_K are the values of the Nernst constant E_0 for silver and potassium respectively, and $[Ag^+]$, etc., are the concentrations of the ions in the two compartments. Hence it follows that

$$E = \frac{RT}{Q}\left(ln \frac{[Ag^+]_2}{[Ag^+]_1} + ln \frac{[K^+]_1}{[K^+]_2}\right) \quad . \quad . \quad . \quad (17)$$

Now since the silver chloride is saturated, we may write

$$[Ag^+]_1 \times [Cl']_1 = [Ag^+]_2 \times [Cl']_2$$

so that

$$\frac{[Ag^+]_2}{[Ag^+]_1} = \frac{[Cl']_1}{[Cl']_2}.$$

Substituting this value in equation (17) we obtain, since the concentrations of the chloride and potassium ions in each compartment may be taken as equal,

$$E = \frac{RT}{Q} ln \frac{[Cl']_1}{[Cl']_2} \frac{[K^+]_1}{[K^+]_2} = \frac{RT}{Q} ln \frac{[K^+]_1^2}{[K^+]_2^2}$$

or

$$E = \frac{2RT}{Q} ln\, c_1/c_2$$

where c_1 and c_2 are the concentrations of the potassium ions in the solutions.

It will be evident that the value of E is entirely independent of the solution pressure and hence of the concentration of the amalgams. Moreover, since no transport occurs, all the silver dissolving off the electrode remains in the solution in the same compartment and the passage of one faraday of electricity through the cell corresponds to an increase of one gram-molecule of silver chloride, which is precipitated in the weaker solution, the reverse process occurring in the stronger solution. Potassium in an amount equivalent to the chloride ions is deposited from the stronger solution on to the amalgam while an equivalent amount dissolves in the weaker solution. The net result is thus, that for every faraday of electricity, one gram ion of potassium chloride and also of silver chloride are transferred from the stronger to the weaker solution by electrical means.

MacInnes and Parker (*loc. cit.*) employed a method, originally suggested by Helmholtz (*Ges. Abhl.*, **1**, 840; **2**, 979) and involving a comparison between the electromotive forces of concentration cells with and without transport, of obtaining the transport number of the ions of the electrolyte.

Thus, for example, the following cell with transport was investigated by Jahn (*Zeit. phys. Chem.*, 1900, **33**, 545) who obtained the results given below:

	c_1	c_2	
Ag | *AgCl, HCl* |	*HCl, KCl* |	*Ag*;	E.M.F. in volts.
	0·03330 *N*	0·003329 *N*	− 0·09162 ± 0·00005
	0·01665 *N*	0·001665 *N*	− 0·09235 ± 0·00005

This cell is evidently reversible with respect to the chloride ion, so that if c_1 and c_2 are the concentrations of this ion in the two solutions the electromotive force is given by

$$E = \frac{RT}{Q}\left(\frac{2U}{U+V}\right) ln\, c_1/c_2 \quad . \quad . \quad . \quad . \quad (19)$$

Tolman and Ferguson (*Journ. Amer. Chem. Soc.*, 1912, **34**, 232) determined the electromotive force of the following cell:

Hg | *HgCl* : *HCl* (c_1)	H_2———H_2	*HCl* (c_2) : *HgCl*	*Hg*
0·02*N*.	1 atm. 1 atm.	0·002*N*.	

E.M.F. − 0·1109 ± 0·001 volts.

This cell contains hydrogen at a pressure of one atmosphere as the common electrode. The use of such gas electrodes will be considered later. The cell is evidently a hydrochloric acid cell without transport, the electromotive force being:

$$E' = \frac{2RT}{Q} ln\, c_1/c_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

A comparison of equations (19) and (20) will show that if the ratio of the concentrations of the chloride ions c_1/c_2 is the same in both cells, then

$$E'/E = U/(U+V)$$

or the ratio of the electromotive forces is equal to the transport number of the cation, namely the hydrogen ion. Making a linear interpolation from the electromotive forces of the first mentioned cells, in order to obtain a value of the voltage of the following cell:

Ag	*AgCl* : *HCl*	*HCl* : *AgCl*	*Ag*
	0·02*N*	0·002*N*.	

MacInnes and Parker obtained the value 0·09210. The ratio E'/E is thus—

$$E'/E = 0{\cdot}09210/0{\cdot}1109 = 0{\cdot}830.$$

This is in excellent agreement with the directly determined value

of the transport number of the hydrogen ion, 0·833, as given by Drucker and Krsnjavi (*Zeit. phys. Chem.*, 1908, **62**, 731).

MacInnes and Parker also obtained the transport number of the potassium ion, by comparing the electromotive forces of the following two cells.

I. *KCl* concentration cell with transport

$$Ag \;\Big|\; \underset{c_1}{AgCl : KCl} \;\Big|\; \underset{c_2}{KCl : AgCl} \;\Big|\; Ag$$

$$E = \frac{RT}{Q}\left(\frac{2U}{U+V}\right) ln\, \gamma_1 c_1/\gamma_2 c_2.$$

The coefficients γ_1, γ_2 are termed "activity coefficients" and will be explained later, when we come to deal with the activity method of treating solutions.

II. *KCl* concentration cell without transport

$$Ag \;\Big|\; \underset{c_1}{AgCl : KCl} \;\Big|\; K_xHg \;\Big|\; \underset{c_2}{KCl : AgCl} \;\Big|\; Ag$$

$$E' = \frac{2RT}{Q}\, ln\, \gamma_1 c_1/\gamma_2 c_2.$$

The results obtained are given in the following table:

Concentrations of *KCl*. c_1	c_2	$\frac{E'}{E}$	Transport Number of K^+ ion. *E.M.F.*	Hittorf.	Moving Boundary.
0·5	0·05	53·57/107·4	0·498	0·496	—
0·1	0·01	54·00/108·9	0·496	0·496	0·493
0·05	0·005	54·7/110·85	0·494	0·496	0·493

The agreement is well within the limits of experimental error.

Gas Cells. The electrodes which we have considered have practically all consisted of a metal in contact with solution, and since metals are conductors of electricity, no difficulty is experienced in determining the electromotive force of the cells. Hydrogen in contact with an acid solution, however, has a certain solution pressure, and therefore, if by some means we can connect the hydrogen to an external circuit, it should be possible to construct a concentration cell with hydrogen electrodes. This has in fact been accomplished by means of the apparatus represented in

Fig. 27. A platinized platinum electrode is arranged so as to be partly in the solution and partly in the hydrogen. Hydrogen is bubbled through the tube B until the pressure of the gas in A is steady. E is the electrode. Let p be the osmotic pressure of the hydrogen ions in the solution. Hydrogen gas consists of diatomic molecules, which tend to form H^+ ions in the solution. Let this tendency be represented as a solution pressure P^-. Then the

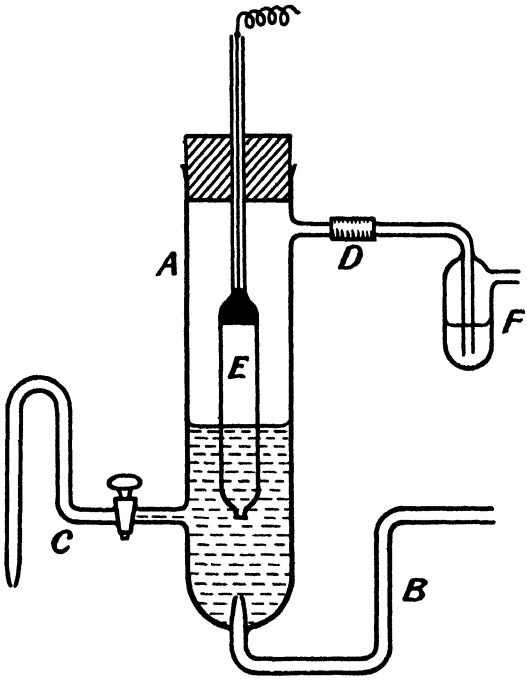

FIG. 27.

potential difference between the hydrogen and the solution is given by

$$E = \frac{RT}{Q} ln \frac{p}{P^-}.$$

Now by Henry's law the solution pressure P^- must be proportional to the square root of the actual pressure of the gas P, so that

$$E = \frac{RT}{Q} ln\, p - \frac{RT}{Q} ln\, \phi . P^{\frac{1}{2}}$$

where ϕ is the proportionality factor.

If now we consider two such electrodes dipping into the same solution, the gas pressures being P_1 and P_2 ($P_1 > P_2$), then the

total electromotive force of the combination will evidently be

$$E = \frac{RT}{Q}(ln\ P_1^{\frac{1}{2}} + ln\ \phi - ln\ P_2^{\frac{1}{2}} - ln\ \phi)$$

$$= \frac{RT}{2Q} ln\ P_1/P_2.$$

The electromotive force thus depends solely upon the gas pressures at the electrodes.

If, on the other hand, we have two electrodes at the same gas pressure dipping into two solutions of, say, hydrochloric acid at different concentrations c_1 and c_2, the net result is an ordinary concentration cell reversible with respect to the cation.

In a similar manner electrodes of oxygen, chlorine, etc., may be prepared. Moreover, by surrounding a piece of platinum foil with bromine or iodine an electrode may be prepared.

Standard Cells and Half Elements.

It is convenient, for many purposes, to have a source of constant E.M.F. and consequently several standard cells have been constructed. It is essential that such cells should be reproducible, that is to say the personal equation should be negligible. Moreover, not only must the electromotive force of the cell be independent of the operator who constructs it, but it should also have as low a temperature coefficient as possible. The cell which best satisfies these conditions is the Weston Cadmium cell. The cell is generally constructed as in Fig. 28. One limb of the H-vessel contains mercury and this is covered with a paste of mercurous sulphate and hydrated cadmium sulphate. The other limb contains a 12·5 per cent. cadmium amalgam, which is prepared by warming the right proportions of the ingredients in a test-tube. The electrolyte consists of saturated cadmium sulphate solution, filled with $3CdSO_4.8H_2O$ crystals. A small air-space is left above the liquid level, and the vessel is closed by successive layers of paraffin wax, cork and sealing wax. All the materials used must be carefully purified. The electromotive force of the cell is given by the expression:

$$1{\cdot}0184 - 0{\cdot}00004(t - 20)$$

where t is the temperature in degrees Centigrade. The temperature coefficient is seen to be exceedingly small, 1/25 millivolts per degree, and the E.M.F. remains constant if none but very small

currents are allowed to pass through the cell. The reaction which serves as the source of E.M.F. may be represented by the equation:

$$Cd \text{ (in satd. amalgam)} + Hg_2SO_4(s). + \frac{8}{3}H_2O \text{ (in solution satd. with } CdSO_4.\frac{8}{3}H_2O) = CdSO_4.\frac{8}{3}H_2O + 2Hg\ (l).$$

Such a standard cell will enable us to determine accurately the E.M.F. of another cell, but it is sometimes desirable to measure, or at least to compare, single electrode potentials and for this purpose it is necessary to prepare a standard electrode or half

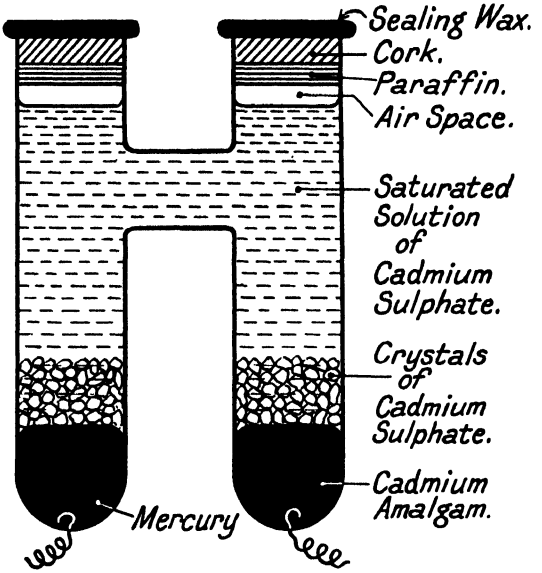

FIG. 28.

element. We have already mentioned the standard normal hydrogen electrode and this is frequently employed as the standard in calculations. The P.D. of this electrode at 25° C. is arbitrarily taken to be zero for the purposes of comparison. The actual P.D. is known approximately to be 0·28 volt. For details of the determination of the absolute values of single electrode potentials, reference should be made to a text-book on electrochemistry. We shall be concerned solely with comparative values based on E.M.F. measurements and referred to the P.D. of the normal hydrogen electrode as zero.

Another standard of frequent use in laboratory practice is the

calomel half element. This electrode consists essentially of pure mercury in contact with a solution of potassium chloride saturated with calomel Hg_2Cl_2. Two types are in use: the normal calomel electrode containing Normal KCl and the Decinormal Calomel electrode, containing 0·1 $N.KCl$. The form in which the electrode is usually found is indicated in the diagram, Fig. 29. It is made up in three layers, viz. (i) mercury, (ii) a mixture of mercury and Hg_2Cl_2 in the form of a paste, (iii) KCl, saturated with mercurous chloride. When the normal calomel electrode is connected up with the standard hydrogen electrode the total E.M.F. of the cell is 0·283 volt. The absolute P.D. is about 0·56 for the Normal Calomel Electrode. For the Decinormal Electrode the absolute P.D. is about 0·61 volt.

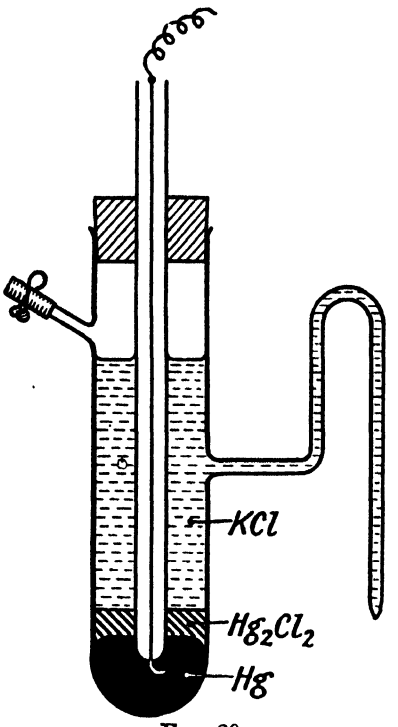

FIG. 29.

A more recent and very useful standard electrode is that known as the "quinhydrone electrode." For details the reader is referred to the original papers. Biilmann, *Trans. Farad. Soc.*, 1923, XIX, 676; Cullen and Biilmann, *J. Biol. Chem.*, 1925, **64**, 727; Cullen and Earle, ib., 1928, **76**, 565; Cullen, ib., 1929, **83**, 539.

By utilizing one or other of these standard potentials a series of values have been obtained for single electrodes. These are, as we have already stated, usually referred to the potential of the combination $Pt \mid H_2 \mid H^+$, as zero, at 25° C. and one atmosphere pressure, the solution being normal. In the following table, Part I, are given the values obtained by Lewis and Randall, taken for the most part from the investigations of Lewis and his associates. References to the original literature are given below the table. The electrode reactions are so arranged that the values for the increase in free energy are simply equal to $(-E_0.Q)$ where E_0 is the electrode potential. In Part II of the table are given some values for the electrode potentials of other elements taken from

the compilation of Abegg, Auerbach, and Luther. These values are of a much lower order of accuracy (cf. Taylor, *Physical Chemistry*, 1931, vol. I, 828). Strictly speaking, the normal hydrogen electrode is regarded as one for which the activity and not the concentration of the hydrions is unity, but the consideration of activity will be deferred till the next chapter. The activity of the ions in the following electrodes is also considered to be unity. Hence the E.M.F. of a cell $H_2 \mid H^+ \mid M^+ \mid M$ will be given by

$$E = E_0 - \frac{RT}{nQ} ln\ 1 = E_0.$$

STANDARD ELECTRODE POTENTIALS AT 25° C.

PART I

	Electrode.	Electrode Reaction.	E_0.
1.	$Li \mid Li^+$	$Li = Li^+ + \ominus$	2·9578
2.	$Rb \mid Rb^+$	$Rb = Rb^+ + \ominus$	2·9242
3.	$K \mid K^+$	$K = K^+ + \ominus$	2·9224
4.	$Na \mid Na^+$	$Na = Na^+ + \ominus$	2·7125
5.	$Zn \mid Zn^{++}$	$\frac{1}{2}Zn = \frac{1}{2}Zn^{++} + \ominus$	0·7581
6.	$Fe \mid Fe^{++}$	$\frac{1}{2}Fe = \frac{1}{2}Fe^{++} + \ominus$	0·441
7.	$Cd \mid Cd^{++}$	$\frac{1}{2}Cd = \frac{1}{2}Cd^{++} + \ominus$	0·3976
8.	$Tl \mid Tl^+$	$Tl = Tl^+ + \ominus$	0·3363
9.	$Sn \mid Sn^{++}$	$\frac{1}{2}Sn = \frac{1}{2}Sn^{++} + \ominus$	0·136
10.	$Pb \mid Pb^{++}$	$\frac{1}{2}Pb = \frac{1}{2}Pb^{++} + \ominus$	0·122
11.	$Fe \mid Fe^{+++}$	$\frac{1}{3}Fe = \frac{1}{3}Fe^{+++} + \ominus$	0·045
12.	$Pt \mid H_2 \mid H^+$	$\frac{1}{2}H_2 = H^+ + \ominus$	0
13.	$Cu \mid Cu^+$	$\frac{1}{2}Cu = \frac{1}{2}Cu^{++} + \ominus$	− 0·3448
14.	$Hg \mid Hg_2^{++}$	$\frac{1}{2}Hg = \frac{1}{2}Hg^{++} + \ominus$	− 0·7986
15.	$Ag \mid Ag^+$	$Ag = Ag^+ + \ominus$	− 0·7995
16.	$Pt \mid S^{--} \mid S$(rhom)	$\frac{1}{2}S^{--} = \frac{1}{2}S$(rhomb.) $+ \ominus$	+ 0·51
17.	$Pt \mid OH^- \mid O_2$	$OH^- = \frac{1}{4}O_2 + \frac{1}{2}H_2O + \ominus$	− 0·3976
18.	$Pt \mid I^- \mid I_2$ (s).	$I^- = \frac{1}{2}I_2$ (s). $+ \ominus$	− 0·5357
19.	$Pt \mid Br^- \mid Br$ (l).	$Br^- = \frac{1}{2}Br_2$ (l). $+ \ominus$	− 1·0659
20.	$Pt \mid Cl^- \mid Cl_2$(g).	$Cl^- = \frac{1}{2}Cl_2$(g). $+ \ominus$	− 1·3594
21.	$Hg \mid HgCl \mid Cl^-$	$Hg + Cl^- = \frac{1}{2}Hg_2Cl_2 + \ominus$	− 0·2700
22.	$Ag \mid AgCl \mid Cl^-$	$Ag + Cl^- = AgCl + \ominus$	− 0·2245
23.	$Hg \mid Hg_2SO_4 \mid SO_4^{--}$	$Hg + \frac{1}{2}SO_4^{--} = \frac{1}{2}Hg_2SO_4 + \ominus$	− 0·6213
24.	$Pt \mid H_2 \mid OH^-$	$\frac{1}{2}H_2 + OH^- = H_2O + \ominus$	+ 0·8280
25.	$Hg \mid HgO \mid OH^-$	$\frac{1}{2}Hg + OH^- = \frac{1}{2}HgO + \frac{1}{2}H_2O + \ominus$	− 0·0984

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(9) Noyes and Toabe, ib., 1917, **39**, 1537.
(13) (23) Lewis and Lacy, 1914, **36**, 804.
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(15) Noyes and Braun, ib., 1912, **34**, 1016.
(19) Lewis and Storch, ib., 1917, **39**, 2544.
(20) Lewis and Rupert, ib., 1911, **33**, 299.
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(24) Lorenz and Böhi, *Zeit. phys. Chem.*, 1909, **66**, 733.
(16) Sammet, ib., 1905, **53**, 641; Maitland, *Z. Elektrochem.*, 1906, **12**, 263.
(25) Brönsted, *Zeit. phys. Chem.*, 1909, **65**, 84; Ming Chow, *J. Amer. Chem. Soc.*, 1920, **42**, 488.

PART II

Electrode.	Electrode Reaction.	E_0.
1. $Ba \mid Ba^{++}$	$\frac{1}{2}Ba = \frac{1}{2}Ba^{++} + \ominus$	2·8
2. $Sr \mid Sr^{++}$	$\frac{1}{2}Sr = \frac{1}{2}Sr^{++} + \ominus$	2·7
3. $Ca \mid Ca^{++}$	$\frac{1}{2}Ca = \frac{1}{2}Ca^{++} + \ominus$	2·5
4. $Mg \mid Mg^{++}$	$\frac{1}{2}Mg = \frac{1}{2}Mg^{++} + \ominus$	1·55
5. $Mn \mid Mn^{++}$	$\frac{1}{2}Mn = \frac{1}{2}Mn^{++} + \ominus$	1·0
6. $Cr \mid Cr^{+++}$	$\frac{1}{3}Cr = \frac{1}{3}Cr^{+++} + \ominus$	0·5
7. $In \mid In^{+++}$	$\frac{1}{3}In = \frac{1}{3}In^{+++} + \ominus$	0·35
8. $Co \mid Co^{++}$	$\frac{1}{2}Co = \frac{1}{2}Co^{++} + \ominus$	0·29
9. $Ni \mid Ni^{++}$	$\frac{1}{2}Ni = \frac{1}{2}Ni^{++} + \ominus$	0·22
10. $Sb \mid Sb^{+++}$	$\frac{1}{3}Sb = \frac{1}{3}Sb^{+++} + \ominus$	− 0·1
11. $Bi \mid Bi^{+++}$	$\frac{1}{3}Bi = \frac{1}{3}Bi^{+++} + \ominus$	− 0·2
12. $As \mid As^{+++}$	$\frac{1}{3}As = \frac{1}{3}As^{+++} + \ominus$	− 0·3
13. $Pd \mid Pd^{++}$	$\frac{1}{2}Pd = \frac{1}{2}Pd^{++} + \ominus$	− 0·82
14. $Au \mid Au^{+}$	$Au = Au^{+} + \ominus$	− 1·5
15. $Pt \mid F^{-} \mid F_2$	$F^{-} = \frac{1}{2}F_2 + \ominus$	− 1·9

It is found that the value of E_0 is a periodic function of the elements. The results are at present only approximate, but when the values of the electrode potential E_0 are plotted against the atomic numbers as in Fig. 30, the typical periodicity exhibited by all fundamental properties of the elements, is observed.

It is evident from our conception of solution pressure and E_0 that the more electropositive an element is, the greater its tendency to form ions and electrons. The more electronegative an element, the greater its tendency to react with an electron to form an anion.

Applications of the Theory of Electrochemistry.

We now propose to consider a few cases where the application of the principles developed in this chapter enable us to elucidate

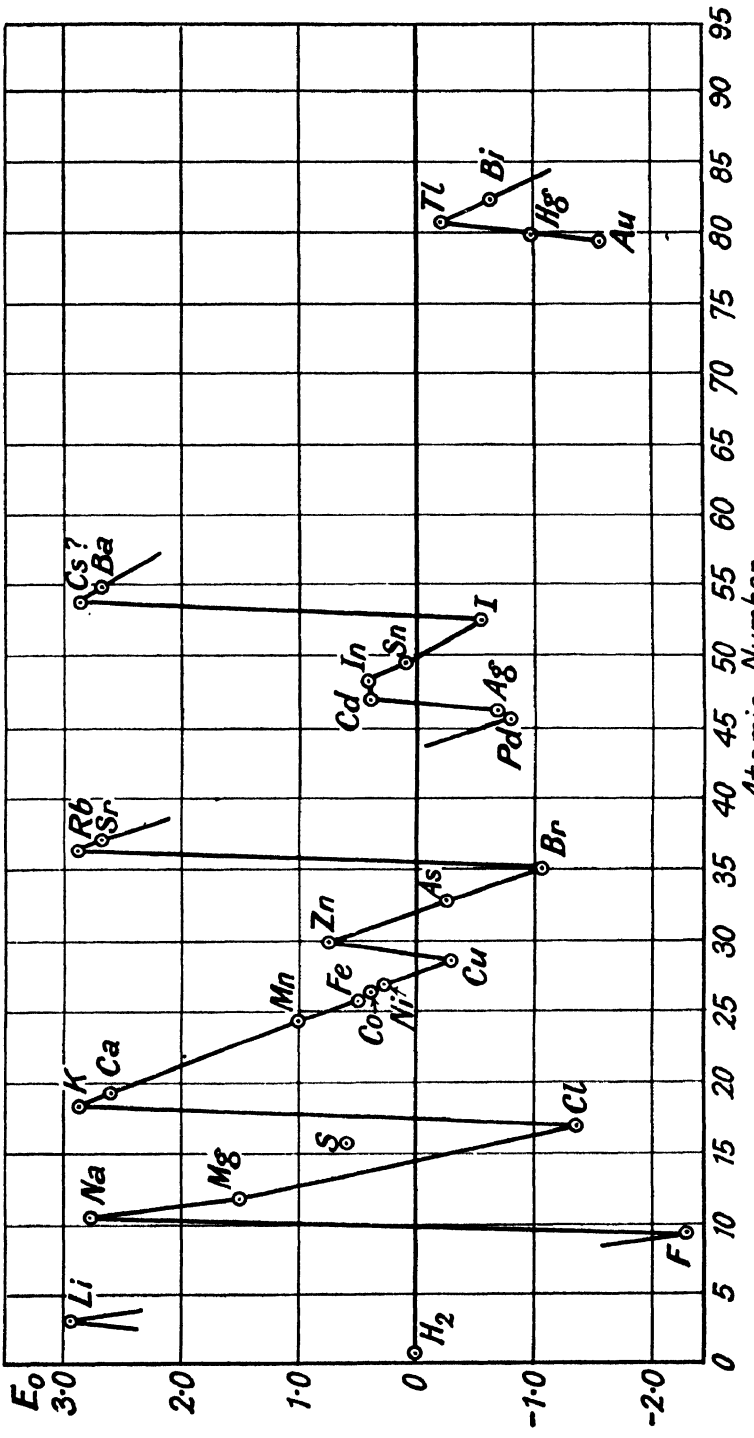

E_0
3·0
2·0
1·0
0
-1·0
-2·0
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95
Atomic Number
Li
Na
K
Rb
Cs?
Mg
Ca
Sr
Ba
Mn
Fe
Co
Ni
Cu
Zn
As
Br
Cd
In
Sn
I
Pd
Ag
Tl
Bi
Hg
Au
S
Cl
F
H_2

FIG. 30.

problems of a chemical nature which would otherwise be somewhat difficult. The first of these is of great interest, namely the determination of the true valency of a substance. It was employed by Ogg to determine the valency of the mercurous ion (*Zeit. phys. Chem.*, 1898, **27**, 285).

Determination of the Valency of an Ion. The question which Ogg set out to determine was whether the mercurous ion should be represented by Hg^{+} or by Hg_2^{++}. He set up the following cell:

Hg	Mercurous (c_1) Nitrate in dil. HNO_3(0·1N)	Mercurous (c_2) Nitrate 0·1 N.HNO_3	Hg
	+	−	

The nitric acid is present so as to prevent the hydrolysis of the salt. Now we have seen that, since this cell is reversible with respect to the mercurous ion the electromotive force is given by

$$E = \frac{RT}{nQ} ln \frac{c_1}{c_2}$$

where n is the valency of the mercurous ion. Now E, c_1 and c_2 can be determined so that n may be calculated. In an actual case where c_1 was $N/2$, c_2 was $N/20$, the electromotive force was found to be 0·029 volts. Hence we have

$$0{\cdot}029 = \frac{0{\cdot}058}{n} log \frac{20}{2} = \frac{0{\cdot}058}{n}$$

whence we obtain $n = 2.$, so that the mercurous ion must be represented by Hg_2^{++}, and the true formula for mercurous nitrate is $Hg_2(NO_3)_2$. Similarly, the correct formula for mercurous chloride will probably be Hg_2Cl_2. It is, of course, necessary to eliminate the liquid-liquid potential difference in making the measurement of the E.M.F. of the cell. This method has the double merit of being direct and of great accuracy.

Determination of the Solubility of Sparingly Soluble Salts. We are here about to describe the method employed by Goodwin (*Zeit. phys. Chem.*, 1894, **13**, 641) in determining the solubility of silver chloride which is so sparingly soluble that the conductivity method is not sufficiently accurate. We determine the electromotive force of some such cell as the following:

Ag	$AgNO_3$ (N/10)	Saturated NH_4NO_3	0·1N.KCl saturated with $AgCl$	Ag.

The cell is reversible with respect to the silver ion so that if c_1 and c_2 are the concentrations of this ion in the two compartments, the E.M.F. of the cell is given by

$$E = \frac{RT}{Q} ln\ c_1/c_2.$$

Now, if we assume complete ionization of the silver nitrate, then c_1 is equal to $N/10$. Hence

$$E = 0{\cdot}058\ log\ \frac{0{\cdot}1}{c_2}.$$

The electromotive force of the cell was found to be 0·450 volts, so that, at 25° C.

$$0{\cdot}450 = 0{\cdot}058\ log\ \frac{0{\cdot}1}{c_2}.$$

Hence we obtain

$$c_2 = 1{\cdot}74 \times 10^{-9}.$$

Now the concentration of chloride ions in the right-hand compartment, if we assume 85 per cent. dissociation, is 0·085, so that the solubility product of silver chloride is

$$1{\cdot}74 \times 10^{-9} \times 0{\cdot}085 = 1{\cdot}48 \times 10^{-10}.$$

Hence the solubility of silver chloride, which is equal to the square root of the solubility product is equal to $1{\cdot}2 \times 10^{-5}$ gram equivalents per litre.

Electrometric Analysis. Since, as we have seen, the potential of an electrode depends upon the concentration of the ions in the solution, it is possible to employ the potential difference observed, instead of an "indicator," in volumetric analysis. Thus, for example, let us consider the cell:

$$Ag \mid AgNO_3\ (c) \mid KNO_3 \mid \text{Calomel or other standard electrode.}$$

We require to determine the concentration of the silver nitrate c. The E.M.F. of the cell will give a measure of the potential of the electrode $Ag \mid AgNO_3$. We now run into the silver nitrate a standard solution of sodium chloride. This precipitates the silver chloride so that the E.M.F. of the cell will change. This alteration in the electromotive force will be gradual at first since the change in the electrode potential depends upon the fractional amount of silver removed. As the amount of chloride approaches equivalence to the amount of silver in the solution, the fraction of silver in

the solution which is removed by each drop of sodium chloride added, rapidly increases, and the E.M.F. changes rapidly in consequence. As we continue to add the chloride, however, the change again becomes very slow. We therefore plot the E.M.F. against the amount of chloride added when a curve of the form shown in Fig. 31 is obtained. The neutral point is given by the point of inflexion on the curve. It is, of course, necessary that the solution of silver nitrate should be thoroughly agitated to ensure rapid mixing, since it is essential that the concentration of the silver nitrate be uniform. The method is very useful and is capable

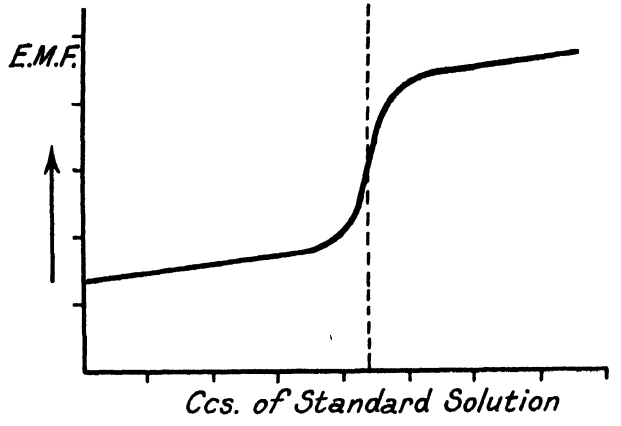


FIG. 31.

of very great accuracy. The point of inflexion can most readily be found by plotting the values of $\frac{\Delta E}{\Delta v}$ against volume of solution added. At the point of inflexion $\frac{\Delta E}{\Delta v}$ is a maximum.

Determination of the Hydrogen Ion Concentration in a Solution. We employ a hydrogen electrode, the potential of which depends upon the concentration of hydrogen ions in the solution. A convenient apparatus is that due to Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35**, 848, 1538) and shown in Fig. 32.

The platinum wire from the electrode is sealed into the end of a glass tube *B*, which, in turn, is sealed near its upper end into a glass tube *A* of wider diameter. Connection between the electrode and the rest of the voltaic circuit can be made by means of a copper wire dipping into mercury in tube *B*. The electrode is

prepared and platinized, and a current of hydrogen passed in through the side-tube *C*, while the lower expanded end of tube *A* is dipped into the acid solution. The hydrogen escapes through the holes *a*, *a*, so arranged that the platinum electrode is partially immersed in the liquid and partially surrounded by gas. The acid solution is connected by an inverted U-tube, filled with a saturated solution of *KCl* (to eliminate the liquid-liquid *P.D.*) with a normal calomel electrode. Carefully purified hydrogen is passed until the hydrogen electrode has acquired its equilibrium potential and the electromotive force of the combination is measured.

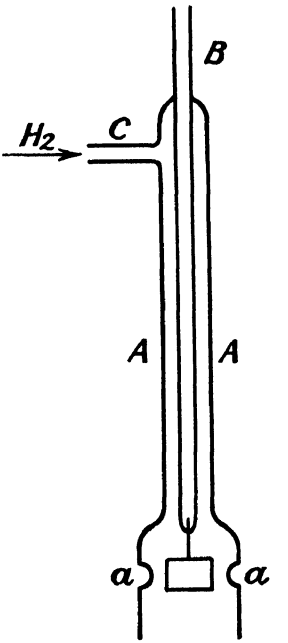


FIG. 32.

Since the potential difference between the liquids is eliminated, the potential of the hydrogen electrode referred to that of the normal calomel electrode is obtained by subtracting the value of the calomel electrode (0·560 volt at 18° C.) from the value of the E.M.F. measured. If, however, as is now customary, one refers the potential of a given hydrogen electrode to the potential of the normal hydrogen electrode in contact with solution, then the E.M.F. of the above cell must be diminished by 0·286 volt, which is the value of the calomel electrode compared with the normal hydrogen electrode at the same temperature. Taking, therefore, the potential of the normal hydrogen ion electrode as zero, the potential of a hydrogen electrode in contact with a solution which is h-normal in respect to hydrogen ions is given by the expression

$$E' = \frac{RT}{Q} ln \frac{1}{h} = 0{\cdot}0001983T \; log \frac{1}{h}.$$

Now if E is the observed E.M.F. of the cell, we have seen that

$$E' = E - 0{\cdot}286$$

so that

$$\frac{E - 0{\cdot}286}{0{\cdot}0001983T} = log \frac{1}{h} = pH.$$

Thus we have a very simple and accurate method of determining the concentration of hydrogen ions present in any given solution.

This method may, evidently, also be employed for titration purposes. Employing the expression just given for the pH of a solution it is found that a neutral solution, i.e. one for which $pH = 7$, corresponds to a value of the E.M.F. of the cell $E = 0{\cdot}686$ volt. at 15° C. In titrating, therefore, we run in small quantities of alkali and determine the E.M.F. after each addition. We plot the values, so obtained, against the volume of alkali added and determine the volume corresponding to 0·686 volts. This is the volume of alkali required to neutralize the solution.

Hydrolysis of Salts. The electrometric method of determining the degree of hydrolysis of salts also depends upon the use of a hydrogen electrode and the determination of the hydrion concentration. Let us consider the hydrolysis of aniline hydrochloride (Denham, *Journ. Chem. Soc.*, 1908, **93**, 41). The reaction may be represented by the equation—

$$C_6H_5.NH_2.HCl + H_2O = C_6H_5.NH_3OH + HCl.$$

The base $C_6H_5.NH_3OH$ will be practically undissociated, while the acid, which is formed in corresponding amount, will be almost completely dissociated. Suppose a fraction x of one mole is dissociated, the volume of the solution containing the mole being V. Then the concentrations of the various constituents are as follows:

$\frac{x}{V}$ is the concentration of the acid and of the base formed.

$\frac{1-x}{V}$ is the concentration of the unhydrolyzed hydrochloride.

The hydrolysis constant is therefore given by

$$K = \frac{x^2}{(1-x)V}.$$

Now we know the value of the volume V, and, if we can determine the hydrion concentration, we can obtain x, since the hydrion concentration is equal to the concentration of acid formed. We therefore determine the E.M.F. of some such cell as the following:

$$H_2 \left| \frac{N}{32}.C_6H_5.NH_2.HCl \right| \begin{matrix} \text{Saturated} \\ NH_4NO_3 \end{matrix} \left| \begin{matrix} \text{Calomel electrode.} \\ \text{Normal.} \end{matrix} \right.$$

The electromotive force of this cell was found to be − 0·4655 volts. Hence the pH. of the solution is given by the following expression for 25° C.

$$pH. = -\frac{E - 0{\cdot}282}{0{\cdot}059} = -3{\cdot}093$$

i.e. $\log (H') = -3{\cdot}093 = \bar{4}{\cdot}907$

so that $(H') = 0{\cdot}000807.$

This is the value of $\frac{x}{V}$. The volume occupied by one mole of hydrochloride, namely V, is 32 litres. Hence the hydrolytic constant is given by

$$K = \frac{(0{\cdot}000807)^2 \times 32}{1 - (0{\cdot}000807 \times 32)} = 0{\cdot}000021.$$

The following table gives the results obtained by Denham by this method.

V.	*E.M.F.*	π_1.	$H \times 10^2$.	$100x$	$K \times 10^4$.
16	0·4567	0·1033	0·1138	1·82	0·21
24	0·4609	0·0991	0·0966	2·32	0·23
32	0·4655	0·0945	0·0807	2·58	0·21
					Mean 0·216

π_1 is Single P.D. of the hydrogen electrode.

The hydrolysis for $V = 32$ is 2·58 per cent., a value agreeing extremely well with that found by Bredig at the same temperature and dilution, namely 2·61 per cent. (Bredig, *Zeit. phys. Chem.*, 1894, **13**, 289).

CHAPTER IX

THE ACTIVITY METHOD OF TREATMENT OF SOLUTIONS

The student should now be fairly familiar with the elementary methods of thermodynamics as applied to dilute solutions. They all depend upon the single assumption that the solute obeys the gas law $P = RTC$, where P is the osmotic pressure, T the absolute temperature, R the gas constant per mole and C the concentration of the solute in the solution. Now, while this assumption gives a fairly satisfactory representation of the experimental data in the case of very dilute solutions of weak electrolytes (or non-electrolytes), it is totally inadequate when we come to deal with electrolytes having a higher electrical conductivity, and which, on Arrhenius's theory, are more completely dissociated into ions.

The anomalous behaviour of these strong electrolytes led G. N. Lewis to elaborate a method of systematizing the various properties of solutions, based on thermodynamical considerations. This is known as the "Activity" method of treatment and is contained in the following publications: *Proc. Amer. Acad.*, 1901, **37**, 49; *Zeit. phys. Chem.*, 1901, **38**, 205; Lewis and Randall, *Thermodynamics*, McGraw-Hill Book Co., 1923. The method has proved to be of great practical utility and it will therefore be presented in some detail. It does not attempt to account for the anomaly of strong electrolytes, but it will be evident, as we proceed, that it does enable us to correlate a large amount of data which would otherwise have very little significance.

Activity Method of Treatment. It is a well-known fact that heat tends to pass naturally and spontaneously from a body at a higher to one at a lower temperature. We have seen reason to regard this as a special case of a much more far-reaching law of nature, namely the Second Law of Thermodynamics. We may, however, regard the phenomenon from a somewhat different point of view and say that every body has a certain tendency to lose heat, or that heat tends to escape from any body, and that the

higher the temperature of the body the greater is the "escaping tendency" of heat from it. If two bodies at different temperatures come into contact, the escaping tendency of heat for the body at the higher temperature is greater than the escaping tendency for the body at the lower temperature, so that heat passes from the former to the latter. The absolute temperature of the body may thus be said to be a measure of this escaping tendency of heat from that body.

In a similar manner, if we have two solutions of aniline, one in water and the other in benzene, for example, the aniline will have a certain tendency to pass from one solution to the other, according to the distribution law, and we may say that the aniline has a certain escaping tendency in both solvents. Equilibrium will evidently be established when the two escaping tendencies are equal.

Let us consider a solid or liquid in contact with its vapour, then the substance may be regarded as having a certain escaping tendency in both phases, i.e. a tendency to pass into the other phase. We desire to obtain some suitable measure of the escaping tendency of a pure substance in such a case. Now it is evident that the **vapour pressure** of the substance gives us a qualitative measure of the escaping tendency, and, in fact, this would serve as a quantitative measure of this property of the system. This is not, however, of much use in practice unless the vapour behaves like an ideal gas, and since no known vapour is strictly ideal and some are quite the reverse, G. N. Lewis introduces the term "Fugacity." This is a "corrected vapour Pressure," that is to say, it is the vapour pressure which would be exerted if the vapour obeyed the gas laws. Now we have seen that for a perfect gas the free energy change accompanying the isothermal transfer of one mole of the gas from a pressure P_1 to a pressure P_2 is given by

$$\Delta F = F_2 - F_1 = \int_{P_1}^{P_2} V dP = RT \ln P_2/P_1.$$

The fugacity, f, should, therefore, obey this law in the case of any substance whatsoever, so that we may write

$$F_2 - F_1 = RT \ln \frac{f_2}{f_1} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If the difference between the two states is reduced to an infinitesimal amount we have

$$F + dF - F = RT\ ln\ (f + df) - RT\ ln\ f$$

so that

$$dF = RT\ d\ ln\ f \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Integrating we obtain

$$F = RT\ ln\ f + B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where B is a constant at any given temperature, i.e. B is a function of temperature alone. This constitutes the mathematical definition of the fugacity of a pure substance in terms of the free energy. Since equation (2) refers to constant temperature it may be expressed in the form

$$\left(\frac{\partial\ ln\ f}{\partial F}\right)_T = \frac{1}{RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and we know that

$$\left(\frac{\partial F}{\partial P}\right)_T = V$$

so that, on combining the two, we obtain

$$\left(\frac{\partial\ ln\ f}{\partial P}\right)_T = \frac{V}{RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

By keeping the temperature constant and integrating this equation we obtain

$$ln\ f = \int \frac{V}{RT} dP + \text{Constant} \quad . \quad . \quad . \quad . \quad (6)$$

If V is known as a function of P this expression enables us to calculate the value of the fugacity at any pressure provided the value at some one pressure is known, i.e. provided the value of the constant at the temperature under consideration is known.

In order to determine how the fugacity of a substance varies with the temperature at constant pressure we proceed as follows: Suppose we have a substance in some given state at which the free energy is F and the fugacity f. Let us imagine it to be converted isothermally to the vapour state and then expanded to an infinitely large volume and an infinitely low pressure. Let F^* be the new value of the free energy, f^* of the fugacity. Then we have by equation (1)

$$F^* - F = RT\ ln \frac{f^*}{f} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Differentiate this expression partially with respect to temperature, the pressure upon each of the two states remaining constant.

$$\left(\frac{\partial F^*}{\partial T}\right)_P - \left(\frac{\partial F}{\partial T}\right)_P = R\,ln\,\frac{f^*}{f} + RT\left(\frac{\partial\,ln\,f^*}{\partial T}\right)_P - RT\left(\frac{\partial\,ln\,f}{\partial T}\right)_P$$

In the gas at very low pressure, the fugacity will be equal to the pressure itself which is constant. Hence $\left(\frac{\partial\,ln\,f^*}{\partial T}\right)_P = \left(\frac{\partial\,ln\,P}{\partial T}\right)_P$ which, of course, is zero. Moreover, by equation (7)

$$R\,ln\frac{f^*}{f} = \frac{F^* - F}{T}$$

so that we have

$$\left(\frac{\partial F^*}{\partial T}\right)_P - \left(\frac{\partial F}{\partial T}\right)_P = \frac{F^*}{T} - \frac{F}{T} - RT\left(\frac{\partial\,ln\,f}{\partial T}\right)_P$$

But by equation V (15) we have

$$\left(\frac{\partial F}{\partial T}\right)_P = \frac{F - H}{T}$$

so that we obtain

$$\left(\frac{\partial\,ln\,f}{\partial T}\right)_P = \frac{H^* - H}{T} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The quantity $H^* - H$ is the increase in the heat content when the substance escapes into a vacuum. It is a very important quantity and has been called the Ideal Heat of Vaporization.

The further consideration of fugacity is beyond the scope of this book and the reader is referred to the original author for the calculations of the fugacity of various substances. We must now, however, proceed to apply this concept of fugacity or escaping tendency to solutions.

In the first place it will be evident to every serious student of chemistry that one of the most ambiguous words in the current vocabulary is the term *concentration*. This is variously expressed in moles per litre of solution, moles per litre of solvent, moles per 100 grams of solvent, grams per litre, and so on. Some of these quantities are convenient for laboratory purposes but they are all more or less arbitrary and G. N. Lewis therefore employs what is, after all, the only logical method of expressing concentration, namely the mole fraction. This is defined as follows : In a solution

containing n_1 moles of X_1, n_2 moles of X_2, n_3 moles of X_3, etc., the mole fraction N_1 of the constituent X_1 is given by

$$N_1 = \frac{n_1}{n_1 + n_2 + n_3 + \ldots} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Similarly, the mole fraction N_2 of the constituent X_2 is

$$N_2 = \frac{n_2}{n_1 + n_2 + n_3 + \ldots}.$$

It is evident that if we add the values of the mole fractions for all the constituents of the solution we obtain

$$N_1 + N_2 + N_3 + \ldots\ldots = 1 \quad . \quad . \quad . \quad . \quad (10)$$

Let the total free energy of such a solution be represented by F. Then it is necessary to see how this quantity is distributed among the various constituents. Let us suppose that all the variables n_2, n_3, n_4, etc., are kept constant, while n_1 changes by an infinitesimal amount. There will be a corresponding change in the free energy F. Let us suppose that the total volume of the solution is very large, so that the addition of one mole of X_1 has no effect on the relative concentrations, then the ratio $\left(\frac{\partial F}{\partial n_1}\right)_{n_2, n_3 \ldots}$ is equal to the change which occurs in the free energy for the addition of one mole of X_1, in other words, it is the free energy of one mole of this constituent in the solution. This is known as the Partial Molal Free Energy $\bar{F}_1$ of the constituent X_1

$$\bar{F}_1 = \frac{\partial F}{\partial n_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Similarly, we may write

$$\bar{F}_2 = \frac{\partial F}{\partial n_2}; \quad \bar{F}_3 = \frac{\partial F}{\partial n_3}, \text{ etc.}$$

We may treat any other property of the system, such as volume, entropy, heat content, etc., in a similar manner and obtain partial molal quantities of the form:

$$\bar{V}_1 = \frac{\partial V}{\partial n_1}; \quad \bar{S}_1 = \frac{\partial S}{\partial n_1}; \quad \bar{H}_1 = \frac{\partial H}{\partial n_1}, \text{ etc.}$$

We may now define the fugacity of a substance in solution, in a similar manner to that adopted for a pure substance, namely by means of the equation

$$\bar{F}_1 = RT \ln f_1 + B_1 \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where B_1 is a function of temperature alone; or in differential form

$$\frac{\partial \ln f_1}{\partial \bar{F}_1} = \frac{1}{RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

As regards the variation of the fugacity of substances in solution, with temperature and pressure, we may write the following expressions corresponding to equations (5) and (8):

$$\left(\frac{\partial \ln f_1}{\partial P}\right)_{TN} = \frac{\bar{V}_1}{RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

$$\left(\frac{\partial \ln f_1}{\partial T}\right)_{PN} = \frac{H_1^* - \bar{H}_1}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

We must now endeavour to determine how the fugacities of the various constituents vary with the composition of the solution. Equation (11) gives us the partial free energy per mole of constituent X_1. But there are altogether n_1 moles of this constituent present, so that the partial molal free energy for that constituent is $n_1.\bar{F}_1$. Hence the total free energy, F, for all the constituents is given by

$$F = n_1.\bar{F}_1 + n_2.\bar{F}_2 + n_3.\bar{F}_3 + \ldots\ldots\ldots \quad . \quad . \quad . \quad (16)$$

If we consider a quantity of solution such that

$$n_1 + n_2 + n_3 + \ldots\ldots = 1$$

then by equation (9) we may replace n_1, n_2, etc., by N_1, N_2, etc., and obtain

$$F = N_1\bar{F}_1 + N_2\bar{F}_2 + N_3\bar{F}_3 + \ldots \quad . \quad . \quad . \quad . \quad (17)$$

Differentiate this expression with respect to N_1, keeping the pressure and temperature constant. We thus obtain, since the free energy is also constant

$$N_1\left(\frac{\partial \bar{F}_1}{\partial N_1}\right)_{TP} + N_2\left(\frac{\partial \bar{F}_2}{\partial N_1}\right)_{TP} + N_3\left(\frac{\partial \bar{F}_3}{\partial N_1}\right)_{TP} + \ldots = 0 \; . \quad (18)$$

Now since, by equation (13) we have

$$d\bar{F}_1 = RT\, d \ln f_1$$

and RT is a constant at constant temperature, equation (18) may be written in the form

$$N_1\left(\frac{\partial \ln f_1}{\partial N_1}\right)_{TP} + N_2\left(\frac{\partial \ln f_2}{\partial N_1}\right)_{TP} + N_3\left(\frac{\partial \ln f_3}{\partial N_1}\right)_{TP} + \ldots = 0 \quad (19)$$

If the solution contains only two constituents, it is evident that

a change in one of the mole fractions, say N_1, must be balanced by an equal change in the other mole fraction N_2 in the opposite direction or

$$dN_1 = -dN_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Substituting this in the equation (19) for two constituents we obtain—

$$N_1\left(\frac{\partial \ln f_1}{\partial N_1}\right)_{TP} = N_2\left(\frac{\partial \ln f_2}{\partial N_2}\right)_{TP} \quad . \quad . \quad . \quad . \quad (21)$$

When the vapours are nearly perfect gases we may substitute partial vapour pressures for fugacities and obtain the approximate relation

$$N_1\left(\frac{\partial \ln p_1}{\partial N_1}\right)_{TP} = N_2\left(\frac{\partial \ln p_2}{\partial N_2}\right)_{TP} \quad . \quad . \quad . \quad . \quad (22)$$

According to equation (12) we have

$$\bar{F}_1 = RT \ln f_1 + B_1.$$

Now if $\bar{F}_1$ and f_1 are both finite it follows that B_1 must also be finite. The partial vapour pressure of any constituent of a solution must approach zero as its mole fraction approaches zero. But as the vapour pressure approaches zero, it becomes equal to the fugacity. Therefore, when $N_1 = 0$, $f_1 = 0$. Hence

$$RT \ln f_1 = -\infty, \text{ and } \bar{F}_1 = -\infty$$

or the partial molal free energy is negative infinity when $N_1 = 0$.

It will be evident that, since the fugacity is a "Corrected Vapour Pressure," we could proceed to deduce all the relations obtained in the elementary treatment of dilute solutions given in Chapter VII, substituting fugacity instead of vapour pressure. We shall, however, content ourselves with deducing Raoult's law by a slightly different method. We shall first of all make the assumption that Henry's law [1] holds for an infinitely dilute solution. This was the assumption from which we started in Chapter VII.

[1] G. N. Lewis deduces Henry's law as follows: If we plot f_2, the fugacity of the solute, against N_2, and observe the slope of the curve when N_2 approaches zero, experiment shows that it is finite, i.e. df_2/dN_2 is constant. But it is an elementary proposition of the calculus that in the neighbourhood of the point $x = 0$, $y = 0$, $dy/dx = y/x$. Hence in the region of the infinitely dilute solution $df_2/dN_2 = f_2/N_2 =$ constant, say, k. That is, $f_2 = kN_2$ which is Henry's law.

Expressed in terms of the fugacity f_2 of the solute this law becomes

$$f_2 = k'c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where c is the concentration in moles per litre. Since in very dilute solution the concentration c is proportional to the mole fraction N_2 of the solute we may write equation (23) in the form

$$f_2 = kN_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Differentiate this expression; we obtain

$$\frac{df_2}{dN_2} = k = \frac{f_2}{N_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Now according to equation (22) we have, at constant temperature and pressure,

$$N_1 \frac{d\ ln\ f_1}{dN_1} = N_2 \frac{d\ ln\ f_2}{dN_2}.$$

Hence

$$N_1 \frac{d\ ln\ f_1}{dN_1} = \frac{N_2}{f_2} \cdot \frac{df_2}{dN_2} = 1.$$

Now we have

$$dN_1/N_1 = d\ ln\ N_1$$

so that

$$d\ ln f_1 = \frac{dN_1}{N_1} = d\ ln\ N_1 \quad . \quad . \quad . \quad . \quad . \quad (26)$$

or on integration

$$ln f_1 = ln\ N_1 + \text{Constant}$$

that is

$$f_1 = f_1^\circ . N_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

where f_1° is the value of f_1 when $N_1 = 1$, and is therefore equal to the fugacity of the pure solvent. This is Raoult's law in terms of fugacities. If we may assume that the vapour of the solvent behaves like a perfect gas, we may substitute the vapour pressure of the solvent for the fugacity and obtain

$$p_1 = p_1^\circ . N_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

It is more usual to express this law in terms of the mole fraction of the solute N_2. Now $N_1 + N_2 = 1$ so that Raoult's law becomes

$$p_1 = p_1^\circ (1 - N_2)$$

or

$$\frac{p_1 - p_1^\circ}{p_1^\circ} = N_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

It will be seen that at very great dilution this is equivalent to the expression deduced in Chapter VII, namely

$$\frac{p_1 - p_1^\circ}{p_1^\circ} = \frac{Cm}{\rho}$$

where m is the molecular weight of the solvent as vapour, ρ is the density of the liquid solvent, C is the concentration in moles per cubic centimetre of solution. Since the solution is dilute we may consider that C is equal to the concentration in moles per c.c. of solvent, and 1 c.c. of solvent contains ρ/m moles. Now

$$N_2 = C/(n_1 + n_2)$$

where n_1 and n_2 are the number of moles of solvent and solute present in 1 c.c. of solution respectively. But since the solution is dilute we may neglect n_2 in comparison with n_1 and obtain

$$N_2 = \frac{C}{\rho/m} = \frac{Cm}{\rho}.$$

Definition of the Ideal Solution. We now propose to define an Ideal or Perfect Solution as a solution which obeys Raoult's law over all ranges of concentration, when that law is expressed in terms of fugacities. This definition is similar, in a sense, to the well-known definition of a perfect gas as one which obeys the gas law, since we are not assuming that any solution actually does obey Raoult's law completely, although experiment shows that, for some dilute solutions, the divergence from the law is small. Raoult's law may, as we have seen, be expressed thus,

$$f_1 = f_1^\circ N_1$$

and extending this to refer to the other constituents we may write

$$f_2 = f_2^\circ N_2; \quad f_3 = f_3^\circ N_3, \text{ etc.}$$

Hence we may restate our definition of the perfect or ideal solution as follows: An ideal solution is one for which the fugacities of each of the constituents are proportional to their respective mole fractions, this proportionality existing at all temperatures and pressures.

Let us now consider two solutions at the same temperature but containing different concentrations of the same substance. Then by Raoult's law

$$f_1 = f_1^\circ N_1; \quad f_1' = f_1^\circ N_1'$$

where f_1, f_1'; N_1, N_1', are the two values of the fugacity and the

mole fraction of the solvent respectively, and f_1° is a constant for any given temperature and pressure. Hence we have

$$\bar{F}_1' - \bar{F}_1 = RT \ln \frac{f_1'}{f_1} = RT \ln \frac{N_1'}{N_1} \quad . \quad . \quad . \quad (30)$$

or in differential form

$$d\bar{F}_1 = RT \, d \ln N_1 \quad . \quad . \quad . \quad . \quad . \quad (31)$$

These are fundamental equations of the Ideal Solution.

G. N. Lewis thus considers that the divergence of solutions of strong electrolytes from the simple gas laws is twofold in origin. It is due, in the first place, to the fact that the vapours of the various constituents are not ideal, i.e. their fugacities are not equal to their vapour pressures; and secondly, to the non-ideal nature of the solution itself, i.e. to the breakdown of Raoult's law. He therefore introduces his concept of **activity.**

Definition of Activity. Lewis chooses some standard state of a pure substance, at which the fugacity is f', and defines the activity of the substance in any other state, at which the fugacity is f, by the relation

$$a = \frac{f}{f'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

The choice of the standard state varies with the particular nature of the problem to be investigated. It is beyond our purpose to follow him further in his treatment of the activity of a pure substance. Suffice it to say, that, in the case of a solution, he equates f' for the solvent to the fugacity f° of the pure solvent at the temperature of the solution. Hence the activity of the solvent is given by the relation

$$a_1 = \frac{f_1}{f_1^\circ} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

Now, if the solution is an ideal one it is evident that this definition enables us to equate the activity of the solvent in the solution to its mole fraction, so that for such a solution

$$a_1 = N_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

The choice of the standard state for the solute is somewhat more variable, but it requires that, for an infinitely dilute solution, the activity of the solute shall be equal to the mole fraction.

$$a_2 = N_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

We may thus say, that for an ideal solution the activities of each of the constituents are equal to their respective mole fractions.

We thus see that the activity is a measure of the effective mole fraction of any constituent of a solution, on the assumption that the solution obeys Raoult's law and other related laws. In the case of aqueous solutions, Lewis has found it better to express the activity in terms of molality, i.e. the number of moles dissolved in 1,000 grams of water, since it is in this and simply related units that the major portion of the enormous mass of experimental data on aqueous solutions is expressed. This means that we can equate the activity to the concentration expressed in the above units and write, for an ideal solution,

$$a_1 = c_1\,; \quad a_2 = c_2, \text{ etc.}$$

It is possible to express the free energy change accompanying a change in the concentration of a solution, in terms of activities. If we consider two solutions, in which the fugacities of the solute are represented by f and f' respectively. Then by equation (12) the difference in the molal free energies of the solute in the two solutions is given by the relation

$$\bar{F}' - \bar{F} = RT \ln \frac{f'}{f} \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

Now the activities of the solute are given by

$$a' = f'/f^\circ\,; \quad a = f/f^\circ$$

so that the ratio f'/f is equal to the ratio of the activities a'/a. Hence equation (36) becomes

$$\bar{F}' - \bar{F} = RT \ln \frac{a'}{a} \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

This is precisely similar to the equation for the free energy of transfer from a region of concentration c' to a region of concentration c when the solution obeys the gas laws. This, of course, is what we should expect if we regard the activity as the effective concentration.

If one of the two states considered is the standard state we have

$$\bar{F} - \bar{F}^\circ = RT \ln \frac{f}{f^\circ} = RT \ln a \quad . \quad . \quad . \quad . \quad (38)$$

Measurement of Activity.

I. **Activity of a Solvent from its Vapour Pressure over a Solution.** In many cases the vapour over the solution may be

regarded as a perfect gas, so that the activity of the solvent a_1 is equal to the ratio p_1/p_1°. This is true for the thallium amalgams, which have been studied by Hildebrand and Eastman at 325° C. (*J. Amer. Chem. Soc.*, 1915, **37**, 2452). The following table gives the values obtained at several values of the mole fraction N_1 of the mercury. The third column gives the ratios of a_1/N_1 for the mercury constituent. This ratio, which should be unity for an ideal solution, indicates the divergence of the actual solution from the perfect state.

ACTIVITY OF MERCURY IN THALLIUM AMALGAMS AT 325° C.

N_1.	$a_1 = p_1/p_1^\circ$.	a_1/N_1.
0·957	0·955	0·998
0·942	0·938	0·996
0·915	0·901	0·985
0·893	0·875	0·980
0·836	0·803	0·961
0·742	0·690	0·930
0·664	0·602	0·907
0·614	0·548	0·893
0·497	0·433	0·871
0·347	0·293	0·844
0·202	0·166	0·822

It will be observed that the ratio a_1/N_1 decreases as N_1 decreases, that is, as the concentration of the thallium increases.

II. **Activity of Solute from its Vapour Pressure.** Lewis and Storch (*J. Amer. Chem. Soc.*, 1917, **39**, 2544) measured the vapour pressure of bromine in dilute solutions in carbon tetrachloride from values of N_2 from 0·004 to 0·025, and found over this range a constant value for the ratio p_2/N_2, namely 0·539. Thus over this limited range the activity of the bromine is equal to the mole fraction.

It should be observed that if we attempt to extrapolate the results obtained to $N_2 = 1$, so as to determine the vapour pressure of the pure liquid bromine we obtain a value 0·539 atmospheres, while the actual vapour pressure of liquid bromine is 0·280 atmospheres. Thus we see that the standard state for bromine as solute is not pure liquid bromine, i.e. in the relation $a_2 = f_2/f_2^\circ = p_2/p_2^\circ$,

p_2° is not equal to the vapour pressure of pure liquid bromine at the same temperature.

III. **Activity of Solute from Distribution between two Solvents.** We have seen that the distribution of a substance between the liquid and vapour phase is only a special case of the distribution between any two phases. Hence we may determine the activity of a solute in one phase from its activity in another phase if we know the distribution between the two phases. Thus Lewis and Storch (*loc. cit.*) employed bromine distributed between carbon tetrachloride and water (slightly acidulated to prevent hydrolysis). The ratio of the molality of bromine in the aqueous layer to the mole fraction in the carbon tetrachloride layer is 0·371. Now in the carbon tetrachloride layer the activity is equal to the mole fraction. Hence the activity in the water layer (measured in terms of molality) is obtained by multiplying the mole fraction in CCl_4 by 0·371.

IV. **Activity from Electromotive Force Measurements.** It will be evident that the equations obtained in Chapter VIII for the electromotive force of cells should really contain activity terms instead of concentrations. We shall defer the consideration of those cells involving ionic concentration until we have dealt in detail with the ionic activities. Such cells as that of Richards and Daniels, however, which consist of thallium amalgams dipping into a single electrolyte may be employed to determine the activity of the thallium in the mercury solution.

Let us consider the cell

Tl in amalgam (N_2) | Thallous chloride | *Tl* in amalgam (N_2').

N_2 and N_2' are the mole fractions of the thallium in the amalgams, and if a_2 and a_2' are the activities of the thallium in the mercury solution, then we may write

$$E = \frac{RT}{nQ} ln \frac{a_2'}{a_2} = \frac{0{\cdot}00019844T}{n} log \frac{a_2'}{a_2} \quad . \quad . \quad . \quad (39)$$

In very dilute amalgams we may equate the activity of the thallium to the mole fraction and obtain

$$E = \frac{0{\cdot}00019844T}{n} log \frac{N_2'}{N_2} \quad . \quad . \quad . \quad . \quad . \quad (40)$$

In the more concentrated amalgams we may use the measured

values of E to determine the variation of activity with mole fraction.

Lewis illustrates the method by employing the data of Richards and Daniels at 20° C. At this temperature equation (39) becomes

$$\log a_2 = \frac{-E}{0{\cdot}05816} + \log a_2' \quad . \quad . \quad . \quad . \quad . \quad (41)$$

We shall assume that the values of N_2' and a_2' are fixed and known, then the values of N_2 and a_2 may be obtained for any other thallium amalgam. In order to determine the values of a_2' and N_2' it is necessary to extrapolate to infinite dilution when $a_2 = N_2$. For such purpose of extrapolation we shall plot the difference between the experimental data and a function chosen with regard to simplification at infinite dilution.

Thus subtracting $\log N_2$ from both sides of (41) we obtain—

$$\log \frac{a_2}{N_2} = \left(\frac{-E}{0{\cdot}05816} - \log N_2\right) + \log a_2' \quad . \quad . \quad (42)$$

If we now plot the quantity in parentheses against N_2, as in Fig. 33

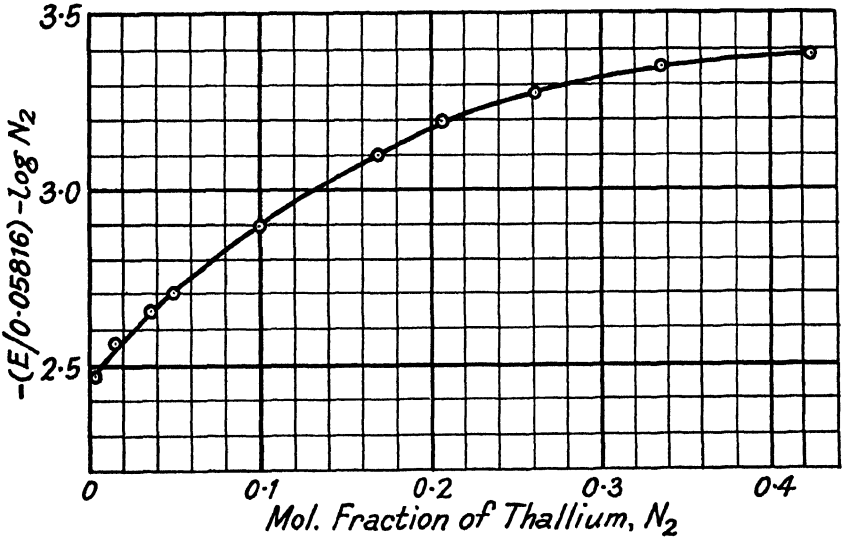


FIG. 33 (from G. N. Lewis).

we note that when $N_2 = 0$ we have by the definition of activity of solute $a_2/N_2 = 1$, or $\log (a_2/N_2) = 0$. The value of the ordinate where the curve cuts the vertical axis is therefore equal to $-\log a_2'$.

The curve is drawn from the experimental data given in the

following table. N_2' is taken as 0·00326, so that $-E$ is equal to the value of the E.M.F. given by Richards and Daniels. The first column gives the mole fraction of thallium; the second gives the values of $-E$ (between the amalgam of the given mole fraction and one in which N_2' is 0·00326). In the next column is given $(-E/0{\cdot}05816 - \log N_2)$, plotted as ordinate in Fig. 33, the fourth gives the values of a_2/N_2 obtained from the plot by subtracting the limiting ordinate $(-\log a_2')$ from the ordinate at the value of N_2 considered. $-\text{Log}\, a_2'$ in the diagram is 2·4689. The last column gives the value of a_2, the activity of the thallium.

This method of determination of the activity is extremely useful, since it does not, in any way, depend upon the vapour state so that it is immaterial whether or no the vapour behaves like a perfect gas.

ACTIVITY OF THALLIUM IN AMALGAMS AT 20° C.

N_2.	$-E$.	$\frac{-E}{0{\cdot}05816} - \log N_2$.	$\frac{a_2}{N_2}$.	a_2.
0·	$-\infty$	2·4689	1	0·0
0·003259	0·00000	2·4869	1·042	0·003396
0·01675	0·04555	2·5592	1·231	0·02062
0·03723	0·07194	2·6660	1·574	0·05860
0·04856	0·08170	2·7184	1·776	0·08624
0·0986	0·11118	2·9177	2·811	0·2772
0·1680	0·13552	3·1045	4·321	0·7259
0·2074	0·14510	3·1780	5·118	1·061
0·2701	0·15667	3·2610	6·196	1·674
0·3361	0·16535	3·3159	7·031	2·363
0·4240	0·17352	3·3558	7·707	3·268
0·428 (sat.)	0·17387	3·3580	7·75	3·316
Tl (liquid supercooled)			8·3	8·3

Calculation of the Activity of One Component of a Binary Solution when the Activity of the Other is Known.

Equation (18) for a binary solution may be written

$$d\bar{F}_1 . N_1 + d\bar{F}_2 . N_2 = 0$$

or

$$d\bar{F}_1 = -\frac{N_2}{N_1} d\bar{F}_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

If we replace $d\bar{F}$ by the equivalent expression $RTd\ ln\ a$, we obtain

$$d\ ln\ a_1 = -\frac{N_2}{N_1} d\ ln\ a_2 \quad . \quad . \quad . \quad . \quad . \quad (44)$$

Integration of this equation gives

$$log\ a_1/a_1' = -\int_{N_2'}^{N_2} \frac{N_2}{N_1} d\ log\ a_2 \quad . \quad . \quad . \quad . \quad (45)$$

It is possible to evaluate the integral directly by determining the area of the curve between two limits. This is not, however, very accurate, and Lewis proposes the following method. Noting that

$$dN_1 = -dN_2 \text{ or } N_1.d\ ln\ N_1 = -N_2.d\ ln\ N_2;$$

$$d\ ln\ N_1 = -\frac{N_2}{N_1} d\ ln\ N_2 \quad . \quad . \quad . \quad . \quad . \quad (46)$$

we may subtract the last equation from equation (44) and find

$$d\ ln\ \frac{a_1}{N_1} = -\frac{N_2}{N_1} d\ ln\ \frac{a_2}{N_2} \quad . \quad . \quad . \quad . \quad . \quad (47)$$

or using common logarithms and integrating

$$log\ \frac{a_1}{N_1} - log\ \frac{a_1'}{N_1'} = -\int_{N_2'}^{N_2} \frac{N_2}{N_1} d\ log\ \frac{a_2}{N_2} \quad . \quad . \quad . \quad (48)$$

This expression may be integrated graphically, by plotting N_2/N_1 as ordinates against $log\ (a_2/N_2)$, the area under the curve, between the points corresponding to the two compositions, gives immediately the difference between the two values of $log\ (a_1/N_1)$. Lewis and Randall employ this method to calculate the activity of the solvent mercury in thallium amalgams. They take one of the compositions as $N_2' = 0$, so that a_1'/N_1' must by definition be unity, since at infinite dilution the mole fraction of the solvent is equal to its activity. Hence $log\ (a_1'/N_1') = 0$ and equation (48) becomes

$$log\ \frac{a_1}{N_1} = -\int_{0}^{N_2} \frac{N_2}{N_1} d\ log\ \frac{a_2}{N_2} \quad . \quad . \quad . \quad . \quad (49)$$

The following are the results obtained:

ACTIVITY OF MERCURY AND THALLIUM IN AMALGAMS AT 20° C.

N_2.	N_2/N_1.	a_2/N_2.	a_1/N_1.
0·00	0·00	1	1
0·005	0·00502	1·06	0·9998
0·01	0·0101	1·15	0·999
0·05	0·0526	1·80	0·986
0·1	0·111	2·84	0·950
0·2	0·250	4·98	0·866
0·3	0·428	6·60	0·790
0·4	0·667	7·57	0·734
0·5	1·000	7·98	0·704

As regards the calculation of the activity of the solute when the activity of the solvent at various values of N is known, we may employ a similar method. Hildebrand and Eastman introduced an empirical equation and Lewis employs it to integrate the expression on the right-hand side of equation (49).

The resulting equation obtained by G. N. Lewis is as follows:

$$log \frac{a_2}{N_2} = \frac{2 \times 0{\cdot}0960}{0{\cdot}263} \left(\frac{1}{1 + 0{\cdot}263 \dfrac{N_1}{N_2}} - \frac{1}{2(1 + 0{\cdot}263 N_1/N_2)^2} \right) . \quad (50)$$

For further discussion of the methods employed in integrating the equation (49) in order to determine the value of the activity of the solute, given that of the solvent, the reader is referred to the original authors (Lewis and Randall, *Thermodynamics*).

Another very important experimental method of determining the activity of the constituents of a solution depends, as one would expect, upon the determination of the depression of the freezing-point of the solvent by the addition of solute. This method is dependent upon one of the series of colligative properties of solutions. Equation VII (13) may therefore be employed to give the activity of the solute directly. The equation involves the latent heat of fusion and in its corrected form may be written

$$a = \frac{L\rho\Delta T}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (51)$$

the activity taking the place of the concentration.

In a similar manner the several other colligative properties may be employed for the determination of activity, but they do not

lend themselves to the degree of accuracy obtained by the freezing-point method. In practice, if we desire an accurate determination of the activity of a solute over a range of dilute and concentrated solutions, a high degree of accuracy may, in general, be most readily obtained by combining freezing-point measurements in dilute solutions with isothermal measurements of the vapour pressure of the solvent in concentrated solutions. These methods may frequently be employed when the E.M.F. methods are inapplicable.

We have seen that, as a strict thermodynamic relation, we must write the free energy change of transfer from one state to another as

$$\bar{F}' - \bar{F} = RT \ln a'/a$$

instead of the similar expression involving concentrations which we employed in the earlier part of this book.

Let us now consider the cycle employed in Chapter VII to deduce the law of mass action in the case of substances in solution. We consider the following reaction:

$$n_1A + n_2B + n_3C + \ldots = n_1'A' + n_2'B' + n_3'C' + \ldots$$

We imagine two equilibrium boxes containing these substances in solution at different partial concentrations, the systems having arrived at a condition of equilibrium. The transfer of n_1 moles of A from box I to box II involves an increase in the free energy of amount

$$\Delta\bar{F} = n_1RT \ln a_{II}/a_I.$$

where a_I and a_{II} are the activities of the solute A in the two boxes. In a similar manner for the transfer of n_2 moles of B in the same direction the free energy increase is

$$\Delta\bar{F} = n_2RT \ln b_{II}/b_I.$$

If we add all such terms over the whole cycle we know that the total change in free energy must be zero since the system is in equilibrium and the processes are conducted in infinitesimal quantities at a time. Hence we have

$$n_1RT \ln a_{II}/a_I + n_2 RT \ln b_{II}/b_I + \ldots = n_1'RT \ln a'_I/a'_{II} + \ldots$$

so that we may write

$$\frac{(a_{II})^{n_1}(b_{II})^{n_2} \ldots}{(a'_{II})^{n_1'}(b'_{II})^{n_2'} \ldots} = \frac{(a_I)^{n_1}(b_I)^{n_2} \ldots}{(a'_I)^{n_1'}(b'_I)^{n_2'} \ldots} = K \quad . \quad (52)$$

which is the well-known law of mass action expressed in terms of activities instead of concentrations.

Having considered, in some detail, the method employed by G. N. Lewis in his treatment of solutions, we are now in a position to discuss its application to that important class of substances known as electrolytes. As the reader is probably aware, Arrhenius sought to explain the various properties of these substances by means of his theory of electrolytic dissociation. According to this theory, electrolytes in solution are partly dissociated into positive and negative ions and these ions are responsible for the conveyance of the current when the solution undergoes electrolysis. At infinite dilution it is assumed that this ionization is complete and the degree of dissociation α is unity. At all other concentrations α is some fraction, which may vary from very small magnitudes to very nearly unity.

Suppose we have a solution of an electrolyte AB at a concentration of c moles per litre of solvent. Then we may represent the dissociation by means of the equation:

$$AB \rightleftharpoons A^+ + B^-.$$

Now if we represent the concentrations of the ions and of the undissociated molecules by the symbols (A^+), (B^-), (AB), and we assume that all the species obey the simple gas law for solutions, then we may apply the law of mass action and obtain the well-known Ostwald dilution law:

$$\frac{(A^+)\,(B^-)}{(AB)} = K \quad . \quad . \quad . \quad . \quad . \quad . \quad (53)$$

where K is a constant. If α be the degree of dissociation we have $(A^+) = (B^-) = \alpha c$; $(AB) = (1 - \alpha)c$, so that equation (53) takes the modified form

$$K = \frac{\alpha^2 c}{(1 - \alpha)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (54)$$

which is the usual equation for the dilution law.

The values of the degree of dissociation α may be obtained from a measurement of the electrical conductivity of the solution. It is supposed that the conductivity due to any ion in a solution is the product of two factors, (*a*) the concentration of that ion and (*b*) its mobility. If the mobility of the ions be assumed to be independent of the concentration of the solution, then the

conductivity of a solution divided by the total ion concentration is constant, but the conductivity divided by the gross concentration in gram-equivalents per litre is dependent upon the degree of dissociation. As the dissociation increases, this quotient, which is known as the equivalent conductivity Λ_v, also increases until at infinite dilution a constant value is obtained, Λ_∞, corresponding to complete dissociation. At any intermediate dilution the degree of dissociation is given by the ratio of the equivalent conductivities at that dilution and at infinite dilution,

$$\alpha = \frac{\Lambda_v}{\Lambda_\infty} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (55)$$

This equation has been modified to allow for the difference in viscosity between solutions at moderate concentrations and the infinitely dilute solution, and the corrected equation is

$$\alpha = \frac{\Lambda_v \eta_v}{\Lambda_\infty \eta_\infty} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (56)$$

The dilution law of Ostwald has been tested for a very large number of electrolytes and the following tables indicate some of the typical results.

I. Kendall (*J. Amer. Chem. Soc.*, 1916, **38**, 1480) has made careful measurements of the equivalent conductivities of solutions of carbon dioxide in water at 25° C. and has calculated the value of the Ostwald Constant K for the reaction:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$K = \frac{(H^+).(HCO_3^-)}{(H_2CO_3)}.$$

DISSOCIATION CONSTANT OF H_2CO_3 AT 25° C.

Concentration. Moles/litre.	$K \times 10^7$.
0·027	3·51
0·019	3·48
0·014	3·49
0·010	3·48
0·0069	3·55
Average . .	3·50

It is evident that for this electrolyte the law is obeyed, well within the limits of experimental error, the value for K, namely $3{\cdot}50 \times 10^{-7}$, indicating a very small degree of ionization.

II. Acetic Acid. Kendall, *Med. Vetenskapsakad. Nobelinst.*, 1911, **2**, No. 38, obtained the values of the dissociation constant of acetic acid at 25° C.

Dissociation Constant of Acetic Acid at 25° C.

Concentration. Moles/litre.	$K \times 10^5$.
1·0	1·40
0·5	1·65
0·25	1·76
0·13	1·81
0·063	1·84
0·032	1·85
0·016	1·85
0·004	1·84
0·002	1·84
0·001	1·84

Here it will be observed that, for the more concentrated solutions, the law is entirely inadequate, although, for the more dilute solutions, the agreement is excellent. It is highly probable, that, in the case of aqueous solutions of carbon dioxide, the law would fail for the higher concentrations, if it were possible to attain them. The value of K for acetic acid again indicates a very small degree of ionization. These are both examples of weak electrolytes.

III. The following are some of the results obtained for strong electrolytes.

(*a*) Dissociation Constant of NH_4Cl at 18° C.

Concentration.	Λv.	α.	K.
1·0	90·7	0·750	2·2
0·5	94·8	0·784	1·4
0·1	103·5	0·856	0·51
0·05	107·8	0·892	0·37
0·01	114·2	0·945	0·16
0·002	118·0	0·976	0·08
0·001	119·0	0·985	0·065
0·0002	120·4	1·000	—
0·0001	120·9 Λ_∞	1·000	—
0·00002	120·9	1·000	—

(*b*) DISSOCIATION CONSTANTS OF *KCl*.

Concentration.	α.	K.
0·1	0·8680	0·571
0·05	0·8968	0·390
0·02	0·9295	0·245
0·01	0·9486	0·175
0·005	0·9638	0·128
0·002	0·9785	0·0895
0·001	0·9866	0·0726

It will be abundantly evident from these data that the Ostwald dilution law fails entirely to represent the behaviour of such strong electrolytes. It is worthy of note that while we have strong electrolytes and weak electrolytes, there does not appear to be a class of electrolytes for which the degree of dissociation lies mid-way between these two types. There is a considerable difference between a dissociation constant of 10^{-7} or 10^{-5} and one of 0·6 to 0·07. We may therefore consider it possible that strong and weak electrolytes differ in some important respect, such for instance as that the latter are only partly dissociated, while the former are completely dissociated at all concentrations. This will be dealt with more fully later in connection with the theory of Debye and Hückel.

It is manifestly imperative to seek to find some explanation of the breakdown of the Ostwald dilution law. It does not appear to be possible to obtain the values of the actual concentrations of the ions of strong electrolytes, either from a determination of the osmotic pressure and related properties or from the electrical conductivity of the solution. No physical interpretation can be attached to the function $\alpha = \dfrac{\Lambda_v \eta_v}{\Lambda_\infty \eta_\infty}$ nor to the van't Hoff factor i.

In the next chapter we shall consider some of the theories which have been advanced to account for this apparent anomaly. However, in the absence of any such theory of the underlying mechanism of the properties of solutions, G. N. Lewis proposes to substitute for concentration terms the empirical activities of the ions and molecules. He thus obtains the Ostwald dilution law in the thermodynamically correct form:

$$K = \frac{a_A \times a_B}{a_{AB}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (57)$$

where a_A and a_B are the activities of the ions A^+ and B^- respectively, a_{AB} is the activity of the undissociated molecule AB.

It is evident that no attempt is made in this method to account for the observed discrepancy between the ionic activities and the values of the ionic concentrations calculated from conductivity data. The assumption is made that owing to some unknown cause the solution is not ideal, so that the ion activities and concentrations cannot be considered to be identical, and the activities are employed as corrected concentration terms.

The Activity Coefficient.

Corresponding to these "corrected" concentrations we may, of course, calculate a "corrected" degree of dissociation. Thus let us consider the dissociation of sodium chloride:

$$NaCl = Na^+ + Cl^-.$$

Now if the concentration of sodium chloride is c moles per litre, and if a_{Na} and a_{Cl} are the activities of the ions then

$$a_{Na}.a_{Cl} = (\gamma.c)(\gamma.c) = \gamma^2c^2$$

where γ is the thermodynamically "corrected" degree of dissociation. It follows that

$$\gamma = (\sqrt{a_{Na}.a_{Cl}})/c \quad . \quad . \quad . \quad . \quad . \quad . \quad (58)$$

This quantity γ is often called the stoichiometric activity coefficient or simply the activity coefficient of the ions, at the particular concentration considered.

In the simple case where the activity of the anion is equal to that of the cation, a condition which often obtains in practice (e.g. in solutions of KCl, $NaCl$, etc.), we have

$$\sqrt{a_A.a_B} = \gamma c = a_A = a_B$$

or, in other words, γ is the coefficient by which the concentration must be multiplied in order to obtain the activities of the ions. The quantity $\sqrt{a_A.a_B}$ is sometimes called the mean ion activity.

In the case of an electrolyte giving more than two ions, e.g. K_2SO_4, if ν is the total number of ions obtained from one molecule, i.e. ν_+ positive and ν_- negative ions, then the mean ion activity is defined by the equation

$$a_\pm = (a_+^{\nu+} + a_-^{\nu-})^{1/\nu} \quad . \quad . \quad . \quad . \quad . \quad (60)$$

The thermodynamic degree of dissociation or activity coefficient is thus given by the relation

$$\gamma = \frac{a_{\pm}}{c(\nu_+{}^{\nu+}.\nu_-{}^{\nu-})^{1/\nu}} \quad . \quad . \quad . \quad . \quad . \quad (61)$$

In the case of strong electrolytes, Lewis departs from his custom of equating the activities of the undissociated molecules to the corrected concentrations in moles per litre. Thus, for strong electrolytes, the concentration of the undissociated molecule is frequently immeasurably small. Hence the value of the dissociation constant would be extremely large. Lewis prefers to equate the dissociation constant to unity so that the activity of the undissociated molecules is equal to the product of the activities of the ions.

$$a_{AB} = a_A.a_B \quad . \quad . \quad . \quad . \quad . \quad . \quad (62)$$

Measurement of Ionic Activities. We must now consider some of the methods which have been employed to determine the activities and the activity coefficients of the various ions. We shall first of all make the assumption that the activities of the positive and negative ions are equal.

I. **Vapour Pressure Measurements.** It is rarely feasible to measure the vapour pressure of the solute in a solution, but where this is possible it furnishes a method of great simplicity. Bates and Kirschman (*J. Amer. Chem. Soc.*, 1919, **41**, 1991) have made a careful study of the partial pressures of hydrogen chloride, bromide and iodide at 25° C. The results are given in the table on page 210, in which the first column gives the molality or concentration in moles per litre; the second, fourth and sixth, the partial pressures of the halides; and the third, fifth and seventh, a quantity which is proportional to the activity coefficient. If a_2 is the activity of one of the undissociated halides, and $a_{\pm}$ is the mean ion activity, we have defined the activity coefficient as $a_{\pm}/m$, where m is the molality, i.e. $\gamma = a_2^{\frac{1}{2}}/m$. Hence if we consider a_2 as proportional to the vapour pressure p, then $p^{\frac{1}{2}}/m$ is a quantity proportional to the activity coefficient and may be written as $k\gamma$.

If these measurements could be carried to high dilutions, k could be determined as the limit approached by $k\gamma$ at infinite dilution. This, however, is experimentally impossible, and we must leave k as an undetermined constant for the present.

ACTIVITY COEFFICIENTS OF HYDROGEN HALIDES AT 25° C.

m.	HCl.		HBr.		HI.	
	$p \times 10^4$.	$k_1\gamma$.	$p \times 10^4$.	$k_2\gamma$.	$p \times 10^4$.	$k_3\gamma$.
4	0·2395	0·001222	—	—	—	—
5	0·6974	0·001669	—	—	—	—
6	1·842	0·002263	0·01987	0·0002351	0·00750	0·0001444
7	4·579	0·003058	0·04868	0·0003152	0·02395	0·0002213
8	11·10	0·004171	0·1171	0·0004280	0·08555	0·0003664
9	25·39	0·005586	0·2974	0·0006058	0·3882	0·0006928
10	55·26	0·007436	0·7763	0·0008815	1·737	0·001317
11	—	—	1·987	0·001280	—	—

MEASUREMENT OF VAPOUR PRESSURE OF SOLVENT. This has already been discussed. It will suffice to give some of Brønsted's results from measurements of the vapour pressure of solutions of sulphuric acid at 20° C. and 30° C., interpolated by G. N. Lewis for 25° C. The method is not susceptible to as great accuracy, for dilute solutions, as the freezing-point method or the method depending on the determination of the electromotive force of concentration cells. For concentrated solutions, however, the accuracy is much greater, as in the case of the following results :—

VAPOUR PRESSURES OF SULPHURIC ACID SOLUTIONS AT 25° C.

N_2.	m.	$p_1/p_1°$.	N_1/N_2.	$10 + \log p_1/p_1°$.	$k\gamma$.
0·02175	1·236	0·959	44·9	9·982	0·00348
0·04255	2·467	0·878	22·5	9·944	0·00350
0·0801	4·88	0·716	11·4	9·856	0·00469
0·1110	6·83	0·545	8·01	9·744	0·00760
0·2014	14·02	0·201	3·96	9·320	0·0227
0·2742	20·94	0·068	2·65	8·851	0·0477

In this table N_2 is the mole fraction and m the molality (or concentration in moles per litre) of H_2SO_4, and the values in the last column are proportional to γ, the proportionality factor being, as yet, unknown, since we cannot extrapolate to infinite dilution.

II. **Measurement of Distribution Ratios.** This method, as we have already seen, is similar to the vapour pressure method.

Rothmund and Drucker (*Zeit. phys. Chem.*, 1903, **46**, 827) measured the distribution of picric acid between benzene and water at 18° C. If we take a_2 as proportional to the concentration in the benzene layer, c_B, and c_w equal to the molality, then $k\gamma = c_B^{\frac{1}{2}}/c_w$. (*N.B.* a_2 is the activity of the undissociated molecules.) The values of $k\gamma$ have been extrapolated to infinite dilution, when γ is unity and the value of k is thus obtained. Dividing the values of $k\gamma$, by this quantity (15·4) we obtain the values of the activity coefficient γ.

ACTIVITY COEFFICIENT OF PICRIC ACID AT 18° C.

c_w.	c_B.	$k\gamma$.	γ.
0·0334	0·1772	12·6	0·82
0·0199	0·0700	13·3	0·86
0·0101	0·0199	14·0	0·91
0·00701	0·0101	14·3	0·93
0·00327	0·00225	14·5	0·94
0·00208	0·000932	14·9	0·97
0·00000	0·000000	15·4	1·00

III. **Activity from Measurements of Electromotive Force.** This is an extremely useful method of determining the activity of the ions in solution. As an example of its application, we may first consider the work of Linhart (*J. Amer. Chem. Soc.*, 1917, **39**, 2532) which is of a very high degree of accuracy. The cell employed is one without transport, namely—

$$Ag \;\Big|\; \underset{c}{AgCl : HCl} \;\Big|\; \underset{1\text{ atm.}}{H_2} \quad \underset{1\text{ atm.}}{H_2} \;\Big|\; \underset{c'}{HCl : AgCl} \;\Big|\; Ag$$

The electromotive force of this cell, in terms of activity coefficients is, as we have seen,

$$E = \frac{2RT}{nQ} \ln \frac{\gamma' c'}{\gamma c} \quad . \quad . \quad . \quad . \quad . \quad . \quad (63)$$

where c and c' are the concentrations of *HCl* in the two compartments, so that γc and $\gamma' c'$ are the mean ionic activities.

If we assume that, in the right-hand cell, the *HCl* is in the standard state, for which $\gamma' c'$ is unity, then equation (63) takes the form

$$E = -\frac{2RT}{nQ} \ln \gamma c \quad . \quad . \quad . \quad . \quad . \quad . \quad (64)$$

or, transforming to ordinary logarithms and substituting the numerical values of the various constants,

$$-E = 0{\cdot}1183 \log \gamma c \quad . \quad . \quad . \quad . \quad . \quad (65)$$

Let us imagine the E.M.F. divided into two portions, E' from the left-hand silver electrode to the hydrogen, E° from the right-hand silver electrode to the hydrogen, then we have

$$E = E^\circ - E' = 0{\cdot}1183 \log \gamma c.$$

Hence $$0{\cdot}1183 \log \gamma = E^\circ - (E' + 0{\cdot}1183 \log c).$$

The quantity in parentheses may be measured and plotted as ordinates against c as abscissæ. It is evident that at infinite dilution $\log \gamma = 0$, so that the ordinate at this point gives the value of E°. Hence the value of γ at any other concentration may be obtained. The following are some of the results:

ACTIVITIES IN AQUEOUS HYDROCHLORIC ACID SOLUTIONS AT 25° C.

c.	γ.	$a\pm$.	a_2. Activity of HCl.	$\overline{F}_2 - \overline{F}_2^\circ$.
0·0005	0·991	0·000496	0·000000246	− 9022
0·001	0·984	0·000984	0·000000909	− 8204
0·002	0·971	0·001942	0·00000377	− 7403
0·005	0·947	0·00474	0·0000228	− 6336
0·01	0·924	0·00924	0·0000855	− 5552
0·02	0·894	0·01788	0·000319	− 4772
0·05	0·860	0·0430	0·00185	− 3732
0·1	0·814	0·0814	0·00664	− 2977
0·2	0·783	0·1566	0·0246	− 2197
0·3	0·768	0·2304	0·0530	− 1742
0·4	0·763	0·305	0·0929	− 1409
0·5	0·762	0·381	0·145	− 1144
0·6	0·770	0·462	0·213	− 917
0·75	0·788	0·591	0·348	− 625
1·00	0·823	0·823	0·676	− 232
2	1·032	2·064	4·17	+ 846
3	1·35	4·05	16·4	+ 1657
4	1·84	7·36	54·2	+ 2367
5	2·51	12·55	158	+ 3000
6	3·40	20·4	416	+ 3575
7	4·66	32·6	1,064	+ 4132
8	6·30	50·4	2,540	+ 4647
9	8·32	74·9	5,607	+ 5117
10	10·65	106·5	11,340	+ 5534
16	43·2	691·0	478,000	+ 7751

It will be observed that the activity coefficient attains a value considerably above unity, at $c = 16$, the value in the table is 43·2. It is therefore somewhat fantastic to regard such a value as a thermodynamic degree of dissociation.

More recently Harned (*Zeit. phys. Chem.*, 1925, **117**, 1) has determined the activity coefficients of *NaOH* and *KOH* for various concentrations. The cells employed were of the type

$$\begin{array}{c|c|c|c|c} H_2 & NaOH\ (c_2) & Na_xHg & NaOH\ (c_1) & H_2 \\ 1\text{ atm.} & & & & 1\text{ atm.} \end{array}$$

The following table gives the values of the E.M.F. at 25° C. Concentrations are expressed in moles per litre.

E.M.F. Measurements at 25° C.

c_2.	c_1.	E.
0·00530	0·01011	− 0·0315
0·01	0·01000	0·0000
0·0202	0·01001	+ 0·0338
0·0526	0·01000	0·0796
0·1047	0·00998	0·1116
0·1081	0·00984	0·1142
0·1934	0·00997	0·1416
0·3975	0·00995	0·1762
0·807	0·01006	0·2103
1·020	0·01016	0·2221
1·517	0·01003	0·2459
2·024	0·01014	0·2630
3·10	0·01012	0·2926

The electrode reactions are

(i) $Na(Na_xHg) = Na^+(c) + \ominus$.

(ii) $\frac{1}{2}H_2$ (1 atm.) $+ OH^-(c). = H_2O + \ominus$.

We may subtract these to obtain the total reaction over the portion

$$Na_xHg \mid NaOH\ (c) \mid H_2\ (1\text{ atm.})$$

namely,

$$Na\ (Na_xHg) + H_2O\ (c) = \tfrac{1}{2}H_2\ (1\text{ atm.}) + OH^- + Na^+.$$

Let the E.M.F. of the two portions be E_1 and E_2, corresponding to concentrations c_1 and c_2, then $E_1 - E_2 = E$ where E is the E.M.F. over the whole cell. Now the change in free energy over the reaction is

$$\Delta F_1 - \Delta F_2 = RT\ ln \frac{a_{Na\cdot(c_1)} \cdot a_{OH'(c_1)} \cdot a_{H_2O(c_2)}}{a_{Na\cdot(c_2)} \cdot a_{OH'(c_2)} \cdot a_{H_2O(c_1)}} = nQ.E.$$

Note that we have not assumed, as formerly, that the activities of the water are the same in both solutions. Transforming to ordinary logs. and substituting the numerical values of the constants we obtain

$$E + 0{\cdot}05915 \log \frac{a_{H_2O(c_2)}}{a_{H_2O(c_1)}} = 0{\cdot}1183 \log \frac{\gamma_2 c_2}{\gamma_1 c_1} \quad . \quad . \quad (66)$$

Now the value of the ratio of the activities of water may be taken as equal to the ratio of the vapour pressures of the water in equilibrium with the solutions, that is—

$$\log p_2/p_1 = \log a_{H_2O(c_2)}/a_{H_2O(c_1)}.$$

Hence we obtain

$$E + 0{\cdot}05915 \log \frac{p_2}{p_1} = 0{\cdot}1183 \log \gamma_2 c_2/\gamma_1 c_1 \quad . \quad . \quad (67)$$

In order to avoid measuring the vapour pressure of the solutions, Harned proceeds as follows. He first of all neglects the correction and obtains approximate values of the activity coefficient γ. He then substitutes these values in an empirical expression which he has found to represent the results in earlier work. The expression is

$$\log \gamma = -\beta c^{\theta'} + \theta . c$$

where β, θ' and θ are all constants. The constants are thus determined with sufficient accuracy and are substituted in a second expression which Harned found to be valid,

$$ln \frac{p_0}{p} = \frac{c}{55{\cdot}5}\left[2 + \frac{4{\cdot}606\ \theta . c}{2} - \frac{4{\cdot}606\beta\theta' . c^{\theta'}}{\theta' + 1}\right] \quad . \quad . \quad (68)$$

The values of the constants determined by Harned are, $\beta = 0{\cdot}288$, $\theta' = 0{\cdot}387$, $\theta = 0{\cdot}122$, and when these are substituted in equation (68) we obtain—

$$ln \frac{p_0}{p} = \frac{c}{55{\cdot}5}[2 + 0{\cdot}3892\ c - 0{\cdot}3701\ c^{0{\cdot}387}] \quad . \quad . \quad (69)$$

The following table contains the results obtained by Harned. The first column gives the concentration in moles per litre, the second column gives the natural logarithms of the ratios of the vapour pressures of $0{\cdot}0202M.$ to p_2, the vapour pressure of the more concentrated solutions. Column 3 contains the correction to be added to the electromotive force, namely $0{\cdot}02568\ ln\ p_c/p_{0{\cdot}0202} = \xi$ (say). The fourth column contains the observed electromotive forces of the cells referred to 0·0202, viz. $E - 0{\cdot}0338$. This was

first corrected in such a way that each concentration would be compared to an exactly 0·01 molal solution, the corrected values being given in column 5. Column 6 gives the corrected values of the E.M.F. obtained by subtracting column 3 from column 5. Column 7 tabulates the values of the ratio of activity coefficients $\gamma_{0\cdot0202}/\gamma_c$. Column 8 contains the values of γ obtained by extrapolating to infinite dilution.

Sodium Hydroxide

1	2	3	4	5	6	7	8
c.	$ln\frac{p_{0\cdot0202}}{p_c}$.	ξ	E_1.	E_2.	E (final).	Ratio $\frac{\gamma_1}{\gamma_2}$.	γ.
0·0202	0·00000	0·000000	0·0000	0·0000	0·0000	1·000	0·880
0·0526	0·00109	− 0·000028	0·0457	0·0457	0·0457	1·070	0·822
0·1047	0·00283	− 0·000073	0·0778	0·0777	0·0776	1·145	0·768
0·1081	0·00294	− 0·000075	0·0804	0·0796	0·0795	1·139	0·773
0·1934	0·00577	− 0·000148	0·1078	0·1077	0·10755	1·179	0·748
0·3975	0·01256	− 0·000322	0·1424	0·1426	0·1423	1·233	0·714
0·807	0·02671	− 0·000686	0·1765	0·1768	0·1761	1·297	0·678
1·020	0·03446	− 0·000884	0·1883	0·1891	0·1882	1·295	0·680
1·517	0·0535	− 0·001373	0·2121	0·2122	0·2108	1·241	0·709
2·024	0·0752	− 0·001929	0·2292	0·2299	0·2280	1·185	0·743
3·1	0·1276	− 0·003276	0·2588	0·2594	0·2561	1·050	0·838

Potassium Hydroxide

c.	$ln\frac{p_{0\cdot03}}{p_c}$.	ξ'.	E_1.	E_2.	E (final).	Ratio $\frac{\gamma_{0\cdot03}}{\gamma_c}$	γ.
0·0300	0·00000	0·000000	0·0000	—	0·0000	1·000	0·857
0·05	0·00068	− 0·000017	0·0241	—	0·0241	1·043	0·822
0·10	0·00236	− 0·000061	0·0572	—	0·0571	1·097	0·789
0·30	0·00915	− 0·000235	0·1113	—	0·1111	1·150	0·746
1·0	0·03534	− 0·000907	0·1750	—	0·1741	1·128	0·760
3·0	0·1376	− 0·00353	0·2511	—	0·2476	0·807	1·062

These results are very conveniently represented by means of the graph in Fig. 34. The ordinates are the activities, the abscissæ are the concentrations in moles per litre. The activity coefficients computed from the original electromotive force, without allowing for the activity of the water, are also plotted (dotted lines). The

extent of the correction is very small in the dilute solutions but amounts to 2 per cent. at 1*M* and 7 per cent. at 3*M* solutions.

Comparison with the degree of dissociation calculated directly from conductivity data, shows that the activity coefficient γ decreases, at first, much more rapidly than α with increasing concentration. γ then passes through a minimum and rises to a value which may, and sometimes does, exceed unity. We thus see that except at high dilutions the values of α obtained do not even approximately give a measure of the activity coefficient. It is found that the activity coefficient varies with the concentration very differently for different substances.

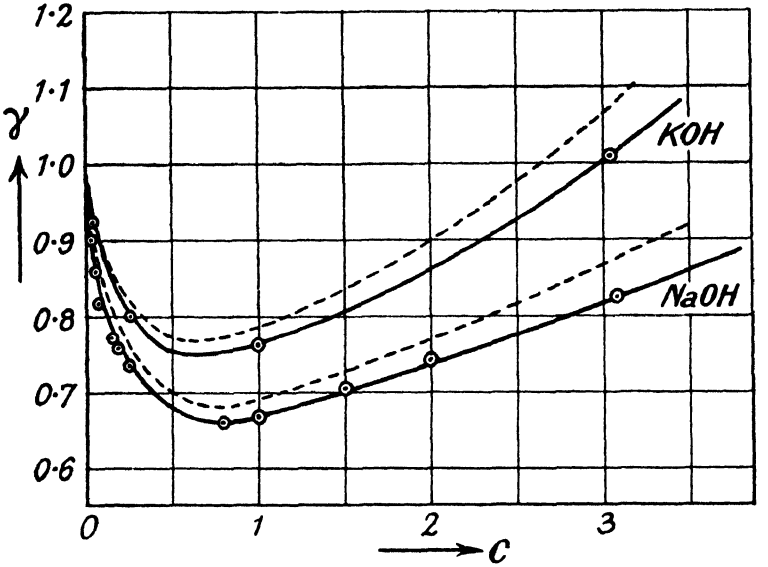


FIG. 34 (from Harned).

IV. **Measurement of Activities from Freezing-point Data.** This method is an extremely useful one provided it is remembered that it is **not** permissible, as some authors have thought, to equate the activity coefficient γ to the degree of ionization calculated by the elementary method. The reason for this lies in the fact that we cannot equate the activity of the undissociated molecule to $(1 - \gamma)c$ where γ is the activity coefficient of the ions.

In dilute solutions, the experimental technique presents many difficulties, but these have largely been overcome by recent work in thermometry in the work of Hausrath (*Ann. Physik.*, (4), 1902, **9**, 522), Bedford (*Proc. Roy. Soc., Lond.*, 1909, **83A**, 454); Adams

(*J. Amer. Chem. Soc.*, 1915, **37**, 494); Harkins and Roberts (*J. Amer. Chem. Soc.*, 1916, **38**, 2676); and Hall and Harkins (*J. Amer. Chem. Soc.*, 1916, **38**, 2658).

Lewis and Linhart have employed these data to calculate the values of the activity coefficients (*J. Amer. Chem. Soc.*, 1919, **41**, 1952).

The rigorous analytical method of calculating the activity from freezing-point lowering is somewhat involved and these authors employ a simple empirical formula connecting the depression of the freezing-point with the concentration of the salt. This expression is

$$nk - t/c = \beta . c^m \quad . \quad . \quad . \quad . \quad . \quad . \quad (70)$$

where n is the number of ions into which one molecule of the salt ionizes; k is the theoretical molecular depression of the freezing-point (in the case of water, $k = 1{\cdot}858°$ per mole of solute dissolved in 1,000 grams of solvent); t is the observed lowering of the freezing-point, produced by a salt of concentration c in moles per 1,000 grams of solvent, β and m are constants. By combining this expression with the thermodynamic equation connecting the free energy change on dilution with the lowering of the freezing-point, they finally obtained

$$log\, \gamma = -\beta\,(m + 1).c^m/2{\cdot}303nkm \quad . \quad . \quad . \quad (71)$$

For details of the calculation the reader is referred to the original authors. The following table gives the results obtained, together with the values of the degree of dissociation α calculated from conductivity data, for a series of different substances at 0·01 Molal solution.

Salt.	*KCl.*	*NaCl.*	$KClO_3$.	K_2SO_4.	$BaCl_2$.	$NaIO_3$.	$CdSO_4$.	$CuSO_4$.	$Li(NO_3)_2$.
γ =	0·925	0·925	0·873	0·687	0·716	0·872	0·338	0·290	0·571
α =	0·941	0·936	0·928	0·872	0·883	0·928	0·614	0·629	0·805

In the case of concentrated solutions this method is no longer applicable, but it is beyond our purpose to follow the methods adopted by Lewis in the solution of this problem. A complete account of the application of freezing-point data to the determination of activity will be found in Lewis and Randall, *Thermodynamics*.

Method of Determining the Activity Coefficient when Data at High Dilution are Lacking.

We have seen that the various methods of calculating the activity coefficient give us some multiple $k\gamma$ of the coefficient itself, and this value of k is obtained by extrapolating to infinite dilution. It often happens, however, that the results obtained by the vapour pressure and electromotive force measurements at high dilutions are not sufficiently accurate. When this is the case the method adopted by G. N. Lewis is to compare the data obtained for the electrolyte under consideration with the data for some substance of a similar type which has been carefully investigated. Thus, for example, the results of Noyes and MacInnes (*J. Amer. Chem.*

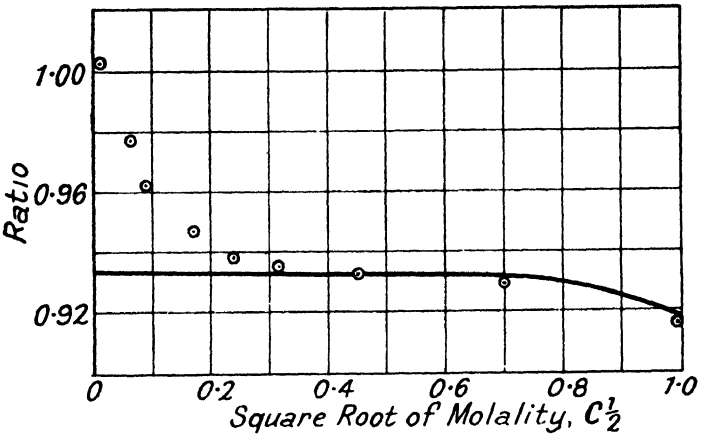


FIG. 35 (from Noyes & MacInnes).

Soc., 1920, **42**, 239) for potassium chloride may be corrected by comparison with those obtained for sodium chloride. The following table gives the results obtained by this method. Column 1 gives the concentration in moles per litre. Column 2 gives the values of γ obtained by Noyes and MacInnes for potassium chloride by extrapolation to infinite dilution. These values are not accurate owing to the uncertainty of the values at high dilution. Column 3 gives the values of the activity coefficient for *NaCl* which have been accurately determined. Column 4 contains the values of the ratio of the activity coefficients in the second and third columns. Now it is reasonable to assume that this ratio should, in some regular manner, approach constancy. These ratios are plotted in Fig. 35 against the square root of the concentration $c^{\frac{1}{2}}$. The smooth

curve neglects the values for dilute solutions and is obtained by extrapolating the values at higher concentrations. The ordinate at zero concentration obtained in this manner is 0·935. If now we divide any other ordinate by this value, and multiply by the activity coefficient of sodium chloride at that concentration, we obtain the activity coefficient of *KCl*. These corrected values are given in the last column of the table. They differ, as a rule, by several per cent. from the values of Noyes and MacInnes.

ACTIVITY COEFFICIENTS OF *KCl* AT 25° C.
(From E.M.F. Data)

Conc. c.	γ (*KCl*) Noyes and MacInnes.	γ (*NaCl*)$_r$	Ratio $\frac{\gamma\ (KCl)}{\gamma\ (NaCl)}$	Corrected values of γ (*KCl*)
0·001	0·979	0·977	1·002	0·977
0·005	0·923	0·946	0·976	0·946
0·01	0·890	0·922	0·964	0·922
0·03	0·823	0·869	0·947	0·869
0·05	0·790	0·842	0·938	0·841
0·1	0·745	0·798	0·934	0·796
0·2	0·700	0·752	0·931	0·749
0·5	0·638	0·689	0·928	0·682
1·0	0·593	0·650	0·912	0·634

The values given in the last column are completely corroborated by freezing-point measurements so that the procedure is justified.

Activity Coefficients in Mixtures of Electrolytes. Several attempts have been made to determine the activity coefficient of electrolytes in mixtures. The results given on the next page, obtained by Harned (*J. Amer. Chem. Soc.*, 1920, **43**, 1808) from electromotive force data, are typical. They refer to the activity coefficient of *HCl* (0·1*M*) in the presence of other chlorides. The first column gives the total concentration, i.e. *HCl* + *MeCl*, in moles per litre. The second column gives the activity coefficient in pure *HCl*; the other columns give γ in the presence of the added salts.

These results do not permit of any simple generalization for the more concentrated solutions. For the more dilute solutions, however (up to 0·2*M* for *KCl* and *LiCl* and even up to 0·5*M* for *NaCl*), the activity coefficient is the same as in pure *HCl*. These data, together with the results obtained from numerous other investigations have led to the formulation of the following simple

Total m.	γ *HCl* in pure *HCl*.	γ *HCl* in *LiCl*.	γ *HCl* in *NaCl*.	γ *HCl* in *KCl*.
0·1	0·81	0·81	0·81	0·81
0·2	0·78	0·78	0·78	0·78
0·5	0·76	0·78	0·76	0·75
1·0	0·82	0·86	0·80	0·75
2·0	1·02	1·09	0·94	0·84
3·0	1·35	1·47	1·17	0·97
4·0	1·84	2·02	1·47	1·17

rule for dilute solutions. In any dilute solution of a mixture of strong electrolytes, of the same valence type, the activity coefficient of each electrolyte depends solely upon the **total** concentration. This is evidently only a limiting law which approaches complete accuracy at infinite dilution.

A considerable amount of very accurate work in this field has been accomplished by means of solubility measurements and we shall now proceed to discuss the results obtained.

Solubility Methods of Determining Activity. The student will already be familiar with the important concept known as the solubility product. Since, as we have seen, however, thermodynamics compels us to substitute activities for concentration terms we must express the product in terms of the former magnitudes. Thus suppose we have a substance AB ionizing as follows:

$$AB \rightleftharpoons A^+ + B^-.$$

We assume that the solution is saturated and in contact with some undissolved salt. Then if a_2 is the activity of the undissociated molecules in the solution, a_+ and a_- are the activities of the positive and negative ions respectively, then

$$a_2 \text{ is a constant}; \quad a_+ \times a_- = \text{Constant}.$$

Now we have defined the activity coefficient γ as

$$\gamma = a_\pm / m_\pm$$

where

$$a_\pm = \sqrt{a_+ . a_-}; \quad m_\pm = m(\nu_+{}^{\nu+} . \nu_-{}^{\nu-})^{1/\nu}.$$

Hence it is evident that the activity coefficient of the salt in the mixture is inversely proportional to the mean molality of its ions.

We shall consider the case of a uni-univalent salt in the presence of another uni-univalent salt with no common ions. In this simple

case $m_{\pm}$ is equal to the solubility of the salt. The following results were obtained by Bray and Winninghoff (*J. Amer. Chem. Soc.*, 1911, **33**, 1663). They refer to the solubility of thallous chloride at 25° C. in the presence of other salts.

Added Salt in Equivalents per Litre.	KNO_3.	KCl.	HCl.	$TlNO_3$.	$BaCl_2$.	Tl_2SO_4.	K_2SO_4.
0·000	0·01607	0·01607	0·01607	0·01607	0·01607	0·01607	0·01607
0·020	0·01716	—	—	—	—	0·01034	0·01779
0·025	—	0·00869	0·00866	0·00880	0·00898	—	—
0·050	0·01826	0·00590	0·00583	0·00624	0·00618	0·00677	0·01942
0·100	0·01961	0·00396	0·00383	0·00422	0·00416	0·00468	0·02137
0·200	—	0·00268	0·00253	—	0·00282	—	—
0·300	0·02313	—	—	—	—	—	0·02600
1·000	0·03072	—	—	—	.	—	0·03416

The activity coefficient is inversely proportional to the mean molality of the ions, i.e. to the solubility of the salt. We therefore plot the reciprocal of the solubility against the total molality of the mixture, or better against the square root of this latter quantity. The proportionality factor is thus evaluated by extrapolation. The value of $1/m_{\pm}$ obtained is 70·3. If, therefore, we divide the values of $1/m_{\pm}$ obtained from the above table by this value 70·3 we arrive immediately at the activity coefficient of thallous chloride in the corresponding solution.

G. N. Lewis has extended the rule mentioned above for dilute solutions to the case of solutions of salts having polyvalent ions. He first of all defines a magnitude which he terms the **ionic strength.**

"In any solution of strong electrolytes let us multiply the stoichiometric molality of each ion by the square of its valence (or charge). The sum of these quantities divided by two (since we have included both negative and positive ions), we shall call the ionic strength and designate by μ. Thus in pure solutions of potassium chloride, magnesium sulphate and barium chloride, all at 0·01M, we have, respectively, $\mu = 0{\cdot}01$, $\mu = 0{\cdot}04$, and

$$\mu = [(4 \times 0{\cdot}01) + 0{\cdot}02]/2 = 0{\cdot}03."$$

The extended form of the rule is then: In dilute solutions, the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength.

Activities of Individual Ions in Strong Electrolytes. The determination of the activity coefficient, which is defined by

$$\gamma = (a_+ \cdot a_-)^{\frac{1}{2}}/m_{\pm}$$

does not require the actual values of the activities of the individual ions to be known. In fact the problem of their determination is fraught with difficulty. The first attempt in this direction was made by MacInnes (*J. Amer. Chem. Soc.*, 1919, **41**, 1086). He assumed that, in a solution of potassium chloride, the activities of the anion and cation are equal. He justifies this assumption on the grounds that the two ions have practically the same weight and mobility. It will be evident, that, once some assumption of this type is made, we can proceed to determine the activities of the separate ions, for the activity of the *Cl'* ion for example will be equal to the mean ionic activity. Hence if the activity coefficient of *HCl* is known at some given concentration, we have

$$(a_H \times a_{Cl})^{\frac{1}{2}}/m = \gamma.$$

G. N. Lewis gives the following provisional table of the activities of individual ions. The top row gives the ionic strength μ. Under the symbol *Me* are included the following ions: Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, Cu^{++}, Zn^{++}, Cd^{++}, except that for Cd^{++} the value is not to be used for calculating the activity coefficient of a halide.

ACTIVITY COEFFICIENTS OF INDIVIDUAL IONS AT VARIOUS VALUES OF THE IONIC STRENGTH

$\mu =$	0·001	0·002	0·005	0·01	0·02	0·05	0·1
H^+	0·98	0·97	0·95	0·92	0·90	0·88	0·84
OH^-	0·98	0·97	0·95	0·92	0·89	0·85	0·81
Cl', Br', I'	0·98	0·97	0·95	9·92	0·89	0·84	0·79
Li^+	0·98	0·97	0·95	0·92	0·89	0·85	0·81
Na^+	0·98	0·97	0·95	0·92	0·89	0·84	0·80
K^+, Rb^+, Cs^+	0·98	0·97	0·95	0·92	0·89	0·84	0·79
Ag^+	0·97	0·96	0·93	0·90	0·85	0·80	0·77
Tl^+	0·97	0·96	0·93	0·90	0·85	0·75	0·64
NO_3'	0·97	0·96	0·94	0·91	0·87	0·77	0·68
ClO_3', BrO_3', IO_3'	0·95	0·93	0·89	0·85	0·79	0·70	0·61
Me^{++}	0·78	0·74	0·66	0·60	0·53	0·43	0·34
SO_4^{--}	0·77	0·71	0·63	0·56	0·47	0·35	0·26
La^{+++}, $Fe(CN)_6^{---}$	0·73	0·66	0·55	0·47	0·37	0·28	0·21

The term activity coefficient, in this table, is employed in a different sense to that hitherto used. It may be defined, here, as the coefficient by which the molal concentration of any ion must be multiplied in order to obtain the activity of that ion.

Influence of Neutral Salts upon the Dissociation of a Weak Acid. McBain and Kam (*Trans. Chem. Soc.*, 1919, **115**, 1332) have obtained some very interesting results in regard to the effect of neutral salts upon the degree of ionization of a weak acid. Experiment shows that the potential of the hydrogen electrode in an aqueous solution of a weak acid, such as acetic acid, is increased by the addition of a neutral salt (e.g. *NaCl*), that is, the apparent concentration of the hydrogen ion is increased.

Now this fact was originally interpreted as indicating a real increase in the dissociation of the acid. McBain and Kam, however, consider that the effect is due, not to an increase in the **concentration** of the hydrogen ions but to an increase in their **activity.** Since equilibrium exists between the ions and the undissociated molecules of acetic acid it follows that any increase in the activity of the ions must be accompanied by a corresponding increase in the activity of the undissociated molecules, the Ostwald Dilution Law being expressed in terms of activities.

But the activity of the undissociated molecules can be determined experimentally from vapour pressure measurements. Hence we have a means of testing the theory. McBain and Kam employed this method and found that " many salts enhance the partial vapour pressure of acetic acid in aqueous solutions by very appreciable amounts. In the case of 2·3 *N.* sodium chloride the increase amounts to no less than 62 per cent." This is greater than the effect observed in the case of other salts investigated : *KCl, KCNS, KNO_3, LiCl.* These salts all showed proportionality between the effect and the concentration of the added salt. Sodium acetate is found to have only a very slight effect on the activity of the hydrogen ion. The behaviour in the case of sodium sulphate was found to be peculiar. Up to 0·35 *N.* there is a slight negative effect; beyond this concentration it becomes positive. The concentrations of the salt employed in these experiments are, of course, well beyond the limits of applicability of the simple generalization given by G. N. Lewis for dilute solutions.

Neutral Salt Catalysis. It is naturally to be expected that the catalytic effect of ions will be proportional to their activities and not, as previously thought, to their concentrations. Harned (*J.A.C.S.*, 1918, **40**, 1461) has therefore attempted to correlate the catalytic activity of potassium chloride with the mean ionic activity of the ions. The reaction studied is the decomposition

of hydrogen peroxide by the iodide ion in the presence of added salt. The catalytic effect is attributed by Harned to the chloride ion, and we saw reason to regard the mean ionic activity of potassium chloride as equal to the activity of the individual ions. As the following table shows, there exists a proportionality between the observed velocity constant of decomposition and the mean ionic activity. The first column contains the concentrations of *KCl* or *NaCl* added; the second column gives the unimolecular velocity constant ($K_1 \times 10^2$) in the presence of *KCl*; column 3 contains the corresponding values of $K_2 \times 10^2$ obtained in the presence of *NaCl*; column 4 gives the mean ion activity $\sqrt{a_+ . a_-}$ of the *KCl* ions; column 5 gives the corresponding figures for *NaCl*; columns 6 and 7 give the ratios of the velocity constants and the mean ionic activity.

CONCENTRATION OF $KI = 0{\cdot}03\ N.$

Conc. of Salt.	$K_1 \times 10^2$.	$K_2 \times 10^2$.	$a_1 = \sqrt{a_+ . a_-}$ for *KCl*.	$a_2 = \sqrt{a_+ a_-}$ for *NaCl*.	$\frac{K_1 \times 10^2}{a_1}$	$\frac{K_2 \times 10^2}{a_2}$
0·000	4·18	4·18	—	—	—	—
0·500	4·31	4·45	0·305	0·311	14·14	14·20
1·000	4·45	4·79	0·584	0·628	7·63	7·65
1·500	4·57	5·20	0·860	1·000	5·32	5·40
2·000	4·70	5·64	1·150	1·397	4·08	4·04
2·500	4·85	6·12	1·433	1·815	3·38	3·32

CONCENTRATION OF $KI = 0{\cdot}02\ N.$

Conc. of Salt.	$K_1 \times 10^2$.	$K_2 \times 10^2$.	$a_1 = \sqrt{a_+ . a_-}$ for *KCl*.	$a_2 = \sqrt{a_+ a_-}$ for *NaCl*.	$\frac{K_1 \times 10^2}{a_1}$.	$\frac{K_2 \times 10^2}{a_2}$.
0·000	2·75	2·75	—	—	—	—
0·500	2·84	2·93	0·305	0·311	9·31	9·40
1·000	2·93	3·17	0·584	0·628	5·02	5·05
1·500	3·02	3·44	0·860	1·000	3·51	3·44
2·000	3·11	3·77	1·150	1·397	2·70	2·70
2·500	3·19	4·19	1·433	1·815	2·22	2·25

Catalytic Activity of the Hydrogen Ion. A considerable amount of work has been done with a view to relating the catalytic effect of the hydrogen ion and the activity of the ion. As an example we may quote some results obtained by Lewis and

Jones (*J. Chem. Soc.*, 1920, **107**, 1120). These authors have determined the velocity constants for the inversion of sucrose at 20° C., in the presence of various mineral acids, and have shown that the velocity constant is directly proportional to the activity of the hydrogen ion. In fact they conclude that the alteration in the velocity constant may be accounted for completely by (*a*) allowing for the stoichiometric correction for the water present, and (*b*) by allowing for the change in the activity of the hydrogen ions. The following table gives some of their results:

TEMPERATURE 20° C. 0·1 $N.H_2SO_4$.

Grams of Sucrose in 100 c.c. of Solution.	Gram-moles of Water per Litre.	$K \times 10^3$ observed.	$\frac{K \times 10^3}{\text{(Water Conc.)}} = K' \times 10^3$.	$H+$ Activity a.	$\frac{K' \times 10^6}{a}$.
0	55·55	4·14*	7·46*	0·060	1·24
10	51·95	4·43	8·53	0·068	1·25
20	48·45	4·79	9·88	0·078	1·27
30	44·99	5·21	11·58	0·0895	1·29
40	41·62	5·54	13·31	0·105	1·27
50	38·09	5·95	15·61	0·118	1·32
60	34·59	6·22	17·97	0·139	1·29
70	30·94	6·29	20·33	0·162	1·25
				Mean	$1·27 \times 10^{-6}$

(Values marked with an asterisk are obtained by extrapolation.)

The student will have observed that while we have not really arrived any nearer to a solution of the problem of the anomaly of strong electrolytes, yet the concept of activity has amply justified its existence owing to the enormous mass of experimental data which it is capable of bringing into harmony, data which had hitherto appeared entirely disconnected. We shall now pass on to a consideration of a method which seeks to probe further into the mystery and to give us an explanation of the anomaly itself.

CHAPTER X

THEORIES OF STRONG ELECTROLYTES

The Inter-Ionic Attraction Theory.

In recent years several attempts have been made to formulate some theory of solutions which would account for the anomalous behaviour of strong electrolytes. Of these, the Inter-ionic Attraction Theory, which we are about to consider, has now gained practically universal acceptance as a means of calculating activity coefficients in the domain of dilute solutions.

Arrhenius, as is well known, regarded electrolytes as being only partially dissociated, except in very dilute solutions. The degree of dissociation could be obtained from conductivity measurements, being given by the ratio Λ_v/Λ_∞ of the equivalent conductivities, or, if we correct for viscosity, $\alpha = \Lambda_v\eta_v/\Lambda_\infty\eta_\infty$. Now the failure of the Ostwald Dilution Law in the case of strong electrolytes may, as we have seen, be due to the fact that the conductivity method is invalid as a means of determining the degree of dissociation. From time to time, suggestions were made that strong electrolytes are completely ionized, and that the variation in their behaviour from that of weak electrolytes may be due to electrical forces between the ions. Thus J. J. van Laar (*Arch. Teyler*, (20), 1900, **7**, 59); Sutherland (*Phil. Mag.*, (vi), 1907, **14**, 1); Bjerrum and others. In 1912, however, Milner undertook a mathematical investigation of the problem, on the assumption that the Coulomb forces acting between the ions prevent their random distribution. The work of Milner did not, however, attract much attention, owing to the mathematical complexity of his treatment, although he showed that his equations represented at least the form of the deviation from the ideal solution. In 1923, however, Debye and Hückel treated the problem again in a manner presenting much less mathematical difficulty. The simplification was due to the introduction of Poisson's equation.

The following papers contain the original work which has led up to the final treatment of the problem given here:

Milner, *Phil. Mag.*, (vi), 1912, **23**, 551; 1913, **25**, 743; Debye and Hückel, *Physik. Zeit.*, 1923, **24**, 185; ib., 1923, **24**, 334; *Rec. trav. chim.*, 1923, **42**, 597; A. A. Noyes, *J. Amer. Chem. Soc.*, 1924, **46**, 1080; Adams, *J. Amer. Chem. Soc.*, 1926, **48**, 621.

The treatment is largely that of A. A. Noyes (*loc. cit.*), except that corrections are made for a confusion between free energy and the total internal energy which was made in his paper and that of Debye and Hückel.

The fundamental idea underlying the treatment of Milner and of Debye and Hückel is that, owing to the electrical attraction between positive and negative ions, there are, on an average, more ions of unlike than of like sign in the neighbourhood of any given ion, and that consequently, when a solution is diluted, the separation of the ions involves an increase of the free energy of the system, owing to the electrical work which must be performed.

The derivation of Debye and Hückel of the free energy change involved in dilution is based upon two general principles. One, the so-called Boltzmann principle, is borrowed from the kinetic theory, and the other, known as Poisson's equation, is derived from the laws of electrostatics, and involves Coulomb's law. It will, therefore, be evident that we are not dealing with a purely thermodynamical treatment of solutions, but a treatment subject to the limitations imposed by the assumption of the applicability of these two principles and the further assumption of complete dissociation.

We shall apply these principles, in the first place, to determine the distribution of the ions of opposite charges around any selected ion, and to evaluate the electrostatic potential that prevails around that ion in consequence of its own charge and of the unequal distribution which it produces in the surrounding ions. The following considerations will become clearer by reference to Fig. 36. In this figure the dot in the centre represents an ion of valence $\pm \nu$ and charge $\pm \nu\varepsilon$, and this charge produces in any spherical shell of volume dv located between the distances r and $r + dr$ a potential P and a density of electric charge D.

The Boltzmann principle may be stated as follows (for an elementary deduction see Jager, *Fortschritte der kinetischen Gastheorie*, Vieweg und Sohn, Braunschweig, 1919, 67–70): When a large number of molecules, possessing an average kinetic energy $\frac{3}{2}kT$ are distributed throughout a given region, in which there

prevail, at different points, different fields of force (and therefore different electrical potentials), whereby any kind of molecule A in any given volume element dv acquires a potential energy E, then the number of such molecules will equal the number n_A of such molecules per unit volume in a place where the potential energy is zero, multiplied by the factor $e^{-E/kT}$ and by the volume dv. That is, if n_A' is the number of molecules which acquire a potential energy E, then

$$n_A' = n_A . e^{-E/kT} . dv \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k is the gas constant per molecule (i.e. $k = R/N$) and n_A is

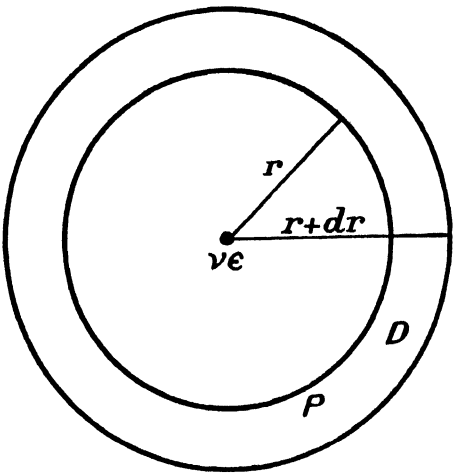


FIG. 36.

the number of molecules of type A per unit volume in the main bulk of the volume where the potential energy is zero.

We apply this principle to determine the distribution of ions in a solution containing, in unit volume, n_A positive ions of A with a valence ν_A and a charge $\nu_A . \varepsilon$; n_B negative ions of valency ν_B and charge $-\nu_B . \varepsilon$; n_C positive ions of valency ν_C and charge $\nu_C . \varepsilon$, n_D negative ions of valency ν_D and charge $-\nu_D . \varepsilon$, etc. Since the potential energy E of any ion is $\pm \nu\varepsilon . P$ when in a region of potential P, there are evidently, by equation (1) the following numbers of these ions in the volume element dv where the potential is P.

$$n_A . e^{-\nu_A \epsilon P/kT} dv ; \; n_B . e^{+\nu_B \epsilon P/kT} dv ; \; n_C . e^{-\nu_C \epsilon P/kT} dv ;$$
$$n_D . e^{+\nu_D \epsilon P/kT} dv ; \text{ etc., etc.} \quad . \quad . \quad . \quad . \quad (2)$$

Developing the exponential quantities in a series by means of the formula

$$e^x = 1 + x + \tfrac{1}{2}x^2 + \ldots.$$

and neglecting all terms after the second, these expressions become

$$n_A(1 - \nu_A \varepsilon P/kT)dv\,;\quad n_B(1 + \nu_B \varepsilon P/kT)dv\,;$$
$$n_C(1 - \nu_C \varepsilon P/kT)dv\,;\ldots\ldots\ldots\ldots \quad (3)$$

(The authors state that they have considered the effect of neglecting these higher terms, and find it to be negligible except at fairly high concentrations.)

The Poisson equation applied to a case where the potential P changes with the distance r by the same amount in all radial directions from a central point has the following form, in which D denotes the density of electricity in the region dv, and K is the dielectric constant of the medium

$$\frac{1}{r}\frac{d}{dr}\left(r^2\frac{dP}{dr}\right) = \frac{d^2P}{dr^2} + \frac{2}{r}\frac{dP}{dr} = -\frac{4\pi D}{K} \quad \ldots \quad (4)$$

This differential equation evidently shows how the potential gradient or field strength dP/dr varies with the electric density D. In order to solve it for P in terms of r we must express D as a function of P or of r. Debye and Hückel show that the former can be done in the following manner. By multiplying the number of ions of each kind present in the volume-element dv (as given by expression (3)) by their respective charges, summing and dividing by the volume dv, and noting that since the solution is electrically neutral,

$$n_A.\nu_A + n_C\nu_C + \ldots = n_B.\nu_B + n_D.\nu_D + \ldots \quad (5)$$

we evidently obtain the density of electricity D in that volume element. That is

$$D = -\frac{\varepsilon^2 P}{kT}(n_A\nu_A^2 + n_B\nu_B^2 + n_C\nu_C^2 + n_D\nu_D^2 + \ldots)$$
$$= -\frac{\varepsilon^2 P}{kT}\Sigma(n\nu^2) \quad \ldots \quad (6)$$

We now substitute this value of D in equation (4) and write a single constant B^2 in place of the resulting coefficient of P, namely we put

$$B^2 = 4\pi\varepsilon^2\Sigma(n\nu^2)/K.kT \quad \ldots \quad (7)$$

The differential equation thus obtained is

$$\frac{d^2P}{dr^2} + \frac{2dP}{rdr} - B^2P = 0 \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The general solution of this equation is of the form

$$P = I\frac{e^{-Br}}{r} + I'\frac{e^{+Br}}{r} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where I and I' are integration constants to be determined from the limiting conditions in our special case.

The constant I' must evidently be equal to zero, since otherwise P would approach infinity (instead of zero) as r approaches infinity. The value of the constant I is determined by Debye and Hückel for the two cases (i) when the central ion may be regarded as a point sphere, (ii) when the ion is regarded as a sphere of definite radius. In the former case its value is $\pm \nu\varepsilon/K$. This value follows from the fact that, when the concentration of the surrounding ions is negligible, so that $\Sigma(n\nu^2) = 0$ and $B = 0$, the expression for the potential must reduce to that caused by a point charge in an ion-free medium, namely to $\pm \nu\varepsilon/Kr$.

This conclusion, as regards the value of I, may also be derived, as is done by Debye and Hückel, from the consideration that it must hold true as r approaches zero, since in the region around the central ion the number of other ions present is negligible. Hence we obtain, for the potential P at a distance r from a positive or negative ion of valence $\pm \nu$, the expression

$$P = \frac{\pm\nu\varepsilon}{K} \cdot \frac{e^{-Br}}{r} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

From this point onwards, we may proceed in two ways. Debye and Hückel employ the following method. They resolve the expression for the potential P into two terms as follows:

$$P = \frac{\pm\nu\varepsilon}{K.r} - \frac{\pm\nu\varepsilon}{Kr}(1 - e^{+Br}) \quad . \quad . \quad . \quad . \quad (11)$$

The first term evidently represents the potential at the distance r that would be caused by the central ion alone, if there were no surrounding ions, and the second term therefore represents the potential at that distance which arises from the "ion atmosphere," that is from the unequal distribution of the positive and negative ions in the neighbourhood of the central ion. This last term has the same value for all small values of r, since for such values the

expression in parentheses reduces to Br upon developing it in a series. But this limiting value is also the potential P_0 at distance zero, and therefore the potential of the ion itself, in so far as this arises from its ion atmosphere. Its value for an ion of charge $\pm \nu\varepsilon$ is seen to be

$$P_0 = \mp \nu\varepsilon . B/K \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Now the increase in the free energy, $\delta F''$, of such an ion which is caused by removing it from its ion atmosphere is evidently

$$\delta F' = \nu^2\varepsilon^2 . B/K \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Hence for the removal, from the influence of their ion atmospheres, of all the ions in any given solution, the increase in the free energy may evidently be found by summing the values of $\delta F'$ for all the separate ions and dividing the result by 2 (since otherwise the effect of separating any pair of ions would be counted twice). In view of the additivity of the free energy effects, we may, moreover, distribute this sum among the different kinds of ions. Thus the free energy increase attending the removal of N ions, constituting one gram-ion, of any particular type of ion of valence ν is given by the following expression; it being understood that all the other ions in the solution are simultaneously removed, and that their removal is attended by other energy effects of a similar type:

$$\Delta F' = N . \varepsilon^2\nu^2 . B/2K \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Resubstituting also the expression for the constant B given by equation (7), we get for this molal free energy change on dilution due to the electric forces

$$\Delta F' = \frac{\sqrt{\pi}\varepsilon^3 . N\nu^2\sqrt{\Sigma(n\nu^2)}}{K^{1\cdot5} . (kT)^{0\cdot5}} . \quad . \quad . \quad . \quad . \quad (15)$$

We may also derive equation (15) from expressions (1) to (9), by the following considerations, which seem worthy of presentation, since the treatment from a different viewpoint affords a certain confirmation of the result, and may serve to make the matter clearer.

We shall consider each ion to be separately removed from all the other ions in the solution, against the forces prevailing between it and those other ions, and formulate the resulting increase in free energy. Consider first any volume element dv, around some selected ion of charge $\pm \nu\varepsilon$, in the form of a spherical shell of radius r and thickness dr, as in Fig. 36. The volume of this shell will be

$4\pi r^2 dr$. The number of ions of various kinds located in any such volume element is given by expression (3), and the resultant charge upon them is given by equation (6) multiplied by the volume dv, i.e. $D.dv$. The free energy increase $\delta F'$ attending the removal of the selected ion from this portion of the ion atmosphere is evidently equal to minus the product of this charge in the volume dv, and the charge on the ion itself $\pm \nu\varepsilon$, divided by the quantity Kr; that is $\delta F'$ is equal to the electrical work which is done upon the system. Hence we have

$$\delta F' = \frac{\pm \nu\varepsilon . \varepsilon^2 . P}{Kr . kT} \Sigma(n\nu^2) . 4\pi r^2 dr \quad . \quad . \quad . \quad (16)$$

or, substituting the value of P given by equation (10),

$$\delta F' = \frac{4\pi\varepsilon^4\nu^2}{K^2 . kT} \Sigma(n\nu^2) . e^{-Br} dr \quad . \quad . \quad . \quad . \quad . \quad (17)$$

To obtain the total free energy increase attending the removal of the selected ion from all the ions, we must evidently sum the separate effects for all the concentric shells surrounding it; in other words, we must integrate equation (17) for values of r between zero and infinity. Carrying out this integration there results,

$$\frac{4\pi\varepsilon^4\nu^2\Sigma(n\nu^2)}{K^2 . kT . B} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

From this expression we may obtain the free energy increase attending the infinite dilution of the solution or the removal of all the ions in it from one another. To do this, we must evidently multiply expression (18) by the number of ions of each particular kind present, sum the products for all the kinds of ions, and divide the result by 2, so as to avoid counting the effect for each pair of ions twice over. Correspondingly, the molal free energy increase accompanying dilution, for any kind of ion of valence $\pm \nu$, is obtained by multiplying expression (18) by the number N of ions in one gram-ion. Doing this and substituting the value of B given by expression (7) we obtain

$$\Delta F' = \frac{\sqrt{\pi}\varepsilon^3 N . \nu^2 \sqrt{\Sigma(n\nu^2)}}{K^{1.5}(kT)^{0.5}} \quad . \quad . \quad . \quad . \quad (19)$$

This equation will be seen to be identical with equation (15).

If we denote by c the concentration in moles per unit volume, then since N is the number of molecules per gram-mole, Nc is

equal to the number of molecules present in unit volume. Moreover k is the gas constant per molecule and Nk is the gas constant per mole, namely R. Replacing n by Nc and kN by R in equation (15) or (19) we obtain

$$\Delta F' = \frac{\sqrt{\pi}\varepsilon^3 . N^2 . \nu^2 \sqrt{\Sigma(c\nu^2)}}{K^{1\cdot5}(RT)^{0\cdot5}} \quad . \quad . \quad . \quad . \quad (20)$$

In order to abbreviate this expression we shall write a single letter b for the product of the natural constants, the value of b being found by putting $\pi = 3{\cdot}142$; $R = 8{\cdot}315 \times 10^7$; $N = 6{\cdot}06 \times 10^{23}$ and $\varepsilon = 4{\cdot}774 \times 10^{-10}$, in the expression

$$b = \varepsilon^3 . N^2 \sqrt{\pi}/R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

$$= 7{\cdot}77 \times 10^{15} \text{ C.G.S. Units.}$$

The equation (20) above now becomes

$$\Delta F' = \frac{b . \nu^2 \sqrt{\Sigma(c\nu^2)}}{K^{1\cdot5}T^{0\cdot5}} \quad . \quad . \quad . \quad . \quad . \quad (22)$$

This expression gives us the difference in the free energy, as a result of the electric forces, of one mole of ions of valence $\pm \nu$, when present at a temperature T in an infinitely dilute solution, and when present in a solution containing these and other ions at such concentration that the sum of the products of the concentration c of each kind of ion by the square of its valence ν is $\Sigma(c\nu^2)$; and the dielectric constant of the solution is K.

It should be noted, as regards this dielectric constant, that we must employ the value of K which prevails in the immediate neighbourhood of the ions, and that this value is greater than that of the solvent as a whole owing to electrostriction.

In the general case where N_A gram-ions of A, N_B gram-ions of B, N_C gram-ions of C, etc., are present, the free energy increase accompanying the dilution, due to the electric forces is evidently given by the following expression, which corresponds to the result of Debye and Hückel when the size of the ions is neglected :

$$\Sigma(N' . \Delta F') = \frac{b\Sigma(N'\nu^2) . \sqrt{\Sigma(c\nu^2)}}{K^{1\cdot5}T^{0\cdot5}} \quad . \quad . \quad . \quad . \quad (23)$$

N' is put for such terms as N_A, N_B, etc., to avoid confusion with the Avogadro number N. For the special case that only two kinds

of ions, of equal valence ν are present at the same molal concentration c, this equation reduces to

$$2\Delta F' = \frac{2b\nu^2\sqrt{2c\nu^2}}{K^{1\cdot5}.T^{0\cdot5}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

or still more simply, for a uni-univalent electrolyte we obtain

$$2\Delta F' = \frac{2b.\sqrt{2c}}{K^{1\cdot5}T^{0\cdot5}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Now this quantity is the free energy increase which accompanies dilution, as a result of the electrical forces acting between the ions. But this is not, by any means, the only change in the free energy on dilution. We must consider the ordinary factor, with which we are already familiar, namely the transfer from a region of concentration c, to a region of infinitely dilute solution where the concentration is c_0. Now we shall assume that, but for the electrical forces acting upon the ions, their behaviour in solution would be similar to that of a perfect gas, that is to say we could apply the simple gas law to the solution. Hence the free energy decrease accompanying dilution, from concentration c to concentration c_0, is, if we neglect the electrical forces,

$$-\Delta F'' = \Sigma RT \ ln \ c/c_0 \quad . \quad . \quad . \quad . \quad . \quad (26)$$

and the total increase in the free energy accompanying dilution is obtained by adding these factors, so that

$$\Delta F = \frac{b\Sigma(N'\nu^2)\sqrt{\Sigma(c\nu^2)}}{K^{1\cdot5}T^{0\cdot5}} - \Sigma \ RT \ ln\frac{c}{c_0} \quad . \quad . \quad . \quad (27)$$

Milner also makes use of the Boltzmann principle of the non-uniform distribution of the ions resulting from the electrical potential due to their attractions and repulsions. But instead of employing the Poisson equation, expressing a relation between potential gradient and space density of the electric charge, he determines the energy change corresponding to this electrical effect, by summing, in the case of a particular configuration of the ions, for each pair of ions which can be formed out of all those present in the solution, the product of their mutual electrical force into the distance between them, multiplying this sum by the probability of the occurrence of this configuration, and summing for every possible configuration of the ions in the solution. The intricate char-

acter of these operations is evident from this statement and the apparently successful treatment of them may well excite admiration.

It was at first thought that Milner's result was two-thirds of that obtained by the method of Debye and Hückel, but the discrepancy was later cleared up by Adams (*loc. cit.*), who showed that, while Debye and Hückel's method leads to the free energy term corresponding to the electrical forces, i.e. to $\Delta F'$, Milner's method leads to the maximum work term $\Delta A'$. As we shall show later, the maximum work term is two-thirds of the free energy term, so that Milner's result agrees well with that of Debye and Hückel. Milner's expression is

$$2\Delta A' = -RT.h.f(h)., \text{ where } h = (\tfrac{8}{3}\pi Nc)^{\frac{1}{2}}\varepsilon^2\nu^2N/KRT \quad (28)$$

In this equation $f(h)$ is a function for which an algebraic expression could not be obtained. To equate this expression with that of Debye and Hückel, namely to $\frac{2}{3}\Delta F'$, we must put

$$h.f(h) = -\tfrac{2}{3}\sqrt{3h^3}.$$

To show how closely this is fulfilled, the values of $h.f(h)$, calculated by Milner for various values of h at 0° C. (and therefore for certain values of the concentration c and the valence ν), are given in the following table, together with the corresponding values of the ratio $-h.f(h)/\frac{2}{3}\sqrt{3h^3}$. This last ratio should be unity if the two expressions are equivalent. The concentrations C are expressed in moles per litre.

$C.\nu^2$.	h.	$-h.f(h)$.	$-h.f(h)./\frac{2}{3}\sqrt{3h^3}$.
0·0001	0·0559	0·0168	1·101
0·001	0·120	0·0525	1·092
0·002	0·152	0·0735	1·0725
0·005	0·206	0·114	1·056
0·01	0·259	0·159	1·044
0·02	0·327	0·222	1·0275
0·05	0·443	0·345	1·0125
0·10	0·559	0·486	1·010
0·20	0·704	0·672	0·984

The agreement is very satisfactory. Milner makes a statement in a footnote of his article (p. 575), without presenting the deriva-

tion, that "it may be shown as an approximation when h is very small" that the expression $h.f(h)$ becomes equal to

$$-\sqrt{3h^3.\pi/2} = -1{\cdot}253\sqrt{3h^3}.$$

This does not seem, however, to accord with his computed values reproduced above, but it may do so in case the ratio increases very rapidly at extremely small concentrations.

We now propose to show that the maximum work term $\Delta A'$ which accompanies dilution, as a result of the electrical forces between the ions, is, in fact, two-thirds of the corresponding free energy change $\Delta F'$. The electrical forces will cause an alteration in the osmotic pressure P of the solution, of amount ΔP. That is ΔP is the difference between the osmotic pressure of the actual solution and that which would obtain if the solution were ideal. Now we have seen that a free energy change is of the form $\int v dp$, so that we may write

$$\Delta F' = \int V d(\Delta P) \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

Now the concentration is expressed in moles per unit volume (i.e. per cubic centimetre) so that $V = 1/c$, and we may write equation (29) in the form

$$d(\Delta P) = c.d(\Delta F') \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

But we have, by equation (22),

$$\Delta F' = \frac{b.\nu^2\sqrt{\Sigma(c\nu^2)}}{K^{1{\cdot}5}T^{0{\cdot}5}}$$

and if we replace all the other terms except c by the single term G, which is evidently constant for any electrolyte at a given temperature, we obtain

$$\Delta F' = G.c^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

Hence on differentiation,

$$d(\Delta F') = \tfrac{1}{2}G.c^{-\frac{1}{2}}.dc$$

so that

$$d(\Delta P) = c.d(\Delta F') = \tfrac{1}{2}G.c^{\frac{1}{2}}dc \quad . \quad . \quad . \quad . \quad (32)$$

Integrating between the limits $c = 0$ and $c = c$, we obtain

$$\Delta P = \tfrac{1}{2}G.\int_0^c c^{\frac{1}{2}}.dc = \tfrac{1}{3}G.c^{\frac{3}{2}} \quad . \quad . \quad . \quad . \quad (33)$$

Now the maximum work factor is, as we have seen in an earlier chapter, of the form $\int pdv$, so that we may write

$$\Delta A' = \int \Delta P . dV$$

or substituting the value of ΔP given by equation (33), and replacing dV by its equivalent $-\frac{1}{c^2}.dc$,

$$\Delta A' = -\int_0^c \tfrac{1}{3}G.c^{\frac{3}{2}}.\frac{1}{c^2}.dc = -\tfrac{1}{3}G.\int_0^c c^{-\frac{1}{2}}.dc = +\tfrac{2}{3}G.c^{\frac{1}{2}} \quad . \quad . \quad (34)$$

which is evidently two-thirds of the value of $\Delta F'$ given in equation (31). Hence we have, corresponding to equation (23),

$$\Delta A' = \frac{2}{3}\frac{b.\Sigma(N'v^2)\sqrt{\Sigma(cv^2)}}{K^{1.5}.T^{0.5}} \quad . \quad . \quad . \quad . \quad (35)$$

or for the special case where only two kinds of ions of equal valence v are present in the solution

$$2\Delta A = \frac{2}{3}.\frac{2bv^2\sqrt{2cv^2}}{K^{1.5}T^{0.5}} \quad . \quad . \quad . \quad . \quad . \quad (36)$$

It will be of interest, before proceeding to the calculation of the osmotic pressure of the solution as a result of these inter-ionic forces, to determine what changes occur in the total internal energy U, and the heat content H of the system, corresponding to these quantities ΔF and ΔA. We may calculate ΔU from ΔA directly, by means of the familiar Gibbs-Helmholtz equation, viz.,

$$\frac{\partial}{\partial T}\left(\frac{-\Delta A}{T}\right) = \frac{\Delta U}{T^2}.$$

Now we have, by equation (34), substituting the value for G and dividing through by T,

$$-\frac{\Delta A}{T} = -\frac{2}{3}\frac{b.v^2\sqrt{\Sigma c}.v^2}{K^{1.5}T^{1.5}}.$$

Differentiating with respect to T we obtain

$$\frac{\partial}{\partial T}\left(\frac{-\Delta A}{T}\right) = \frac{-2bv^2\sqrt{\Sigma cv^2}}{3}\left(-1.5K^{-2.5}T^{-1.5}.\frac{dK}{dT} - 1.5K^{-1.5}T^{-2.5}\right)$$
$$= \frac{\Delta U}{T^2}.$$

Hence we have

$$\Delta U = \tfrac{2}{3} b\nu^2 \sqrt{\Sigma c\nu^2} \left(\frac{3}{2} T^{+0.5} . K^{-2.5} \frac{dK}{dT} + \tfrac{3}{2} K^{-1.5} T^{-0.5} \right)$$

$$= \frac{b\nu^2 \sqrt{\Sigma c\nu^2}}{K^{1.5} T^{0.5}} \left(\frac{T . dK}{K . dT} + 1 \right)$$

$$= \frac{b\nu^2 \sqrt{\Sigma c\nu^2}}{K^{1.5} T^{0.5}} \left(\frac{d \ln K}{d \ln T} + 1 \right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

If the dielectric constant were independent of temperature, $\frac{d \ln K}{d \ln T}$ would be zero so that the factor in parentheses would become unity and we should have

$$\Delta U = \frac{b\nu^2 \sqrt{\Sigma c\nu^2}}{K^{1.5} T^{0.5}} = \Delta F \quad . \quad . \quad . \quad . \quad . \quad (38)$$

The best available measurements, however, over a wide range of temperature, of the dielectric constant of water, are those of Lili Kockel (*Ann. Physik.*, (4), 1925, **77**, 417–18). Between 10° C. and 100° C., his results may be represented, within the limits of experimental error, by the equation,

$$K = 400{,}000\ T^{-1.5} \quad . \quad . \quad . \quad . \quad . \quad (39)$$

Below 8° C. the relation is less simple, as would be expected.

Differentiating equation (39), we have

$$dK = -\ 1{\cdot}5 \times 400{,}000\ T^{-2.5} . dT$$

so that

$$\frac{dK}{K} = -\ \frac{1{\cdot}5 \times 400{,}000 T^{-2.5}}{400{,}000 T^{-1.5}} . dT$$

$$= -\ 1{\cdot}5 . dT/T$$

or

$$\frac{d \ln K}{d \ln T} = -\ 1{\cdot}5$$

Substituting this value in equation (37), we obtain

$$\Delta U = \frac{-\ 0{\cdot}5\ b\nu^2 \sqrt{\Sigma c\nu^2}}{K^{1.5} T^{0.5}} .$$

In other words, when account is taken of the temperature coefficient of the dielectric constant of the medium a value of ΔU is obtained, in the case of water, which is half as large as, and opposite in sign to, the corresponding value of the free energy change ΔF

$$\Delta U = -\ \tfrac{1}{2} \Delta F \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

In a precisely similar manner, we may obtain the value of the change in the heat content from the corresponding equation

$$\frac{\partial}{\partial T}\left(\frac{-\Delta F}{T}\right) = \frac{\Delta H}{T^2}.$$

The resulting value of ΔH is evidently,

$$\Delta H = \frac{3\,b\nu^2\sqrt{\Sigma c\nu^2}}{2\,K^{1\cdot5}T^{0\cdot5}}\left(\frac{d\ ln\ K}{d\ ln\ T} + 1\right) \quad . \quad . \quad . \quad . \quad . \quad (41)$$

and if we substitute the value of the temperature coefficient given above for the case of water, we obtain

$$-\Delta H = \tfrac{3}{4}.\Delta F \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

ΔH is, of course, the heat absorbed during dilution as a result of the electrical forces.

We may now attempt to determine the osmotic effects of these electrical forces. It is evident that they will act in such a way as to reduce the effective osmotic pressure, i.e. the observed osmotic pressure will be less than that which would be exerted by an ideal solution. We may adopt either of two methods.

The first of these has already been followed in deducing equation (33). Applied to the case where we have two types of ions of equal valency ν, this equation becomes

$$\Delta P = \frac{2b\nu^2c\sqrt{2c\nu^2}}{3\,.K^{1\cdot5}T^{0\cdot5}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

Hence the osmotic pressure of a solution of concentration c will be given by

$$P = P_0 - \frac{2}{3}\frac{b\nu^2c\sqrt{2c\nu^2}}{K^{1\cdot5}T^{0\cdot5}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

where P_0 is the pressure which would be exerted if the solution were ideal. But we may write, for an ideal solution $P_0 = 2RTc$ (since there are two ion types), so that

$$P = 2RTc - \frac{2}{3}\frac{b\nu^2c\sqrt{2c\nu^2}}{K^{1\cdot5}T^{0\cdot5}} \quad . \quad . \quad . \quad . \quad . \quad (45)$$

or, for the general case

$$P = RT\Sigma c - \frac{b\,.(\Sigma c\nu^2)^{1\cdot5}}{3K^{1\cdot5}T^{0\cdot5}} \quad . \quad . \quad . \quad . \quad . \quad (46)$$

The second method depends upon the application of Kinetic principles. We employ the virial equation of Clausius, namely,

$$PV = \tfrac{1}{3}nmu^2 - \tfrac{1}{3}\Sigma(f.r) \quad . \quad . \quad . \quad . \quad . \quad (47)$$

In this equation, $\Sigma(f.r)$, called the virial, denotes the sum for all the pairs of ions in the volume V of the solution, of the force f between the ions and their distance r apart. The equation was originally put forward to represent the behaviour of a gas. In the case of the ions of a solution, if we assume its applicability the force f is of the form X/r^2, so that $f.r = X/r$. The virial is evidently the difference between the free energy which the molecules possess in a perfect solution and that which obtains in an actual solution. This is, however, the quantity ΔF calculated by Debye and Hückel. Hence we have, if we write $2RT$ for $\frac{1}{3}nmu^2$, for the case where two types of ions of the same valence ν are present

$$PV = 2RT - \frac{1}{3}\frac{2b\nu^2\sqrt{2c\nu^2}}{K^{1.5}T^{0.5}} \quad . \quad . \quad . \quad . \quad . \quad (48)$$

If, now, we substitute the value for $V = 1/c$ we obtain

$$P = 2RTc - \frac{2}{3}\frac{bc\nu^2\sqrt{2c\nu^2}}{K^{1.5}T^{0.5}}$$

which is identical with equation 45, so that the two methods are seen to yield the same results.

Deduction of an Expression for the Activity Coefficient of the Ions. It is manifestly of great interest and importance to relate the equations of Debye and Hückel to the earlier concept of activity. This may be done very simply as follows. We have seen, by equation 27, for the transfer of a single gram-ion from a solution of concentration c to an infinitely dilute solution, that the free energy change is

$$-\Delta F = RT\ ln\ c/c_0 - \frac{b\nu^2\sqrt{c\nu^2}}{K^{1.5}T^{0.5}} \quad . \quad . \quad . \quad . \quad (49)$$

But, by our definition of activity, it is evident that the decrease in free energy due to the dilution is represented by the equation

$$-\Delta F = RT\ ln\ a/a_0$$

where a and a_0 are the activities in the solution and in an infinitely dilute solution respectively. But if γ is the activity coefficient of the ion in the solution at concentration c, then γc is the activity. In the infinitely dilute solution the activity is equal to the concentration c_0, so that the free energy decrease is given by

$$-\Delta F = RT\ ln\ \gamma c/c_0 \quad . \quad . \quad . \quad . \quad . \quad (50)$$

Combining equations (49) and (50) we obtain

$$RT\ ln\ \gamma c/c_0 = RT\ ln\ c/c_0 - \frac{bv^2\sqrt{cv^2}}{K^{1\cdot5}T^{0\cdot5}}.$$

Hence the activity coefficient is given by the equation

$$ln\ \gamma = -\frac{bv^2\sqrt{cv^2}}{R.(KT)^{1\cdot5}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (51)$$

In this expression $R = 8{\cdot}2 \times 10^7$ and $b = 7{\cdot}77 \times 10^{15}$ when the concentration is measured in moles per cubic centimetre. At 0° C. and 25° C. these expressions become

$$log\ \gamma = -0{\cdot}346\ v^2\sqrt{cv^2} \text{ at } 0°\text{ C.} \quad . \quad . \quad . \quad (52)$$
$$log\ \gamma = -0{\cdot}357\ v^2\sqrt{cv^2} \text{ at } 25°\text{ C.}$$

The corresponding expressions for the activation function for a substance of two ions A and B are

$$log\ \frac{(\gamma_A)^{1/\nu_A}.(\gamma_B)^{1/\nu_B}}{\nu_A + \nu_B} = \begin{cases} 0{\cdot}346\sqrt{\Sigma cv^2} \text{ at } 0°\text{ C.} \\ 0{\cdot}357\sqrt{\Sigma cv^2} \text{ at } 25°\text{ C.} \end{cases} \quad . \quad . \quad (53)$$

A. A. Noyes (*J. Amer. Chem. Soc.*, 1924, **46**, 1098) has subjected the theory to a fairly thorough experimental examination assuming complete ionization of the substances, first with the aid of the values of the activity coefficient derived by Lewis and Randall from freezing-point data and electromotive force data; and second with the help of activity coefficients derived from most of the suitable series of solubility-effect measurements existing in the literature.

The numerical factor of $\sqrt{\Sigma cv^2}$ must be regarded as uncertain for the following reasons: (1) the dielectric constant prevailing in the immediate neighbourhood of the ions, which is the one theoretically involved, must be considerably greater than that of the water as a whole; (2) the size of the ions which has been neglected in the calculation, has an effect which becomes appreciable at fairly small concentrations. Both these factors operate in the same direction and lead us to expect that the numerical factor will be considerably less than that calculated by equation (53) corresponding to the equations of Debye and Hückel; and it seems probable that a better expression of the theory may be afforded by adopting a value for the numerical factor, say five-

sixths as large as that given. Doing this we may write for the solvent water at 0° C. and 25° C. the following values of the activation function of equation (53).

$$0{\cdot}288\sqrt{\Sigma cv^2} \text{ at } 0^\circ \text{ C. and } 0{\cdot}298\sqrt{\Sigma cv^2} \text{ at } 25^\circ \text{ C.} \quad . \quad (54)$$

The following are some of the results given by Noyes (*loc. cit.*). At the head of each group, in the rows designated Theory (Eq. 53) and Theory (Eq. 54) are given the values of the activation product, as calculated by equations (53) and (54) respectively.

EXPERIMENTAL AND THEORETICAL VALUES OF THE ACTIVATION PRODUCT COMPARED.

Valence Type.	Temp. °C.	Substance.	Conc. in Moles per 1,000 grams Water.				
			0·01.	0·02.	0·05.	0·10.	0·20.
1 × 1	25	Theory Eq. 53 .	0·792	0·720	0·594	0·480	0·254
		Theory Eq. 54 .	0·823	0·761	0·650	0·542	0·421
		HCl	0·854	0·801	0·740	0·662	0·612
		LiCl	0·852	0·799	0·711	0·647	0·600
		NaCl . . .	0·852	0·799	0·710	0·639	0·568
		KCl	0·852	0·799	0·706	0·630	0·561
		KOH . . .	0·852	0·799	0·706	0·629	—
1 × 1	0	Theory Eq. 53 .	0·799	0·728	0·604	0·491	0·366
		Theory Eq. 54 .	0·827	0·768	0·658	0·552	0·433
		KNO_3 . . .	0·841	0·770	0·652	0·537	—
		$AgNO_3$ . . .	0·816	0·735	0·613	0·523	0·429
		KIO_3, $NaIO_3$.	0·780	0·707	0·586	0·472	—
2 × 1	0	Theory Eq. 53 .	0·557	0·436	0·271	0·157	—
		Theory Eq. 54 .	0·614	0·501	0·336	0·214	—
		$BaCl_2$ . . .	0·607	0·530	0·429	0·355	—
		K_2SO_4 . . .	0·571	0·481	0·359	0·273	—
2 × 2	0	Theory Eq. 53 .	0·406	0·279	0·133	0·058	0·018
		Theory Eq. 54 .	0·472	0·346	0·187	0·093	0·035
		$MgSO_4$ . . .	0·405	0·322	0·227	0·166	0·119
		$CuSO_4$ . . .	0·405	0·322	0·216	0·158	0·110
		$CdSO_4$ . . .	0·405	0·324	0·221	0·160	—
3 × 1	0	Theory Eq. 53 .	0·332	0·210	0·085	0·031	0·007
		Theory Eq. 54 .	0·339	0·272	0·128	0·055	0·016
		$La(NO_3)_3$ . .	0·474	0·388	0·286	0·224	0·176

Owing to the uncertainty, referred to above, as to the exact theoretical value of the numerical factor in equation (53), a more satisfactory test of the theory is obtained by plotting the values of $-\log \frac{(\gamma_A)^{1/\nu_A}(\gamma_B)^{1/\nu_B}}{\nu_A + \nu_B}$ as ordinates against the values of $\sqrt{\Sigma(cv^2)}$

as abscissæ. Along the lower side of the plot are given the corresponding values of the ionic strength $\frac{1}{2}\Sigma cv^2$. The theoretical values of the activation function, corresponding to the form of equation (53), at 25° C., are shown by the lower of two broken straight lines; and the values corresponding to a factor two-thirds as large are shown by the upper broken straight line. The values required by equation (54) would lie in between these.

The theory, as expressed by equation (53), evidently requires: (1) that these graphs be straight lines for all salts; (2) that they

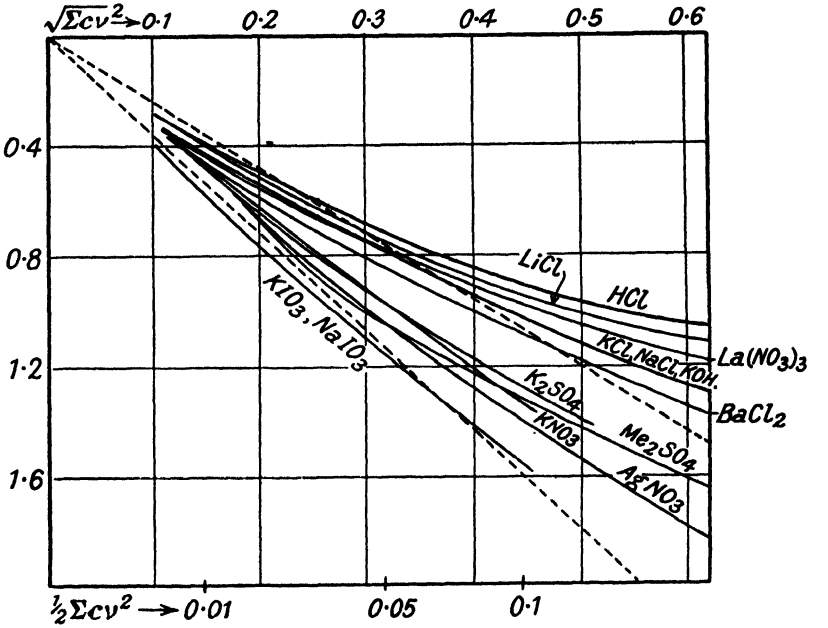


FIG. 37.

ACTIVATION VALUES FROM FREEZING-POINT AND ELECTROMOTIVE DATA (From A. A. Noyes.)

coincide for different substances of the same valence type; (3) that they coincide for substances of different valence types; and (4) that they have the slope corresponding to the factor 0·346 at 0° C. and 0·357 at 25° C.

The first requirement, that the graphs be straight lines, i.e. that the logarithm of the activation product be proportional to the square root of the concentration, is evidently well fulfilled for all the uni-univalent substances, up to an ionic strength of 0·05 Molal, and for all these substances except hydrogen chloride and lithium chloride, up to an ionic strength of 0·1 M. The principle does not

seem to be obeyed so closely by the salts of higher valence types, but the accuracy of the results is hardly great enough to decide.

The other requirements are only approximately fulfilled as will be seen from a study of the graph. The general conclusions of A. A. Noyes may be summarized as follows: Even at fairly small concentrations different salts of the same valence type show considerable variations in the values of their activation product, instead of giving identical values as required by theory. Thus at 0·05 M. the nine uni-univalent but chemically very different substances, whose activation products have been determined, have activation products varying from 0·59 to 0·74; and the two uni-bivalent salts, barium chloride and potassium sulphate have the products 0·43 and 0·36. Nevertheless, the results considered as a whole with respect to the functional relations predicted, and even with respect to the average value of the numerical coefficient, are strikingly in accord with the requirements of the theory, as shown by the following statements.

As required by equation (53), for nearly all the single substances up to ionic strengths of 0·05, and often of 0·1 M. the logarithm of the activation product is proportional to the square root of the concentration of the substance, and therefore, when plotted against this quantity, it gives a linear graph. Moreover, the effect of the valence of the ions is, in general, that predicted by the theory, as is shown by the fact that the uni-univalent, uni-bivalent and bi-bivalent substances (as also one uni-tervalent substance), all give graphs of the logarithmic activation function against the quantity Σcv^2, which lie within a narrow sheaf—one no wider than that including the various salts of the same valence type. Finally the average slope of the curves for all the substances corresponds approximately to a numerical coefficient having a value of about five-sixths of that given by the theory.

This and subsequent work has shown conclusively that the limiting equations obtained by Debye and Hückel do give a correct account of the behaviour of electrolytes at high dilutions. We shall now consider the various suggestions which have been advanced for the case of salt solutions at higher concentrations.

Theories of Concentrated Salt Solutions. It has been known for some time that as the concentration of a salt solution is increased, the activity coefficient at first decreases in the range of dilute

solutions, passes through a minimum value and then rapidly increases again. Harned and his co-workers have made a careful study of this phenomenon: Harned, *J. Amer. Chem. Soc.*, 1925, **47**, 676, 684, 689, 930; 1926, **48**, 126. The table on page 215 illustrates this behaviour of the activity coefficient admirably, for the case of sodium and potassium hydroxides.

Now the theory of Debye and Hückel, which, as we have seen, gives a fairly accurate reproduction of the behaviour of very dilute solutions, involves several physical assumptions, viz.:

(i) We assume that all forces other than Coulomb forces between the ions can be neglected.

(ii) We assume that corrections for the overlapping of the ionic atmospheres can be neglected.

(iii) The solvent between the ions is regarded as behaving like the pure solvent in bulk.

The first assumption implies that the theory is strictly applicable only to an electrolyte which is completely dissociated into point ions. As the solutions become more concentrated, however, it is no longer legitimate to neglect the size of the ions. Now, the ionic dimensions will be equivalent to a force of repulsion between them, since they prevent the charges coming together. But the inter-ionic attraction acts in the direction of a decrease in the activity coefficient, so that the ionic size will tend to increase the activity coefficient. Debye and Hückel have made allowance for a distance of closest approach of the ions. They obtain the following modified form of equation (52)

$$\log \gamma = - \frac{0{\cdot}357\nu^2\sqrt{c\nu^2}}{1+A.\sqrt{c\nu^2}} \quad . \quad . \quad . \quad . \quad . \quad (55)$$

where A is a constant which is related to the "apparent ionic diameter," or the mean value of the distance a within which one ion may approach another, by the equation

$$A = 0{\cdot}232 \times 10^8 \times a \quad . \quad . \quad . \quad . \quad . \quad (56)$$

The constant A differs for different electrolytes, but it was found to be of the right order of magnitude. Equation (55) is a considerable improvement on the simpler equation (52) for solutions from 0·005 to 0·1 molal. It does not, however, account satisfactorily for the behaviour of more concentrated solutions. In

fact, it was subsequently shown by O. Schärer (*Physikal. Zeit.*, 1924, **25**, 145; A., 1924, ii, 455) that experimental values for this additional constant A are negative in the case of dilute solutions of thallous chloride in dilute aqueous thallous nitrate. The reason for this anomaly is the neglect of terms other than those of the first order in the derivation of equation (3), since these terms become significant at concentrations where the effect of the ionic size is important. The Debye-Hückel theory does not therefore lend itself readily to quantitative extension on this basis, to the case of concentrated solutions.

The implication that the electrolyte is completely dissociated into ions has also received consideration. Debye and Hückel assume not only that the ionization of the electrolyte is complete, but that the resulting ions are free, i.e. that no electrical association occurs. Bjerrum (*Kgl. Danske. Videnskabs. Selsk. Math.-fys. Medd.*, 1926, **7**, (9), 1) has investigated the problem of ionic association. Ions of opposite sign which have approached one another to such an extent that the work necessary to separate their electrical charges is greater than four times the mean kinetic energy per degree of freedom $\left(\frac{4kT}{2}\right)$ are regarded as associated. The net external electrical effect of such a combination will, of course, be zero, i.e. the ion pair will behave electrically like an unionized molecule. Bjerrum calculates the number of such ion pairs by employing the Boltzmann principle and the thermodynamic law of mass action in terms of activities. To the remaining "free" ions he applies the original Debye-Hückel theory. He expresses the probability of association as a function of the distance between the ionic charges, and finds that the probability first diminishes, then passes through a minimum and finally increases as the distance between the ions is decreased. It follows that the minimum association will occur when the sum of the ionic radii of positive and negative ions is just equal to the distance corresponding to the minimum probability. With either larger or smaller sums of the ionic radii greater association would be expected. The amount of ionic association also depends upon the kind of ion under consideration. Thus the symmetrical, "noble gas type" of ion has a smaller tendency to combine electrically with lithium or sodium ions than the unsymmetrical hydroxyl ion. The values for the ionic radii obtained by Bjerrum are certainly

more plausible than those obtained from the extension of the Debye-Hückel theory when no regard is taken of the higher order terms. The question is obscured, however, by the fact that the ions are surrounded by a solvent sheath and this will undoubtedly have an effect upon the degree of association.

H. Müller (*Physikal. Zeit.*, 1927, **28,** 324; 1928, **29,** 78) and T. H. Gronwall (*Proc. Nat. Acad. Sci.*, 1927, **13,** 198) have recently considered the effect of the size of the ions upon their activity coefficients and Gronwall, Lamer, and Sandved (*Physikal. Zeit.*, 1928, **29,** 358) have carried out a solution of the fundamental equations of Debye and Hückel as far as terms of the fifth order, for the case of binary electrolytes. Their results give values for the ionic radii which are perhaps more plausible than those of Bjerrum, without any assumption of ionic association being employed.

R. H. Fowler (*Statistical Mechanics*, 1929) while investigating the second assumption of Debye and Hückel, that the corrections for overlapping of the ion atmospheres may be neglected, showed that the neglect of higher order terms is equivalent to assuming that the potential energy of an ion, due to the field and atmosphere of another ion is small in comparison with its kinetic energy of translation. The overlapping of the ion atmospheres may, under these conditions, be safely neglected. Gronwall, Lamer and Sandved (*loc. cit.*) also confirm the view that there is greater probability of finding an ion in a region where its potential energy is great compared with its kinetic energy, than would have been predicted by the theory of Debye and Hückel. As a result the radius of the ion atmosphere, namely $1/B$ of equation (12),[1] will be reduced, and the properties of the solution so modified that, if compared with the simple theory of Debye and Hückel, the electrolyte will appear to be incompletely dissociated. Kramers (*Proc. K. Akad. Wetensch. Amsterdam*, 1927, **30,** 145) showed that for aqueous solutions of uni-univalent electrolytes the neglect of the higher order terms is permissible, in the deduction of the potential due to the ion atmosphere, for solutions below 0·01N. at

[1] $1/B$ is sometimes termed the radius of the ionic atmosphere, since by equation (12) the potential P_0, due to the ionic atmosphere, acting on an ion is given by $P_0 = \nu\varepsilon B./K$. But the potential at distance r due to charge $\nu\varepsilon$ is, in a medium of dielectric constant K, $P_0 = \nu\varepsilon/Kr$, so that the ionic atmosphere behaves as though it were a sphere of radius $r = 1/B$.

25° C., for solutions in methyl alcohol, which has a lower dielectric constant, the limiting value is $M/600$. This is in agreement with the experimental results.

As regards the third assumption of Debye and Hückel, namely that the solvent between the ions behaves like the pure solvent in bulk, the use of the macroscopic dielectric constant of the solvent has been justified by Debye and Pauling (*J. Amer. Chem. Soc.*, 1925, **47**, 2129) for sufficiently dilute solutions. The effect of stronger solutions of electrolytes on the polarization and dielectric constant of the solvent has been investigated by Hückel (*Physik. Zeit.*, 1926, **26**, 93). He shows that when the solvent is more polarizable than the ions, there arise, in addition to the Coulomb forces, forces of repulsion between the ions, which result in an increase in the activity coefficients, eventually above unity. Moreover, the change in the dielectric constant with the increase in the concentration of the electrolyte makes the self-potential of the ion, which was neglected in the simple theory of Debye and Hückel for very dilute solutions, appear as a significant quantity in the region of more concentrated solutions. Since the dielectric constant decreases with increasing concentration of the electrolyte, it follows from equation (51) that it will tend to increase the activity coefficients. This is in qualitative agreement with experiment. Hückel's equation is as follows:

$$\log \gamma = -\frac{0{\cdot}356\nu_1\nu_2\sqrt{c\nu^2}}{1 + A\sqrt{c\nu^2}} + B\sqrt{c\nu^2} - \log(1 + Rc) \quad . \quad (57)$$

The last term is merely employed to convert $\log f$ to $\log \gamma$, where f is the mean activity of the electrolyte divided by its mole fraction. The important term is the linear one $B\sqrt{c\nu^2}$, where B is a constant. This term was derived from theoretical considerations which involve the change in dielectric constant with change in concentration. It was deduced on the basis of the assumption that the dielectric constant varies linearly with concentration. This equation has been tested by Hückel, *Physik. Zeit.*, 1925, **26**, 93; Scatchard, *J. Amer. Chem. Soc.*, 1925, **47**, 2098; Harned, ib., 1926, **48**, 326; Harned and Åkerlöf, *Physik. Zeit.*, 1926, **27**, 411; Harned and Douglas, *J. Amer. Chem. Soc.*, 1926, **48**, 3095; Lucasse, *Z. phys. Chem.*, 1926, **121**, 254; Harned, *J. Amer. Chem. Soc.*, 1929, **51**, 416.

The following tables show some of the results obtained:

HCl.			*NaCl.*		
c.	γ obs.	γ calc.	*c.*	γ obs.	γ calc.
0·001	0·965	0·966	0·001	0·966	0·965
0·005	0·928	0·929	0·005	0·928	0·928
0·01	0·904	0·905	0·01	0·903	0·903
0·05	0·829	0·831	0·05	0·821	0·819
0·1	0·796	0·795	0·1	0·778	0·775
0·2	0·766	0·766	0·2	0·732	0·729
0·5	0·757	0·757	0·5	0·678	0·678
1·0	0·810	0·811	1·0	0·656	0·658
1·5	0·903	0·896	1·5	0·658	0·662
			2·0	0·670	0·674
			2·5	0·690	0·692
			3·0	0·714	0·715
			3·5	0·749	0·739
			4·0	0·779	0·764

$SrCl_2$.			*NaOH.*		
c.	γ obs.	γ calc.	*c.*	γ obs.	γ calc.
0·01	0·729	0·729	0·0053	0·932	0·925
0·02	0·662	0·664	0·01	0·901	0·901
0·05	0·571	0·575	0·0202	0·862	0·869
0·07	0·540	0·543	0·0526	0·805	0·813
0·1	0·512	0·512	0·1081	0·757	0·764
0·2	0·465	0·463	0·1934	0·732	0·730
0·5	0·427	0·431	0·3975	0·699	0·686
0·7	0·427	0·436	0·807	0·664	0·666
1·0	0·449	0·454	1·020	0·666	0·670
			1·517	0·694	0·695
			2·024	0·728	0·734
			3·1	0·82	0·85

The values of the constants A and B and also of $a \times 10^8$ are given in the following table :

Electrolyte.	*A*.	*B*.	$a \times 10^8$.
HCl	0·940	0·0713	4·05
NaCl	0·840	0·0320	3·62
$SrCl_2$	1·018	0·03	4·39
NaOH	0·66	0·05	2·87

The value of the constant R is 0·018 x where x is the total number of ions into which one molecule of the salt ionizes.

It will be observed that there is quite good agreement between the experimental values of the activity coefficient and those calculated on the basis of equation (57). The maximum deviation in the case of hydrochloric acid, in the concentration range from 0·001 to 1 molal is 0·24 per cent., and in the case of sodium chloride from 0·001 M. to 3 M., it is 0·6 per cent. The calculation in the case of strontium chloride is an average one for a bi-univalent salt, and the experimental values are not so accurate.

Although the linear term, $B\sqrt{cv^2}$, in equation (57) was derived from the assumption of a linear variation of the dielectric constant with the concentration of the solution, the existing data [1] on the dielectric properties of salt solutions show a variation with concentration of quite a different order of magnitude from the ones fitting Hückel's calculations. Thus Gronwall and Lamer (*Science*, 1926, **64**, 122) find that the dielectric constant of solutions of electrolytes begins by increasing from 50 to 100 times more rapidly than Hückel's expression indicates. It soon reaches a minimum value and then starts to increase slowly, until in very concentrated solutions it is considerably larger than the value for pure water. It is probably better, therefore, to regard the linear term in equation (57) as empirical, especially as the dielectric constant is certainly not the only factor to be considered.

Finally, it is necessary to consider the question of the solvation of the ions. This has been discussed from several different points of view and an excellent bibliography and review of the work up to 1922 is given by Fricke (*Zeit. Elektrochem.*, 1922, **28**, 161). The general conclusions are: (*a*) that the hydrogen ion is in all probability definitely associated with one molecule of water, giving the ion H_3O^+. This is based on the evidence of Goldschmidt (*Zeit. phys. Chem.*, 1924, **114**, 1, and earlier papers), Fajans (*Naturwissensch.*, 1921, **9**, 733); Brønsted (*J. Phys. Chem.*, 1926, **30**, 777) and others; (*b*) that as regards the other ions there is considerable evidence for solvation from measurements of transport numbers. Unfortunately transference measurements are incapable of giving us the degree of hydration of individual ions. They only yield the algebraic sum of the effects due to the separate ions.

[1] Walden, Ulich and Werner, *Zeit. phys. Chem.*, 1925, **116**, 261.

and some assumption is necessary in order to calculate the actual hydration numbers. Up to the present no reliable method of obtaining these numbers is available, the values calculated hitherto varying with the experimental method employed and the specific assumption made in the calculation.

Bjerrum in 1920, before the method of Debye and Hückel had been elaborated, attempted to calculate ionic hydration values from activity data in concentrated solutions (*Z. anorg. Chem.*, 1920, **109**, 275). We may proceed as follows: Let us consider the dissociation of a uni-univalent electrolyte AC to be represented by the equilibrium

$$CA \rightleftharpoons C^+ + A^-.$$

The Ostwald dilution law in the thermodynamically correct form is

$$K = \frac{a_+ . a_-}{a_2}$$

where a_+, a_- and a_2 are the activities of the ions C^+, A^- and of the undissociated molecule respectively. As in the preceding chapter, we shall take the value of K to be unity and write

$$a_2 = a_+ . a_-.$$

Let us now assume that the cause of the divergence of strong electrolytes from the simple law of Ostwald in terms of concentrations is due to the hydration of the molecules. We have the following equilibria in the solution of such an electrolyte:

(i) $AC \rightleftharpoons C^+ + A^-$
(ii) $C^+ + h.H_2O \rightleftharpoons C^+ . hH_2O$
(iii) $A^- + j.H_2O \rightleftharpoons A^- . jH_2O$

where $C^+ . hH_2O$ and $A^- . jH_2O$ are the ion hydrates. Denote by a_w, a_h and a_j the activities of the water molecule, and the two ion hydrates respectively. Combining the three equations we obtain for the equilibrium constant K' the relation

$$K' = \frac{a_h . a_j}{a_2 . a_w^{(h+j)}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (58)$$

If as before we equate K' to unity we obtain the equation

$$a_2 = a_+ . a_- = \frac{a_h . a_j}{a_w^{(h+j)}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (59)$$

Bjerrum assumed complete dissociation of the electrolyte and calculated his activities from electromotive force data. Taking logarithms of (59) we obtain

$$\log a_+ . a_- = \log a_h . a_j - (h + j) . \log a_w \quad . \quad . \quad . \quad (60)$$

Substituting activity coefficients

$$\log \gamma c = \log \gamma' c - \frac{h + j}{2} \log a_w \quad . \quad . \quad . \quad . \quad (61)$$

where γ' is the square root of the activity coefficient product of the hydrated ions. Now the activity of the water a_w is equal to p/p_0 the ratio of the vapour pressures, so that equation (61) becomes

$$\log \gamma = \log \gamma' - \frac{h + j}{2} \log \frac{p}{p_0} \quad . \quad . \quad . \quad . \quad (62)$$

In very dilute solutions the second term of the right-hand side becomes negligible since p/p_0 approaches unity. Hence in dilute solutions we have

$$\log \gamma = \log \gamma' = - \frac{\beta(m + 1)}{2{\cdot}303 . nkm} \quad . \quad . \quad . \quad (63)$$

by equation IX (71). This equation was employed by Bjerrum to calculate the activity coefficients of various electrolytes when suitable values of $(h + j)$ are substituted. The following table gives some of the results obtained for the halides:

c	*HCl.*		*KCl.*		*NaCl.*		*LiCl.*	
	$(h + j) = 11$		$(h + j) = 4.$		$(h + j) = 6.$		$(h + j) = 12.$	
	γ Obs.	γ Calc.	γ Obs.	γ Calc.	γ Obs.	γ Calc.	γ Obs.	γ Calc.
0·01	0·924	0·924	0·903	0·898	0·906	0·906	0·922	0·920
0·05	0·860	0·857	0·816	0·821	0·834	0·833	0·843	0·849
0·1	0·814	0·825	0·779	0·775	0·792	0·791	0·804	0·812
0·5	0·762	0·767	0·659	0·654	0·682	0·682	0·754	0·738
1·0	0·823	0·823	0·613	0·592	0·652	0·652	0·776	0·784
2·0	1·032	(1·186)	0·566	0·559	0·672	0·679	0·936	(1·14)
3·0	1·35	(2·15)	0·575	0·567	0·722	(0·781)	1·20	(2·13)

The agreement between the observed and calculated values is very good as far as 1 *M.* for lithium chloride and hydrochloric acid and as far as 2 molal for sodium chloride and 3 *M.* for potassium chloride. It is evident that the theory gives the trend in the activity coefficients, i.e. first a decrease to a minimum value followed by an increase to values above unity. Further applications of this theory are to be found in the papers of Schreiner, *Z. anorg. Chem.*, 1921, **115**, 181; 1921, **116**, 102; 1922, **121**, 321. This theory is consequently of considerable interest, although little importance can be attached to the actual hydration values employed, and it probably gives us a qualitative account of the reasons for the trend in the activity coefficients in the region of concentrated solutions.

This method assumes hydrates of definite composition, i.e. probably chemical compounds. It is not, however, necessary to assume that the valencies actually play a part in the hydration. When a salt dissolves in water, the volume of the solution is normally less than the sum of the volumes of the water plus the salt, and the diminution in volume is greater, for a given amount of salt, the more dilute the solution. This contraction on solution is known as **electrostriction.** It is attributed primarily to a contraction of the water owing to the attractions of the water dipoles by the ions.

Webb (*J. Amer. Chem. Soc.*, 1926, **48**, 2589) obtained an expression for the free energy change accompanying the hydration of a chemically unhydrated ion, as a function of its radius, by calculating the difference in energy necessary to charge the ion in a vacuum, and that necessary to charge the ion in water and to compress the solvent in the vicinity of the ions. He took account of the fact that the dielectric constant of a molecular medium is not constant in the neighbourhood of the ions. He also calculated the partial molal volume of an ion at great dilution, as a function of its effective radius in solution, allowing a correction for the electrostriction effect. The solution of the two resulting equations, which may be obtained in the case of an electrolyte for which the free energy change of hydration and the partial molal volume are known, gave the radii of the individual ions, and hence the free energy change accompanying the hydration of those ions. His values are given in the following table:

Ion . . .	*Na*	*K*	*Rb*	*Cs*	*F*	*Cl*	*Br*
Radius . .	1·505	1·873	2·02	2·19	1·75	2·238	2·382
ΔF . . .	99	81·9	76·9	71·5	87·0	70·1	66·2
Ion . . .	*I*	*H*	*Ag*	*Tl*	*Zn*	*Cd*	*Hg*
Radius . .	2·60	< 0·5	1·57	1·96	1·04	1·15	1·11
ΔF . . .	61·0	249·6	95·5	78·6	525	473	486

The radii are given in Ångstrom units (1 Å. = 10^{-8} cms.) and the free energy changes in kilogram-calories per mole.

It is interesting to note that the values obtained for the ionic radii follow the same order as those given by Bragg (*Proc. Roy. Inst. Gt. Brit.*, III, 1925, **24**, No. 119, 614) and by Wasantjerna (*Soc. Scient. Fenn. Comm. Math.-Phys.*, 1923, **1**, 38) for the radii of ions in crystals; moreover, the difference is roughly constant, the effective radii of the ions in solution being about 0·47 Å. greater than those of Bragg for radii in crystals. If these values for the ionic radii are approximately correct it is evident that the mean free paths of the ions must be extremely small. Webb concludes that the values of the free energy change accompanying hydration are sufficiently accounted for by the electrical effects, in all cases except that of hydrogen. Consequently he considers that the hydration of ions other than the hydrogen ion is probably physical and not chemical.

We have already mentioned that as a general rule a considerable shrinkage in volume, known as the electrostrictive effect, accompanies the solution of an electrolyte. This is not always the case, however, since the volume of a solution of lithium iodide is actually greater than the sum of the volumes of the salt plus the water. Baxter and Wallace (*J. Amer. Chem. Soc.*, 1910, **38**, 70) showed that the water volume in concentrated halide solutions of a given molality manifest the following order:

$$V_{LiI} > V_{LiBr} > V_{LiCl} > V_{NaI} > V_{NaBr} > V_{NaCl} > V_{KI} > V_{KBr} > V_{KCl}$$

This is exactly the order of the activity coefficients of the solutions of these electrolytes at the given molality. Moreover, it is exactly the order obtained for the dissociation of water itself, into H^+

and OH' ions, in the presence of these salts at the given concentration.

This markedly parallel behaviour is extremely significant and seems to indicate that the influence of the solvent is of fundamental importance in interpreting the trend of the activity coefficients in strong solutions of electrolytes. The limiting theory of Debye and Hückel, which only takes account of the inter-ionic attraction, leads to the view that the activity coefficient of all electrolytes decreases continuously with increasing concentration. Qualitatively the influence of hydration is an increase in the size of the ions, together with an increase in the effective concentration of the ions owing to the removal of the water. Both these effects are in the direction of an increase of the activity coefficient. They are represented to some extent by the constant A in Hückel's equation (equation (57)). Harned and Douglas (*J. Amer. Chem. Soc.*, 1926, **48**, 3095) also consider that polarization occurs by the deformation of the solvent molecules, owing to the electrical field of the ions. This will have the effect of reducing the attractive forces between the ions, i.e. it will act in opposition to the effect considered in the simple theory of Debye and Hückel, with the consequent increase of the activity coefficient. This theory is in accord with the observed order of the electrostrictive effects, mentioned above. Lithium iodide, which causes an expansion in the water molecules, causes the greatest dissociation of these molecules and also possesses the highest activity coefficient. Moreover, this theory does not necessarily conflict with the equation of Hückel, where the linear term $B\sqrt{cv^2}$ is introduced to allow for the change in the dielectric constant of the medium with concentration. Harned suggests that it is probably this polarizing influence of the ions of the electrolyte on the solvent molecules which causes the change in the macroscopic dielectric constant of the medium.

Calculation of Conductivity of Solutions. Debye and Hückel have further applied their theory to the calculation of the conductivity of strong electrolytes. The problem presents greater difficulties than the calculations of activity, osmotic pressure, etc., since we are dealing, in conductivity measurements, with ions in motion.

The kernel of the theory of Debye and Hückel is contained, as

we have seen, in the fact that there are, on an average, surrounding any given ion in a solution, more ions of unlike than of like sign. These neighbouring ions have been referred to as the **ionic atmosphere.** Now let us consider the effect of an applied electromotive force, resulting in the passage of a current of electricity through the solution. In an infinitely dilute solution the ions attain a velocity which is just balanced by the mechanical resistance of the liquid medium. When, however, the solution is more concentrated, inter-ionic forces come into operation and tend to modify the velocity of the ions.

The effects of the inter-ionic attraction are twofold, and both act in such a direction as to oppose the motion of the ions and hence to decrease their velocity. The first effect arises as follows: As an ion moves, it tends to cause the formation of an ion atmosphere around it. The result is that an atmosphere is continually forming in front of the ion and dying away behind it. Now the ion atmosphere is of opposite sign to the moving ion, so that if this process of formation and disappearance does not occur instantaneously, the ion will be continually moving away from that portion of the atmosphere which has the greatest density of charge. This dissymmetry of the ion atmosphere will therefore result in a retardation of the ion. Debye and Hückel have shown that there is, in fact, an appreciable time required for this creation and dispersal of the ion atmosphere, and this time interval is known as the **period of relaxation** and denoted by τ. To a first approximation the radius of the ionic atmosphere $1/B$ is doubled during the time of relaxation, which for an electrolyte like potassium chloride with ions of equal mobility is given by the expression

$$\tau = \frac{\rho}{B^2.kT} \text{ seconds} \quad . \quad . \quad . \quad . \quad . \quad . \quad (64)$$

where k is the gas-content per molecule and ρ is the frictional constant of the ion, defined as the force opposing an ion moving with unit velocity, and is given by $\rho = (1{\cdot}5 \times 10^{-7})/l_0$, where l_0 is the mobility of the ion. For a potassium chloride solution in water at 25° C. containing c moles per litre, this gives

$$\tau = 0{\cdot}55 \times 10^{-10}/c \text{ seconds.}$$

It is evident that an increase in the ionic velocity produces an increased dissymmetry in the ionic atmosphere, with the consequent reduction in the field intensity, which we may call the dissymmetry

term, and this varies directly with the velocity, for small velocities. The actual dissymmetry is small; for example in an external field of 1 volt per centimetre, a potassium ion in a 0·001 *N.* solution will move approximately through 7/100,000 of the radius of its ionic atmosphere during its period of relaxation, but even the slight dissymmetry thus produced is sufficient to cause an appreciable retardation of the ion owing to the relatively enormous size of the electronic charge.

According to Debye and Hückel, the retarding effect upon the ion due to the time of relaxation is given by

$$\text{Retarding Effect} = \frac{\varepsilon^2.Z.v}{6.K.kT}\sqrt{\frac{8\pi N\nu^2.c}{K.kT}}$$

where v is the velocity of the ion under the E.M.F., c is the concentration in moles per cubic centimetre, Z is a resistance factor equal to f/v, i.e. to the resultant force upon the ion divided by the steady velocity. The other letters have their usual significance.

The second effect of the ion atmosphere upon the ionic mobility is due to the increased viscous resistance caused by the movement of the ions of the atmosphere in the opposite direction to the central ion. Since the ions are assumed to carry a certain amount of solvent with them, the viscous resistance to ionic motion is greater than if the solvent were at rest. Debye and Hückel assumed the validity of Stokes' law and obtained an expression for the additional frictional force due to the ionic atmosphere, which like the dissymmetry term varies inversely as the radius of the ionic atmosphere and so is proportional to the square root of the concentration c. Debye and Hückel call this term the electrophoretic term owing to the similarity between this phenomenon and that of electrophoresis or the migration of colloid particles in an electric field as a result of their charge.

After correcting for both these effects the resulting equation of Debye and Hückel was of the form

$$\frac{\Lambda_\infty - \Lambda c}{\Lambda_\infty} = \left\{A.\left(\frac{l'}{\bar{l}} + \frac{l'}{\bar{l}}\right) + \beta b\right\}\sqrt{c} \quad . \quad . \quad . \quad (65)$$

where Λ_c is the equivalent conductivity at concentration c, Λ_∞ is the equivalent conductivity at infinite dilution, l', l' are the mobilities of the cation and anion respectively at infinite dilution, A and β are constants which can be evaluated for any specific

solvent and b is the mean radius of the ion. The first term represents the effect of the period of relaxation, the second term the electrophoretic effect.

This equation reduces to the form

$$\Lambda_c = \Lambda_\infty - x\sqrt{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad (66)$$

which is identical with the empirical equation used by Kohlrausch for the conductivities of dilute aqueous solutions of electrolytes. Comparison with experimental results shows that the coefficient of $\sqrt{c}$ in equation (66) is of the right order of magnitude if a value is assumed for the ionic radius of 10^{-8} cm. in accordance with X-ray data. But if the value of b is calculated from the ionic mobilities at infinite dilution, assuming Stokes' law to hold, the observed and calculated values of the coefficient are not in exact agreement; e.g. for potassium chloride solutions in water at 25° C. they are 0·461 and 0·547 respectively.

Onsager (*Physikal. Zeit.*, 1926, **27**, 388; 1927, **28**, 277; *Trans. Farad. Soc.*, 1927, **23**, 341) has recently made some important modifications of the Debye and Hückel theory as applied to conductivity. He pointed out that these authors, in calculating the retardation due to the dissymmetry of the ionic atmosphere, had considered an ion moving with a constant velocity in the solution and had neglected the Brownian movement. He therefore recalculated the retardation due to this effect and introduced the necessary correction. He also shows that the electrophoretic effect may be calculated without the aid of Stokes' law, a relationship which cannot strictly be applied to particles of ionic dimensions. Onsager's equation is therefore independent of the magnitide of the ionic radius.

The limiting formula of Onsager, which only applies to dilute solutions, is, in the case of a binary electrolyte having two ions of equal valence ν,

$$\Lambda_c = \Lambda_\infty - \left(\frac{5{\cdot}78 \times 10^5}{(KT)^{3/2}}\nu^2.\Lambda_\infty + \frac{58{\cdot}0\nu}{(KT)^{\frac{1}{2}}\eta}\right)\sqrt{2\nu c} \quad . \quad (67)$$

This equation contains no terms which cannot be evaluated so that the theory can be directly tested by comparing the calculated with the experimental values of the conductivity of any strong electrolyte in any solvent at any temperature. This relation is evidently also in agreement with the empirical equation of Kohl-

rausch mentioned above. For uni-univalent electrolytes in water at 18° C. Onsager's equation becomes:

$$\Lambda_c = \Lambda_\infty - (0{\cdot}224\Lambda_\infty + 50{\cdot}5)\sqrt{c} \quad . \quad . \quad . \quad (68)$$

The equation of Onsager has been tested for water and for a number of organic solvents. For a summary of this work and references to the literature, see *Annual Reports of the Chemical Society* (1930, p. 335). The results of these measurements show that for uni-univalent salts in each of the solvents the relation between Λ_c and $\sqrt{c}$ is linear, as is predicted by the theory. The following table gives the percentage deviation from Onsager's equation in the case of these solvents. With the exception of water, for which the measurements are at 18° C., the temperature is 25° C. The percentage deviation is naturally

$$100\left(\frac{x \text{ obs.} - x \text{ calc.}}{x \text{ calc.}}\right)$$

where x is the constant in the corrected form of equation (66).

	Water.	*MeOH.*	*EtOH.*	CH_3NO_2.	CH_3CN.	Acetone.
$\eta_{25°}$	0·01056	0·00545	0·01080	0·00627	—	0·00308
$K_{25°}$. . . .	81·3	30·3	25	37	36	21
LiCNS . . .	17 [1]	− 1	18	weak	—	(960)
NaCNS . .	3 [1]	− 2	24	weak	—	250
KCNS . . .	6 [1]	0	37	188	—	122
RbCNS . . .	—	0	54	—	—	122
CsCNS . . .	− 6 [1]	10	78	—	—	124
LiI	—	—	10	300	—	96
KI	− 8·8	− 10	38	73	17	58
$LiClO_4$ . . .	− 12	− 2	10	430	—	54
$NaClO_4$ . . .	15 [2]	8	52	175	—	73
LiPicrate . .	− 32	—	16	—	410	270
NaPicrate . .	—	3	104	—	106	190
$AgNO_3$ . . .	15	70	130	—	84	weak
NEt_4.*Pic*. . .	− 10	17	75	− 1·5	6	34
NEt_4I . . .	—	33	102	2	5·7	98
NEt_4ClO_4 . .	—	40	164	9	24	68

[1] These values refer to the chlorides, not to the thiocyanates, as no accurate measurements of the latter have been made in water.

[2] This value is for potassium perchlorate.

It will be seen that in each of the first five solvents there are some salts which show close agreement with theory, and it is

significant that, with few exceptions, any large deviation from ideal behaviour is in the direction that can be explained by ionic association, namely that $x_{obs.}$ is greater than $x_{calc.}$ The body of evidence appears to be sufficient to justify the use of the Debye-Hückel-Onsager equation as a working hypothesis to represent the behaviour of an ideal electrolyte, and we have therefore a new means of investigating the degree of association of electrolytes in the dilute range where the theory can be applied with safety.

The results given in the above table show that there is a marked difference between the first three solvents which contain a hydroxyl group and the last three which have no such group. The hydroxylated solvents favour complete ionization of the electrolyte while tending to suppress the individual characteristics of the salt. Ulich (*Zeit. angew. Chem.*, 1928, **41**, 443, 467, 1075, 1141) refers to this effect as " nivellierend " or levelling. With the non-hydroxylic solvents the case is just the reverse, the solutions are usually weak electrolytes and the chemical characteristics predominate. This effect cannot be ascribed to the dielectric constant, since methyl alcohol has a lower constant than nitromethane, nitrobenzene, or acetonitrile, in which three solvents uni-univalent salts may act as weak electrolytes.

Another difference between the two classes of solvents is that in the alcohols the tendency to association in any series of salts with the same anion increases with the atomic number of the cation, while in the non-hydroxylic solvents the association increases in the order $K^{\cdot} < Na^{\cdot} < Li^{\cdot\cdot}$ (with the possible exception of the perchlorates in acetone), and the lithium salt is often a weak electrolyte when the potassium salt is highly ionized. The relative tendencies of the anions to promote ionic association are not quite so marked, but are in the order

$$(ClO_4', \ Pic', \ I') < (Br', \ NO_3') < (Cl', \ CNS')$$

although there are varieties from this scheme.

In the alcohols, the tetra-substituted ammonium salts show the maximum deviation from the theoretical slope of the conducitvity curve, while in the non-hydroxylic solvents they give results which agree most closely with the theory. There seems to be a general tendency for the association to increase as the dielectric constant decreases, for a given type of solvent, but this is not always true.

According to the Debye-Hückel-Onsager theory, the influence of

the solvent upon the conductivity is that due to its dielectric constant and also to the effect of the viscosity upon the ionic mobility. In addition to these effects, however, we must also take into consideration the solvation of the ions. This causes an increase in the size of the ions owing to the associated solvent, with the result that they can no longer approach one another so closely as if no solvation occurred. The net result is a decrease in the tendency of the ions to associate or recombine. This would seem to explain, in part at least, the difference between the hydroxylic compounds and those which do not contain a hydroxyl group. The former are incapable of forming a chemical linkage with the anion so that association readily occurs and the resulting electrolyte is weak. On the other hand, water and alcohols are capable of forming solvates of both ions so that the tendency to associate is weak and the electrolyte is almost completely dissociated. This question has been considered by Bjerrum (*Kgl. Danske. Videnskabs. Selsk. Math.-fys. Medd.*, 1926, **7**, (9), 1).

CHAPTER XI

CHEMICAL AFFINITY

The problem of Chemical Affinity is one which has attracted attention from very early times, but the first attempts at a systematic treatment were made by J. R. Glauber (1648) and Robert Boyle (1664), who proposed to arrange chemically related substances in series according to their power of displacing one another from chemical combination. The first of these "Affinity Tables" were compiled by St. F. Geoffroy (1718) and G. E. Stahl (1720) and these were later extended by T. Bergmann (1775), G. de Morveau (1781), T. Kirwan (1790) and others. Anomalies soon began to arise, however, and it became evident that other factors besides the actual nature of the reacting substances must be taken into consideration. Of these factors, the influence of mass seems to have been appreciated to some extent by Bergmann, for he states that "in order to displace *B* from its combination with *A*, it is frequently necessary to employ two, three or maybe six times the amount of *C* actually required to saturate *A*." He does not, however, appear to have realized the full significance of these observations.

The need for finding some method of measuring affinity quantitatively very soon became apparent, and the first attempt in this direction was made by Wenzel (1777). The magnitude of a mechanical force is measured by its action upon the motion of a particle. Hence Wenzel proposed to determine the magnitude of the mysterious force, known as chemical affinity, by determining the velocity of the chemical reaction occurring between the substances under consideration. He was thus led to undertake an investigation into the rates of solution of a number of metals in acids, and he came to the important conclusion that "chemical action is proportional to the amount of substance taking part in the reaction."

There are several objections, however, to regarding the rate of reaction as a true measure of chemical affinity. Thus, for instance,

we know that the speed of a chemical reaction may be influenced, to a remarkable degree, by the presence or absence of certain substances, known as catalysts, which do not themselves take any ultimate part in the reaction. It is therefore evident that we can hardly regard the reaction velocity as even an approximate measure of the affinity.

A second suggestion, at first sight a more plausible one, was put forward by Thomsen in 1854 and supported by Berthelot (1867). This was that the heat evolved in the course of a chemical reaction is a measure of the affinity of the reactants. It will be seen later that, in some cases, the heat of reaction is very nearly equal to the affinity, but there is one very obvious objection to our employing this principle of Thomsen and Berthelot, namely that some reactions are known which occur with **absorption** of heat. Thus, for instance, when ammonium nitrate is dissolved in water, or ice is added to salt, the temperature of the system falls, showing that heat has been absorbed. Moreover, Berthelot's principle would preclude the possibility of a balanced reaction, since, if heat is evolved in one direction, the reverse direction must involve an absorption of heat. But, as is well known, many balanced reactions exist, and, in fact, it is useful to regard all reactions as balanced theoretically, even where they appear to proceed to completion. Hence the Berthelot principle must be rejected as a reliable method of measuring the affinity.

Our study of thermodynamics has, however, given us the clue to the factor which will best serve as a true measure of the affinity, namely the free energy decrease which occurs during the reaction. A reaction takes place in a given system when that system is capable of a decrease in the free energy and the further the system is originally from the equilibrium state, the greater is this free energy decrease. The first successful solution of the problem is due to Helmholtz (*Sitzerungber. der Akad. der Wiss. Berlin*, 1882), but he did not pursue it. It was really rediscovered by van't Hoff in 1883.

It is therefore necessary to set about measuring the free energy change accompanying various reactions and this will give us a measure of the affinity of the reacting substances under the conditions of the experiment. We propose in this chapter to give a few examples of the determination of these magnitudes.

We shall consider, first of all, a homogeneous gaseous re-

action, as, for example, the reaction between hydrogen and iodine—

$$H_2 + I_2 \rightarrow 2HI.$$

It is required to determine the affinity of hydrogen for iodine per mole of each constituent. That is, we require the free energy decrease accompanying the reaction as it is expressed above. Now, by equation VI (5) we have

$$-\Delta F = RT \ln K_c - RT\Sigma n \ln C \quad . \quad . \quad . \quad (1)$$

Hence if we have hydrogen and iodine at arbitrary chosen concentrations reacting to give hydrogen iodide at some other known concentration, it is only necessary to know the equilibrium constant at the given temperature and to substitute these values in equation (1) to obtain the affinity per mole of hydrogen. If the initial concentrations of iodine and hydrogen and the final concentration of hydrogen iodide are all unity, equation (1) takes the simplified form

$$-\Delta F = RT \ln K_c. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Hence the affinity may be determined if we know the equilibrium constant of the reaction. Bodenstein (*Zeit. phys. Chem.*, 1897, **22**, 1) has investigated this reaction very thoroughly. From his results values of K may be calculated. For one mole of hydrogen and of iodine the constant has the form

$$K_c = \frac{C^2_{HI}}{C_{H_2} \times C_{I_2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

At 300° C. the value of K is found to be 80, so that ($T = 573°$ Abs.).

$$\text{Affinity} = -\Delta F = RT \ln K$$
$$= \frac{2 \times 573}{0{\cdot}4343} \log 80$$
$$= +5{,}000 \text{ calories.}$$

At 500° C. (773° Abs.) $K = 41$, approximately, so that

$$\text{Affinity} = -\Delta F = \frac{2 \times 773}{0{\cdot}4343} \log 80$$
$$= +5{,}760 \text{ calories.}$$

The heat evolved in this reaction is + 2,800 calories, which is considerably less than the affinity. This is an example of the failure of the Thomsen-Berthelot principle.

In a similar manner we may calculate the free energy decrease or affinity of the reactants in the formation of water vapour from

its dissociation constant at high temperatures. The following are some of the results obtained by Nernst and von Wartenberg (Set I), *Nacht. Kgl. Ges. Wiss. Göttingen*, 1905, p. 35; Löwenstein (Set II), *Zeit. phys. Chem.*, 1905, **54**, 715; von Wartenberg (Set III), *Zeit. phys. Chem.*, 1906, **56**, 715; Langmuir (Set IV), *J. Amer. Chem. Soc.*, 1906, **28**, 1357. The second column gives the temperature in degrees absolute, the third column gives the percentage dissociation. Column 4 gives the equilibrium constant calculated from the relation

$$K_p = \frac{(H_2O)}{(H_2).(O_2)^{\frac{1}{2}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where the brackets indicate partial pressures.

Column 5 gives the values of the affinity per mole of water formed, i.e. the free energy decrease when 1 mole of hydrogen at 1 atmosphere pressure reacts with $\frac{1}{2}$ mole of oxygen at 1 atmosphere pressure to give 1 mole of water vapour at 1 atmosphere pressure. This quantity is evidently given by the relation

$$-\Delta F = RT \ln K_p = \frac{2 \times T}{0{\cdot}4343} \log K_p$$

DISSOCIATION OF WATER VAPOUR

Set.	Temp.	Percentage Dissociation.	K_p.	$-\Delta F$.	Observer.
I .	1397	0·0078	$2{\cdot}05 \times 10^6$	+ 40610	Nernst and von Wartenberg.
	1480	0·0184	$5{\cdot}66 \times 10^5$	+ 39200	
	1561	0·0340	$2{\cdot}26 \times 10^5$	+ 38490	
II .	1705	0·0326	$2{\cdot}3 \times 10^4$	+ 34240	Löwenstein.
	1783	0·0778	$1{\cdot}82 \times 10^4$	+ 34970	
	1863	0·211	$6{\cdot}70 \times 10^3$	+ 33590	
	1968	0·373	$3{\cdot}79 \times 10^3$	+ 32445	
III .	2155	1·18	$1{\cdot}094 \times 10^3$	+ 30150	von Wartenberg.
	2257	1·77	$0{\cdot}590 \times 10^3$	+ 28805	
IV .	1325	0·00325	$7{\cdot}65 \times 10^6$	+ 42010	Langmuir.
	1354	0·0049	$4{\cdot}13 \times 10^6$	+ 41340	
	1393	0·0069	$2{\cdot}47 \times 10^6$	+ 41010	
	1433	0·0103	$1{\cdot}35 \times 10^6$	+ 40440	
	1455	0·0142	$8{\cdot}35 \times 10^5$	+ 39670	
	1474	0·0141	$8{\cdot}45 \times 10^5$	+ 40230	
	1531	0·0255	$3{\cdot}47 \times 10^5$	+ 39055	
	1550	0·0287	$2{\cdot}91 \times 10^5$	+ 38910	

It will be observed that the free energy decrease is greater the lower the temperature.

This method of determining the affinity or free energy decrease accompanying a reaction from a knowledge of the equilibrium constant may evidently be employed also in the case of reactions in solutions.

Thus we may calculate the affinity of the ions of, say, a weak acid from a knowledge of the dissociation constant.

When we come to deal with solids, we may, in the first instance, regard the reaction as occurring in the vapour state, and determine the affinity or free energy decrease in that state from the equilibrium constant. It is better, when this is done, to place the suffix (*g*) after the formula for the solid substance, to show that we are considering only the vapour state.

A case of great interest is that investigated by Schottky (*Zeit. phys. Chem.*, 1908, **64**, 422) namely, the affinity of ice for various salts, anhydrous and hydrated. We may regard the problem as follows: We imagine one mole of water vapour to be vaporized from ice at equilibrium pressure and transferred to the salt, by the three-stage distillation process. The free energy decrease is evidently, if we assume the gas laws for the vapour

$$-\Delta F = RT \ln p_0/p_1$$

where p_0 is the pressure of water vapour in contact with ice, p_1 is the pressure of water vapour in contact with the salt under consideration; p_1 is also the dissociation pressure of the product formed. Thus in the case of the affinity of ice for $CuSO_4.3H_2O$, p_1 is the equilibrium vapour pressure of the trihydrate and also the dissociation pressure of the pentahydrate. It is therefore only necessary to make a series of vapour pressure measurements in order to calculate the affinity of ice for the trihydrate. In this case we are evidently determining the decrease in free energy in passing from solid ice under its own vapour and solid trihydrate under its equilibrium vapour pressure, to the pentahydrate under its dissociation pressure p_1.

The following table gives Schottky's values for the free energy decrease or affinity of the reaction, together with the values of $-\Delta H$ the heat evolved during the reaction. These latter values are obtained from Thomsen's values by subtracting 1,440 calories, the latent heat of fusion per mole at 0° C. The last column gives

the difference between the free energy decrease and the heat evolved, thus showing the divergence from the Thomsen-Berthelot principle.

Reaction.			$-\Delta H$.		$-\Delta F$.		$-\Delta H - (-\Delta F)$
$CuSO_4.3H_2O$	+	$2H_2O$	1190		840		+ 350
$ZnSO_4.H_2O$	+	$5H_2O$	554		480		+ 74
$MnSO_4.H_2O$	+	$4H_2O$	336		359		− 23
$FeSO_4.6H_2O$	+	H_2O	200		275		− 75
$Na_2S_2O_3$	+	$5H_2O$	1056		962		+ 94
$NaBr$	+	$2H_2O$	656		585		+ 71
$BaCl_2$	+	H_2O	2010		1410		+ 160
$SrCl_2.2H_2O$	+	$4H_2O$	790		753		+ 37
$Na.Ac.$	+	$3H_2O$	1284		907		+ 377
$Na_2HPO_4 2H_2O$	+	$5H_2O$	640		424		+ 216
$Na_2HPO_4 7H_2O$	+	$5H_2O$	640		280		+ 360
$CuSO_4.H_2O$	+	$2H_2O$	1645		1045		+ 600
Na_2HPO_4	+	$2H_2O$	1410		860		+ 550
$(COOH)_2$	+	$2H_2O$	1560		810		+ 750
$BaCl_2.H_2O$	+	H_2O	2230		1060		+ 1170
$ZnSO_4.6H_2O$	+	H_2O	1810		450		+ 1360
$MgSO_4.6H_2O$	+	H_2O	2060		590		+ 1470
$SrCl_2.$	+	$2H_2O$	2930		1430		+ 1500
$CuSO_4$	+	H_2O	4860		2350		+ 2510
$MnSO_4$	+	H_2O	3990	>	1130	Difficult to measure owing to small p.	< 2860
$ZnSO_4$	+	H_2O	6880		2350		+ 4530

It is evident that there is a marked difference between the heat evolved during the reaction and the free energy decrease accompanying it. The values given above are not all very accurate, however, owing to the difficulty of measuring the small vapour pressures exerted by some of the hydrates.

We now propose to determine, as an example of a very general and useful method, the affinity of oxygen for iron at 1,000° Abs. at atmospheric pressure. The reaction considered is

$$Fe\ (s) + \tfrac{1}{2}O_2 = FeO\ (s)$$

the suffix s indicating that the iron and the ferric oxide are in the solid state. We shall, however, confine ourselves, for the present, to the same reaction in the vapour phase

$$Fe\ (g). + \tfrac{1}{2}O_2 = FeO\ (g).$$

It is evident that if we could measure the dissociation pressure of

the oxide, we should have a direct method of measuring the affinity, for

$$-\Delta F = RT\ ln\ K_p - RT\Sigma n\ ln\ p$$
$$= RT\ ln\ \frac{(FeO)}{(Fe).(O_2)^{\frac{1}{2}}} - RT\ ln\ \frac{(FeO)}{(Fe).(1)}$$

where the factors in brackets indicate partial pressures of the vapours. The value of the oxygen pressure in the second term is unity. Hence we have,

$$-\Delta F = RT\ ln\ 1/p_{O_2}.$$

This, however, is not possible in practice. We have to employ a less direct method of determining the affinity.

Let us consider the reaction

$$FeO(g) + C(g) = Fe(g) + CO.$$

The affinity of this reaction is evidently

$$-\Delta F_1 = RT\ ln\ p$$

where p is the equilibrium pressure of the carbon monoxide. The following results are given for p by Schenk, Semiller, and Falcke (*Ber.*, 1907, **40**, 1708).

$T°$ K.	p.	$log\ p$.
829	73·2 mm.	1·866
869	164·2 ,,	2·215
939	386·0 ,,	2·566

Extrapolating to 1,000° K. we obtain the value of p, 810 mm. = 1·06 atmospheres. Hence we obtain, for the free energy decrease under 1 atmosphere pressure,

$$-\Delta F_1 = + RT\ ln\ 1{\cdot}06$$
$$= + 1{\cdot}98 \times 2{\cdot}303 \times 1{,}000 \times 0{\cdot}0253$$
$$= + 114 \text{ calories.}$$

We shall next turn our attention to the dissociation of carbon dioxide at 1,000° K. From the data given by Nernst, *Lehrbuch*, 5 Aufl., p. 680, we obtain the percentage dissociation to be $1{\cdot}58 \times 10^{-7}$. The reaction is $CO_2 = CO + \frac{1}{2}O_2$ and the affinity under 1 atmosphere pressure is therefore

$$-\Delta F_2 = \frac{p_{CO} \times (p_{O_2})^{\frac{1}{2}}}{p_{CO_2}}.$$

Putting $p_{CO} = p_{O_2} = 1{\cdot}58 \times 10^{-7}$; $p_{CO_2} = 1$ atmosphere we obtain

$$-\Delta F_2 = -1{\cdot}98 \times 2{\cdot}303 \times 1{,}000 \times log\,(1{\cdot}58 \times 10^{-7})^{3/2}$$
$$= -47{,}200 \text{ calories.}$$

Boudouard gives the equilibrium conditions for the reaction

$$2CO = C + CO_2$$

at 1,000° K. and 1 atmosphere pressure as 67 per cent. by volume of carbon monoxide, 33 per cent. carbon dioxide. Hence the affinity of the reaction is given by the relation

$$-\Delta F_3 = RT\ ln\ p_{CO_2}/p_{CO}^2 = RT\ ln\ \frac{0{\cdot}33}{(0{\cdot}67)^2}$$
$$= -1{\cdot}98 \times 2{\cdot}303 \times 1{,}000 \times 0{\cdot}134$$
$$= -610 \text{ calories.}$$

Now by adding these last two quantities with the direction and therefore the sign reversed, we obtain the free energy change of the reaction $(-\Delta F_4)$

$$CO + \tfrac{1}{2}O_2 + C + CO_2 = CO_2 + 2CO$$

i.e.

$$C + \tfrac{1}{2}O_2 = CO,$$

$$-\Delta F_4 = \Delta F_2 + \Delta F_3$$

that is

$$-\Delta F_4 = 47{,}200 + 610 = 47{,}810 \text{ calories.}$$

If, now, we subtract reaction (1) from reaction (4) we obtain the desired reaction

$$Fe + \tfrac{1}{2}O_2 = FeO\ ;\ (-\Delta F)$$

and

$$-\Delta F_4 - (-\Delta F_1) = -\Delta F$$

i.e.

$$-\Delta F = +47{,}810 - 114$$
$$= +47{,}696 \text{ calories.}$$

Thus we see that the free energy decrease accompanying the reaction represented by the following equation

$$Fe\,(g) + \tfrac{1}{2}O_2 = FeO\,(g)$$

regarded as occurring entirely in the vapour state at 1,000° K. and an oxygen pressure of 1 atmosphere is + 47,696 calories. But throughout the reaction the pressures of the vapours of iron and ferrous oxide are the equilibrium vapour pressures at 1,000° K. The effect of the oxygen pressure may be neglected. Now the free energy change occurring when a substance is vaporized at

the equilibrium vapour pressure is evidently zero, so that we have actually determined the affinity of the reaction

$$Fe\,(s) + \tfrac{1}{2}O_2 = FeO\,(s).$$

That is, by applying the van't Hoff isotherm to the reaction in the condensed state we may calculate the affinity of the complete reaction.

The heat of reaction determined by Le Chatelier for this reaction is 64,950 calories which is evidently considerably greater than the affinity or free energy decrease. This is thus another instance of the complete breakdown of the Thomsen-Berthelot principle.

Another method of determining the affinity of oxygen for iron consists in employing hydrogen as the reducing agent in lieu of carbon. These methods have a very wide application, since the free energy is an extensive property of the system, so that free energy changes are additive.

Electrical Method of Measuring Affinity. We have already seen that one of the simplest and most direct methods of determining the free energy change which accompanies a reaction is by means of an electric cell. If E is the electromotive force of the cell then the free energy decrease $-\Delta F$ is given by

$$-\Delta F = nQ.E$$

where Q is the charge on the ion, and n is the valency of the ion with respect to which the cell considered is reversible. As an example, we may consider the Daniell cell. The reaction is apparently

$$Zn + CuSO_4 = Cu + ZnSO_4.$$

But this is not the actual reaction which occurs in the cell, since both the copper and zinc sulphates may be assumed to be completely ionized, so that the net reaction of the cell is

$$Zn\,(s) + Cu^{++} = Zn^{++} + Cu\,(s).$$

If the sulphates are both present at the same concentration ($0{\cdot}1N$) the electromotive force is approximately 1·1 volts. Hence we have

$$-\Delta F = n.Q. \times 1{\cdot}1 \text{ volt coulombs or joules.}$$

$Q = 96{,}540$ coulombs, n is 2, and 4·2 joules = 1 calorie, so that

$$-\Delta F = \frac{2}{4{\cdot}2} \times 96{,}540 \times 1{\cdot}1$$

$$= 50{,}570 \text{ calories.}$$

It is evident that this value is the difference between the free energy decrease of the following reactions

$$Zn\ (s) = Zn^{++}\ (-\Delta F_1)$$

and $$Cu\ (s) = Cu^{++}\ (-\Delta F_2)$$

i.e. $$-\Delta F = (-\Delta F_1) - (-\Delta F_2).$$

It is now permissible to equate this quantity to the value of $-\Delta F$ obtained from the van't Hoff isotherm

$$-\Delta F = RT\ ln\ K - RT\ \Sigma n\ ln\ C$$

$$= RT\ ln\ \frac{C_{\epsilon Zn^{++}} . C_{\epsilon Cu}}{C_{\epsilon Cu^{++}} . C_{\epsilon Zn}} - RT\ ln\ \frac{C_{Zn^{++}} . C_{\epsilon Cu}}{C_{Cu^{++}} . C_{\epsilon Zn}}$$

where $C_{\epsilon Cu}$, $C_{\epsilon Zn}$ are the partial concentrations of metal in solution, unionized and in equilibrium with the solid metal, $C_{\epsilon Zn}{}^{++}$, $C_{\epsilon Cu}{}^{++}$ are the equilibrium concentrations of zinc and copper ions in the solution and $C_{Cu}{}^{++}$, $C_{Zn}{}^{++}$ are the actual concentrations of the ions in the cell. Now we have arbitrarily chosen the concentrations of the zinc and copper sulphate to be both equal to 0·1 *N.*, so that the above equation simplifies to

$$-\Delta F = RT\ ln\ \frac{C_{\epsilon Zn^{++}}}{C_{\epsilon Cu^{++}}} = RT\ ln\ K' \quad . \quad . \quad . \quad (5)$$

Let us now substitute the value of $-\Delta F$ determined from the electromotive force data; we obtain

$$RT\ ln\ K' = 50{,}570 \text{ calories.}$$

The temperature is 25° C., i.e. 298° K. Hence converting to ordinary logs.

$$log\ K' = \frac{50{,}570}{1{\cdot}98 \times 2{\cdot}303 \times 298} = 37.$$

Hence the equilibrium constant K' is 10^{37}. It is manifestly impossible to determine a constant of such a magnitude by the ordinary methods of analysis, but the electromotive force of the cell has thus provided us with a very simple and accurate method of calculating this quantity.

Again let us consider the cell

$$Ag \mid AgCl;\ KCl\ (c);\ HgCl \mid Hg,$$

i.e. electrodes of silver and mercury surrounded respectively by solid silver chloride and mercurous chloride and both immersed in a solution of potassium chloride. The reaction occurring is

$$Ag\ (s) + HgCl\ (s). = AgCl + Hg\ (l).$$

The electromotive force of the cell is 0·0455 volts and hence the decrease in the free energy is given by the following expression at 298° K.

$$-\Delta F = 0{\cdot}0455 \times 96{,}540 \times \frac{1}{4{\cdot}2} \text{ calories}$$

$$= +\ 1{,}046 \text{ calories.}$$

One very interesting series of affinity measurements may be obtained from the electromotive force of gas cells containing hydrogen or oxygen. Thus, for example, we may consider the following cell

$$H_2\,(1 \text{ atm.}) \mid 1.N.HCl \mid 1.N.NaOH \mid H_2\,(1 \text{ atm.}).$$

The actual reaction which occurs in the cell is, if we assume complete dissociation of the acid and alkali and of the resulting salt,

$$H^+ + OH' = H_2O.$$

It is a well-known fact that the heat of neutralization of dilute mineral acids by dilute strong alkalies is a constant, viz. 14,000 calories approximately, and is really the heat of formation of 1 mole of undissociated water from its ions. By determining the electromotive force of the above cell, and correcting for the liquid-liquid potential difference, we may calculate the affinity or free energy decrease of this reaction. The electromotive force at room temperature (after correction) is 0·81 volts, so that the free energy decrease is given by

$$-\Delta F = 0{\cdot}81 \times 96{,}540 \times \frac{1}{4{\cdot}2}$$

$$= 18{,}620 \text{ calories.}$$

This measurement also provides us with a method of calculating the dissociation constant K_w of water. We proceed as follows: By the van't Hoff isotherm we have

$$-\Delta F = RT\ ln\ \frac{C_{\epsilon H_2O}}{C_{\epsilon H+}.C_{\epsilon OH'}} - RT\ ln\ \frac{C_{H_2O}}{C_{H+}.C_{OH'}}.$$

Now $C_{H_2O} = C_{\epsilon H_2O}$ and C_{H+} and $C_{OH'}$ are both unity, so that this equation becomes

$$-\Delta F = -RT\ ln\ C_{\epsilon H+}.C_{\epsilon OH'} = -RT\ ln\ K_w.$$

Substituting the value of $-\Delta F$ obtained from the electromotive force of the cell we have

$$-\Delta F = -RT\ ln\ K_w = 18{,}620.$$

Hence on transforming to ordinary logarithms and inserting the values of the temperature and of R

$$log\ K_w = -\frac{18{,}620}{2{\cdot}303 \times 1{\cdot}98 \times 290}$$

$$= -\ 14{\cdot}08$$

so that $$K_w = 10^{-14}$$

which is in excellent agreement with values obtained by other methods.

A similar method to the one just employed consists in determining the electromotive force of the cell

$$O_2 \mid N.HCl \mid N.NaOH \mid O_2.$$

The oxygen dissolves giving hydroxyl ions, thus setting up a solution pressure. The net result is a neutralization of the hydrions and the hydroxyl ions as before $H^+ + OH' = H_2O$, and oxygen is transferred in the process from the acid side to the alkali side.

A third method of the same type depends upon the use of the cell:

$$H_2 \mid Electrolyte \mid O_2.$$

The most suitable electrolyte to employ is hydrochloric acid. In this cell both the hydrogen and the oxygen dissolve in the electrolyte, forming hydrogen and hydroxyl ions which combine to form undissociated water. The hydrogen pole will naturally be negative and the oxygen pole positive, owing to the removal of the ions.

Affinity of Oxidation-Reduction Processes from E.M.F. Measurements.

Suppose we have a solution of stannous chloride in contact with a solution of ferric chloride. We know that the two solutions tend to react, the iron being reduced to the ferrous condition and the tin oxidized to the stannic state. Now suppose we set these solutions up in the form of a galvanic cell, by inserting platinum electrodes into the two solutions, thus

$$Pt \mid Ferric\ Chloride \mid Stannous\ chloride \mid Pt.$$

Then by measuring the electromotive force of the cell we may

calculate the affinity or free energy decrease of the process. The cell reaction is

$$Sn^{++} + 2Fe^{+++} = Sn^{++++} + 2Fe^{++}.$$

In a similar manner by measuring the electromotive force of the following cell

$$Pt \mid FeSO_4 \mid KMnO_4 \mid Pt$$

we can obtain the free energy decrease accompanying the reaction

$$MnO_4' + 5Fe^{\cdot\cdot} + 8H^{\cdot} = Mn^{\cdot\cdot} + 5Fe^{\cdot\cdot\cdot} + 4H_2O$$

under the conditions which happen to obtain in the cell at the instant of measurement. It is evident that the value of the electromotive force obtained, and consequently of the free energy decrease calculated, depends upon the concentration of each of the ion types. The calculation of the affinity for some particular concentrations can, of course, be performed by means of the van't Hoff Isotherm. In the stannous chloride, ferric chloride cell, since the reaction corresponds to the transfer of two electrons, the free energy decrease will be $E.2Q$. Hence we have

$$2Q.E = -\Delta F = RT\ ln\ K - RT\ ln \frac{(Sn^{++++})\,(Fe^{++})^2}{(Sn^{++})\,(Fe^{+++})^2}$$

where K is of the same form as the last term only involving equilibrium concentrations.

We shall, however, confine ourselves to a somewhat simpler case which was investigated by Peters (*Zeit. phys. Chem.*, 1895, **26**, 193). He used as one of his elements the standard calomel electrode (Normal), the potential difference of which is known (0·56 volts). This serves as the reducing agent. The other element consisted of a platinum wire dipping into a solution of a mixture of ferrous and ferric chlorides. We may represent the cell as follows:

$$Pt \left| \begin{matrix} Fe^{+++} \\ Fe^{++} \end{matrix} \right| \begin{matrix} Hg_2Cl_2 \\ Hg_2{}^{++} \end{matrix} \Big| Hg$$

In the left-hand section the reaction occurring is

$$2Fe^{+++} + 2\ominus = 2Fe^{++}$$

while in the right-hand section the reaction is

$$2Hg\ (\text{metal}) - 2\ominus = Hg_2{}^{++}.$$

The net reaction of the cell is therefore the sum of these two processes, namely,

$$2Fe^{+++} + 2Hg = 2Fe^{++} + Hg_2{}^{++}.$$

The free energy decrease accompanying the reaction is given by the van't Hoff isotherm which for this reaction takes the form

$$-\Delta F = RT\ ln\ \frac{C^2{}_{\epsilon Fe++} \cdot C_{\epsilon Hg_2++}}{C^2{}_{\epsilon Fe+++} \cdot C^2{}_{\epsilon Hg}} - RT\ ln\ \frac{C^2{}_{Fe++} \cdot C_{Hg_2++}}{C^2{}_{Fe+++} \cdot C^2{}_{Hg}}.$$

Now for the calomel electrode we know that

$$C_{Hg_2++} = C_{\epsilon Hg_2++} = \text{Constant}$$

and also the concentration of mercury (unionized) in the solution C_{Hg} is a constant, so that we may transform this expression and write

$$-\Delta F = RT\ ln\ \frac{C^2{}_{\epsilon Fe++}}{C^2{}_{\epsilon Fe+++}} - RT\ ln\ \frac{C^2{}_{Fe++}}{C^2{}_{Fe+++}}$$

$$= RT\ ln\ K - RT\ ln\ \frac{C^2{}_{Fe++}}{C^2{}_{Fe+++}}.$$

Now since the reaction represented above involves the transfer of two electrons, the electromotive force is equal to one-half the free energy decrease, so that

$$E = \tfrac{1}{2}RT\ ln\ K - \tfrac{1}{2}RT\ ln\ \frac{C^2{}_{Fe++}}{C^2{}_{Fe+++}}.$$

The first term of this expression $\frac{1}{2}RT\ ln\ K$ is usually termed the **normal potential** of the process, and denoted by E_0. E is called the reduction potential, since the reaction as considered is a reduction. Hence we have

$$E = E_0 - RT\ ln\ \frac{C_{Fe++}}{C_{Fe+++}}.$$

By means of this equation Peters calculated the value of E_0 and hence of the equilibrium constant K. Mixtures of ferrous and ferric salts in known concentration were employed in the left-hand section, and as an approximation it was assumed that the ioniza-

tion of these salts is complete so that the ion concentration is equal to that of the salt. The following table gives some of Peters' results:

Ratio of $Fe++$ and $Fe+++$ in per cent.		E in Volts.	P.D. of the ferri ferro Electrode in Volts.	E_0 in Volts.	$\sqrt{K}$ Calculated $= \frac{C_{\epsilon Fe++}}{C_{\epsilon Fe+++}}$
Ferri	Ferro				
0·5	99·5	0·296	0·856	0·428	
1	99	0·312	0·872	0·427	
2	98	0·331	0·891	0·428	Mean value
10	90	0·375	0·935	0·430	$10^{7\cdot45}$
50	50	0·427	0·987	0·427	
90	10	0·483	1·043	0·428	
99	1	0·534	1·094	0·419 ?	

The values of E_0 are in excellent agreement with one another as we should expect from the theory. The actual value of the constant K is very high. It requires that for equilibrium the ratio of the ferrous ion to the ferric ion is over 7,000,000. The net result is that for any ratio obtainable in practice it is always the reduction process which occurs.

We have now considered, briefly, some of the methods of determining directly the free energy decrease or affinity of reactions. One of the most important methods of determining the affinity, however, is dependent upon the famous theorem of Nernst which we shall consider in the next chapter. In this method we calculate the free energy change from the change in the heat content which accompanies the reaction and which is given by the heat of reaction at constant pressure.

Variation of Affinity with Temperature. Before proceeding, however, to a discussion of the Nernst Heat Theorem, we must consider briefly the effect of temperature upon the free energy change of a reaction. It is necessary to employ the Gibbs-Helmholtz equation in the form

$$\Delta H - \Delta F = T\left(\frac{\partial(-\Delta F)}{\partial T}\right)_P \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Now we know that for any reaction at constant pressure

$$\Delta H = q_p$$

where q_p is the heat absorbed at constant pressure. Hence we may write

$$q_p - \Delta F = T\left(\frac{\partial(-\Delta F)}{\partial T}\right)_P \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This equation shows that if, for any temperature, we know the heat of reaction at constant pressure, and also the value of the affinity then we may calculate the temperature coefficient of the affinity at this temperature. This is the most general form of the equation. Many authors, however, have gone somewhat astray at this point. They have defined affinity in such a manner that it may be calculated from the electromotive force of some suitable cell, which evidently depends upon a reaction proceeding at **constant pressure.** They then make the arbitrary assumption, which is not by any means invariably true, that the volume is approximately constant, so that the affinity $-\Delta F$ is equal to the decrease in the work content $-\Delta A$. They then apply the equation

$$\Delta U - \Delta A = T\left(\frac{\partial(-\Delta A)}{\partial T}\right)_v$$

and hence

$$q_v - \Delta A = T\left(\frac{\partial(-\Delta A)}{\partial T}\right)_v.$$

This equation is undoubtedly true for reactions at constant volume, but since the reactions usually considered do not occur at constant volume, but at the constant pressure of the atmosphere, it seems to be unnecessary to employ the approximation, especially as our heat measurements refer, in most cases, to constant pressure.

We may transform equation (6) so as to refer immediately to the electromotive force of a cell, by equating $-\Delta F$ to $n.Q.E.$ We obtain

$$\frac{\Delta H}{nQ} + E = T\left(\frac{\partial E}{\partial T}\right)_P \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

If, now, we measure the electromotive force of the cell for a series of temperatures, we may, by plotting the values obtained against temperature, obtain the value of the temperature coefficient $\left(\frac{\partial E}{\partial T}\right)_P$ for any given temperature from the slope of the curve. Knowing the value of E for that temperature we may calculate the heat of

reaction ΔH, by substituting directly in equation (8). The values of ΔH so obtained are much more accurate than those calculated from calorimetric measurements.

The following table contains a series of values, calculated in this manner, for the reaction:

$$\tfrac{1}{2}H_2 + HgCl = HCl\,(0{\cdot}1\ M) + Hg$$

from the electromotive force of the cell

$$H_2 \mid HCl\,(0{\cdot}1\ M) \mid HgCl \mid Hg.$$

In this case $n = 1$ so that

$$\Delta H = Q\left(T\frac{\partial E}{\partial T} - E\right)$$

Temperature.	ΔH.
20° C.	− 7995 cals.
25° C.	− 8291 ,,
30° C.	− 8471 ,,
35° C.	− 8609 ,,
40° C.	− 8694 ,,
45° C.	− 8774 ,,

The available calorimetric data give a value of $\Delta H = -8{,}000$ calories approximately at 18° C., but the above figures are more accurate. The equation (8) is therefore of great importance in the determination of the heat of a reaction at constant pressure.

CHAPTER XII

THE THIRD LAW OF THERMODYNAMICS

We have now considered in some detail the scope and methods of what is known as Classical Thermodynamics. It has taught us, among other things, that a decrease in the free energy of any system is the necessary criterion of a reaction occurring in that system and we have seen reason to regard the measure of this free energy decrease as a measure of affinity. Now although this view involves the rejection of Berthelot's principle, that the heat of a reaction is the measure of affinity, yet it is an undoubted fact that in many cases the free energy decrease and the heat evolved by the system at constant pressure are very nearly the same, so that the principle served for a time to give an approximate measure of affinity in certain cases. Moreover, it is often possible to determine the heat of a reaction, either directly, or indirectly from specific heat data and the use of Kirchhoff's law, when the free energy change is not so readily obtained. It would therefore be a distinct advantage if it were possible, by any method, to calculate the free energy decrease $-\Delta F$ from the heat of reaction q_p (= heat absorbed) or ΔH.

The only relationship between these two quantities ΔF and ΔH, which may be obtained on the basis of classical theory is that known as the Gibbs-Helmholtz equation and, as we have seen, takes the form:

$$\Delta H - \Delta F = T\left(\frac{\partial(-\Delta F)}{\partial T}\right) \quad . \quad . \quad . \quad . \quad (1)$$

We have already seen that if measurements of $-\Delta F$ and of its temperature coefficient $\frac{\partial(-\Delta F)}{\partial T}$ are available, e.g. from measurements of electromotive force, then it is possible to calculate the heat effect ΔH with a very high degree of accuracy. The reverse process, however, is not so simple, as the following considerations

will show. We may, by dividing through by T^2, write equation (1) in the form—

$$\frac{T\left(\frac{\partial(-\Delta F)}{\partial T}\right) - (-\Delta F)}{T^2} = \frac{\Delta H}{T^2}$$

which is the same as

$$\frac{\partial}{\partial T}\left(\frac{-\Delta F}{T}\right) = \frac{\Delta H}{T^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Integrating this expression we obtain

$$\frac{-\Delta F}{T} = \int \frac{\Delta H}{T^2} dT + \text{Constant} \quad . \quad . \quad . \quad . \quad (3)$$

We thus see that in order to calculate the free energy change from the heat effect it is necessary to evaluate the integration constant, and this can only be done, on the basis of the first two laws of thermodynamics, if we know the value of $-\Delta F$ for some one temperature. The integration of the first term on the right-hand side has already been considered in Chapter VI. We express ΔH as a function of temperature as follows:

$$\Delta H = \Delta H_0 + \Delta\alpha' T + \frac{\Delta\beta'}{2} T^2 + \frac{\Delta\gamma'}{3} T^3 + \quad . \quad . \quad (4)$$

where the coefficients are those contained in the expression for the change in the specific heat at constant pressure as a result of the reaction (Equation VI (22))

$$\Delta C_p = \Delta\alpha' + \Delta\beta' T + \Delta\gamma' T^2 + \ldots\ldots \quad . \quad . \quad . \quad (5)$$

Hence we may write

$$\frac{\Delta H}{T^2} = \frac{\Delta H_0}{T^2} + \frac{\Delta\alpha'}{T} + \frac{\Delta\beta'}{2} + \frac{\Delta\gamma'}{3} T + \ldots \quad . \quad . \quad . \quad (6)$$

and on integrating we obtain

$$\int^T \frac{\Delta H}{T^2} dT = a + \frac{-\Delta H_0}{T} + \Delta\alpha' \, ln \, T + \frac{\Delta\beta'}{2} T + \frac{\Delta\gamma'}{6} T^2 + \ldots . \quad (7)$$

where a is the constant of integration. Hence by equation (2) we have

$$+\Delta F = \Delta H_0 + IT - \Delta\alpha' T . ln \, T - \frac{\Delta\beta'}{2} T^2 - \frac{\Delta\gamma'}{6} T^3 + \ldots . \quad (8)$$

where $I = -a$.

From thermal data we can determine every quantity in this equation with the exception of the integration constant I, and it is to Nernst that we owe the suggestion which has enabled us to evaluate this constant I without it being necessary to make any free energy measurements at all. This suggestion is known as the **Nernst Heat Theorem** and is a part of what is now considered to rank as the **Third Law of Thermodynamics.**

We have already mentioned that in many cases the free energy decrease $-\Delta F$ is approximately equal to the heat evolved during the reaction at constant pressure, $-\Delta H$. Now Richards (*Zeit. phys. Chem.*, 1902, **42**, 129) in studying the electromotive force and the heat of reaction in various cells at low temperatures, showed that as the temperature is decreased these two quantities ΔF and ΔH become more and more nearly equal. It is therefore reasonable to assume that at absolute zero, we may write

$$\Delta F = \Delta H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

or the free energy change and the heat of reaction are equal. This is not, however, quite sufficient. Experiment shows that, not only do these two quantities approach one another as the temperature is decreased, but they do so very rapidly in the neighbourhood of absolute zero, so that in the immediate neighbourhood of the zero point the divergence between ΔF and ΔH is practically negligible. Nernst, in a paper "Ueber die Berechnung chemischer Gleichgewichte aus thermischer Messungen" (*Nachr. kgl. Ges. Wiss., Göttingen; Math-physik. Klasse*, 1906, p. 1) expressed this by saying that not only do the free energy change and the heat change of a reaction approach one another at low temperatures but they do so asymptotically, so that we may write

$$\lim_{T=0} \frac{d\Delta F}{dT} = \lim_{T=0} \frac{d\Delta H}{dT} = 0 \quad . \quad . \quad . \quad . \quad (10)$$

Graphically this may be represented as in Fig. 38. In the left-hand diagram the upper curve representing ΔF and the lower curve representing ΔH meet at the zero point, but the tangents at that point do not coincide. In the right-hand diagram, however, the tangents at the zero point are identical and are parallel to the temperature axis. This latter diagram therefore represents the true state of affairs according to Nernst's Theorem, and not the left-hand diagram.

Nernst originally considered that this principle was applicable to all pure substances in the condensed state, i.e. solid or liquid, since the vapour phase is naturally absent at absolute zero. As we shall see, however, there is considerable experimental evidence against its applicability to liquids, while there is ample verification of the principle in the case of crystalline solids. It therefore seems preferable to limit the heat theorem to the crystalline state, although it is probable that the divergence in the case of amorphous solids is small.

The principle which we have just stated is itself sufficient to enable us to calculate the free energy change from the heat of reaction although it is not a complete statement of the Third Law.

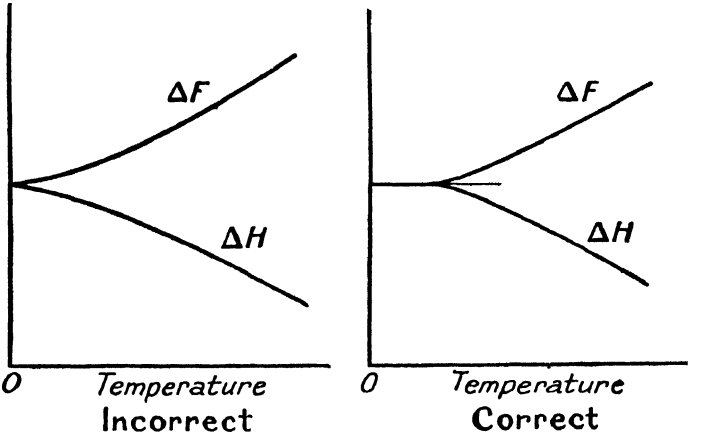


FIG. 38.

It is not permissible, however, as Nernst thought at first, to do this by employing equations (4) and (8) directly since this assumes their applicability at low temperatures, and as we shall soon see the equations VI (21), and (22), for specific heats, which give the values of the coefficients, are no longer valid in the neighbourhood of absolute zero.

Instead we shall proceed as follows : Let us consider the reaction

$$A + B = C + D$$

occurring entirely in the solid state. Then each substance may be assumed to have a certain vapour pressure which may be denoted by P with the appropriate subscript. Then if we denote the heat of vaporization of these substances by ΔH_A, ΔH_B, etc., and neglect

the volume of the solid in comparison with that of the vapour, the Clapeyron equation for substance A takes the form

$$\frac{d \ln P_A}{dT} = \frac{\Delta H_A}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

provided the vapour is regarded as behaving like a perfect gas.

Now we have seen in Chapter III that $\frac{dH}{dT} = C_p$ at constant pressure, so that we may write

$$\frac{d\Delta H_A}{dT} = \Delta C_{p_A}$$

where ΔC_p is the difference between the heat capacities of the vapour and the solid. Integrating this expression between absolute zero and $T°$ K. we obtain

$$\Delta H_A = \Delta H_{0A} + \int_0^T \Delta C_{p_A} dT \quad . \quad . \quad . \quad . \quad (12)$$

Substituting this value of ΔH_A in equation (11) and integrating we have

$$\ln P_A = -\frac{\Delta H_{0A}}{RT} + \int \frac{\int_0^T \Delta C_{p_A} dT}{RT^2} dT + i_A \quad . \quad . \quad (13)$$

where i_A is an integration constant, termed by Nernst the "True Chemical Constant." We can integrate the third term in this expression by parts,

$$\int \frac{\int_0^T \Delta C_{pA} dT}{RT^2} dT = -\frac{\int_0^T \Delta C_{pA} dT}{RT} + \int_0^T \frac{\Delta C_{pA}}{RT} dT$$

The second term of this equation is by equation (12) equal to

$$(\Delta H_A - \Delta H_{0A})/RT$$

so that equation (13) becomes

$$\ln P_A = -\frac{\Delta H_A}{RT} + \int_0^T \frac{\Delta C_{pA} dT}{RT} + i_A \quad . \quad . \quad . \quad (14)$$

Similar expressions may be obtained for $\ln P_B$, $\ln P_C$, and $\ln P_D$.

Now we may imagine the reaction to proceed via the vapour phase, by supposing that one mole of A and one mole of B are vaporized and react to form C and D which are then condensed to the solid form. Let us denote the equilibrium vapour pressures by the small letters p_A, p_B, etc. Applying the law of mass action we have

$$K_p = \frac{p_C \times p_D}{p_A \times p_B} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

We may now apply the well-known equation obtained in Chapter VI, namely,

$$\frac{d \ln K_p}{dT} = \frac{\Delta H_R}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where ΔH_R is the heat of the reaction **in the gaseous phase,** at constant pressure. This equation may be integrated in a more accurate manner than that adopted in Chapter VI by a similar method to that just employed and we thus obtain

$$\ln K_p = -\frac{\Delta H_R}{RT} + \int_0^T \frac{\Delta C_{pR} dT}{RT} + i_R \quad . \quad . \quad . \quad . \quad (17)$$

where

$$\Delta C_{pR} = \Delta C_{pC} + \Delta C_{pD} - \Delta C_{pA} - \Delta C_{pB}.$$

The free energy decrease accompanying the reaction is given by the van't Hoff isotherm in the form

$$-\Delta F = RT \ln K_p - RT\Sigma \ln P$$

or $$\Delta F = RT (\ln P_C + \ln P_D - \ln P_A - \ln P_B - \ln K_p) \quad (18)$$

If, now, we substitute the expressions for $\ln P_A$, etc., and for $\ln K_p$ from equations (13) and (17) we obtain

$$\Delta F = (\Delta H_A + \Delta H_B + \Delta H_R - \Delta H_C - \Delta H_D) + RT\int \frac{(\Delta C_{pC} + \Delta C_{pD} - \Delta C_{pA} - \Delta C_{pB} - \Delta C_{pR})}{RT} dT + (i_C + i_D - i_A - i_B - i_R)RT \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Now it is evident that the first term of this expression, namely,

$$\Delta H_A + \Delta H_B + \Delta H_R - \Delta H_C - \Delta H_D = \Delta H_S$$

where ΔH_S is the heat of the reaction in the solid phase. Moreover

$$(\Delta C_{pC} + \Delta C_{pD} - \Delta C_{pA} - \Delta C_{pB} - \Delta C_{pR}) = -\Delta C_{pS}$$

where ΔC_{pS} is the heat capacity of the resultants C and D, minus the heat capacity of the reactants A and B in the solid phase. The quantity ΔF is evidently equal to the free energy change accompanying the process in the solid phase, and we may therefore write

$$\Delta F = \Delta H_S - T\int_0^T \frac{\Delta C_p dT}{T} + (i_C + i_D - i_A - i_B - i_R)RT \quad . \quad (20)$$

This equation is derived from purely thermodynamic principles except for the assumptions that the vapour behaves like a perfect gas and that the volume of the solid is negligible in comparison with that of the vapour. Both of these assumptions are sufficiently accurate to warrant our using this equation to represent the behaviour of the system in the neighbourhood of absolute zero. Moreover, we have not as yet assumed the validity of the Nernst Heat Theorem. We may now, however, integrate equation (1) by a similar method to that just adopted. By equation V (15) we have $\left(\frac{\partial F}{\partial T}\right)_P = -S$, so that, we may write

$$\frac{d\Delta F}{dT} = -\Delta S \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

But by the Nernst principle this quantity approaches zero in the neighbourhood of absolute zero, or

$$\lim_{T=0} \Delta S = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Now classical thermodynamics gives us the following relation for the change of entropy as a result of a chemical reaction:

$$\Delta S = \int_0^T \Delta C_p d \ln T + I_0 \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where I_0 is a constant of integration. Substituting this value in (1) we obtain

$$\Delta F = \Delta H - T \cdot \int_0^T \frac{\Delta C_p dT}{T} - I_0 T.$$

Comparing this expression with equation (20), we evidently obtain

$$I_0 = -R(i_C + i_D - i_A - i_B - i_R) \quad . \quad . \quad . \quad . \quad (24)$$

But by the Nernst Heat Theorem we have seen that $\lim_{T=0} \Delta S = 0$.

Applying this to equation (23) it follows that

$$I_0 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

This is the important fact which emerges on the application of the Nernst Heat Theorem to a chemical reaction. Substituting in equation (24) gives

$$i_R = i_C + i_D - i_A - i_B \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

or the integration constant of the reaction given by equation (17) is equal to the algebraic sum of the "true" chemical constants, of the reacting substances.

The value for the free energy change of the reaction now becomes

$$\Delta F = \Delta H - T\int_0^T \frac{\Delta C_p dT}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

This simple expression, which as we have seen follows immediately from the accurate integration of the Clapeyron equation on applying the Heat Theorem, enables us to determine ΔF entirely from heat measurements provided we have data for the specific heats of all the reacting substances down to absolute zero. Alternatively we could calculate $ln\ K_p$ from a knowledge of the true chemical constants of the materials, obtained from measurements of specific heats at low pressures, by means of equation (17) and then, substituting the vapour pressures of the solids, we could obtain the free energy change. This latter method is evidently, however, much more laborious, and is never employed in practice in free energy determinations. Unfortunately, at first, owing to the erroneous views adopted as regards the specific heats at absolute zero, the latter method was used together with the empirical equations (6) and (8) which are only valid at ordinary temperatures. We do not intend to spend any time, however, in considering these investigations. It will suffice to point out the error underlying them.

We have seen that the Nernst Heat Theorem may be expressed in the following mathematical form:

$$\lim_{T=0} \Delta C_p = 0\,; \quad \lim_{T=0} \Delta S = 0\,. \quad . \quad . \quad . \quad . \quad (28)$$

The first part of this statement tells us that for crystalline solids undergoing any change at absolute zero the specific heat of the system does not change, or, in other words, the sum of the specific heats of the reactants is equal to the sum of the specific heats of the resultants. Nernst interpreted this to mean that all substances at absolute zero have the same **finite** heat capacity. He then proceeded to calculate this value by extrapolating the empirical expressions given in Chapter VI to this temperature.

In 1907, however, Einstein (*Ann. Physik.*, 1907, **22**, 180) derived, from Planck's radiation formula, an equation for the heat capacity of a system of simple harmonic oscillators, and, since all forms of matter at low temperatures may presumably be regarded as made up of different sorts of these oscillators, he predicted that the heat capacity of all forms of matter would approach zero at the absolute zero of temperature. Now, although Einstein's equation is not in exact agreement with experimental data, this prediction has been amply verified for all known forms of real matter. Thus we see that Nernst's assumption of a finite limit for C_p at absolute zero, may be regarded as disproved, and we may state that the vanishing of ΔC_p in the neighbourhood of absolute zero depends upon the fact that C_p is itself zero for all substances at that temperature. Actually experiment shows that, in the neighbourhood of absolute zero, C_p diminishes with such rapidity that not only C_p but also the ratio C_p/T approaches zero. However, we shall only assume for our formulation of the Third Law that this ratio is finite, and write

$$\lim_{T=0} C_p = 0\,; \qquad \lim_{T=0} C_p/T \text{ is zero or finite.}$$

The second part of the Nernst Heat Theorem states that $\lim_{T=0} \Delta S = 0$.

Now classical thermodynamics gives us the following relation (Equation III (42))

$$\int dS = \int C_p . d\ ln\ T = \int \frac{C_p}{T} dT \quad . \quad . \quad . \quad . \quad (29)$$

and we may therefore evaluate the integral $\int dS$ between any two temperature limits, simply by plotting values of the ratio C_p/T as ordinates against the absolute temperatures as abscissæ as in

Fig. 39. The area below the curve, say between T_1 and T_2, gives us the difference between the entropies of the system at these two temperatures. If one of the temperatures considered is absolute zero, it is evident that since the area from $T = 0$ to $T = T$ is finite, the entropy change in passing from absolute zero to any temperature must be a finite positive quantity. *That is to say, the entropy of all substances must be at its lowest possible value at absolute zero.* On integrating equation (19), we obtain

$$\int_{}^{T} dS = C_p \ln T + S_0$$

where S_0 is the integration constant and is equal to the value of

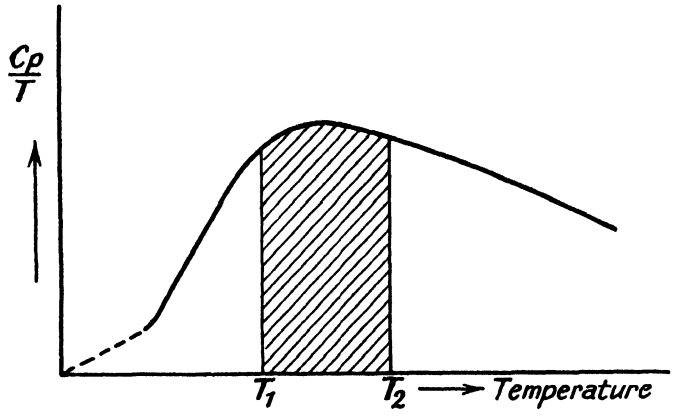


Fig. 39.

the entropy at absolute zero. This constant is entirely undetermined on the basis of the first two laws of thermodynamics.

Since, however, it is found to be impossible for any substance to have a value of the entropy less than S_0 for that substance, Planck (*Ber. deut. chem. Ges.*, 1912, **45**, 5) suggested that we should equate S_0 to zero. Suppose we do this for all the elements. Then imagine a chemical reaction occurring at absolute zero, e.g. $Pb + I_2 = PbI_2$. Since the entropy change accompanying the reaction is zero, by Nernst's principle, it follows that the entropy of lead iodide is likewise zero. Thus we arrive at the important conception of absolute values of entropy, and the entropy function takes on an altogether new significance. It is now no longer a somewhat vague abstraction but a useful and powerful implement in the hands of the investigator.

We are now in a position to state the Third Law of Thermodynamics in its most comprehensive and fundamental form, namely: Every substance has a finite positive entropy, but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfectly crystalline substances. Mathematically we may write the law in the form

$$\lim_{T=0} C_p = \lim_{T=0} S = 0 \quad . \quad . \quad . \quad . \quad (30)$$

The statement of the Third Law which we have just given is confined to perfectly crystalline substances. It is therefore necessary to justify this limitation and we propose to give some of the evidence which has been accumulated, before passing on to the applications of the Third Law.

Let us first of all consider the question of solutions. What evidence is there that the entropy of a solution at absolute zero, i.e. a solid solution or a supercooled liquid solution, is greater than the sum of the entropies of the pure constituents? Suppose we produce one mole of a perfect solution from its pure constituents. These constituents are assumed to be sufficiently similar in properties that they form an approximately ideal solution. Let the mole fractions of the constituents X_1 and X_2 be N_1 and N_2 respectively. Then the free energy change accompanying the transfer of N_1 moles of X_1 from the pure substance to the solution will be $N_1RT\ ln\ \frac{N_1}{1}$, the mole fraction in the pure substance being unity. Similarly, the free energy change accompanying the transfer of N_2 moles of X_2 is $N_2RT\ ln\ N_2$. Hence the total increase in free energy accompanying the formation of one mole of solution is

$$\Delta F = N_1.RT\ ln\ N_1 + N_2.RT\ ln\ N_2 \quad . \quad . \quad . \quad (31)$$

But we have seen that $-\Delta S = \frac{d\Delta F}{dT}$. Hence by differentiating equation (21) we obtain

$$-\Delta S = \frac{d\Delta F}{dT} = N_1.R\ ln\ N_1 + N_2.R\ ln\ N_2 \quad . \quad . \quad (32)$$

Let us take the case, for example, where $N_1 = N_2 = 0{\cdot}5$. Then

$$\Delta S = -R\ ln\ 0{\cdot}5 = +R\ ln\ 2 = 1{\cdot}4 \text{ calories per degree.}$$

This entropy difference is a constant for any temperature provided the resulting solution is ideal. If, now, the solution remains perfect down to absolute zero the same entropy difference will persist, so that if the value of S_0 for the pure components is zero, the value of S_0 for the solution will be 1·4 calories per degree, per mole of solution. On the other hand, if the solution becomes less perfect at lower temperatures, as often happens, it might be possible for this departure from the ideal state to bring about a reduction of the entropy of the solution so that it would become zero at 0° K. Now we have seen that

$$\frac{d\Delta S}{dT} = \frac{\Delta C_p}{T}$$

so that a reduction in the entropy difference between solution and components involves a positive value for ΔC_p, where ΔC_p is the difference between the heat capacity of the solution and the sum of the heat capacities of the components. This was tested experimentally by Gibson, Parks and Latimer (*J. Amer. Chem. Soc.*, 1920, **42**, 1542) who measured the specific heats of supercooled ethyl alcohol, propyl alcohol and their equimolecular mixture, from room temperature down to 86° K. Throughout the range they found no appreciable difference between the heat capacity and the sum of the heat capacities of the constituents, i.e. ΔC_p was found to be zero within the temperature range measured. It is therefore safe to assume that the diminution in the entropy in this range is negligibly small. Commenting on these results, G. N. Lewis says:

It is true that a difference might appear at still lower temperatures, but it was pointed out by Lewis and Gibson (*J. Amer. Chem. Soc.*, 1920, **42**, 1529) that even if this phenomenon were to occur in some solutions, it could hardly occur in such a way as to reduce ΔS_0 to zero for all types of solutions. Thus with a mixture of two almost identical organic isomers we should expect ΔC_p to be nearly zero, and therefore ΔS to be nearly constant, over a wide range of temperature. This reasonable surmise becomes a conviction when we consider the extreme case of a mixture of two isotopes. Here we have substances which are so nearly identical in properties that as yet no way has been found for bringing about their separation. We even know isotopes which have not only the same atomic number but the same atomic weight. It seems hardly conceivable that two such isotopes would suffer any measurable change in heat capacity on mixing, and therefore we must conclude that in such a case the entropy change on mixing remains essentially constant down to the absolute zero.

In fact one such solution has already been thoroughly investigated. Ordinary lead is known to be a mixture of isotopes, and yet its specific heat at low temperatures follows quantitatively the course that would be predicted from the behaviour of other metals.

Not only does the Third Law appear to break down in the case of solutions, however, but the work of Gibson and co-workers on the specific heat of supercooled liquids led Lewis and Gibson (*loc. cit.*) to predict that the entropy of a pure supercooled liquid would be considerably greater than that for pure crystalline solids. The most decisive evidence on this point is the work of Gibson and Giauque (*J. Amer. Chem. Soc.*, 1923, **45**, 93). Their results for the molecular heats of amorphous and crystalline glycerol are

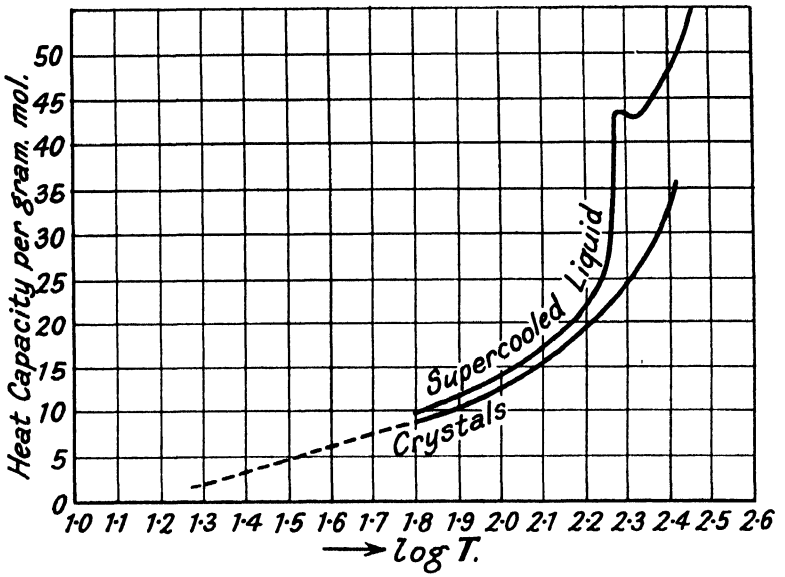


FIG. 40.

shown in Fig. 40 where they are plotted against *log T*. The entropy of fusion for glycerol is 15·02 calories per degree. In order to establish the Third Law for supercooled liquids, the integral

$$\Delta S = \int \Delta C_p d \ln T$$

must be equal to this. The area between the curves of the plot multiplied by 2·303 and taken between the limits 0° K. and $T°$ K., where $T°$ is the melting-point of crystalline glycerol, gives us the value of this integral.

Gibson and Giauque obtained for this area only 9·39, leaving a discrepancy of 15·02 − 9·39 = 5·63 calories per degree. The dotted portion of the curve for the crystals is due to Simon (*Ann. Physik.*, 1922, **68**, 241) who determined the specific heat down to liquid hydrogen temperatures. The upper curve, due to the supercooled liquid, manifests a sharp break which suggests a change in phase, but the evidence seems to be against this, especially as the two curves do not quite coincide even at the lowest temperatures investigated. It is, of course, possible that the liquid curve might diverge again at still lower temperatures and it would be very desirable to obtain further data on the subject. Wietzel (*Zeit. anorg. Chem.*, 1921, **116**, 71) has obtained similar results in the case of crystalline and amorphous quartz, but here again the data do not extend to sufficiently low temperatures to be quite conclusive. In view of these experiments, however, it seems preferable to limit the Third Law to the case of pure crystalline solids, as we have already done.

Experimental Evidence for the Nernst Heat Theorem. From the foregoing considerations it will be evident that the most direct methods of testing the heat theorem or of applying it to the calculation of free energy changes, depend upon the use of the equation

$$\Delta F = \Delta H - T\int_0^T \frac{\Delta C_p dT}{T}$$

$$= \Delta H - T\Delta S \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

The change in entropy accompanying the reaction, ΔS, may be determined from a consideration of the C_p curves of the reacting substances. C_p is plotted against $ln\ T$ when the area below the curves gives $\Delta S'$ for the particular substance under consideration from absolute zero to the temperature of the experiment. The algebraic sum of all these terms $\Delta S'$ gives the entropy change ΔS for the reaction. If one or more of the reacting substances is in the gaseous phase it is evidently only necessary to add the entropy change of vaporization to this value. Having obtained the entropy change accompanying the reaction, the calculation of the free energy change from the heat of reaction may be accomplished by direct substitution in equation (33).

The necessity of obtaining accurate specific heat data at low temperatures was realized by Nernst himself, and, in fact, his method of measuring this function has been followed in all the recent work at low temperatures. The substance, of which the specific heat is to be measured, is placed in a container which is supplied with an electrical heating coil and a thermocouple or resistance thermometer. A measured amount of electrical energy is supplied to the heating coil, and the rise in temperature is measured. In order to prevent heat exchange with the surroundings by conduction, the container is suspended in a vacuum. Radiation is prevented by wrapping the container in silver foil. Since a very high vacuum may be obtained and radiation is negligible at low temperatures, the leakage of heat is practically eliminated. The principal source of error lies in the uncertainty of the temperature measurements, since below 90° K. both thermocouples and resistance thermometers behave in an anomalous manner and calibration is difficult. For details the following references should be consulted: Nernst, *J. Phys.*, (4), 1910, **9,** 721; Nernst, Koref and Lindemann, *Sitz. ber. Preuss. Akad.*, 1910, 247, 262; Nernst, *Ann. Physik.*, 1911, **36,** 395; Eucken, *Phys. Zeit.*, 1909, **10,** 586; Eucken and Schwers, *Sitz. ber. Preuss. Akad.*, 1914, p. 369; Kammerlingh, Onnes and Keesom, *Proc. Amsterdam Akad.*, 1914, 894.

The following illustrations of the applicability of the Nernst Heat Theorem will give the student an idea of the application of the principle to the calculation of free energy change. They are taken from Lewis and Randall's book already mentioned.

I. Let us consider the reaction Sulphur (Rhombic) = S (Monoclinic). From the measurements of Nernst (*Ann. Physik.*, 1911, **36,** 345) and Wigland (ib., 1907, **22,** 64) on the specific heats of the two common crystalline forms of sulphur, the entropy per gram atom of rhombic sulphur at 25° C., S°_{298}, is 7·6 calories per degree. It is usual, especially in America, but more recently also in other countries, to measure free energy changes, etc., at 25° C. or 298° K. This has the advantage of standardizing the data. The data on the specific heat of monoclinic sulphur are not good enough for a very accurate determination of the entropy of this substance, but they permit an estimate which shows the entropy of this form to be two or three tenths of a unit higher than that of the rhombic form. By means of free energy data for this reaction we obtain

$\Delta F^\circ_{298} = 17$; and the heat of reaction is found to be $\Delta H^\circ_{298} = 82$. Hence

$$\Delta S^\circ_{298} = \frac{1}{T}(\Delta H^\circ_{298} - \Delta F^\circ_{298})$$
$$= \frac{82 - 17}{298} = 0{\cdot}22.$$

II. We may now consider the transformation of white tin into grey tin. Brønsted (*Zeit. phys. Chem.*, 1914, **88**, 479) investigated the specific heats of these substances and obtained the following results:

T° K.	*log T*.	C_p (white) obs.	C_p (grey) obs.	C_p (grey) calc.
79·8	1·9020	4·64	3·80	3·80
87·3	1·9410	4·87	4·07	4·07
94·8	1·9768	5·07	4·30	4·31
194·9	2·2898	6·20	5·66	5·60
197·2	2·2949	6·23	5·71	5·64
205·2	2·3122	6·25	5·75	5·69
248·4	2·3952	6·36	5·87	5·86
256·4	2·4089	6·37	5·88	5·88
264·3	2·4221	6·38	5·89	5·90
273·0	2·4362	6·39	5·90	5·93
288·1	2·4596	6·40	5·91	5·97

The last column contains values calculated with the aid of Debye's equation for specific heats (*vide infra*). It will be evident that the agreement with the observed values is good.

We now plot the values of *log T* given in Column 2 as abscissæ against the values of C_p for each of the allotropes as ordinates. The curves are extrapolated to absolute zero and the area below the curve between the limits $T = 0$ and $T = 298$, is determined in both cases. This area multiplied by 2·303 gives us the absolute value of the entropy of the substance at 25° C. since the value at absolute zero is zero. Doing this we obtain for white tin $S^\circ_{298} = 11{\cdot}17$, while for grey tin we obtain $S^\circ_{298} = 9{\cdot}23$. Hence for the reaction *Sn* (white) = *Sn* (grey) we have

$$\Delta S^\circ_{298} = 9{\cdot}23 - 11{\cdot}17 = -1{\cdot}94 \text{ calories per degree.}$$

Brønsted has also made a careful investigation of the heat of this reaction and the free energy change at 25° C. The difference

between his values divided by the absolute temperature, 298°, gives $\Delta S^\circ_{298} = -1{\cdot}87$. The difference between these two values is only 0·07 and Brønsted's measurements thus form an excellent confirmation of the Third Law.

III. Entropy of Iodine. The measurements of the specific heat of iodine are not sufficiently trustworthy to enable us to determine the entropy of this substance. Günther (*Ann. Physik.*, 1916, **51**, 828) attributes this fact to a slow transition between two forms of iodine. We may, however, proceed as follows: Let us determine the E.M.F. of the cells

(*a*) $Pb \mid PbI_2 \mid PbClO_4\ aq. \mid PbI_2 \mid I_2(s).$

(*b*) $Pb \mid PbI_2 \mid KI\ aq. \mid AgI \mid Ag$

We thus obtain the free energy change of the reactions

(*a*) $Pb + I_2\,(s) = PbI_2;\ \Delta F^\circ_a$

(*b*) $Pb + 2AgI = PbI_2 + 2Ag;\ \Delta F^\circ_b.$

The heats of these reactions may also be obtained. Denote these by ΔH°_a and ΔH°_b. Hence for reaction (*a*)

$$\Delta S^\circ_{298} = \frac{1}{298}(\Delta H^\circ_a - \Delta F^\circ_a) = -1{\cdot}2 \text{ calories per degree.}$$

Similarly for reaction (*b*) we obtain $\Delta S^\circ_{298} = -8{\cdot}0$ calories per degree. Now from the work of Lewis and collaborators, we have for Pb, $S^\circ_{298} = 15{\cdot}5$; for PbI_2, $S^\circ_{298} = 41{\cdot}3$; for Ag, $S^\circ_{298} = 10{\cdot}2$; and for AgI, $S^\circ_{298} = 26{\cdot}8$; all these values being obtained from specific heat measurements. Hence for reaction (*a*)

$$S^\circ_{298}(Pb) + 2S^\circ_{298}(\tfrac{1}{2}I_2) = S^\circ_{298}(PbI_2) + 1{\cdot}2$$

or

$$15{\cdot}5 + 2S^\circ_{298}(\tfrac{1}{2}I_2) = 41{\cdot}3 + 1{\cdot}2.$$

Hence $S^\circ_{298}(\tfrac{1}{2}I_2(s)) = 13{\cdot}5$.

On the other hand, by combining reactions (*a*) and (*b*) we obtain

$$Ag + \tfrac{1}{2}I_2\,(s) = AgI;\ \Delta S^\circ_{298} = +3{\cdot}4 \text{ calories per degree.}$$

Hence we have

$$S^\circ\,(Ag) + S^\circ\,(\tfrac{1}{2}I_2\,(s)) = S^\circ\,(AgI) - 3{\cdot}4$$

or

$$10{\cdot}2 + S^\circ\,(\tfrac{1}{2}I_2\,(s)) = 26{\cdot}8 - 3{\cdot}4$$

so that $S^\circ_{298}(\tfrac{1}{2}I_2\,(s)) = 13{\cdot}2$. The difference between these two values for the entropy of iodine at 25° C. is 0·03, so that we have again an excellent experimental verification of the Heat Theorem.

IV. A fourth interesting example is the calculation of the entropy of oxygen, by three different methods. From the measurements

of Eucken of the specific heats and the heats of transformation of various forms of oxygen we obtain for the entropy of oxygen at 25° C. as gas, $S°_{298}(\frac{1}{2}O_2, g) = 24{\cdot}1$.

From a similar investigation by Eucken of carbon monoxide we obtain, $S°_{298}(CO, g) = 45{\cdot}6$. For carbon in the form of graphite, specific heat measurements give $S°_{298} = 1{\cdot}3$. The free energy change and heat change of the following reaction have been obtained: $\Delta F°_{298} = -32{,}510$, $\Delta H°_{298} = -26{,}140$.

$$C \text{ (graph.)} + \tfrac{1}{2}O_2 = CO\,; \quad \Delta S°_{298} = 21{\cdot}4.$$

Hence
$$1{\cdot}3 + S°(\tfrac{1}{2}O_2, g) = 45{\cdot}6 - 21{\cdot}4$$

so that
$$S° (\tfrac{1}{2}O_2, g) = 22{\cdot}9.$$

The third method, which is very reliable, is based on the measurements of Günther (*Ann. Physik.*, 1916, **51**, 828), of the specific heat of mercuric oxide. This gives $S°_{298}(HgO, s) = 16{\cdot}3$. The entropy of mercury is known to be $S°_{298}(Hg, l) = 17{\cdot}8$. Consider the following reaction: $Hg\ (l) + \frac{1}{2}O_2 = HgO$.
We have $\Delta F°_{298} = -13{,}810$; $\Delta H°_{298} = -21{,}600$. Hence we may write

$$\Delta S°_{298} = \frac{-21{,}600 + 13{,}810}{298} = -26{\cdot}1.$$

We thus obtain

$$S° (Hg, l) + S° (\tfrac{1}{2}O_2, g) = S° (HgO) + 26{\cdot}1$$

$$17{\cdot}8 + S° (\tfrac{1}{2}O_2, g) = 16{\cdot}3 + 26{\cdot}1$$

or
$$S° (\tfrac{1}{2}O_2, g) = 24{\cdot}6.$$

These three values, 24·1, 22·9, 24·6, are very satisfactory when we consider the number of different experiments required for their calculation.

These experiments have given us at least an indication of the methods of employing the Third Law, and have served to show the excellent experimental basis upon which it rests.

In addition to experimental methods of determining the specific heat of solids at low temperatures, various attempts have been made to obtain a theoretical formula for the specific heat on the basis of the quantum theory. The most successful of these formulæ is that due to Debye (*Ann. Physik.*, 1912, **39**, 789). He considers a monatomic solid as a homogeneous isotropic elastic medium, and assumes the heat energy to be present in the form of vibrations which range all the way from ordinary sound waves up to vibra-

tions of a limiting frequency, ν_0, which presumably corresponds to the frequency of the individual atom, ν, of the Einstein equation. The total number of these vibrations is not infinite, as is assumed in the ordinary theory of elasticity but is equal to $3N$, the number of degrees of freedom of a solid body containing N atoms. From the theory of elasticity Debye obtains an expression for the number of vibrations dz which lie between ν and $\nu + d\nu$,

$$dz = 9N\frac{\nu^2 d\nu}{\nu_0^3}.$$

Employing this value he gets for the specific heat at constant volume

$$C_v = \frac{9N.k}{\nu_0^3}\int_0^{\nu_0} \frac{e^{h\nu/kT}}{(e^{h\nu/kT}-1)^2}\left(\frac{h\nu}{kT}\right)^2 \nu^2 d\nu$$

where h is the well-known Planck constant, k is the gas constant per atom. It will be observed that the expression gives C_v, as indeed do all the theoretical formulæ obtained by this method. We may, however, obtain C_p very simply by means of equation III (35), viz.

$$C_p = C_v + \frac{\alpha^2 VT}{\beta}$$

where α is the coefficient of expansion, β is the compressibility of the substance considered. The values calculated by Brønsted for the specific heat of grey tin illustrate the applicability of this formula. When T is large it takes the approximate form $C_v = 3R$. When T is small it reduces to $C_v = aT^3$, where a is a constant.

It will be evident from the foregoing considerations that it is highly desirable to have at our command a table of the entropies of all the various elements. A considerable amount of useful work has been done in this direction and the following table taken from Taylor's *Treatise on Physical Chemistry* (1931) contains the most recent values. A very useful collection of free energy data will be found in the *International Critical Tables*, vol. VII, 1930.

Largely owing to the untiring efforts of G. N. Lewis and his collaborators an enormous mass of free energy data has been accumulated, and tables of the free energy changes accompanying the synthesis of various compounds have been compiled. Before closing this chapter we propose to give one illustration due to G. N. Lewis of the limitless applications of these data.

ATOMIC ENTROPIES AT ONE ATMOSPHERE AND 298° K.

Hydrogen ($\frac{1}{2}H_2$)	17·00	Iron	6·8
Hydrogen (H)	28·75	Cobalt	7·2
Helium	30·13	Nickel	7·2
Lithium	7·6	Copper	8·0
Beryllium	7·3	Zinc	9·7
Carbon (diamond)	0·6	Bromine ($\frac{1}{2}Br_2$, l)	16·3
Carbon (graphite)	1·4	Bromine (Br, g)	41·7
Nitrogen ($\frac{1}{2}N_2$)	22·98	Krypton	39·18
Oxygen ($\frac{1}{2}O_2$)	24·51	Zirconium	9·5
Oxygen (O)	38·04	Molybdenum	7·5
Neon	34·95	Ruthenium	6·9
Sodium	12·46	Rhodium	7·6
Sodium (g)	36·73	Palladium	8·9
Magnesium	8·12	Silver	10·2
Aluminium	6·73	Cadmium	11·68
Silicon	4·54	Tin (white)	12·45
Sulphur (rhombic)	7·70	Tin (grey)	10·73
Chlorine ($\frac{1}{2}Cl_2$, g)	26·3	Iodine ($\frac{1}{2}I_2$, s)	13·95
Argon	37·00	Iodine (I, g)	43·20
Potassium	16·5	Xenon	40·53
Potassium (g)	38·3	Lanthanum	13·7
Calcium	10·4	Cerium	13·8
Titanium	6·6	Tungsten	8·1
Chromium	5·8	Osmium	7·8
Manganese	7·3	Iridium	8·7
Gold	11·0	Platinum	10·0
Mercury (l)	18·3	Lead	15·5
Mercury (g)	41·8	Radon	42·11
Thallium	14·8	Thorium	13·6
Chlorine (Cl, g)	39·40	Uranium	11·1

Note.—Elements having a nuclear spin s have an entropy, both in the elementary state and in compounds, that is greater by an amount $R\ ln\ (2s+1)$ per gram atom than it would be if the element had no nuclear spin. If the thermal data are obtained to a sufficiently low temperature, the entropy as calculated from them would include this term $R\ ln\ (2s+1)$ but only in the case of elementary hydrogen is this known to be included. Thus the values given for molecular and atomic hydrogen in the table are higher by an amount $R\ ln\ 2$ than they would be if the hydrogen atom did not have a nuclear spin of one half. For thermodynamic calculations it will be necessary to add the quantity $R\ ln\ 2$ per gram atom of hydrogen to the entropy of hydrogen compounds as obtained experimentally. In the case of other elements that have nuclear spins no difficulty will arise because the entropies of an element and its compounds as determined experimentally will each be less than the theoretical values by the amount $R\ ln\ (2s+1)$ per gram atom of the element.

Some years ago a distinguished chemist proposed some experiments to determine whether nitrogen under pressure would hydrolyze to give aqueous ammonium nitrite according to the equation

$$N_2 + 2H_2O = NH_4^+ + NO_2^-$$

G. N. Lewis proposed to answer the question immediately from the free energy tables. He obtained the following data from his tables

$$2H_2O\ (l) = \text{Elements};\ \Delta F^\circ_{298} = +\ 113{,}120 \text{ cals.}$$
$$\text{Elements} = NH_4^+;\ \Delta F^\circ_{298} = -\ 18{,}930 \text{ cals.}$$
$$\text{Elements} = NO_2^-;\ \Delta F^\circ_{298} = -\ 8{,}500 \text{ cals.}$$

Hence the free energy change accompanying the reaction under consideration is given by

$$\Delta F^\circ_{298} = 113{,}120 - 18{,}930 - 8{,}500 = 85{,}690 \text{ cals.}$$

Now, from the van't Hoff isochore,

$$-\Delta F^\circ_{298} = RT \ln K_c.$$

Substituting the value of ΔF°_{298} obtained we obtain

$$K_c = \frac{(NH_4^+)\,(NO_2^-)}{(N_2)} = 10^{-63}.$$

In other words, the reaction would be far too small to be detected, by the ordinary methods of analysis, i.e. down to about 10^{-6} M.

CHAPTER XIII

HETEROGENEOUS SYSTEMS

Our considerations have hitherto been confined mainly to the case of homogeneous systems such as gases or liquids, although it will be evident that we have made no attempt to confine ourselves rigidly to such systems. In the present chapter, however, we propose to consider more particularly the applications of thermodynamic principles to heterogeneous systems, systems consisting of more than one phase. This is a field of great importance and much of the pioneer work is due to the celebrated J. Willard Gibbs.

The most important generalization resulting from the application of thermodynamics to such systems is that known as Gibbs' Phase Rule. It is beyond the scope of this book to attempt to give an account of this rule and its practical utility. We shall, however, proceed to give a deduction of the rule on the basis of thermodynamics.

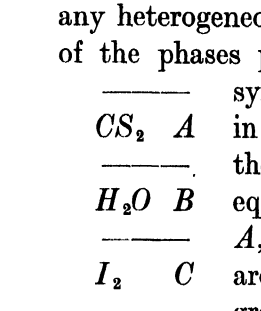
The phase rule deals in a general kind of way with heterogeneous equilibria. The systems considered may be undergoing a chemical or a physical change, but the phase rule is only applicable when a condition of true equilibrium exists. The only changes considered in its deduction are those of temperature and pressure. Other accompanying changes due to the action of light, capillarity, electricity, magnetism, etc., are left out of account. It is of great importance as a means of classification of the various kinds of heterogeneous reactions. It renders possible the grouping together of a large number of apparently disconnected phenomena and has actually led to the discovery of new substances and to a knowledge of the conditions under which they can exist.

It is, first of all, necessary to define the various terms employed in the formulation of the phase rule, and this we shall now proceed to do.

I. **Phase.** A phase is a mass of substance which is physically and chemically homogeneous. It is separated from the other phases

by a definite boundary of separation, known as the surface. It is evident that, in any system, there can only be one gaseous phase, since gases are completely miscible. Any substance is, in general, capable of existing in more than one phase provided the conditions, temperature, pressure, etc., are suitable. Thus, for instance, the substance benzene can exist in the three phases solid, liquid, and vapour. Water is capable, as work upon the phase rule has demonstrated, of existing in either seven or eight different phases, vapour, liquid, and several allotropic forms of solid. The phase rule defines the conditions under which some of these various phases can exist together in equilibrium.

II. **Degree of Freedom.** We know that the equilibrium in any heterogeneous system is independent of the absolute amounts of the phases present. Thus, for example, suppose we have a system of three phases in contact *A*, *B*, *C*, e.g. Iodine in contact with water and carbon disulphide. If the system is in equilibrium we do not upset this equilibrium by removing some of any of the phases *A*, *B*, *C*, and this is true even when the three phases are not all in immediate contact. Thus, in the diagram, *C* is not in contact with *A* directly, but, by the Nernst Distribution Law, the ratio of the concentrations of *C* in *A* and *B* is a constant, independent of the absolute quantities of *A* and *B* present. Thus the concentration of iodine in water and that of iodine in the carbon disulphide are fixed, since iodine is present and the solutions are saturated, so that we have no degrees of freedom of concentration in this system. In this system we have also the temperature and pressure to take into consideration, so that the total number of degrees of freedom is two. The total number of variables of the system is, however, greater than this, but, as we have seen, several of these variables are interdependent, so that change in one necessitates a change in others. The number of degrees of freedom may be defined as the least number of the variables of a system which must be arbitrarily fixed in order to define the system completely. In the case of a gas in the pure state, we have three variables, pressure, temperature and volume. But only two of these are independent, the third being fixed automatically according to the gas law $PV = RT$ per mole. Hence the number of degrees of freedom of such a gas is two. In the case of a liquid in contact with its saturated vapour



the number of degrees of freedom is one, since, if we fix the temperature, the vapour pressure is automatically fixed.

III. **Components of a System.** To define the composition of any given phase several methods may be adopted, but whichever way we choose, we require to express the concentration in terms of the components present. We define the **number of components of a system** as the least number of independently variable constituents by means of which we can represent the composition of all the phases present **in the form of a chemical equation.** For example, consider the case of an anhydrous salt in contact with its saturated solution. We have three phases, solid salt, liquid solution, and vapour. Two components may, however, be employed to express the composition of each of the phases, i.e. salt S and water. In the liquid phase, if we express concentration as parts of component in 100 parts of solution, by weight, we have, if x grams of S are dissolved in 100 parts of solution, the composition $xS : (100 - x)H_2O$. The solid phase has the composition 100 S, and the vapour phase has the composition 100 H_2O. Now we might have chosen the three components H_2, O_2, and S to represent the compositions of the different phases, but these are not all independently variable, since the ratio of hydrogen to oxygen is the same in all the phases, viz. 2 : 1, as in water. Again consider the system obtained when calcium carbonate is heated, viz. the equilibrium

$$\underset{\text{solid}}{CaCO_3} \rightleftharpoons \underset{\text{solid}}{CaO} + \underset{\text{gas}}{CO_2}$$

Here we have a two component system, since we can express the composition of each phase in terms of any two of the three substances, $CaCO_3$, CaO, CO_2. It is quite immaterial which pair of these substances we choose. Thus, suppose we take $CaCO_3$ and CaO as the two components. Then the composition of the various phases is given by

Phase	Molecular Composition.	Percentage by Weight.
$CaCO_3$	$100\ CaCO_3 + 0\ CaO$	$100\ CaCO_3 + 0\ CaO$
CaO	$0\ CaCO_3 + 100\ CaO$	$0\ CaCO_3 + 100\ CaO$
CO_2 (gas)	$100\ CaCO_3 - 100\ CaO$ $(= 100\ CO_2)$	$\frac{100}{44}(100\ CaCO_3 - 56\ CaO)$

It is usual to avoid the use of negative quantities, however, in expressing the composition of a phase, so that in the above case we usually take CaO and CO_2 as the components. We then obtain as the molecular concentrations the following:

Phase.	Molecular Concentration.
$CaCO_3$ (solid)	100 CaO + 100 CO_2
CaO (solid)	100 CaO + 0 CO_2
CO_2 (gas)	0 CaO + 100 CO_2

Another example is that of reciprocal salts and water, the salts being in solution, $AB + CD = AD + CB$, thus

$$NH_4Cl + NaNO_3 = NH_4NO_3 + NaCl.$$

These four substances form a four component system whether the solid phases are present or not. We may take as the components, three of the salts and water. Again if we heat ammonium chloride the system may be represented by one component, NH_4Cl. In the gaseous phase we have dissociation according to the equation

$$NH_4Cl = NH_3 + HCl$$

but, since neither of the gases formed are removed from the gaseous phase the ratio of NH_3 to HCl in the gaseous phase is a constant, and equal to that in ammonium chloride. This is an excellent illustration of the difference between a chemical constituent and a component of a system. The vapour phase is represented by one component although some of the NH_4Cl is dissociated so that there are three chemical constituents. Of course if we add NH_3 or HCl to the system we can no longer represent it by the one component NH_4Cl, we obtain a two component system, since the ratio NH_3/HCl is not fixed throughout. One further case will perhaps serve to make the point clear. Let us consider copper sulphate crystals, $CuSO_4.5H_2O$. This substance on heating gives the tri-hydrate and finally the anhydrous salt. There are four phases, the vapour and three solid phases. The number of components is two, $CuSO_4$ and H_2O. Out of these two components we can build up each phase. One is not enough, since we could not then obtain the different hydrates.

The phase rule is an expression which defines the relation between the number of phases p, the number of degrees of freedom f, and

the number of components of a system n, when the system is in equilibrium. Now we have seen that the thermodynamic criterion of equilibrium for any system under constant temperature and pressure is

$$(dF)_{TP} = 0.$$

Thus suppose we consider one of the components X, say, present in two phases I and II. If equilibrium exists between the two phases, the free energy change accompanying the transfer of say one mole of X from phase I to phase II is zero. In other words, the free energy per mole of X in phase I is equal to the free energy per mole of the same component X in phase II. Expressed mathematically we may write

$$\bar{F}_{\mathrm{I}.X} = \bar{F}_{\mathrm{II}.X}$$

where $\bar{F}_{\mathrm{I}.X}$ and $\bar{F}_{\mathrm{II}.X}$ are the partial free energies per mole of X in I and II. If three phases are present, we may define the condition of equilibrium by two equations thus

$$\bar{F}_{\mathrm{I}.X} = \bar{F}_{\mathrm{II}.X} = \bar{F}_{\mathrm{III}.X}.$$

Similarly, if there are four phases we require three equations. Hence if there are p phases we have $(p - 1)$ thermodynamic equations. But there are n components so that the total number of thermodynamic equations which are necessary, in order to define completely the equilibrium condition is $n(p - 1)$. Now in any such system we can also alter the temperature and pressure. These represent two of the variables of the system. Moreover, it is evident that each of the components may be at different concentrations in each of the phases. Let us fix our attention upon one component X. Concentration terms are essentially ratio terms and may be expressed as the number of moles of X divided by the total number of moles present. If there are n components present in each phase, then it follows that there are $n - 1$ ratios necessary to define the composition of each phase completely. But there are p phases, so that the total number of such ratios is $p(n - 1)$. Hence the total number of possible variables of the system is

$$N = p(n - 1) + 2.$$

Of this number we have seen that only a limited number are independent, this number being the number of degrees of freedom f. Now the number of degrees of freedom is evidently the number

of possible variables for which there are no thermodynamic equations which must be satisfied. That is

$$f = N - n(p - 1)$$
$$= p(n - 1) + 2 - n(p - 1)$$

so that $$f = n - p + 2$$

or the number of degrees of freedom of any system which is in equilibrium is equal to the number of components of the system minus the number of phases present plus 2. This is the famous **phase rule** of Gibbs.

The investigation of heterogeneous equilibria in the light of this phase rule has attained to enormous proportions and we do not propose to consider the matter further. Excellent accounts of the methods employed and the results obtained will be found in Findlay's *Phase Rule* and Clibbens' *Phase Theory*. We shall now pass on to a brief consideration of surface phenomena in the light of thermodynamics.

Surface Tension. It is a well-known fact that owing to the cohesive forces between the molecules of a fluid, the surface of

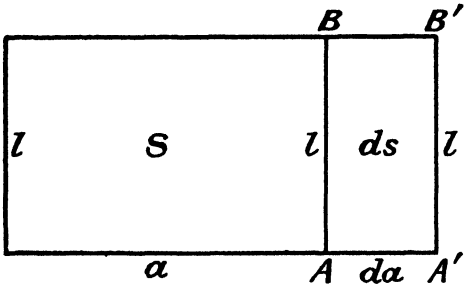


FIG. 41.

that fluid, i.e. the boundary between the fluid and some other phase, behaves as though it were subject to a force acting tangentially and tending to separate two portions of that surface meeting along any line in the surface, of length l, with a force σl. The force per unit length σ is known as the Surface Tension. Let us consider a rectangular portion of the surface of length a and width l, area is $s = al$ (Fig. 41). Suppose we stretch the surface by an amount ds in area, by moving end AB a distance da to $A'B'$. The force acting along the line AB is σl. Hence the work done upon the system is

$$\sigma l \times da = \sigma ds.$$

This work is necessary in order to increase the surface area by an amount ds, so that the work required to increase the area by unity will be σ. Now in considering this work term we have not taken into account any change in the volume of the system as a whole and we must therefore equate σ to the free energy change of the system when the surface is increased by unity. Let us consider a two-phase system, such as water in contact with its vapour. If we change the area of the surface of separation, there will, in general, be a volume change. Let us suppose that the temperature of the system is constant and determine the change of surface tension with pressure. Now the free energy is entirely dependent upon the pressure and the surface, since the volume depends upon the surface and the pressure, i.e. we may write $F = \emptyset\ (s, P)$ where $\emptyset\ (s, P)$ merely indicates the fact that F is a function of s and P alone. Hence by analogy with equation I (25) we have

$$\left[\frac{\partial}{\partial P}\left(\frac{\partial F}{\partial s}\right)_P\right]_s = \left[\frac{\partial}{\partial s}\left(\frac{\partial F}{\partial P}\right)_s\right]_P \quad . \quad . \quad . \quad . \quad (1)$$

or since the surface tension σ is equal to the free energy increase per unit increase in the surface, i.e. to $\left(\frac{\partial F}{\partial s}\right)_P$, and $\frac{\partial F}{\partial P} = V$, we obtain—

$$\left(\frac{\partial \sigma}{\partial P}\right)_s = \left(\frac{\partial V}{\partial s}\right)_P \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This equation gives us the dependence of the surface tension upon the pressure of the system, the surface being maintained constant.

In a similar manner we may write—

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial s}\right)_T\right]_s = \left[\frac{\partial}{\partial s}\left(\frac{\partial F}{\partial T}\right)_s\right]_T \quad . \quad . \quad . \quad . \quad (3)$$

But we have

$$\frac{\partial F}{\partial s} = \sigma \text{ and } \frac{\partial F}{\partial T} = -S$$

so that

$$\left(\frac{\partial \sigma}{\partial T}\right)_s = -\left(\frac{\partial S}{\partial s}\right)_T \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

or replacing $-S$ by its equivalent $\frac{1}{T}(F - H)$, we obtain—

$$\left(\frac{\partial \sigma}{\partial T}\right)_s = \frac{1}{T}\left[\left(\frac{\partial F}{\partial s}\right)_T - \left(\frac{\partial H}{\partial s}\right)_T\right] \quad . \quad . \quad . \quad (5)$$

or

$$T\left(\frac{\partial\sigma}{\partial T}\right)_s = \sigma - \left(\frac{\partial H}{\partial s}\right)_T \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This expression is evidently equivalent to the Gibbs-Helmholtz equation in the form

$$\Delta F - \Delta H = T\left(\frac{\partial \Delta F}{\partial T}\right).$$

The expression $\sigma - T\left(\frac{\partial\sigma}{\partial T}\right)_s$ is frequently termed the total surface energy, but the name is rather ill-chosen, depending upon the use of the Gibbs-Helmholtz equation in the alternative form connecting ΔA and ΔU. If M is the molecular weight and v is the specific volume $\sigma(Mv)^{\frac{2}{3}}$ is known as the molar surface free energy, and $\left(\sigma - T\left(\frac{\partial\sigma}{\partial T}\right)_s\right)(Mv)^{\frac{2}{3}}$ is sometimes known as the total molar surface energy.

Frankenheim (*Journ. f. prakt. Chem.*, 1841, **23**, 401 ; *Lehre von der Kohäsion*, 1836, p. 86) found experimentally that the change of surface tension with temperature is linear for temperatures sufficiently far removed from the critical point of the substance under consideration. That is, we may write

$$\frac{\partial\sigma}{\partial T} = \text{Constant}\,; \quad \sigma = A + BT \quad . \quad . \quad . \quad . \quad (7)$$

where A and B are constants.

Eötvös (*Wied. Ann.*, 1886, **27**, 452) obtained empirically the following linear expression

$$\sigma(Mv)^{\frac{2}{3}} = k(T_c - T) \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where T_c is the critical temperature of the substance, k is a constant which is the same for all non-polar liquids. This equation states that the molar surface free energy is directly proportional to the difference between the temperature of experiment and the critical temperature of the liquid under consideration.

Ramsay and Shields (*Zeit. phys. Chem.*, 1893, **12**, 433) have modified this equation by inserting another constant ε which has usually a value about 6. The revised equation is

$$\sigma(Mv)^{\frac{2}{3}} = k(T_c - T - \varepsilon) \, . \quad . \quad . \quad . \quad . \quad (9)$$

Liquids containing hydroxyl groups have abnormal values of k.

If, now, we differentiate this expression of Ramsay and Shields we obtain

$$\left(\frac{\partial\sigma}{\partial T}\right) = -k/(Mv)^{\frac{2}{3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

which is evidently negative. Hence by equation (6)

$$\left(\frac{\partial H}{\partial s}\right)_T = \sigma - T\left(\frac{\partial\sigma}{\partial T}\right) = \sigma + k/(Mv)^{\frac{2}{3}}$$

which is positive. Thus we see that an increase in the surface is accompanied by an increase in the heat content, that is, by absorption of heat, or a cooling effect.

Let us now differentiate equation (10) with respect to temperature keeping the surface constant. We obtain

$$\frac{\partial^2\sigma}{\partial T^2} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

But by equation (6)

$$\left(\frac{\partial H}{\partial s}\right)_T = \sigma - T\left(\frac{\partial\sigma}{\partial T}\right)_s$$

so that on differentiating with respect to temperature, keeping the surface area constant we obtain

$$\frac{\partial^2 H}{\partial T\partial s} = -T\left(\frac{\partial^2\sigma}{\partial T^2}\right)_s \quad . \quad . \quad . \quad . \quad . \quad (12)$$

But since H is a function of T and s we may write

$$\frac{\partial^2 H}{\partial T\partial s} = \frac{\partial^2 H}{\partial s\partial T} = \frac{\partial}{\partial s}(C_p) \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Hence we obtain

$$\left(\frac{\partial C_p}{\partial s}\right) = -T\left(\frac{\partial^2\sigma}{\partial T^2}\right) = 0 \quad . \quad . \quad . \quad . \quad . \quad (14)$$

or the specific heat of the liquid at constant pressure is independent of the size of the surface. In other words, the surface layer has not a characteristic specific heat of its own, but the same as the liquid in bulk. This, in fact, is the significance of the constant k in the expressions of Eötvös and Ramsay and Shields.

When association of the molecules takes place we may have more than one molecular type present. One or other of these types may accumulate in the surface, causing a variation in the specific heat as compared with the bulk of the liquid. The coefficient k would not then be constant. Thus in the case of water,

if we assume that the liquid consists of double molecules, the variation of k is from about 1·59 between 3° C. and 40° C. to 2·27 between 150° C. and 210° C. The following are some of the values of the constant k for non-associated liquids, given by Freundlich.

Substance.	k.	Observer.
Nitrogen	2·00	Baly and Donnan [1]
Oxygen	1·92	,, ,, ,,
Argon	2·02	,, ,, ,,
Chlorine	2·10	Marchand [2]
Carbon monoxide	2·00	Baly and Donnan [1]
Silicon tetrachloride	2·03	Ramsay and Shields [3]
Sulphuryl chloride	2·16	,, ,, ,,
Ethyl ether	2·17	,, ,, ,,
Carbon tetrachloride	2·11	,, ,, ,,
Carbon bisulphide	2·02	,, ,, ,,
Benzene	2·10	,, ,, ,,
Aniline	2·05	,, ,, ,,
Nitrobenzene	2·23	,, ,, ,,
Pyridine	2·23	,, ,, ,,

[1] Baly and Donnan, *Journ. Chem. Soc.*, 1902, **81**, 907.
[2] Marchand, *Journ. d. chim. phys.*, 1913, **11**, 573.
[3] Ramsay and Shields, *Zeit. phys. Chem.*, 1893, **12**, 433.

Since the surface tension σ has the form of a free energy quantity, we may write $\sigma = \Delta F$, where ΔF is the increase in the free energy accompanying unit increase in the surface area. Now, by equation (6) we have

$$T\left(\frac{\partial\sigma}{\partial T}\right)_s = \sigma - \left(\frac{\partial H}{\partial s}\right)_T.$$

Put $\frac{\partial H}{\partial s} = \Delta H_s$, then ΔH_s is the heat change corresponding to the free energy increase ΔF, i.e. to the increase in the surface area of one unit. We may now differentiate this equation and obtain

$$\frac{\partial\left(\sigma - \left(\frac{\partial H}{\partial s}\right)_T\right)}{\partial T} = \frac{\partial(\sigma - \Delta H_s)}{\partial T} = -T\frac{\partial^2\sigma}{\partial T^2} = 0$$

provided the σ, T curve is linear.

We may now apply the Nernst Heat Theorem to the case of

surface tension in the following manner. We have seen that this theorem states

$$\lim_{T=0} \Delta F = \lim_{T=0} \Delta H; \text{ and } \lim_{T=0} \frac{\partial \Delta F}{\partial T} = \lim_{T=0} \frac{\partial \Delta H}{\partial T} = 0.$$

Hence we may write, that in the neighbourhood of absolute zero $\sigma = \Delta H_s$, and

$$\lim_{T=0} \frac{\partial \sigma}{\partial T} = \lim_{T=0} \frac{\partial H_s}{\partial T} = 0.$$

The σ, T curve for any substance must therefore approach the temperature axis asymptotically in the neighbourhood of absolute zero.

Adsorption. When two or more homogeneous phases are brought into contact, the surface of separation is not merely a two-dimensional boundary, but it has a certain definite thickness. That is to say, when we pass from one phase to another, instead of the abrupt change from one into the other which we might expect, there is a region in which the concentrations of the two phases are markedly different from those in the main bulk. Thus, for instance, if porous charcoal is present in a gas, the surface of separation contains a layer of gas molecules at a concentration much higher than that in the pure gaseous phase. Moreover, it is found by experiment that these gas molecules are very tenaciously held by the surface, especially at low temperatures. This phenomenon is known as **Adsorption.** Another familiar example is obtained in the purification of organic substances by boiling with animal charcoal, when the dissolved colouring matters are adsorbed and may thus be separated from the solution.

Gibbs (*Scientific Papers*, vol. II) showed on the basis of thermodynamics, that if any substance is dissolved in a liquid and thus decreases the surface tension of that liquid, e.g. at the liquid-air interface, then that substance will exist in a **higher** concentration in the surface layer than in the bulk of the solution, that is, it will be adsorbed at the surface. We now propose to give one of the several proofs of this principle.

Suppose we have a system consisting of a solution of volume V and osmotic pressure P, in contact with the atmosphere, the surface under consideration being that between the liquid and the atmo-

sphere. The solution is separated from a quantity of pure solvent by a semi-permeable membrane, which is arranged in the form of a piston. We now imagine the following cycle of changes to be carried out upon the system.

I. The surface area is increased by an amount ds. This involves an increase in the free energy of $\sigma.ds$. The volume of the solution is regarded as having remained constant during this process. The osmotic pressure of the solution may, however, have altered, since some of the solute may have been adsorbed upon the new portion of the surface. Let the new osmotic pressure be $\left(P + \frac{\partial P}{\partial s}ds\right)$.

II. The volume of the solution is now increased by the amount dV by means of the semi-permeable membrane. The work done by the system is evidently $\left(P + \frac{\partial P}{\partial s}ds\right).dV$, and since this is not an increase of the system as a whole, but merely a process occurring in it, this is equal to the decrease in free energy of the system. The surface area is regarded as constant during this last operation. The surface tension has changed, however, to $\left(\sigma + \frac{\partial \sigma}{\partial V}dV\right)$.

III. The surface is now caused to contract to its initial area, when there is an increase in the free energy of amount $-\left(\sigma + \frac{\partial \sigma}{\partial V}dV\right)ds$. The osmotic pressure has now returned to its initial value P.

IV. The volume of the solution is now decreased by the amount dV, by pushing the semi-permeable membrane further in. This involves an increase in the free energy of amount PdV.

The cycle is now complete and since it has been accomplished isothermally and reversibly, by hypothesis, the total change in the free energy of the system must be zero. Hence we may write

$$\Delta F = \sigma.ds - \left(P + \frac{\partial P}{\partial s}ds\right)dV + \left(\sigma + \frac{\partial \sigma}{\partial V}dV\right)ds + PdV = 0$$

or

$$\frac{\partial \sigma}{\partial V} = -\frac{\partial P}{\partial s} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

This equation states that if the surface tension increases with increase in V, that is with decrease in the concentration, then the osmotic pressure of the solution will decrease with increase in the surface area. That is to say, if a substance lowers the surface tension of a liquid when it is dissolved in that liquid, then an

increase in the area corresponds to an increase in the adsorption of the solute at the surface.

Let us now suppose that this volume V of solution contains n moles of solute, so that, if no adsorption occurred, the concentration would be $\frac{n}{V}$ moles per unit volume. This is not, however, the actual concentration since the surface contains an excess which we shall denote by Γ per unit area. The true concentration in the bulk of the solution when the area is s will be $c' = \frac{n - \Gamma s}{V}$. The quantity Γs, may, of course, be either positive or negative according as the adsorption is positive or negative. We can now write equation (15) in the form—

$$\frac{\partial \sigma}{\partial c'} \cdot \frac{\partial c'}{\partial V} = \frac{\partial P}{\partial c'} \cdot \frac{\partial c'}{\partial s} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

But we have

$$\frac{\partial c'}{\partial V} = - \frac{n - \Gamma s}{V^2}; \quad \frac{\partial c'}{\partial s} = - \frac{\Gamma}{V}$$

so that equation (16) becomes

$$c' \frac{\partial \sigma}{\partial c'} = - \Gamma \frac{\partial P}{\partial c'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Thus far we have not introduced any hypothesis as to the nature of the solution. Equation (17) is therefore a perfectly general thermodynamic equation. If, now, we introduce the assumption that the solution obeys the gas law, we may write $P = RTc'$, so that we obtain

$$\Gamma = - \frac{c'}{RT} \cdot \frac{\partial \sigma}{\partial c'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

This equation shows at once that if the surface tension increases as c' increases then the adsorption is negative, and vice versa.

The experimental verification of this equation of Gibbs presents considerable difficulty. The only direct tests of its validity, having any quantitative value are those of McBain and of Harkins. McBain and Davies (*J. Amer. Chem. Soc.*, 1927, **49**, 2230) arranged a long almost horizontal tube containing a solution through which a slow and steady stream of uniform nitrogen bubbles could be passed without appreciable pulsation or pumping action. Much attention was given to the elimination of mixing effects, pressure

irregularities and other factors which would prevent the attainment of normal adsorption equilibria. At the upper end of the tube, the air bubbles with their liquid films were collected, drained of excess solution, and collected in a separate container. The difference between the amount of solute in the froth removed and that in an equal amount of the remaining solution—corrected for the gradual change—gave the amount of solute adsorbed at the liquid-gas interface of the bubbles passed through. The size and number of bubbles being known, the area of the surface could be calculated, and hence the value of Γ was obtained in grams per square centimetre. In all cases the results obtained were definitely greater than, but closely parallel to, the theoretical values. In similar experiments with 0·05 N sodium oleate solutions, an adsorption amounting to $1{\cdot}5 \times 10^{-9}$ equivalents of oleate radical per sq. cm. of surface was obtained (Laing, McBain, and Harrison, *Sixth Colloid. Symp.*, 1928, p. 63). The theoretical value should be zero, since the surface tension is found to be independent of the concentration of the oleate. Harkins and Gans (*Fifth Coll. Symp.*, 1927, p. 40, *Sixth Coll. Symp.*, 1928, p. 36) have also failed to confirm Gibbs' equation. The results indicate that the Gibbs expression gives values of the right order in some cases, but it appears as though the experimental technique is not sufficiently accurate as yet to enable a decisive test to be made. In any case it is somewhat premature to reject the equation of Gibbs, as McBain seems inclined to do, especially as it is a direct result of thermodynamic reasoning.

It is evidently much easier to determine adsorption experimentally in the case of rigid surfaces such as those of charcoal or silica gel. It is not possible to apply the Gibbs equation quantitatively to such a case, however, since the changes in free energy or surface tension with concentration defy measurement. At very low concentrations the distribution of a gas or solute between an adsorbent and the adjacent phase follows Henry's law. This is only an approximation for low concentrations, however, for the adsorption does not, in general, increase linearly with concentration. Over limited ranges, the adsorption may be expressed by means of the well-known adsorption isotherm,

$$a = k.c^m \text{ or } \log a = \log k + m \log c \quad . \quad . \quad . \quad (19)$$

where a is the weight of substance adsorbed per gram of solid adsor-

bent, c is the equilibrium concentration of the substance in the bulk and k and m are empirical constants. In most cases the constant m is found to decrease with increasing concentration or decreasing temperature, and this decrease indicates an approach to a condition of saturation which is inconsistent with the parabolic equation (19). The Freundlich isotherm can therefore be employed only as an interpolation formula within a limited concentration range.

The following numbers refer to ammonia adsorbed on meerschaum at 0° C. a is measured in c.cs. per gram of adsorbent, and c is replaced by pressure.

$$k = 54{\cdot}83\,; \quad m = 0{\cdot}184.$$

P. in cm. *Hg*.	a (Observed).	a (Calculated).
0·500	48·3	48·3
3·713	72·3	69·8
21·500	95·3	96·4
57·56	117·0	116·0

Since adsorption decreases with rise in temperature, it is to be expected, on the basis of Le Chatelier's principle that it will take place with absorption of heat. This is in agreement with the quantitative experiments of Titoff (*Zeit. phys. Chem.*, 1910, **74**, 641), Lamb and Coolidge (*J. Amer. Chem. Soc.*, 1920, **42**, 1146) and others. The majority of these data refer to what is termed the Integral Heat of Adsorption, that is the initial conditions are not definitely fixed—charcoal as free from gas as possible and pure gas—and adsorption is continued until atmospheric pressure is reached.

The differential heat of adsorption which corresponds to the heat of dilution, is defined as the quantity of heat which is developed upon transition from one state of equilibrium between adsorbent and gas to another state of equilibrium, i.e. from one equilibrium pressure to another. It is useful to distinguish between the **isosteric** heat of adsorption and the **isobaric** heat of adsorption.

The isosteric heat of adsorption is such that the amount adsorbed is kept constant while the pressure and temperature are varied. It is analogous to the heat of evaporation of a mixture. We are concerned with this mainly in the region of intermediate and high

pressures, in which the amount adsorbed changes but little. It is determined by the Clapeyron equation. If q is the heat evolved per mole of substance adsorbed we may write

$$q = RT^2 \frac{d \ ln \ p}{dT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

This equation was tested by Titoff and satisfactorily confirmed.

The isobaric heat of adsorption corresponds to the heat of a reaction in a condensed system, the amount adsorbed changes while the pressure remains practically constant. It concerns us most in the region of small pressures. In that region, as the isothermal indicates, the amount adsorbed changes rapidly while the pressure change is small.

Characteristics of Adsorption Equilibria. Freundlich gives the following characteristics of adsorption equilibrium as distinct from chemical equilibrium:

1. Adsorption obeys the isotherm $a = k \, . \, c^m$.
2. The variability of m with the adsorbed substance is small.
3. The variability of the constant k with the nature of the solid adsorbent is small.
4. The system attains the equilibrium state very rapidly.
5. The effect of temperature upon the equilibrium is relatively small.

Donnan's Theory of Membrane Equilibria. Suppose we have two solutions separated by a membrane which is permeable to one of the solutes, but not to the others. We might expect, at first, that this solute would diffuse through the membrane until the concentration on both sides had attained the same value. This, however, is not found to be the case, except when no non-diffusible substances are present. Donnan (*Zeit. Elektrochem.*, 1911, **17**, 572) on the basis of thermodynamics, has evolved a theory of such equilibria which has had a far-reaching and successful application in the fields of colloidal and physiological chemistry.

Suppose we have a salt, such as Congo red, which is the sodium salt of an organic acid, in solution in water. The salt will be practically completely ionized into $Na^{\cdot}$ ions and R' ions. The latter are incapable of diffusing through a membrane of collodion or parchment. We now place some of this solution in one side of a vessel which is divided into two compartments by a membrane. On the other side is placed a solution of common salt which is

ionized into $Na^{\cdot}$ and Cl'. We may represent this initial state by the diagram

$$\begin{array}{c|c} Na^{\cdot},\ R' & Na^{\cdot},\ Cl' \\ \text{I} & \text{II} \end{array}$$

The sodium chloride will diffuse from II to I until a condition of equilibrium is attained which may be represented by

$$Na^{\cdot},\ R',\ Cl' \mid Na^{\cdot},\ Cl'.$$

Let us assume that this equilibrium obtains in the system and imagine that an infinitesimally small quantity of $NaCl$ is transferred across the boundary. The change in the free energy will be

$$\Delta F = dn.RT\ ln\frac{a_{Na^{\cdot}\,\text{I}}}{a_{Na^{\cdot}\,\text{II}}} + dn.RT\ ln\frac{a_{Cl'\,\text{I}}}{a_{Cl'\,\text{II}}}$$

where dn is the number of moles transferred, from compartment II to compartment I, $a_{Na^{\cdot}\text{I}}$, $a_{Na^{\cdot}\text{II}}$, etc., are the activities of the ions in the respective compartments at the equilibrium point. But the characteristic of equilibrium is that this free energy change shall be zero, so that the above expression vanishes, or we have

$$a_{Na^{\cdot}\,\text{I}} \times a_{Cl'\,\text{I}} = a_{Na^{\cdot}\,\text{II}} \times a_{Cl'\,\text{II}} \quad . \quad . \quad . \quad (21)$$

It is unnecessary to take into consideration any potential difference which may exist between the two compartments since we are considering the transfer of equivalent quantities of $Na^{\cdot}$ and Cl' ions. If we carry out an exactly similar process for the undissociated sodium chloride molecules we obtain

$$dF = dn.RT\ ln\frac{a_{NaCl\,\text{I}}}{a_{NaCl\,\text{II}}} = 0$$

or

$$a_{NaCl\,\text{I}} = a_{NaCl\,\text{II}}.$$

Combining this equation with equation (21), we obtain the well-known law of mass action in terms of activities—

$$\frac{a_{Na^{\cdot}\,\text{I}} \times a_{Cl'\,\text{I}}}{a_{NaCl\,\text{I}}} = \frac{a_{Na^{\cdot}\,\text{II}} \times a_{Cl'\,\text{II}}}{a_{NaCl\,\text{II}}} = \text{Constant.}$$

Donnan deals with dilute solutions for which it is legitimate to write equation (21) in the approximate form involving concentrations. He assumes for simplicity that the solutes $NaCl$ and NaR are both completely dissociated and that the volumes of liquid on both sides of the membrane are the same.

The initial state of the system may be represented by the diagram—

$$\begin{array}{cc|cc} Na^{\cdot}, & R' & Na^{\cdot}, & Cl' \\ c_1 & c_1 & c_2 & c_2 \end{array}$$

while the final state may be represented as follows:

$$\begin{array}{ccc|cc} Na^{\cdot} & , R', & Cl' & Na^{\cdot} & , Cl' \\ c_1 + x & c_1 & x & c_2 - x & c_2 - x \end{array}$$

where c_1, c_2 are the initial concentrations in gram-ions per litre. x is the quantity which has diffused across the membrane. The percentage of $NaCl$ which has diffused is therefore $\frac{x}{c_2}100$. The equilibrium distribution ratio of the $NaCl$ is $\frac{c_2 - x}{x}$.

We may now write equation (21), substituting concentration terms for activities, as follows—

$$(c_1 + x)x - (c_2 - x)^2$$

or

$$x = \frac{c^2{}_2}{(c_1 + 2c_2)}$$

whence

$$\frac{x}{c_2} = \frac{c_2}{c_1 + 2c_2}$$

so that

$$\frac{c_2 - x}{x} = \frac{c_1 + c_2}{c_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

This equation gives us the distribution ratio of the sodium chloride in the presence of Congo red. Now if c_2, the concentration of the inorganic salt, is small compared with c_1, we may write

$$\frac{x}{c_2} = \frac{c_2}{c_1} \text{ and } \frac{c_2 - x}{x} = \frac{c_1}{c_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

As an example let us suppose that the concentration of the sodium chloride is one-hundredth that of the organic salt, i.e. $c_2 = \frac{c_1}{100}$ then $\frac{x}{c_2} = \frac{1}{100}$, or only 1 per cent. of the sodium chloride diffuses across the membrane.

If on the other hand c_1 is small compared with c_2, it follows that

$$\frac{x}{c_2} = \tfrac{1}{2} \text{ or } \frac{c_2 - x}{x} = 1$$

or the equilibrium state is characterized by equal concentrations of salt on both sides of the membrane. This is, as we should expect, the condition which obtains when no organic salt is present. The following table shows the variation of the distribution of sodium chloride between the solutions as a function of the concentrations of the *NaR* and *NaCl* itself:

Initial Concentration of *NaR* in I.	Initial Concentration of *NaCl* in II.	Initial Ratio *NaR*/*NaCl*.	Percentage *NaCl* diffused from II.	Distribution Ratio at Equilibrium.
c_1.	c_2.	c_1/c_2.	$100\frac{x}{c_2}$.	$\frac{c_2 - x}{x}$.
0·01	1	0·01	49·7	1·01
0·1	1	0·1	47·6	1·1
1	1	1	33	2·0
1	0·1	10	8·3	11·0
1	0·01	100	1·0	99·0

The equilibrium point is obviously independent of the fact that *NaCl* was initially present in compartment II. The same point would have been reached if some had been present in compartment I. This effect is very remarkable since we see that in spite of the permeability of the membrane to sodium chloride, the amount which diffuses may be practically negligible if a sufficient concentration of the organic salt of sodium *NaR* is present on the further side. It is evident that this phenomenon will be of great importance in physiology, where membranes play a very large part in controlling the body functions. The unequal distribution of sodium chloride on two sides of a parchment membrane owing to the presence of Congo red on one side has been experimentally demonstrated by Harris in Donnan's laboratory.

Influence on Osmotic Pressure Measurements. It will be evident that it is impossible to measure the osmotic pressure of an organic salt *NaR* directly in the presence of diffusible inorganic salts such as *NaCl*, since the unequal distribution of the *NaCl* is manifested by an inequality of the osmotic pressure due to this salt on the two sides of the membrane. We can, however, proceed as follows. Let us assume that the salts are completely dissociated and that the ions obey the gas laws. Then if P_0 is the true

osmotic pressure of a solution of NaR of concentration c_1, we may write

$$P_0 = 2.RT.c_1.$$

Let P be the opposing osmotic pressure of the sodium chloride, then assuming the equilibrium arrangement already discussed—

$$P = 2(c_2 - x)RT - 2xRT = 2(c_2 - 2x)RT.$$

Hence the observed osmotic pressure will be

$$\begin{aligned} P_1 = P_0 - P &= 2RTc_1 - 2RT(c_2 - 2x) \\ &= 2RT(c_1 - c_2 + 2x) \end{aligned}$$

or putting $x = \dfrac{c^2{}_2}{c_1 + 2c_2}$ we obtain

$$\frac{P_1}{P_0} = \frac{c_1 + c_2}{c_1 + 2c_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

If c_1, the concentration of the organic salt whose osmotic pressure we desire to measure, is small compared with c_2, then $P_1 = \frac{1}{2}P_0$ or the observed osmotic pressure is one-half the true osmotic pressure. If c_2 is small compared with c_1, we naturally obtain $P_1 = P_0$. The following table illustrates these relationships:

Ratio c_2/c_1.	Ratio P_1/P_0.
0·1	0·92
1	0·67
2	0·60
10	0·52

The observed osmotic pressure of an electrolytically dissociated non-dialysing substance is thus lowered by the addition of an electrolyte having a common ion. This has been experimentally verified by Donnan and Harris (*J. Chem. Soc.*, 1911, **99**, 1554); Donnan and Allmand (ib., 1914, **105**, 194); Donnan and Garner (ib., 1919, **115**, 1313) and Biltz (*Zeit. phys. Chem.*, 1913, **83**, 625).

Effect of an Electrolyte without a Common Ion.

We may treat this case in a precisely similar manner to the simpler one just considered. The initial conditions may be represented by—

$Na^{\cdot}$, R'	$K^{\cdot}$, Cl'
c_1 c_1	c_2 c_2
I	II

while the final state is represented by

$$\begin{array}{cccc|ccc} Na^{\cdot} & , K^{\cdot} & , Cl' & , R' & K^{\cdot} & , Cl' & , Na^{\cdot} \\ c_1 - z & x & y & c_1 & c_2 - x & c_2 - y & z \end{array}$$

The solutions on either side of the membrane must be electrically neutral so that $z = x - y$, i.e. the number of ions of $Na^{\cdot}$ which pass from I to II must equal the algebraic sum of the number of moles of $K^{\cdot}$ and the number of moles of Cl' (according to the sign of their electric charge) which pass from II to I.

Let us now consider the transfer of a small quantity dn gram-ions of $Na^{\cdot}$ from I to II, and a simultaneous transfer of an equivalent quantity dn gram ions of $K^{\cdot}$ in the reverse direction. The electrical work will be zero since the quantities are equivalent and the change in free energy will be given by

$$dF = dn\ RT ln \frac{(Na^{\cdot})\,\mathrm{II}}{(Na^{\cdot})\,\mathrm{I}} + dnRT\ ln\ \frac{(K^{\cdot})\,\mathrm{I}}{(K^{\cdot})\,\mathrm{II}} = 0$$

so that

$$\frac{(Na^{\cdot})\,\mathrm{II}}{(Na^{\cdot})\,\mathrm{I}} = \frac{(K^{\cdot})\,\mathrm{II}}{(K^{\cdot})\,\mathrm{I}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Again by transferring dn moles of $Na^{\cdot}$ and dn moles of Cl' from I to II we obtain

$$\frac{(Na^{\cdot})\,\mathrm{I}}{(Na^{\cdot})\,\mathrm{II}} = \frac{(Cl')\,\mathrm{II}}{(Cl')\,\mathrm{I}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

and by transferring dn moles of $K^{\cdot}$ and dn moles of Cl' from I to II we obtain

$$\frac{(K^{\cdot})\,\mathrm{I}}{(K^{\cdot})\mathrm{II}} = \frac{(Cl')\,\mathrm{II}}{(Cl')\,\mathrm{I}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

Combining these three equations and substituting the values of the equilibrium concentrations we obtain

$$\frac{(Na^{\cdot})\,\mathrm{I}}{(Na^{\cdot})\,\mathrm{II}} = \frac{(K^{\cdot})\,\mathrm{I}}{(K^{\cdot})\,\mathrm{II}} = \frac{(Cl')\,\mathrm{II}}{(Cl')\,\mathrm{I}} = \frac{c_1 + c_2}{c_2} = r \quad . \quad . \quad . \quad (27)$$

As an example we may consider the case where the ratio c_1/c_2 is 100, i.e. where the organic salt is present in great excess. The following changes from the initial state will occur:

(1) 99 per cent. of the $K^{\cdot}$ ions originally present in II will diffuse into I.

(2) Only 1 per cent. of the Cl' ions originally present in II will diffuse into I.

(3) Only 1 per cent. of the $Na^{\cdot}$ ions originally present in I will diffuse into II.

If on the other hand c_1 is small compared with c_2, we have $r = \frac{c_2}{c_2} = 1$ or the equilibrium distribution corresponds to equal concentrations of $Na^{\cdot}$, $K^{\cdot}$ and Cl' on both sides of the membrane, as we should expect. It will therefore be evident that the presence of the organic salt has a marked effect upon the diffusion of the salt. In fact it appears in the above case where $c_1/c_2 = 100$, as though there has been a marked preferential effect for the potassium ions, since 99 per cent. of these ions diffuse into I while only 1 per cent. of the Cl' ions diffuse.

Hydrolytic Decomposition of Salts by Membranes. We shall now consider the case of a non-dialysable salt on one side of a membrane with **pure water** on the other. The initial ionic concentrations may be represented as follows:

$Na^{\cdot}$, R'	Pure
c_1 , c_1	water
I	II

The Na^+ ions will pass through the membrane into compartment II where they will form dissociated sodium hydroxide, and a corresponding number of H^+ ions must diffuse into compartment I. The equilibrium state may be represented by the following diagram:

$Na^{\cdot}$, $H^{\cdot}$, R'	$Na^{\cdot}$, OH'
$c_1 - x$, x c_1	x x

We shall once more assume complete dissociation of all the electrolytes present, and that the volumes of the two compartments are equal. We shall also assume that the concentration of the hydrions in I at equilibrium is large compared to that in pure water. Let us imagine the transfer of dn gram-ions of $Na^{\cdot}$ and dn gram-ions of OH' from I to II. Since the system is in equilibrium the free energy change will be zero, that is

$$dF = dn.RT\ ln\ \frac{(Na^{\cdot})\,\mathrm{II}}{(Na^{\cdot})\,\mathrm{I}} + dnRT\ ln\ \frac{(OH')\,\mathrm{II}}{(OH')\,\mathrm{I}} = 0$$

so that we may write

$$\frac{(Na^{\cdot})\,\mathrm{I}}{(Na^{\cdot})\,\mathrm{II}} = \frac{(OH')\,\mathrm{II}}{(OH')\,\mathrm{I}} \quad \ldots\ldots \quad (28)$$

Substituting the values for the equilibrium concentrations we obtain—

$$\frac{c_1 - x}{x} = \frac{x}{(OH')\,\mathrm{I}}.$$

Now if K_w is the ionization constant for water we have

$$(x)(OH') = K_w,$$

so that we may write

$$\frac{c_1 - x}{x} = \frac{x^2}{K_w}$$

or

$$x^3 = K_w(c_1 - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

If x is small compared with c_1, this expression becomes

$$x^3 = K_w.c_1$$

or

$$x = (K_w.c_1)^{\frac{1}{3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

The following table shows the type of results obtained at 25° C., $K_w = 10^{-14}$:

c_1.	x.	$100x/c_1$.
0·01	5×10^{-6}	0·05 per cent.
0·1	1×10^{-5}	0·01 „ „
1	2×10^{-5}	0·002 „ „

This equation is, as we have stated, derived on the assumption that the two compartments have the same volume. If, however, the volume of compartment II is v times the volume of I then the equation takes the form

$$x = (K_w.v^2.c_1)^{\frac{1}{3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

Although the extent of this hydrolysis is very small, it must always occur when we have an electrolyte, one ion of which cannot pass through a membrane, separated from pure water by such a membrane. Not only will this hydrolysis affect the observed osmotic pressures of electrolytic colloids, but this process explains the removal by dialysis of only one of the ions of an electrolyte absorbed by a gel. The gel itself acts as a membrane and if it is only permeable to one of the ions of the electrolyte, this ion alone will diffuse and be removed by the surrounding water, leaving the other ion in the form of acid or base according as to whether it was the anion or the cation of the electrolyte originally present.

If the acid formed by hydrolysis HR is a weak acid there will evidently be a decrease in the hydrogen ion concentration in compartment I, and consequently the degree of hydrolysis will be greater.

We shall confine ourselves to the case when the acid is a very weak one, that is when the dissociation constant K_a of the acid is very small. We may represent the equilibrium conditions as follows :

I					II	
$Na^{\cdot}$	$, OH'$	$, HR,$	R'		$Na^{\cdot}$	$, OH'$
$c_1 - x$	$y - x$	y	$c_1 - y$		x	x

Here y is the concentration of HR undissociated. Corresponding to the y gram-ions of $H^{\cdot}$ which are thus removed from the solution, there will be y OH' ions present in compartment I. But x gram-ions of OH' have diffused into compartment II leaving a concentration of $(y - x)$ OH' ions. Let $(H^{\cdot})_1$ be the concentration of hydrions in compartment I, then we may write

$$(y - x)(H^{\cdot})_1 = K_w$$
$$(c_1 - y)(H^{\cdot})_1 = K_a y$$

so that dividing one expression by the other

$$\frac{c_1 - x}{y - x} = \frac{K_a}{K_w} y.$$

But by equation (28) which is still applicable to the present case

$$\frac{c_1 - x}{x} = \frac{x}{(OH')_1} = \frac{x}{y - x} \quad . \quad . \quad . \quad . \quad . \quad (33)$$

so that

$$y = \frac{c_1 x}{c_1 - x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

Substituting this value in equation (32) we obtain

$$x^3 = \frac{K_w}{K_a}(c_1 - x)\,(c_1 - 2x). \quad . \quad . \quad . \quad . \quad (35)$$

If x is small in comparison with c_1 $\left(\text{i.e. } x \text{ is less than } \frac{c_1}{100}\right)$ this equation takes the approximate form

$$x^3 = \frac{K_w}{K_a} c_1^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

The following values for x will indicate the order of magnitude of this effect of a small dissociation constant:

$c_1 = 1$; $K_w = 10^{-14}$; the values of x are calculated from equation (36).

$K_a = 10^{-5}$; $x = 10^{-3}$; $100x = 0{\cdot}1$

$K_a = 10^{-8}$; $x = 10^{-2}$; $100x = 1{\cdot}0$.

These hydrolytic effects have been investigated experimentally and the results have served to confirm the theory.

Membrane Potential Difference. In any of the experiments considered there is a definite potential difference between the two sides of the membrane. This potential difference between the solutions at equilibrium is due to the difference between the concentrations of the ions on the two sides. We may consider the case of the following equilibrium condition

$$\underset{\text{I}}{Na^{\cdot};\ R';\ Cl'} \mid \underset{\text{II}}{Na^{\cdot};\ Cl'}$$

Let E be the potential difference between the two compartments, the potential of II being taken as greater than that of I. Suppose the extremely small quantity $Q.dn$ coulombs of positive electricity is transferred isothermally from II to I. This involves a decrease in the free energy of $-Q.dnE$, due to the electrical work done. In addition there is a free energy change due to the transfer of the ions. pdn gram-ions of $Na^{\cdot}$ have passed from II to I involving a decrease in the free energy of $pdn.RT\ ln\ \frac{(Na^{\cdot})\,\text{I}}{(Na^{\cdot})\,\text{II}}$ and simultaneously qdn gram-ions of Cl' have passed in the reverse direction involving a decrease in the free energy of $q.dnRT\ ln\ \frac{(Cl')\,\text{II}}{(Cl')\,\text{I}}$. p and q are the transport numbers of the $Na^{\cdot}$ and Cl' ions respectively, so that $p + q = 1$. The total change in the free energy must be zero since the system is in equilibrium, hence

$$-Q.dn.E + p.dn.RT\ ln\ \frac{(Na^{\cdot})\,\text{I}}{(Na^{\cdot})\,\text{II}} + q.dn.RT\ ln\ \frac{(Cl')\,\text{II}}{(Cl')\,\text{I}} = 0.$$

Now we have seen that

$$\frac{(Na^{\cdot})\,\text{I}}{(Na^{\cdot})\,\text{II}} = \frac{(Cl')\,\text{II}}{(Cl')\,\text{I}} \text{ and } p + q = 1.$$

Hence we obtain

$$-E = \frac{RT}{Q}\ ln\ \frac{(Na^{\cdot})\,\text{II}}{(Na^{\cdot})\,\text{I}} = \frac{RT}{Q}\ ln\ \lambda \quad . \quad . \quad . \quad (37)$$

Now for the particular case investigated we have seen that

$$\lambda = \frac{x}{c_2 - x} = \frac{c_2}{c_1 + c_2}.$$

Hence we obtain

$$E = \frac{RT}{Q} ln \frac{c_1 + c_2}{c_2}$$

$$= \frac{RT}{Q} ln \left(1 + \frac{c_1}{c_2}\right) \quad . \quad . \quad . \quad . \quad (38)$$

If c_2 is small in comparison with c_1 this expression becomes

$$E = \frac{RT}{Q} ln\, c_1/c_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

If on the other hand c_1 is small in comparison with c_2 the potential difference approximates to zero, as we should expect, for in the limit in which there is no *NaR* present at all, the *NaCl* will distribute itself in equal concentration on each side of the membrane. The following table illustrates the numerical values of the potential difference E obtained for a series of arbitrarily chosen ratios c_1/c_2.

c_1/c_2	1	10	100	1000
E	+0·017	+0·060	+0·116	+0·174

In a similar manner we may consider the case represented by the following diagram, *KCl* replacing the sodium chloride of the case just considered:

$$\underset{\text{I}}{Na^{\cdot}, K^{\cdot}, Cl', R'} \;\Big|\; \underset{\text{II}}{Na^{\cdot}, K^{\cdot}, Cl'}.$$

In this case if we consider the transfer of $Q.dn$ coulombs of positive electricity from compartment II to compartment I this will be carried by $(p.dn)$ $Na^{\cdot}$ ions and $(q.dn)$ $K^{\cdot}$ ions moving from II to I and $(s.dn)$ Cl' ions moving in the reverse direction from I to II. The free energy increase due to the transfer alone will be

$$p.dn\, ln \frac{(Na^{\cdot})\,\text{I}}{(Na^{\cdot})\,\text{II}} + q.dn\, ln \frac{(K^{\cdot})\,\text{I}}{(K^{\cdot})\,\text{II}} + s.dn\, ln \frac{(Cl')\,\text{II}}{(Cl')\,\text{I}}.$$

In this equation we have

$$p + q + s = 1.$$

There is also a free energy change due to the potential difference

between the two compartments. If this P.D. be represented by E where compartment II is reckoned as positive, then the free energy increase of the system or the work done upon the system (at constant pressure) due to the electrical forces is $-E.Q.dn$. Hence the total increase in the free energy is given by

$$\Delta F = -E.Q.dn + dn.RT\left(p\,ln\frac{(Na^{\cdot})\,\mathrm{I}}{(Na^{\cdot})\,\mathrm{II}} + q\,ln\frac{(K^{\cdot})\,\mathrm{I}}{(K^{\cdot})\,\mathrm{II}} + s\,ln\frac{(Cl')\,\mathrm{II}}{(Cl')\,\mathrm{I}}\right)$$

Since the system is in equilibrium this free energy change must be zero. Now we have seen by equation (27) that

$$\frac{(Na^{\cdot})\,\mathrm{I}}{(Na^{\cdot})\,\mathrm{II}} = \frac{(K^{\cdot})\,\mathrm{I}}{(K^{\cdot})\,\mathrm{II}} = \frac{(Cl')\,\mathrm{II}}{(Cl')\,\mathrm{I}} = \frac{c_1 + c_2}{c_2} = r.$$

Hence we obtain

$$E = \frac{RT}{Q}\,ln\ r = \frac{RT}{Q}\,ln\frac{c_1 + c_2}{c_2} \quad . \quad . \quad . \quad . \quad (40)$$

If c_2 is small in comparison with c_1 this expression reduces to

$$E = \frac{RT}{Q}\,ln\ c_1/c_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

Again from a consideration of the case of membrane hydrolysis where pure water is present originally upon one side of the membrane, we obtain

$$E = \frac{RT}{Q}\,ln\,\lambda$$

where λ is given by the equations

$$\lambda = \frac{(Na^{\cdot})\,\mathrm{II}}{(Na^{\cdot})\,\mathrm{I}} = \frac{(H^{\cdot})\,\mathrm{II}}{(H^{\cdot})\,\mathrm{I}} = \frac{(OH')\,\mathrm{I}}{(OH')\,\mathrm{II}}.$$

But we have seen that

$$\lambda = \frac{x}{c_1 - x}.$$

Confining ourselves to the case where x is small, we may write

$$\lambda = \frac{x}{c_1} = \frac{\sqrt[3]{K_w.c_1}}{c_1}.$$

Hence we obtain

$$E = \frac{RT}{Q}\,ln\,\frac{c_1}{\sqrt[3]{K_w.c_1}} \quad . \quad . \quad . \quad . \quad . \quad (42)$$

The following are the values calculated from this equation for 25° C.

c_1.	E.
1·0	+ 0·30
0·01	+ 0·19

In a similar manner we may consider the case when the HR formed is a weak acid of dissociation constant K_a.

These considerations have had an extensive application especially in the realm of colloid chemistry. For a consideration of the various aspects of the theory in regard to its application to the case of proteins, see Loeb, *Proteins and the Theory of Colloidal Behaviour*.

Conclusion

It might possibly be thought from the discussion in the preceding pages that the principles of thermodynamics may be infallibly applied to every possible type of system under whatever set of conditions may happen to obtain at the moment. This is, however, by no means the case, and it may be of interest, before closing this book, to consider briefly the more obvious limitations of the principles which we have developed.

The consideration of the First and Second Laws of Thermodynamics showed us that they are essentially laws of experience which are based entirely upon negative evidence—the non-occurrence of certain events. Now whilst the mass of this evidence is so overwhelming as to make any doubt of the universal validity of these laws appear almost unthinkable, it is well to bear in mind that it is negative evidence. Many authors have extended these two laws to include the whole universe. This is the idea underlying the well-known statement of Clausius that

> "Die Energie der Welt ist constant,
> Die Entropie der Welt strebt einen Maximum zu."

This view does not, however, appear to be entirely warranted by the information at our disposal. In the first place, it makes the assumption that the universe is a finite system in complete thermal isolation, and whilst the recent theories of Einstein lend some support to this assumption, the question is still open to discussion. Again the problem as to whether or not living beings are capable of bringing about a violation of the Second Law is still unsolved. However, these questions are purely speculative and have little bearing upon the practical applications of our subject.

More fundamental limitations are involved in the fact that the Second Law is, as we have seen, a statistical principle based upon the laws of probability. It states that any thermally isolated system tends to a condition of maximum probability which is characterized by a maximum value of the entropy function. The statistical considerations underlying this law only refer to systems

containing a very large number of units. It is evident, therefore, that such a principle must, in view of its statistical nature, be limited in its application. Thus, for example, suppose we consider a system containing a large number of molecules of some substance which is undergoing a chemical change. A good example of such a system is a radioactive substance. We can apply probability considerations and the principles of thermodynamics to the whole system and determine the rate of the reaction at any instant. That is to say, we may calculate the number of molecules which will undergo transformation in any given interval of time. But if we consider, for the moment, some one individual molecule, or even a small cluster of such molecules, we are entirely at a loss. The given molecule or molecules may or may not be among the number which will undergo transformation in the given interval, and thermodynamics is powerless to predict the answer. Thus it appears that, as regards microscopic systems, that is systems containing only a few units (whether these be molecules or stars), the Second Law is no longer applicable.

Another limitation of thermodynamic principles, and one which has been brought prominently before the notice of chemists and physicists in recent years, is the consideration that they rest upon the assumption that energy transformations are always continuous in nature. This assumption is involved in the fact that we have regarded the energy quantities, U, F, A, etc., to be continuously variable functions of the system. The admissibility of this assumption is by no means unquestioned as regards certain classes of phenomena, notably the emission and absorption of radiation by matter. In fact, the fundamental postulate of Planck's Quantum Theory is that radiation is absorbed and emitted discretely and not continuously.

However, in spite of these limitations, or perhaps because of them, Thermodynamics has been and still is a very useful and powerful tool in the hands of the investigator, both in the more theoretical and academic aspects of chemistry and also, to a rapidly increasing extent, in the technical applications of chemistry to industrial processes.

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