The apparatus here described has proved very efficient, and we are able to obtain very satisfactory duplicate results in two combustions of the same substance. Practically no trouble is experienced in obtaining a constant temperature of the calorimeter system either at the beginning or end of a combustion; in fact, with the room temperature even 5° higher than that of the calorimeter water, constant readings have been obtained. With this calorimeter, the time required for a combustion is much less than usual, inasmuch as long preliminary and final periods are avoided and the calculation is materially simplified.

NUTRITION LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON,
BOSTON, MASSACHUSETTS.

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A SIMPLE SYSTEM OF THERMODYNAMIC CHEMISTRY BASED UPON A MODIFICATION OF THE METHOD OF CARNOT.

BY EDWARD W. WASHBURN.

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CONTENTS.

1. Introduction. 2. Description of the perfect thermodynamic engine. 3. The vapor pressure of a pure substance. 4. The homogeneous physical mixture. 5. Homogeneous chemical equilibrium. 6. Heterogeneous chemical equilibrium. 7. Electromotive force. 8. The colligative properties of a solution. 9. Summary and conclusion.

1. Introduction.

In order to determine the maximum amount of work which can be obtained from a given amount of heat by a fall in temperature, Carnot, in 1824, performed an "imaginary experiment," the Carnot Cycle. In performing this "experiment" Carnot made use of the simplest and most familiar example of a mechanism for obtaining work from heat, the cylinder and piston of the steam engine. He realized clearly that in order to obtain the desired relation he had only to *imagine* a mechanism which could operate under the most ideal conditions, one which represented the limit approached by all actual machines of the same class, as the losses due to friction, heat radiation and conduction, incomplete external compensation, etc., became indefinitely small. The reversible cyclical process thus invented by Carnot and later slightly modified by the work of Clapeyron and of Clausius, constitutes to-day the basis for the derivation of the mathematical formulation of the Second Law of Thermodynamics. Resting upon this law, the whole structure of thermodynamics has since been built up.

In the process of constructing our systems of thermodynamic chemistry, two general methods may be distinguished. The first of these, the analytic method, starts with Clausius' formulation of the Second Law in terms of entropy. The manner in which the entropy function might be used with advantage by the chemist was first illustrated by Horstmann, who applied it to many problems in chemical equilibrium. The later advocates of the analytic method, however, have not found it convenient to restrict themselves to the entropy function, but have defined and made use of a number of other thermodynamic functions. Willard Gibbs, in his masterly contributions to thermodynamic chemistry, defined four of these functions, his ε, ψ, χ and ζ functions; the ζ function, or the so-called Gibbs thermodynamic potential, being the one most commonly employed to-day. The system invented by Gibbs has been followed by Duhem, Planck, van der Waals, van Laar, and others, usually however receiving some modification at the hands of each investigator. Thus Planck, instead of using Gibbs' Zeta function, prefers another potential which he defines as equal to $-\zeta/T$, where T is the absolute temperature; and recently G. N. Lewis has constructed a very simple analytic system of thermodynamic chemistry by introducing two new functions, the fugacity, Ψ, and the activity, ξ, which are connected with each other by the equation, $\Psi = \xi RT$, and whose relation to Gibbs' Zeta function is expressed by the equation $\zeta = RT\ln\Psi + f(T)$. Although here classed among the analytic methods, this system owes a large part of its increased simplicity to the fact that its fundamental equations are derived by employing the second general method instead of starting with the entropy function as might have been done.

The second general method of constructing a system of thermodynamic chemistry is the Carnot method, or, as it is usually called to-day, the cyclical process method. This has been the favorite method among chemists, and to it we owe most of our advances in this branch of chemistry, as illustrated by the work of such men as van't Hoff, Ostwald, Arrhenius and Nernst. It is the simplicity of the processes involved in this method and the consequent protection against error which constitute its great advantages over the more intricate and abstruse, but yet not necessarily more rigorous methods based upon the entropy and thermodynamic potential functions. This has been well stated by Mach in his comment upon the discoverer of the second law: "Carnot, by whose ideas the whole of thermodynamics is ruled to-day, ... affords us the most pleasing picture of a genius who, without apparent exertion and without the labored application of intricate and cumbersome scientific methods, but solely through the consideration of the simplest processes, is able, almost without effort, to perceive the most fundamental truths."

The cyclical process method of deriving thermodynamic equations as applied by many of its advocates has been the subject of considerable adverse criticism mainly upon two grounds: (1) As usually carried out, the cyclical process consists of a series of steps, usually four, in each of which certain amounts of work and of heat are involved, the desired result being obtained by combining properly all the work and heat terms of the various steps in the cycle. The complete process is consequently rather long in some instances and is regarded by some writers as very cumbersome compared with some of the corresponding analytic methods. (2) In writing down the work and heat terms for the various steps of the cycle, it is customary to introduce some assumption such as the perfect gas law or one of the laws of dilute solutions, with the result that a rigorous, purely thermodynamic equation is not obtained, but only an approximate one containing one or more arbitrary assumptions. The possibility of introducing these assumptions is the most serious objection which can be offered to the cyclical process method, as carried out at present. So general is this practice, that in the text-books employing this method one looks almost in vain for exact thermodynamic equations such as those relating to chemical equilibrium, for example.

In the following pages a modification of the Carnot method will be described which eliminates completely both of these objections: (1) the cycle is reduced to a single step and the desired relation can be written down simply by inspection; (2) the differential equation so obtained will always be entirely rigorous because it is impossible to introduce into the process any assumptions except the Second Law of Thermodynamics. This gain in simplicity and exactness is accomplished by joining together the various pistons of the ordinary cycle so as to form a single complete engine which we shall call the Perfect Thermodynamic Engine. After describing the construction and operation of this engine, its application will be illustrated by using it in order to derive a number of the more important relations of thermodynamic chemistry. While the treatment of the subject in the following pages must necessarily be rather concise, it can, I believe, be followed easily by any chemist familiar with the elements of thermodynamics and the calculus.

2. The Perfect Thermodynamic Engine.

Figures 1, 2 and 3 illustrate different types of the engine, the essential parts of which are the following (see Fig. 1):

Two *reaction chambers* (**E** and **E′**) contain the system under consideration. Each chamber is placed in a *reservoir* (**R** and **R′**) of infinite heat capacity for the purpose of maintaining a constant temperature within the chamber. Each chamber is fitted with a set of *cylinders* (**A, B, D, A,′ B′, D′**, etc.) which connect with it through suitable *semipermeable membranes*, **aa, a′a′**. The cylinders are fitted with frictionless pistons (**A, B, D, A′, B′, D′**, etc.), some of which are semipermeable, others impermeable. Each corresponding pair of pistons is connected by a rigid piston rod, thus forming a *compound piston* (**AA′, BB′, DD′**, etc.). The piston rods have zero heat capacities and are non-conductors of heat and electricity, and the two reservoirs, **R** and **R′**, are otherwise insulated from each other so that no irreversible transfer of heat can take place between them. During the *operation* of the engine the following conditions must be fulfilled: (1) The two reservoirs must never differ from each other, in temperature, by more than an infinitesimal amount; when such a difference exists, the temperature of **R** will be designated by T and that of **R′** by $T + dT$; (2) The pressure difference against the two heads of a compound piston must never exceed an infinitesimal amount; the pressures exerted against the pistons of **E** will be designated by p, P, etc., those exerted against the pistons of **E′**, by $p + dp$, $P + dP$, etc. The *operation* of the engine consists in the movement of the com-

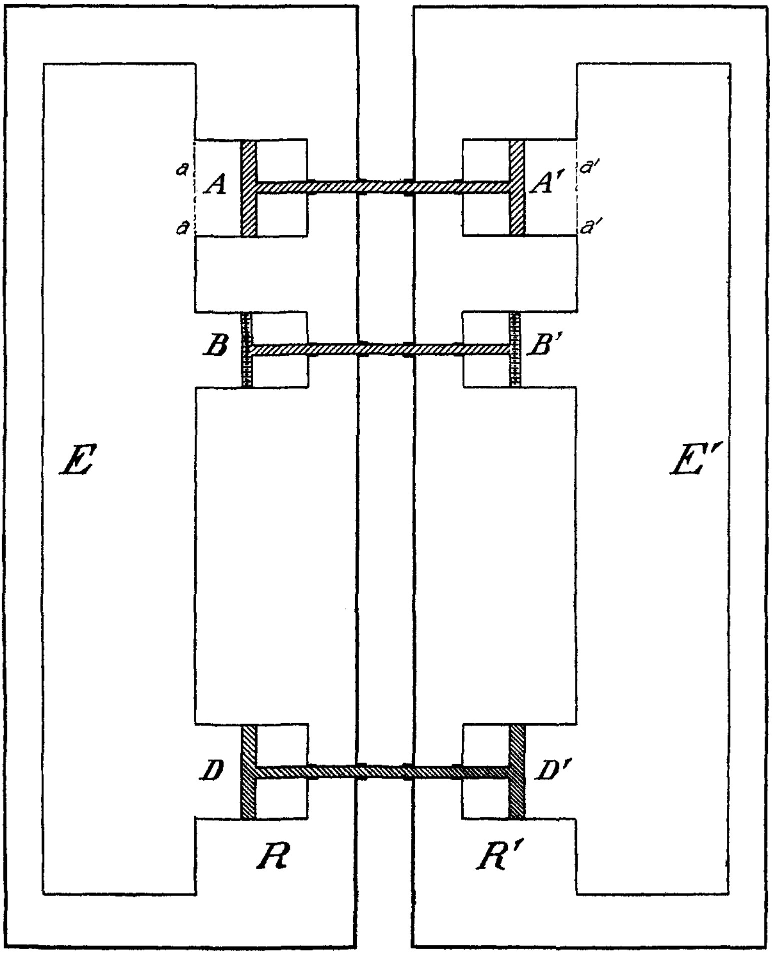

Fig. 1.

pound pistons through finite distances, accompanied by corresponding processes which take place within the reaction chambers. Other conditions which must be fulfilled during this operation are (3) that each compound piston must always move so as to produce the maximum amount of external work, there being applied to it a compensating external pressure substantially equal to the pressure difference on the two piston-heads; and (4) that the rates of motion of all the pistons must be so regulated that the equilibrium within the reaction chambers remains undisturbed. In other words, the engine must operate reversibly.

By the Second Law of Thermodynamics, the following two theorems, regarding the work produced during the *operation* of the engine, are true:

Theorem I.—The total work produced during the isothermal *operation* (temperature of **R** = temperature of **R**′) of the engine is equal to zero.

Theorem II.—When the engine operates as a heat engine (temperature of **R** $= T$, that of **R**′ $= T + dT$), the total work produced is equal to $Q\ dT/T$, where Q is the heat absorbed from reservoir **R**′.

It should also be noted that the algebraic expression for the work produced by any compound piston during the operation of the engine will have a positive sign when the motion is from right to left and a negative sign when the motion is from left to right. Since one complete "operation" of the engine, as we shall use the term, is not a complete cycle, it will be necessary to demonstrate the truth of these two theorems. This will be done in the next section, in which certain other details concerning the construction and operation of the engine will also be described.

3. The Vapor Pressure of a Pure Substance.

The equilibrium between vapor and liquid (or vapor and solid) in a one-component system may be altered: (1) by changing the total pressure on the liquid (or solid) phase at constant temperature; (2) by changing the temperature of the system while keeping the pressure on the liquid (or solid) phase constant; or (3) by changing the temperature of the system and at the same time allowing the total pressure on the liquid (or solid) phase to vary in such a manner that it is always equal to the vapor pressure. We shall make use of the perfect thermodynamic engine in order to determine the separate effects of these different factors upon the vapor pressure of a pure liquid. The treatment for the case of a pure solid is perfectly analogous.

The Pressure Coefficient (T = *const.*).—We shall use the engine shown in Fig. 1, omitting, however, pistons and cylinders **BB**′. The arrangement of the engine is as follows:

Chamber **E**: Filled with the liquid whose vapor-pressure, acting through the membrane **aa** (permeable to vapor only) against piston **A**, is p. Total pressure on liquid, acting against piston **D**, is P. Temperature of **R** = T.

Chamber **E′**: Exactly as **E** except that the total pressure on the liquid, acting against piston **D′**, is $P + dP$ and the vapor-pressure, acting against piston **A′**, is $p + dp$.

To operate the engine allow piston **AA′** to move reversibly toward the left until one mol of the vapor in cylinder **A** condenses through the membrane into chamber **E** and an equal volume v is evaporated from chamber **E′** into cylinder **A′**. At the same time and at such a rate as not to disturb the equilibrium in either chamber, piston **DD′** moves reversibly toward the right through the volume V occupied by one mol of the liquid under the pressure P. The work done by piston **AA′** is vdp, and that done by piston **DD′** is $-VdP$. By the Second Law (*i. e.*, Theorem I) the total work is equal to zero, which gives us the equation

$$vdp - VdP = 0 \tag{1}$$

or

$$(\partial p/\partial P)_T = V/v, \tag{2}$$

an equation first obtained by Poynting.[1]

If the vapor obeys the perfect gas laws, equation (2) assumes the form

$$(\partial \ln p/\partial P)_T = V_0(1-\alpha P)/RT \tag{3}$$

where V_0 is the molecular volume of the liquid under zero pressure and α is the mean coefficient of compressibility of the liquid as defined by the equation, $\alpha = (V_0 - V)/V_0 P$. The equation can now be integrated. Since the right-hand member of equation (2) is necessarily positive, the vapor pressure always increases with increase in pressure on the liquid phase. The coefficient, $(\partial p/\partial P)_T$, is small for temperatures considerably removed from the critical temperature (thus for water at 0°, $(\partial p/\partial P)_{T=273°} = 3.6 \cdot 10^{-6}$ mm. per atmosphere) but increases with the temperature and becomes equal to 1 at the critical temperature.

Proof of Theorem I.—We have assumed Theorem I in writing equation (1). In order to demonstrate the truth of this theorem for the present case, it is only necessary to show that the engine can be restored to its original condition without leaving any residual effect in the surroundings. Turning, therefore, to our engine after the completion of the operation, we notice that as regards the vapor, the final state of the system differs from its original state in that we have (in cylinder **A′**) $1 + dx$ mols of vapor occupying the volume v under the pressure $p + dp$ instead of having (in cylinder **A**) 1 mol of vapor occupying the volume v under the pressure p. This means that while only one mol of liquid has been produced in chamber **E**, $1 + dx$ mols of liquid have been evaporated from chamber **E′**, dx being obviously expressed by the relation $dx = (\partial x/\partial p)_{v,T}dp$. But the removal of this dx mol of liquid from chamber **E′** would, unless

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[1] Poynting, *Phil. Mag.* [5], **12**, 32 (1881).

compensated in some manner, cause a corresponding change in the total pressure in this chamber, because it will be remembered that during the operation of the engine, piston-head **D′** moves toward the right simply through the volume V of one mol of liquid under pressure P, not through the volume of $1 + dx$ mols of liquid under the pressure $P + dP$. To avoid this pressure change a little device, **X** (not shown in Fig. 1, but shown in Fig. 1*a*), acts automatically during the operation of the engine to maintain a constant pressure in chamber **E′**. This device applies the constant pressure $P + dP$ to a little auxiliary piston, π', which, during the operation of the engine, gradually introduces reversibly into chamber **E′**, such an amount, dx' mol, of liquid as suffices to maintain the constant pressure $P + dP$ within this chamber. During this process (which we need not consider as a part of the "operation" of the engine for reasons stated below) the device **X** gives out the energy $(P + dP)dV'$.

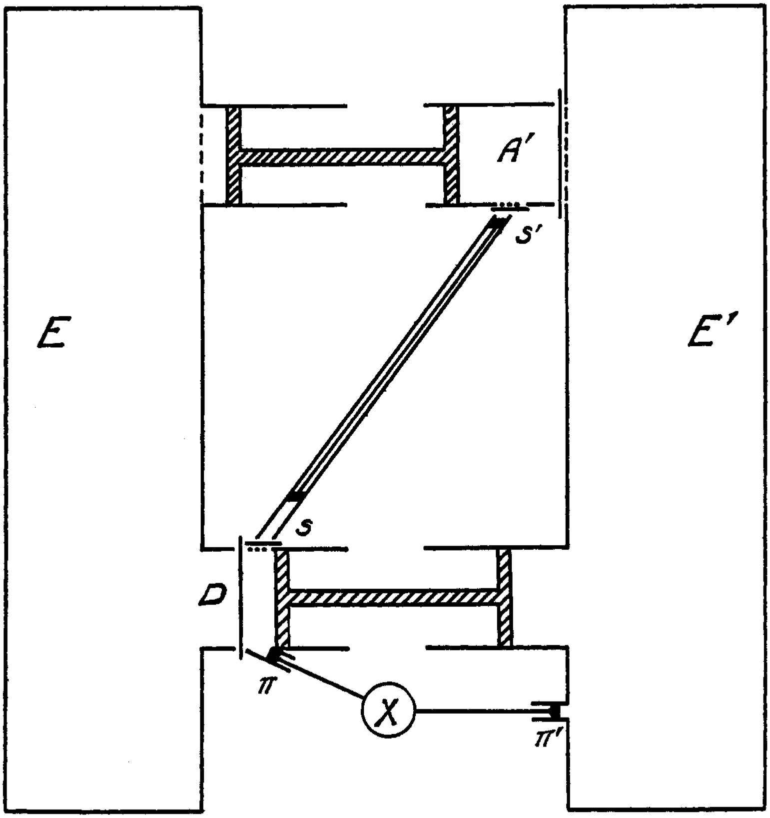

Fig. 1*a*.

As soon as the "operation" of the engine has been completed, another automatic device (shown in Fig. 1*a*) immediately acts to restore the system to its original condition. This device is the little compound piston ss′. The head s′ rests against a slider which separates it from cylinder **A′** and which at the conclusion of the "operation" of the engine slides back so that the vapor pressure $p \pm dp$ acts against the piston head s′. Below the piston head s is contained dx mol of vapor at the pressure p separated from cylinder **D** by a semipermeable membrane and by an impermeable slider which on sliding back puts the dx mol of vapor into communication with the liquid in cylinder **D**, with which it is in equilibrium. The action of this device is as follows: When the "operation" of the engine has been completed the one mol of liquid in cylinder **D** and the $1 + dx$ mols of vapor in cylinder **A′** are automatically cut off from the rest of the engine (as shown in Fig. 1*a*), the little sliders at s and s′ move back and piston ss′ moves downward drawing dx mol of vapor out of cylinder **A′** (the pressure consequently dropping to p) and condensing it as liquid into the one mol of liquid in cylinder **D,** whose pressure thereby is raised to $P + dP$. *At the same time*[2] the little piston, π, which is attached to the device **X** moves downward through the volume dV'. The system is now in its original condition, *i. e.*, we have 1 mol of vapor under the pressure p and $1 + dx'$ mols of liquid under the pressure $P + dP$, which was the condition of the system before the operation of the engine.

Let us consider the work produced by the action of these various automatic devices which serve to restore the system to its original condition. The piston ss′ moves through the volume dv under the pressure dp and therefore performs the work $dp\,dv$, which is a differential of the second order and consequently negligible. During the movement of the little piston π the device **X** takes up the energy $(P + dP)dV'$. But this is the same amount of energy which it gave out previously to piston π'. The operation of the device **X**, therefore, involves no work. The total work involved in restoring the system to its original condition, after an "operation" of the engine, is therefore made up of differentials of a higher order than the first and is consequently entirely negligible in comparison with the work performed during the "operation" itself. Although we have shown this to be true only for the simple case just considered, it is clear that it must also be true for any engine of this type, in which the intensity factor of some form of energy is different in the two chambers because of a difference dP in the total pressures on the chambers, and whose operation consists in removing one or more substances from one chamber and forcing them into the other by means of

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[2] Strictly speaking, the movement of piston π should not begin until such a portion of the dx mol has been forced into **D,** as suffices to raise its pressure to $P + dP$.

compound pistons moving in a manner analogous to the simple case just considered. *Theorem* I *is therefore true.*

The Temperature Coefficient (P = *const.*).—Let us now consider the effect of temperature changes upon the vapor pressure of a liquid which is under constant external pressure P, such changes as would occur for example on heating the liquid in an open vessel exposed to the atmospheric pressure. As in the previous case, we will make use of the engine shown in Fig. 1, omitting cylinder **BB′**. The arrangement is as folllows:

Chamber **E**: Filled with the liquid whose vapor pressure acting through the semipermeable (*i. e.*, only to the vapor) membrane against piston **A** is p. Total pressure on liquid, acting against piston **D**, is P. Temperature of **R** = T.

Chamber **E′**: Exactly as **E** except that the temperature of **R′** is $T + dT$ and the vapor pressure, acting against piston **A′**, is $p + dp$.

The operation of the engine is the same as in the preceding case. Piston **AA′** moves reversibly toward the left under the pressure dp, until 1 mol of the vapor in cylinder **A** is condensed into **E** and an equal volume evaporated from **E′** into cylinder **A′**. Piston **DD′** moves toward the right, under zero pressure, through the volume V occupied by one mol of the liquid, in **E**. The work done by piston **AA′** is vdp, that done by piston **DD′** is zero. We have, therefore, by the Second Law (*i. e.*, *Theorem* II),

$$vdp = L_P dT/T \qquad (4)$$

or

$$(\partial p/\partial T)_P = L_P/vT, \qquad (5)$$

an equation previously obtained by Lewis.[3]

L_P, the heat absorbed from reservoir **R′**, is the molecular heat of vaporization of the liquid under constant pressure. Since this is a positive quantity, the vapor pressure always increases with rise in temperature. If the vapor behaves as a perfect gas, we can put $v = RT/p$ in equation (5), which gives us

$$(\partial \ln p/\partial T)_P = L_P/RT.^2 \qquad (6)$$

To integrate, it is only necessary to express L_P as a function of T, which can be readily done by means of the thermodynamic relation,

$$\partial L_P/\partial T = c_p - C_P, \qquad (7)$$

where c_p and C_P are the molecular heat capacities of vapor and liquid respectively, under constant pressure.[4]

Proof of Theorem II.—Let us now return to our engine and compare its final state with its initial state. As regards the vapor we have (in

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[3] *Proc. Amer. Acad.*, **37**, 53 (1901); *Z. physik. Chem.*, **38**, 205 (1901).

[4] Equation 7 also contains the assumption that the vapor behaves as a perfect gas. The purely thermodynamic equation for the temperature coefficient of L_P is

$$(\partial L_P/\partial T)_P = c_p - C_P + L_P/T - (L_P/v)(\partial v/\partial T)_p. \qquad (7a)$$

cylinder **A′**) $1 + dx$ mols of vapor occupying the volume v at the temperature $T + dT$ and pressure $p + dp$ instead of having (in cylinder **A**) 1 mol of vapor at the temperature T and pressure p. dx is defined by the equation $dx = (\partial x/\partial p)_{v,T}(\partial p/\partial T)_P dT + (\partial x/\partial T)_{v,p} dT$, and may, in general, be either positive or negative since the second term of this expression is essentially negative. $1 + dx$ mols of liquid have consequently evaporated from chamber **E′** during the operation and in order to prevent a consequent change in pressure in this chamber, the automatic device **X** acts just as in the preceding case to introduce dx mol of liquid into **E′**, replacing that which evaporates into cylinder **A′**, and thereby performs the work PdV.

At the completion of the operation of the engine, the $1 + dx$ mols of vapor are cut off from cylinder **A′** and brought into reservoir **R**, whereupon the temperature returns to T. By means of the piston ss′ (Fig. 1*a*) dx mol is then removed from it (its pressure thereupon falling to p) and condensed into the 1 mol of liquid which has been cut off from chamber **E** and whose pressure is thereby raised to $P + dP$. The work involved in this operation is that done by piston ss′, which is $dp\,dv$. The one mol of liquid is now brought into reservoir **R′** (whereupon its temperature returns to $T + dT$) and is connected to the device **X**, which removes dx mol from it, its pressure thereby falling to P. The whole system is now in its original condition. The work absorbed by the device **X** in this last step is $P\,dV$, the same amount which it previously gave out. Therefore the restoration of the system to its original condition after the operation of the engine does not leave any residual effects in the surroundings as far as work is concerned. As regards the heat absorbed from reservoir **R′** during the restoration, it is clear that since the temperature change is infinitesimal, the heat absorbed must be a differential quantity and consequently negligible in comparison with the finite amount of heat L_p absorbed during the operation of the engine. *Theorem* II *is therefore true.*

These two examples suffice to show that the restoration of the system to its original condition after the operation of the engine involves no work or heat terms which need to be considered. The whole effective work of the process is therefore performed entirely by the compound pistons of the engine and we may therefore, in the future, confine our consideration solely to these pistons and apply Theorems I and II directly to them. The various automatic devices which have been described for restoring the system to its original condition are understood to be a part of every engine, but since their action does not involve any work it will not be necessary to pay any attention to them in the future.

The Temperature Coefficient ($P = p$).—The latent heat of vaporization of a liquid is usually determined by condensing (in a calorimeter) the vapor of the boiling liquid. Under these conditions the liquid always vaporizes, not under constant pressure at all temperatures, but under its own vapor pressure at each temperature. The temperature coefficient of the vapor pressure under these conditions can be at once written down, by using the engine shown in Fig. 1. The arrangement is exactly as in the preceding case except that the pressure against piston **D** is p and that against piston **D′** is $p + dp$. The operation is the same as before and we obtain at once the relation

$$vdp—Vdp = L_p dT/T \tag{8}$$

or

$$(\partial p/\partial T)_{P=p} = L_p/(v—V)T \tag{9}$$

which is the familiar Clausius-Clapeyron equation.

L_P and L_p, the latent heats of vaporization of a liquid under the pressure P, and under its own vapor pressure, p, respectively, will not differ much unless the difference between P and p is large or the difference between v and V is small. In the case of water, for example, if $P = 1$ atmosphere, the difference between L_P and L_p could never exceed 0.005 per cent. L_p is the one which is usually determined experimentally, but A. W. Smith[5] has recently made a very accurate determination of L_P by bubbling air through water, the temperature of which was kept constant by electrical heating.

Solid-liquid Equilibrium.—By filling the chambers of the engine with a pure solid and the cylinders with the pure liquid in equilibrium with it, we can study the effects of temperature and pressure upon such a system, in exactly the same way as for the liquid-gas or solid-gas equilibrium described above, the equations obtained being identical in form with those just derived.

4. The Homogeneous Physical Mixture.

In this section we shall make use of the perfect thermodynamic engine in deriving the equations expressing the effects of pressure, composition and temperature upon the partial vapor pressures and the osmotic pressures for any homogeneous physical mixture. Before taking up the derivations, however, it will be necessary to define accurately the term "osmotic pressure" as we shall use it.

Consider any homogeneous liquid mixture of n components (A, B, C, etc.) under the external pressure P. Let us take any one of the components, A for example, in the pure liquid state and subject it to such an external pressure P_A that its vapor pressure shall be equal to its partial vapor pressure from the mixture. If now the pure liquid A be placed in communication with the mixture through a membrane permeable only to A, the system will be in equilibrium as respects the passage of A into

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[5] *Phys. Rev.*, **25**, 145 (1907).

or out of the mixture. The difference between the pressures P_A and P is called the "osmotic pressure." For the simplest type of mixture it depends only upon the specific volume and compressibility of the pure substance A and upon its mol fraction in the mixture, for a given value of T and P. It would seem preferable therefore to speak of this pressure difference as the "osmotic pressure" of the substance A, since it is essentially determined by the properties of this substance. Principally on account of historical reasons, however, it is customary to speak of this pressure difference as the "osmotic pressures" of all the other components of the mixture except the substance A. In what follows it is essential that this pressure difference shall be referred directly to the substance which is present in the pure liquid state, and we will therefore speak of it as "the osmotic pressure referred to A as the solvent" or, briefly, as "the osmotic pressure referred to A." *In any homogeneous (gaseous, liquid or solid) mixture, therefore, the osmotic pressure* Π_A *referred to any constituent,* A, *is defined by the equation,* $\Pi_A = P - P_A$, *where* P *is the external pressure on the mixture and* P_A *is the external pressure on the pure substance* A *(in the same state of aggregation) when it is in equilibrium with the mixture through a membrane permeable only to itself.*[6]

The following treatment, together with the equations obtained, is equally applicable to a solid, liquid or gaseous homogeneous, physical mixture of any number of components, but in developing our equations we shall find it convenient to fix our attention upon a homogeneous liquid mixture of say four components. The composition of the mixture is expressed by the equation $N_A + N_B + N_M + N_N = 1$, where N_X represents the mol fraction of any constituent X. The mol fraction of any constituent (A, for example) is defined by the equation $N_A = n_A/(n_A + n_B + n_M + n_N)$, where n_A, n_B, etc., represent the number of mols of the various constituents in any given quantity of the mixture.

The Pressure Coefficient (N, T = *const.*).—1. Vapor Pressures: Using the engine shown in Fig. 2, the arrangement is as follows (Temperature of **R** = temperature of **R′** = T):

Chamber **E**: Filled with the liquid mixture under the total pressure P applied by means of piston **D**. The partial vapor pressures of the various constituents (each acting through a membrane permeable only to its own vapor) are, p_A acting against piston **A,** p_B against **B,** p_M against **M,** and p_N against **N**.

Chamber **E′**: Filled with the liquid mixture under the total pressure $P + dP$ applied by piston **D′**, the partial vapor pressures being $p_A + dp_A$ acting against piston **A′**, $p_B + dp_B$ against B′, $p_M + dp_M$ against **M′** and $p_N + dp_N$ against **N′**.

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[6] This definition is essentially the same as that given by A. A. Noyes (*Z. physik. Chem.*, 35, 707 (1900)). Its advantages over the more common one will become evident as we proceed.

At the beginning of the operation each of the four vapor pistons is at the right-hand end of its stroke, so that piston heads **A′**, **B′**, **M′**, and **N′** are in contact with the semipermeable membranes separating the cylinders from **E′**. The operation of the engine consists in the simultaneous movement of all four vapor pistons toward the left until 1 mol of the mixture has been evaporated from **E′** and condensed into **E**. At the same time piston **DD′** moves toward the right through the volume $(\Sigma\overline{V})$ of one mol of the liquid mixture. By the Second Law (Theorem I) the total work is equal to zero, giving us the equation,

$$N_Av_Adp_A + N_Bv_Bdp_B + N_Mv_Mdp_M + N_Nv_Ndp_N - (\Sigma\overline{V})dP = 0 \qquad (10)$$

or

$$(N_Av_A\partial p_A + N_Bv_B\partial p_B + N_Mv_M\partial p_M + N_Nv_N\partial p_N/\partial P)_{N,T} = (\Sigma\overline{V}) \qquad (11)$$

which for brevity we shall write in the form

$$[(\Sigma N_Av_A\partial p_A)/\partial P]_{N,T} = (\Sigma\overline{V}). \qquad (12)$$

In these equations V_x is the volume of one mol of the substance X in the vapor state under the pressure p_x.

2. Osmotic Pressures: If the cylinders contain the pure components in the liquid state instead of the gaseous state the respective partial pressures are osmotic pressures instead of vapor pressures, and allowing the engine to operate as before, we can write down at once the equation

$$[(\Sigma N_AV_A\partial\Pi_A)/\partial P]_{N,T} = -(\Sigma N\overline{V}) \qquad (13)$$

in which V_A, V_B, etc., represent the molecular volumes of the pure substances A, B, etc., in the liquid state under the pressures $P - \Pi_A$, $P - \Pi_B$, etc., respectively.[7]

The Composition Coefficient (*P*, *T* = *const.*).—1. Vapor Pressures: We shall now proceed to determine the effect of a slight change in the composition of a mixture, upon the partial vapor pressures of its constituents. Let us change the mol fraction of constituent A, for example, from N_A to $N_A + dN_A$. The arrangement of the engine is exactly as in the preceding except that the total pressure acting against **D** and **D′** is P for both chambers, the dp differences in the partial vapor pressures being due to the fact that the composition of the mixture in chamber **E′** has been altered by the addition of dN_A mols. of A. The operation of the engine is exactly as above and we have by the Second Law (Theorem I),

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[7] The expression $(\Sigma N\overline{V})$ is used to represent the volume of one mol of the mixture because this volume may be regarded as equal to the sum of the partial volumes of the components as expressed by the equation $N_A\overline{V}_A + N_B\overline{V}_B + N_M\overline{V}_M + N_N\overline{V}_N = \Sigma N\overline{V}$, in which V_A, V_B, etc., represent the *partial* molecular volumes of the respective constituents in the mixture. The partial molecular volume of any constituent is equal to the increase in the volume of an infinite amount of the mixture when one mol of the constituent is added to it. Similar relations may be stated for the quantities $(\Sigma N\overline{L})$ and $(\Sigma N\overline{D})$ which appear in equations (18) and (19).

$$N_A v_A dp_A + N_B v_B dp_B + N_M v_M dp_M + N_N v_N dp_N = 0, \tag{14}$$

or

$$[(\Sigma N_A v_A \partial p_A)/\partial N_A]_{P,T} = 0. \tag{15}$$

2. Osmotic Pressures: As in the preceding case, if the cylinders contain the pure liquid components the operation of the engine gives us the equation

$$-[(\Sigma N_A V_A \partial \Pi_A)/\partial N_A]_{P,T} = 0. \tag{16}$$

The Temperature Coefficient (*P*, *N* = *const.*).—1. Vapor Pressures: The arrangement and operation of the engine is exactly the same as in the preceding case except that the composition is identical in both chambers and the temperature of R = T and that of R′ = $T + dT$. The Second Law (Theorem II) gives us at once the relation

$$N_A v_A dp_A + N_B v_B dp_B + N_M v_M dp_M + N_N v_N dp_N = (\Sigma NL)dT/T \tag{17}$$

or

$$[(\Sigma N_A v_A \partial p_A)/\partial T]_{P,N} = (\Sigma NL)/T \tag{18}$$

where (ΣNL) is the latent heat of vaporization of one mol of the mixture at constant pressure and composition.[7]

2. Osmotic Pressures: With the pure liquids in the cylinders we obtain the equation

$$-[(\Sigma N_A V_A \partial \Pi_A)/\partial T]_{P,N} = (\Sigma N\overline{D})/T \tag{19}$$

where $(\Sigma N\overline{D})$ is the latent heat of separation of one mol of the mixture into its pure liquid components under equilibrium conditions. Its exact meaning is clearly evident from the operation of the engine.[7]

Discussion.—The equations which we have just derived involve nothing but the two laws of thermodynamics and they contain all the information which thermodynamics alone is capable of yielding regarding the relations existing among the partial vapor pressures or osmotic pressures for a homogeneous mixture. We shall not, in the present paper, discuss these important equations further, although many interesting examples of their transformations and applications in special cases present themselves. It will be sufficient to note here that if the vapors behave as perfect gases, the vapor pressure equations assume the forms

$$[(\Sigma N_A \partial \ln p_A)/\partial P]_{N,T} = (\Sigma NV)/RT, \tag{20}$$

$$[(\Sigma N_A \partial \ln p_A)/\partial N_x]_{P,T} = 0, \tag{21}$$

and

$$[(\Sigma N_A \partial \ln p_A)/\partial T]_{N,P} = (\Sigma NL)/RT^2. \tag{22}$$

The equation of Duhem-Margules for the partial vapor pressures of a binary mixture is a form of equation (21). It will also be noticed that the equations derived in section (1) for a pure substance are special forms of these equations for a one-component system.

By making the two chambers of our engine infinite in volume and removing only one constituent we can obtain the following equations for the partial vapor pressure or osmotic pressure referred to *one constituent alone.*

$$(\partial p_A/\partial P)_{N,T} = \bar{V}_A/v_A. \quad (23) \qquad (\partial \Pi_A/\partial P)_{N,T} = -\bar{V}_A/V_A. \quad (23a)$$

$$(\partial p_A/\partial T)_{N,P} = \bar{L}_A/v_A T. \quad (24) \qquad (\partial \Pi_A/\partial T)_{N,P} = -\bar{D}_A/V_A T. \quad (24a)$$

The absence of an equation for one constituent, corresponding to equation (15), will be noticed. Thermodynamics is incapable of yielding any information concerning the changes in the partial vapor pressure (or osmotic pressure) of one constituent of a mixture, with a change in the composition of the mixture, other than the information contained in equation (15).

Since $\bar{V}_A$ may be either positive or negative,[7] the partial vapor pressure of a constituent of a mixture, unlike the vapor pressure of a pure substance (see page 472), may be in some cases increased and in others decreased by increasing the total pressure on the mixture. L_A, the partial molecular heat of vaporization of any constituent, A, is the heat absorbed when one mol of A is vaporized reversibly from an infinite amount of the mixture. If the vapor obeys the perfect gas laws equation (24) becomes

$$(\partial \ln p_A/\partial T)_{N,P} = (L_A - D_A)/RT^2, \quad (25)$$

where L_A is the molecular heat of vaporization of the *pure liquid* A, and D_A is the heat *absorbed* when one mol of liquid A is mixed with an infinite amount of the mixture. $-D_A$ is obviously the ordinary molecular *heat of dilution* of a solution with one of its components, A. The equation now contains only quantities which can be readily measured.

In a similar way equation (24a) for the *temperature coefficient of osmotic pressure* can be put in a more practical form if we replace $\bar{D}_A$ by $(D_A - \Pi_A V_A)$, which is equal to it by the First Law. If we choose to refer the heat of dilution to *unit volume* of solvent instead of to one mol we have $q = -D_A/V_A$ and equation (24a) assumes the familiar form of the Helmholtz equation

$$(\partial \Pi_A/\partial T)_{P,N} = (\Pi - q)/T. \quad (26)$$

5. Chemical Equilibrium: A. Homogeneous.

Let us consider any chemical equilibrium, expressed by the equation

$$a\mathrm{A} + b\mathrm{B} + \ldots . \rightleftarrows m\mathrm{M} + n\mathrm{N} + \ldots . \quad (27)$$

in which a mols of the substance A react with b mols of the substance B, etc., to form m mols of the substance M and n mols of the substance N, etc. The substances entering into the reaction are in equilibrium with each other in any homogeneous phase and there may or may not also be present in the phase one or more other substances which do not take part in the reaction: a solvent or an indifferent gas, for example. As in the preceding section the composition of the phase is represented by the equation

$$N_A + N_B + \ldots . + N_M + N_N + \ldots . + N_1 + N_2 + \ldots . = 1 \quad (28)$$

where N_X is the mol fraction of the constituent X, numercial subscripts referring to substances which do not take part in the chemical equilibrium.

Our problem is to determine in what direction and to what extent the chemical equilibrium is displaced by, (1) increasing the concentration (*i. e.*, the mol fraction) of one of the reacting substances, (2) increasing the total pressure on the phase, and (3) increasing the temperature of the system. In deriving our fundamental equations, it will be simpler to fix our attention chiefly upon some particular phase, and we shall choose a gaseous phase, which, in addition to the reacting substances, contains also an indifferent gas which we shall call constituent, 1. It would correspond to a solvent if we were dealing with a liquid or solid solution.

[The treatment of chemical equilibrium in a homogeneous liquid or solid phase is quite analogous, it being simply necessary to replace partial gas pressure p_X by the osmotic pressure Π_X. It will be sufficient, therefore, in the following treatment, to indicate parenthetically (in brackets) the necessary changes in the process and the corresponding equations for these cases.]

Arrangement of the Engine.—We shall make use of the engine shown in Fig. 2. The arrangement is as follows:

Chamber **E**: Filled with the gaseous mixture as described above, the composition of the mixture being represented by the equation

$$N_A + N_B + \ldots + N_M + N_N + \ldots . + N_1 = 1.$$

The substances A, B. ., M, N. . are in chemical equilibrium as expressed by the equation

$$a\text{A} + b\text{B} + \ldots \rightleftarrows m\text{M} + n\text{N} + \ldots .$$

The partial pressures of the substances taking part in the equilibrium act through suitable semipermeable membranes against the pistons as follows: p_A against piston **A,** p_B against piston **B,** p_M against piston **M** and p_N against piston **N**. The total pressure on the system is applied by means of piston **D**.

Chamber **E′**: Analogous in every respect to chamber **E** except that the equilibrium has been slightly displaced by some cause so that the partial pressures from this chamber have become $p_A + dp_A$ against piston **A′**, $p_B + dp_B$ against piston **B′**, etc.

[For a liquid (or solid) phase in the chamber, the cylinders are filled with the pure substances A, B, M, N, etc., in the liquid (or solid) state and the pressures on the pistons are osmotic pressures, Π_A and $\Pi_A + d\Pi_A$, Π_B and $\Pi_B + d\Pi_B$, etc.]

The operation of the engine consists in the movement of pistons **AA′**

and **BB**′ toward the left until *a* mols of A and *b* mols of B have been forced into **E** and drawn out of **E**′; and the simultaneous movement of pistons **MM**′ and **NN**′ toward the right, removing *m* mols of M and *n* mols of N from **E** (as fast as they are formed by the reaction of A and B which are being introduced by pistons **AA**′ and **BB**′) and forcing them into E′ (as fast as they are required to replace, by reaction, the A and B which are being removed by pistons **AA**′ and **BB**′). The equilibrium is not disturbed in either chamber. The work done by pistons **AA**′, **BB**′, **MM**′ and **NN**′ is

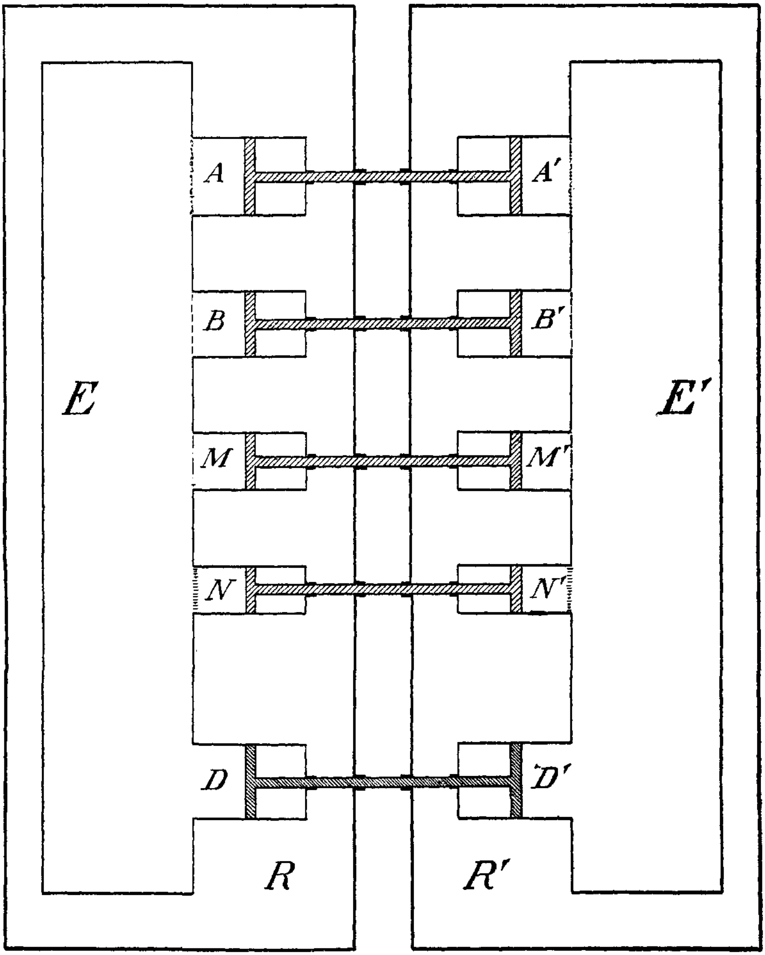

Fig. 2.

$$av_{\mathrm{A}}dp_{\mathrm{A}} + bv_{\mathrm{B}}dp_{\mathrm{B}} + \ldots - mv_{\mathrm{M}}dp_{\mathrm{M}} - nv_{\mathrm{N}}dp_{\mathrm{N}} - \ldots,$$

or more briefly,

$$\Sigma\pm av_A dp_A \quad [\text{for liquid or solid, } \Sigma\mp aV_A d\Pi_A].$$

The ± sign indicates that terms relating to the reacting substances are to be taken with a positive sign and those relating to the products of the reaction with a negative sign.

By the Second Law (Theorems I and II), this work is equal to (1) zero, or (2) QdT/T according as the displacement of the equilibrium in chamber **E′** is brought about by changing (1) the composition, or the total pressure, or (2) the temperature. We shall consider each effect separately.

The Composition and Pressure Coefficients (*P, T = const. or N, T = const*).—Keep the *total pressure* and the temperature in **E** and **E′** the same and displace the equilibrium in **E′** by changing the mol fraction of (say) A from N_A to $N_A + dN_A$; *or*, keep the *composition* and temperature the same in both **E** and **E′** and change the total pressure on **E′** from P to $P + dP$ by means of piston **D′**. In either case the operation of the engine gives us at once the equation

$$av_A dp_A + bv_B dp_B + \ldots\ldots - mv_M dp_M - nv_N dp_N - \ldots = 0 \qquad (29)$$

or

$$\left(\frac{\Sigma\pm av_A \partial p_A}{\partial N_A}\right)_{P,T} = 0 \qquad (30) \qquad \left[\left(\frac{\Sigma\mp aV_A \partial\Pi_A}{\partial N_A}\right)_{P,T} = 0 \qquad (30a)\right.$$

$$\left(\frac{\Sigma\pm av_A \partial p_A}{\partial P}\right)_{N,T} = 0 \qquad (31) \qquad \left.\left(\frac{\Sigma\mp aV_A \partial\Pi_A}{\partial P}\right)_{N,T} = 0 \qquad (31a)\right]$$

These equations contain everything which thermodynamics alone is capable of teaching us concerning a chemical equilibrium at constant temperature. To proceed further it is necessary to know the functional relation between p and v for the system under consideration. To illustrate, let us assume that this relation is $pv = RT$, *i. e.*, the perfect gas law. Putting $v_X = RT/p_X$ for each substance in equation (30), the equation becomes

$$RT d\ln\frac{p_A^a \cdot p_B^b \cdots}{p_M^m \cdot p_N^n \cdots} = 0. \qquad (32)$$

This equation can obviously only be true if

$$\frac{p_A^a \cdot p_B^b \cdots}{p_M^m \cdot p_N^n \cdots} = const. = K_p, \qquad (33)$$

which is the mathematical formulation of the law of chemical mass action in terms of partial pressures. It can be expressed in terms of *mol fractions* or *volume concentrations* by substituting $p_X = N_X P$ or $p_X = C_X RT$, respectively, in equation (33), giving

$$\frac{N_A^a . N_B^b \cdots}{N_M^m . N_N^n \cdots} = K_p P^{\Delta x} (= K_N \text{ for constant } P), \qquad (34)$$

and

$$\frac{C_{\mathrm{A}}^{a} \cdot C_{\mathrm{B}}^{b} \cdots}{C_{\mathrm{M}}^{m} \cdot C_{\mathrm{N}}^{n} \cdots} = K_{p}(RT)^{\Delta x} = K_{C}, \tag{35}$$

where Δx—the change in the number of mols which results from the reaction—is written for $(m + n + \ldots . - a - b - \ldots)$.

It is evident, from the preceding, that the Law of Mass Action for a gaseous phase (*i. e.*, equation (33)) expresses the condition of chemical equilibrium *only* for a system in which the substances taking part in the reaction are all perfect gases. And of the perfect gas laws only those of Boyle and Avogadro are involved. It is not essential that the law of Gay-Lussac (*i. e.*, $p = kT$) be obeyed. To state, therefore, that any chemical equilibrium (in a gaseous phase or dilute solution) does not obey the Mass Action Law is simply to state that the pressure (gaseous or osmotic) of at least *one* of the substances concerned in the equilibrium does not obey the law of Boyle-Avogadro. Notwithstanding the fact that this law has been shown to be both a necessary and sufficient condition for the validity of the Law of Mass Action, the belief seems still to be held in some quarters that the latter law may after all have a wider and more general application. T. B. Robertson, for example, in a recent paper,[8] considers the conditions for chemical equilibrium in a system in which the equation $p(v - d) = RT$ is obeyed instead of the perfect gas law. He concludes that such a system must *also* obey the Law of Mass Action.[9] This conclusion must be regarded as erroneous. The equation $p(v - d) = RT$ does *not* lead to the Mass Action Law but to quite a different expression, as will be evident by substituting $v = RT/p + d$, in equation (30) and integrating. This gives the relation

$$RT \ln p_{\mathrm{A}}^{a} \cdot \mathrm{p}_{\mathrm{B}}^{b} \cdots / p_{\mathrm{M}}^{m} \cdot p_{\mathrm{N}}^{n} \cdots = const. - \Sigma \pm a p_{\mathrm{A}} d_{\mathrm{A}} \tag{36}$$

in which the last term represents the series

$$a p_{\mathrm{A}} d_{\mathrm{A}} + b p_{\mathrm{B}} d_{\mathrm{B}} + \ldots - m p_{\mathrm{M}} d_{\mathrm{M}} - n p_{\mathrm{N}} d_{\mathrm{N}} - \ldots$$

Similarly for *each* equation of state there is a *corresponding* law of chemical equilibrium but the Law of Mass Action belongs *only* to systems obeying the Boyle-Avogadro law.

The Temperature Coefficient (P, N = *const.*).—Keep the composition and total pressure the same in **E** and **E**$'$ and displace the equilibrium in **E**$'$ by changing the temperature of **R**$'$ from T to $T + dT$. The operation of the engine gives us the equation

$$a v_{\mathrm{A}} dp_{\mathrm{A}} + b v_{\mathrm{B}} dp_{\mathrm{B}} + \ldots - m v_{\mathrm{M}} dp_{\mathrm{M}} - n v_{\mathrm{N}} dp_{\mathrm{N}} - \ldots = QdT/T \tag{37}$$

or

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[8] *J. Physic. Chem.*, **10**, 522 (1907).

[9] This conclusion seems to have been accepted by other investigators, apparently without question. It is quoted by the Earl of Berkeley (*Proc. Roy. Soc.*, A**79**, 131 (1907)) in support of certain conclusions regarding the application of van der Waals' equation to solutions and it is even beginning to appear in the text-books. See, for example, the last edition of Morgan's "Elements of Physical Chemistry," p. 239.

$$\left(\frac{\Sigma^{\pm} a v_{\mathrm{A}} \partial p_{\mathrm{A}}}{\partial T}\right)_{P,[N=f(T)]} = \frac{Q_p}{T} \quad (38) \qquad \left[\left(\frac{\Sigma^{\mp} a V_{\mathrm{A}} \partial \Pi_{\mathrm{A}}}{\partial T}\right)_{P,[N=f(T)]} = \frac{Q_\pi}{T} \quad (38a)\right]$$

where Q_p is the heat *evolved* by the reaction when it proceeds from left to right according to equation (27) and does the maximum external work. If we assume the *perfect gas law* this equation becomes

$$(\partial \ln K_p/\partial T)_{P,N} = Q_p/RT^2, \qquad (39)$$

where K_p is defined by equation (33). We may substitute, $K_p = K_c(RT)^{\Delta x}$ (equation (35)) and $Q_p = U - \Delta xRT$ (by the first law of thermodynamics) and obtain the familiar equation of van't Hoff,

$$d\ln K_c/dT = U/RT^2, \qquad (40)$$

where K_c is defined by equation (35) and U, the change in total energy, is the heat evolved when the reaction takes place (from left to right) without external work.[10]

6. Chemical Equilibrium. B. Heterogeneous.

The Composition Coefficient (*P*, *T* = *const.*).—The arrangement and operation of the engine for this case are in general exactly the same as for the corresponding case of homogeneous equilibrium, except that

[10] General Equations.—The results just obtained for the effects of composition, pressure and temperature can, if desired, be expressed in a single general equation. For example, suppose we wish to find a general equation by means of which K_N can be calculated for a given gaseous mixture at any temperature or pressure. We have the general expression

$$d\ln K_N = (\partial \ln K_N/\partial P)_T dP + (\partial \ln K_N/\partial T)_P dT. \qquad (41)$$

From equation (34), by taking the logarithm of both sides and differentiating, we obtain

$$(\partial \ln K_N/\partial P)_T = \Delta x/P. \qquad (42)$$

From equations (34) and (39) we obtain

$$(\partial \ln K_N/\partial T)_P = (\partial \ln K_p/\partial T)_P = Q_p/RT^2. \qquad (43)$$

But by the first law of thermodynamics,

$$Q_p/RT^2 = U + \Delta xRT/RT^2 = U/RT^2 + \Delta x/T \qquad (44)$$

and

$$U = U_0 + \Sigma(\mathrm{a}h_{\mathrm{A}})T. \qquad (45)$$

Consequently,

$$(\partial \ln K_N/\partial T)_P = U_0/RT^2 + \Sigma(\mathrm{a}h_{\mathrm{A}})/RT + \Delta x/T \qquad (46)$$

and combining with (41) and (42) we obtain finally,

$$d\ln K_N = \Delta x dP/P + U_0 dT/RT^2 + [\Sigma(\mathrm{a}h_{\mathrm{A}}) + R\Delta x]dT/RT \qquad (47)$$

which, on integration, yields

$$\ln K_N = \ln I + \Delta x \ln P + \frac{(\Sigma(\mathrm{a}h_{\mathrm{A}}) + R\Delta x)}{R}\ln T - \frac{U_0}{RT} \qquad (48)$$

or, written in the exponential form

$$K_N = IT^b P^{\Delta x} e^{-\frac{U_0}{RT}} \qquad (49)$$

in which I is the integration constant and b is written for $(\Sigma(\mathrm{a}h_{\mathrm{A}}) + R\Delta x)/R$. This is Gibbs' formula for gas dissociation, and has, I believe, heretofore never been derived except by the use of Gibbs' thermodynamic potential. Van Laar even goes so far as to state (*Sechs Vorträge*, p. 69) that it is not possible to derive it in any other way.

substances present in a second state of aggregation are not removed from one chamber and forced into the other during the operation of the engine, but are simply allowed to vaporize (or dissolve) in one chamber and condense (or precipitate) in the other as the reaction progresses. This, of course, necessitates the movement of the pressure piston, **DD′**, through the corresponding volume change; but since it moves under zero pressure it does no work, and the differential equation obtained is therefore identical with the one for homogeneous equilibrium *with the omission of all terms referring to substances present in a second state of aggregation.* These omissions may be indicated by placing the symbol $\textcircled{2}$ inside the summation sign. Thus in place of equation (30) [and (30*a*)] we have:

$$\left(\frac{\Sigma_{\overset{\pm}{\textcircled{2}}} a v_{\mathrm{A}} \partial p_{\mathrm{A}}}{\partial N_{\mathrm{A}}}\right)_{P,T} = 0 \quad (50) \qquad \left[\left(\frac{\Sigma_{\overset{\mp}{\textcircled{2}}} a V_{\mathrm{A}} \partial \Pi_{\mathrm{A}}}{\partial N_{\mathrm{A}}}\right)_{P,T} = 0\right] \quad (50a)$$

It is customary to derive the laws of heterogeneous chemical equilibrium, from the corresponding laws of homogeneous equilibrium—the Mass Action Law for example—by assuming that the pressures or concentrations of substances present in a second state of aggregation are constants. While this gives the correct result and is a convenient aid to the memory, as a general method of proof it must be condemned, because the assumption upon which it is based is not only unnecessary but is apt to be misleading. This can be illustrated by considering a specific example.

The law of the constancy of the solubility product for difficultly soluble substances which dissociate in solution is almost invariably derived by first assuming the Mass Action Law and then assuming that the concentration of the undissociated portion is a constant so long as an excess of the solid phase is present. Now in the case of aqueous solutions of strong electrolytes, Stieglitz has recently called attention to the fact that since the Mass Action Law does not hold even approximately for these substances, any derivation based upon this law cannot be applied to their solutions. He therefore concludes[11] that there is no theoretical basis for the Solubility Product Law in the case of strong electrolytes.

This criticism of the method of derivation in the case of strong electrolytes is quite justified, but the conclusion which is drawn regarding the lack of theoretical foundation for the law in these cases is unjustified. In order to derive the Solubility Product Law it is not only unnecesssary to assume the Mass Action Law but it is not even necessary to know what

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[11] Stieglitz, THIS JOURNAL, 30, 954 (1908). After recalculating Arrhenius' solubility data and finding good agreement with the Solubility Product Law, he concludes: "In view of these facts and also in view of the results of the complete calculation of Arrhenius' data on the solubility of the silver salts, which removed the last *theoretical* foundation for the solubility product constant, we may well consider it for the present to be an approximate empirical principle."

the law is which regulates the equilibrium between the dissociated and undissociated portions of the dissolved solute. This can be made clear by applying the engine as indicated above (p. 487) to a saturated solution of a solute, BC for example, which dissociates in solution according to the equation

$$BC \rightleftarrows B + C.$$

We obtain at once the equation[12]

$$V_B d\Pi_B + V_C d\Pi_C = 0 \qquad (51)$$

where $d\Pi$ in both cases may be *either* $(\partial\Pi/\partial N_B)dN_B$ or $(\partial\Pi/\partial N_C)dN_C$.

If A and B are "normal solutes" and the solution is sufficiently dilute it can be readily shown that equation (51) takes the form

$$C_B \cdot C_{C'} = const. = (\alpha_0 S_0)^2 \qquad (53)$$

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[12] If the operation is carried out in the manner described in the preceding sections, the cylinders of the engine will contain pure liquid B (resp. C) and π_B (resp. π_C) will denote the difference in pressure upon the solution and the pure liquid B (resp. C) which is necessary to establish equilibrium; or as we have called it (see p. 478), "the osmotic pressure referred to B (resp. C) as the solvent." In case B and C happen to be ions, some difficulty will doubtless arise in the minds of some readers as to the validity of a process which makes use of a cylinder filled with pure liquid ion. If so, the arrangement of the engine can be easily changed so that the cylinders shall contain *solutions* of the ions separated from the chambers by membranes permeable only to the ion in question. The pistons then would be permeable only to the solvent and the osmotic pressure (π_B' resp. π_C') would be the *ordinary* osmotic pressure of the solute, in the present instance an ion. Thus, looking at Fig. 3 a moment, the movement of piston BB′ toward the left would necessitate the flow of pure solvent toward the right through piston B′ into cylinder B′ where it would dilute the solution of B-ion contained in this cylinder. But this solution would then no longer be in equilibrium with the solution in chamber E′ and the ion B^+ would pass from E′ through the semipermeable membrane into cylinder B′ until the equilibrium was restored. The motion of piston BB′ toward the left would therefore result in drawing B^+-ion out of chamber E′ and forcing it into Chamber E, just as in the general case where the cylinders are filled with the pure liquids. Piston CC′ would do the same for C-ion, so that we would obtain the equation

$$V_{B'} d\pi'_{B'} + V_{C'} d\pi'_{C'} = 0, \qquad (52)$$

which is identical in form with equation (51) above and for dilute solutions leads to the same result when integrated. Thus if the ions are "normal solutes" and the solution is "sufficiently dilute," we can write for each ion

$$\pi' = CRT,\ d\pi' = RTdC \text{ and } V = 1/C$$

which gives us

$$RTd \ln C_{B'} C_{C'} = 0,$$

or

$$C_{B'} . C_{C'} = \text{const} = (\alpha_0 S_0)^2. \qquad (53)$$

The exact significance of the term "normal solute" will be treated more fully in a future communication, in which a set of equations for solutions will be derived without making any assumption regarding the concentration of the solution. The equations for "dilute solutions" which are developed in the present paper will there be shown to be only special cases of a more general set of equations for solutions of any concentration. For the present the term "normal solute" may be understood to refer to any solute "whose osmotic pressure in dilute solution obeys the gas laws."

which is the Solubility Product Law. S_0 and α_0 are, respectively, the solubility of BC in the pure solvent and its degree of dissociation in this solution. Since the Solubility Product Law is found to hold, at least approximately, for solutions of strong electrolytes of the uni-univalent type, it is evidence that the ions in these solutions are approximately "normal solutes" (*i. e.*, their osmotic pressures are proportional to their concentrations in dilute solution), and that the deviations from the Mass Action Law for strong electrolytes must be attributed *chiefly* to the failure of the Boyle-Avogadro law in the case of the unionized molecules. This conclusion has been pointed out recently by A. A. Noyes,[13] who offers a very suggestive provisional hypothesis to account for the abnormal behavior of the unionized molecules in such solutions.

The Pressure Coefficient (N, T = *const.*).—In the case of heterogeneous equilibrium, when piston **DD′** applies a pressure P to chamber **E** and $P + dP$ to chamber **E′**, the operation of the engine is accompanied by a motion of this piston through the volume change which results from the chemical reaction and a work term, $\Delta V dP$, appears in the equation which was absent in the corresponding case of homogeneous equilibrium (q. v. p. 484). Otherwise the operation remains the same and the final equation obtained is in all other respects identical with the corresponding one for homogeneous equilibrium, but *with the omission of all terms referring to substances present in a second state of aggregation.* Thus, corresponding to equation (31) [and (31*a*)] for homogeneous equilibrium, we obtain in the case of heterogeneous equilibrium the equation

$$\left(\frac{\Sigma\overset{\pm}{\underset{\smile}{(2)}} av_\mathrm{A}\partial p_\mathrm{A}}{\partial P}\right)_{N,T} = \Delta V \quad (54) \text{ and } \left[\left(\frac{\Sigma\overset{\mp}{\underset{\smile}{(2)}} aV_\mathrm{A}\partial \Pi_\mathrm{A}}{\partial P}\right)_{N,T} = \Delta V_\pi\right]. \quad (54a)$$

The exact meaning of ΔV is clearly evident from the operation of the engine. It is equal to the increase in the total reaction volume of all substances present in a second state of aggregation, which results when the reaction proceeds from left to right in the sense of equation (27). This can be illustrated by considering some specific examples.

Suppose the reaction under consideration is

$$a\mathrm{A} + b\mathrm{B} \rightleftarrows m\mathrm{M} + n\mathrm{N} \quad (55)$$

in which A and M are gases and B and N solids. Applying equation (54) to this case, or better, using the engine directly, we obtain the equation

$$av_\mathrm{A}dp_\mathrm{A} - mv_\mathrm{M}dp_\mathrm{M} = \Delta V dP. \quad (56)$$

ΔV here is obviously equal to the reaction volume of N minus the reaction volume of B. Now the reaction volume of N is nV_N, where V_N is the

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[13] A. A. Noyes, This Journal, 30, 351 (1908).

molecular volume of *solid* N under the pressure P. Similarly the reaction volume of B is bV_B, so that $\Delta V = nV_N - bV_B$. If we assume the perfect gas laws for A and M, equation (56) becomes

$$RTd\ln p_A^a/p_M^m = (nV_N - bV_B)dP \qquad (57)$$

or

$$(\partial \ln K_p/\partial P)_{T,N} = (nV_N - bV_B)/RT. \qquad (58)$$

Another example: Let us consider a solid BC in contact with its saturated solution in which it exists in a state of partial dissociation, the equilibrium between the solid and its dissociation products in solution being expressed by the equation

$$BC \rightleftarrows B + C. \qquad (59)$$

How will an increase of pressure affect this equilibrium? Operate the engine so that solid BC dissolves in chamber **E′**, under the pressure $P + dP$ and its dissociation products are removed osmotically and an equivalent amount forced into chamber **E**, where they at once combine to form solid BC under the pressure P. This gives us the equation

$$V_B d\Pi_B + V_C d\Pi_C = \Delta V dP, \qquad (60)$$

in which ΔV is the decrease in volume which results when one reaction weight (= one mol in this case) of solid BC dissolves in its saturated solution. If B and C are "normal solutes"[12] and the solution is dilute it can be shown that equation (60) becomes

$$RTd\ln(\alpha_0 S_0)^2 = \Delta V dP \qquad (61)$$

or

$$[\partial \ln(\alpha_0 S_0)^2/\partial P]_{N,T} = \Delta V/RT \qquad (62)$$

in which S_0 is the solubility of BC (expressed as mols per 1000 grams of solvent) under the pressure P and α_0 is its degree of dissociation in the saturated solution. This is obviously an equation giving the pressure coefficient of the logarithm of the solubility product.[19]

The Temperature Coefficient (N, P, = *const.*).—From what has been said in the preceding portions of this section, it is evident that the operation of the engine for this case gives us the general equation

$$\left(\frac{\Sigma \overset{\pm}{②} a v_A \partial p_A}{\partial T}\right)_{N.P} = \frac{QdT}{T} \quad (63), \quad \left[\left(\frac{\Sigma \overset{\mp}{②} a V_A \partial \Pi_A}{\partial T}\right)_{N.P} = \frac{Q_\pi dT}{T}\right] \quad (63a)$$

We will reserve until some future time the further discussion of the general case, and will consider here a specific example, the temperature coefficient of the solubility product for an electrolyte.

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[19] In case B and C happen to be ions we may modify the operation of the engine as explained in note (12). In this case we shall, however, obtain the same final equations (*i. e.*, equation (62)).

Let us apply the engine directly: We have in both chambers a saturated solution of an electrolyte BC in contact with an excess of the solid. Chamber **E** is at $T°$ and chamber **E**′ at $T + dT°$. The operation of the engine consists in the solution of one mol of solid BC in chamber **E**′, accompanied by its simultaneous removal osmotically in the form of solutions of B-ion and C-ion by means of pistons **B**′ and **C**′, as described in note 12. The reverse process, of course, occurs in chamber **E**. The equation for the operation is (cf. eq. 52):

$$V_{B'}d\Pi'_{B'} + V_{C'}d\Pi'_{C'} = QdT/T \qquad (64)$$

If the ions as "normal solutes" and the solution is "sufficiently dilute" we can write for each ion, $\Pi' = CRT$, $d\Pi' = RTdC + RCdT$, and $V = 1/C$, which gives

$$RTd\ln C_{B'}.C_{C'} + 2RdT = QdT/T, \qquad (65)$$

or

$$RT^2d\ln(\alpha_0S_0)^2 = (Q - 2RT)dT, \qquad (66)$$

or

$$(\partial\ln(\alpha_0S_0)^2/\partial T)_{P.N} = U/RT^2. \qquad (67)$$

U, the increase in internal energy, is equal to the heat absorbed when a system composed of one mol of solid BC and $1000/2\alpha_0S_0$ grams of pure solvent, both under the pressure P and at the temperature T, changes, without the production of any work, into a system composed of a solution of BC in which the solute exists only in the form of its ions. Such a solution cannot be obtained in reality but the corresponding heat effect can be measured, which is all that is necessary. It is perhaps worth while to consider a numerical example illustrating the use of equation (67).

Let us compare the directly measured value of U with the value calculated by means of the expression

$$2RT^2(d\ln\alpha_0/dT + d\ln S_0/dT) = U, \qquad (68)$$

in the case of orthonitrobenzoic acid. The value of U for this acid obtained by calorimetric measurements at 20° is 4040 ± 100 cal.[14] The value of $(d\ln S_0/dT)_{20°}$ has been determined by Noyes and Sammet[15] and found to be 0.03335. From their conductivity measurements at 15° and 25°, we obtain $\alpha_{15°} = 0.386$ and $\alpha_{25°} = 0.311$, whence $\Delta\ln\alpha/\Delta t$ for this temperature interval comes out —0.0216, which we shall take as the

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[14] From a determination made in this laboratory by Mr. D. A. MacInnes. We hope to extend this investigation in the near future and will therefore defer the description of the method until its completion.

[15] Noyes and Sammet, *Z. physik. Chem.*, 43, 529 (1903).

value of $(d\ln\alpha_0/dT)_{20°}$. Adding these values we obtain $d\ln(\alpha_0 S_0)/dT = 0.0118$, which, when multiplied by $2RT^2$ (*i. e.*, $2 \times 1.98 \times 293 \times 293$) gives 4020 Cal. as the calculated value of U, which is in good agreement with the directly measured value.

In interpreting their experimental results, Noyes and Sammet use the equation of van't Hoff[16] for the temperature coefficient of the *total* concentration of a saturated solution of an ionized solute, namely,

$$d\ln iS/dT = L/iRT^2, \qquad (69)$$

in which i $(= 1 + \alpha)$ is the van't Hoff coefficient. We would have obtained this equation, if in using the engine we had removed osmotically from chamber **E′** not simply one mol of the solute in the form of its ions but one mol of the solute in the form of both ions and undissociated molecules, in the proportions in which they exist together in the saturated solution. Then, in order to obtain the equation in the above form, we should have had to assume that the undissociated molecules were "normal solutes" as well as the ions. In other words, the van't Hoff equation involves an unnecessary number of assumptions. It is an equation which can be obtained by combining two equations, one involving only the ions (*i. e.*, equation (67)) and another similar one involving only the undissociated molecules.

The recent work of A. A. Noyes and his associates[17] has shown us the necessity for differentiating between ions and undissociated molecules with regard to their behavior as solutes. There is all the more reason for doing this since the assumption that they behave alike in this respect is quite unnecessary in the majority of cases. All of our equations for solution, which contain the van't Hoff factor i, are derived on the assumption that both ions and undissociated molecules are "normal solutes." Consequently, if a given equation is found to be in agreement with the results of experiment, it does not necessarily mean that this assumption is correct, for agreement might still occur if both the ions and undissociated molecules deviated, but in opposite directions, from the behavior of the normal solute. If the equation is not in agreement with the results of experiment, it does not tell us whether the disagreement is due to the behavior of the ions or the undissociated molecules, or both. And yet it is quite possible to decide this question, for in nearly every case the equation containing the van't Hoff i can be broken up into two simpler equations, one of which involves only the ions and the other only the undissociated molecules. An example of this occurs in the case of orthonitrobenzoic acid, described above. Noyes and Sammet found that the van't Hoff equation (eq. (69)) *was not* in agreement with the results of their experiments with this acid. We have seen that equa-

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[16] van't Hoff, *Z. physik. Chem.*, **17**, 147, 546 (1895).

[17] Carnegie Inst. Pub., No. 63.

tion (67), which involves only the ions, *is* in good agreement with the experimental results. Consequently the deviation from the van't Hoff equation must be ascribed, for the most part at any rate, to the abnormal behavior of the undissociated portion. Whether it is to be attributed to the partial association of the unionized molecules (as Noyes and Sammet suggest) or to the presence of two isomeric forms of these molecules is not yet certain.[18]

Before leaving this subject attention should be called to the fact that we have in equation (67) a very valuable method for studying the behavior of ions (apart from the unionized molecules) with respect to the Gay-Lussac law for the effect of temperature upon osmotic pressure in dilute solutions.[18]

7. Electromotive Force.

The Perfect Thermodynamic Engine is generally applicable to the derivation of all types of electromotive force equations which are based directly upon the Second Law. In the present paper, however, we shall confine the consideration to the electromotive force of concentration cells. The type of engine used is shown in Fig. 3. It differs from the preceding forms only by the addition of the parts **W** and $\eta\eta'$. **W** is a device which permits the easy passage of ions but which resists any mass flow of the solution from one chamber to the other, thus permitting a difference of pressure to be maintained in the two chambers, if desired. η and η' are two reversible electrodes which can be connected with each other (through a suitable compensating external E. M. F. to ensure operation under equilibrium) by means of the key **K**.

Concentration Cells (T, P = *const.*) —(*a*) *The Nernst Equation.*— As an example of this case let us consider a simple concentration cell with reversible silver electrodes and with silver nitrate as the electrolyte. Using the engine shown in Fig. 3, omitting cylinder **AA′**, and with temperature of **R** and **R′** = T, and pressure against **D** and **D′** = P, the arrangement of the engine is as follows:

Chamber **E**: Filled with a solution of silver nitrate of concentration C and provided with a reversible silver electrode η which has a potential E. Cylinder **B** contains a solution of silver ion which is in equilibrium, through the semipermeable membrane, with the silver ion in the chamber. Piston **B**, which is impermeable only to silver ion, is under the "osmotic pressure" $\Pi'_{Ag^{\cdot}}$. Cylinder **C** is arranged similarly with respect to NO_3-ion, the "osmotic pressure" against piston **C** being $\Pi'_{NO'_3}$.

Chamber **E′**: Similar to **E** except that the solution has concentration $C + dC$, the potential of the electrode η' is E + dE and the osmotic

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[18] We hope to pursue this question further experimentally in this laboratory, as well as the general question of the temperature coefficients of the osmotic pressures of ions as distinct from the unionized molecules.

pressures are $\Pi'_{Ag.} + d\Pi'_{Ag.}$ against piston B′ and $\Pi'_{NO'_3} + d\Pi'_{NO'_3}$ against piston C′.

To operate the engine, close the key K and allow one equivalent (*F*) of electricity to flow reversibly. The passage of this current is accompanied by the electrical transference of n_a equivalents of electrolyte from chamber E′ to chamber E (*i. e.*, from cathode to anode). n_a is the ordinary or Hittorf transference number of the anion.[20] To compensate

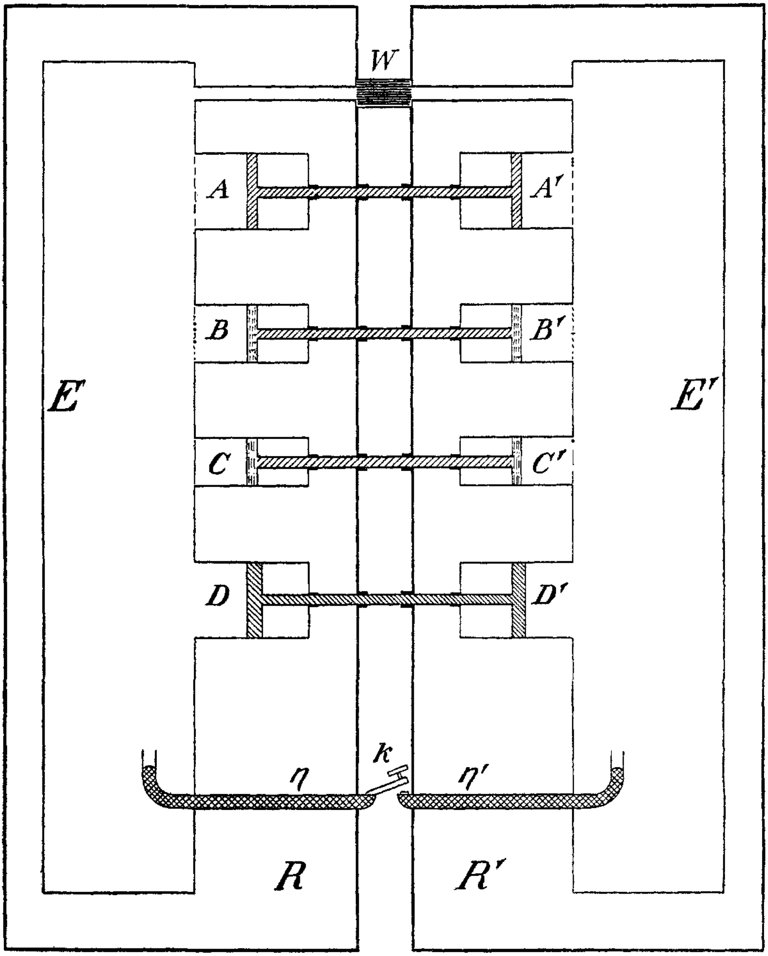

Fig. 3.

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[20] In general, both solvent and electrolyte are transferred by the current. For the present purpose it is not necessary to differentiate between these two factors but only to know the *total* effect referred to solute alone, and this is expressed by the ordinary Hittorf transference number. An equation involving the "true transference number" (see Washburn, THIS JOURNAL, 31, 323 (1909)) can be readily obtained by

for this effect and maintain equilibrium, pistons **BB′** and **CC′** move reversibly toward the right removing n_a mols of each ion from **E** and forcing them into **E′**. By the Second Law the total work is equal to zero, or

$$FdE = n_a[V_{Ag^{\cdot}}d\Pi'_{Ag^{\cdot}} + V_{NO_3'}d\Pi'_{NO_3'}]. \tag{70}$$

If we assume the ions to be normal solutes and the solution dilute, this equation becomes

$$dE = (2n_aRT/F)d\ln C_{Ag^{\cdot}}. \tag{71}$$

In order to integrate we need to know n_a as a function of $C_{Ag^{\cdot}}$. If we assume it to be independent of the concentration we obtain the Nernst equation on integrating.

$$E - E' = \Delta E = (2n_aRT/F)\ln C_{Ag^{\cdot}}/C'_{Ag^{\cdot}}. \tag{72}$$

If $C_{Ag^{\cdot}} = \alpha C$ and $\alpha = \Lambda_c/\Lambda_\infty$ this equation becomes

$$E - E' = \Delta E = (2n_aRT/F)\ln\Lambda_cC/\Lambda_{c'}C', \tag{73}$$

in which Λ_c indicates the equivalent conductance of the solution at the concentration C.

It should be noticed that *this equation contains no assumption regarding the relation which exists between the ions and undissociated molecules in the solution.* It requires only that the ions be "normal solutes," the behavior of the undissociated molecules in this respect not being involved. Another important characteristic of the equation is the fact that *it is not influenced by errors in the value of the equivalent conductance at infinite dilution.* It offers therefore *another* method of studying the behavior of ions apart from their relation to the undissociated molecules (cf. page 489).

(*b*) *The Helmholtz Equation.*—Using the engine shown in Fig. 3 but omitting cylinders **BB′** and **CC′** the arrangement is as follows:

Chamber **E**: Filled with a solution of (say) HCl of any concentration C and provided with a reversible calomel electrode η having the potential E. The vapor pressure of HCl from the solution acts through the semipermeable membrane against piston **A** with a pressure p.

Chamber **E′**: The same as **E** except that the concentration of the solution is $C + dC$, the potential of η' is $E + dE$ and the vapor pressure acting against piston **A′** is $p + dp$.

The operation of the engine is evident and gives us at once the relation

$$FdE = n_Kvdp. \tag{74}$$

If the vapor obeys the perfect gas law this becomes

$$dE = (n_KRT/F)d\ln p \tag{75}$$

which on integration, assuming n_K const., gives the Helmholtz equation,

$$E - E' = (n_KRT/F)\ln p/p'. \tag{76}$$

introducing into the engine a vapor piston by means of which solvent can be vaporized from one chamber and condensed into the other.

n_K is here the Hittorf transference number of the cation. Obviously an exactly similar equation can be obtained in terms of the partial vapor pressures of the *solvent* from the two solutions.

These two examples will be sufficient to illustrate the use of the engine in deriving E. M. F. equations. The requisite arrangement and operation of the engine for the derivation of pressure or temperature equations (*e. g.*, the Gibbs-Helmholtz equation) will be readily understood from the corresponding cases of vapor pressure, chemical equilibrium, etc., which have been described in the preceding pages.

8. The Colligative Properties of a Solution.

The quantities osmotic pressure, vapor-pressure lowering, freezing-point lowering, boiling-point raising,[21] etc., which lie at the basis of our methods of molecular weight determination in solution, have played such important rôles in the development of the modern theory of solutions, that a clear conception of the thermodynamic relations which connect them with one another is of fundamental importance. In many cases, the derivations of these relations which are given in the text-books contain the assumption that the solution is dilute and involve one of the laws of dilute solutions. Even in an elementary text, the only excuse that can be offered for introducing such assumptions is that the derivation of the exact relation is too complicated for the student to grasp at this stage. But even on such grounds, this procedure can scarcely be justified if it leaves the student with the idea that the relation between osmotic pressure and freezing-point lowering, for example, is in any way dependent upon the law which connects either of these quantities with the concentration. In the following pages it will be shown that by means of the thermodynamic engine the exact relations can be written down at once. These relations are, of course, differential equations. The method of integration varies with the nature of the solvent and the accuracy with which it is possible to measure the various quantities concerned. In the present paper the methods of integration will only be indicated briefly for some of the simplest cases.

The type of engine used is shown in Fig. 1. Both chambers are filled with the solution under investigation. Piston **AA′** is a "vapor piston," that is, as it moves toward the left, for example, it draws the vapor of the solvent out of chamber **E′** and condenses it into chamber **E**. Piston **BB′** is an osmotic piston. As it moves toward the left it allows solvent to enter chamber **E′** by passing through the semipermeable head **B′**, while at the same time solvent is removed in a similar manner from chamber **E**, the space behind the two piston heads being filled with pure

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[21] Following the suggestion of Ostwald, we shall call these quantities the colligative properties of the solution.

solvent. Piston **DD′** is the total pressure piston. It moves to the right or left during the operation of the engine whenever a volume change in the chambers renders it necessary, but since in the following treatment we shall deal always with a solution under constant external pressure (that of the atmosphere for example), this piston will move only under a pressure difference of zero. Consequently no work is involved in its motion and it will not be necessary to consider it at all during the operation of the engine.

For the solution we will take any homogeneous liquid mixture of any number of constituents, A, B, C, etc. Since the terms solvent and solute are perfectly arbitrary for such a solution, let us regard A as the solvent and the other constituents as solutes.

Osmotic Pressure and Vapor Pressure (P, T = *const.*).—To ask the question, How does the vapor pressure of the solvent from any solution vary with the osmotic pressure? is equivalent to asking the question,[22] How does the vapor pressure of the pure liquid solvent vary with the total pressure upon it? and this relation has already been derived. It is equation (2) which may be written as follows (since by definition $d\Pi = -dP$):

$$(\partial p/\partial \Pi)_{P.T} = -V/v. \tag{77}$$

In order to integrate we need only know v and V as functions of p and Π, respectively. Assuming the gas laws for the vapor we have $v = RT/p$. If V_0 is the molecular volume of the liquid under the pressure P (*i. e.*, when $\Pi = 0$, see p. 478) and α is its coefficient of compressibility between P and $P - \Pi$ $(\alpha = (V_0 - V)/V_0(P - \Pi - P))$, then $V = V_0(1 + \alpha\Pi)$. Substituting in equation (77) and integrating we have

$$RT\int d\ln p = -V_0\int(1 + \alpha\Pi)d\Pi,$$

or

$$RT\ln p = -V_0(\Pi + {}^1/_2\alpha\Pi^2) + RT\ln p_0,$$

in which the quantity p_0 in the integration constant is the vapor pressure of the pure solvent under the pressure P and at the temperature T. This gives us finally

$$\Pi + {}^1/_2\alpha\Pi^2 = -(RT/V_0)\ln p/p_0. \tag{78}$$

In many cases the term containing α is negligible and by expanding the logarithm term into a series we can obtain a more convenient form for ordinary use:

$$\Pi = \frac{RT}{V_0}\left[\left(\frac{p_0 - p}{p_0}\right) + {}^1/_2\left(\frac{p_0 - p}{p_0}\right)^2 + {}^1/_3\left(\frac{p_0 - p}{p_0}\right)^3 + \ldots\right] \tag{79}$$

The ordinary equation for dilute solutions is obtained by neglecting all but the first term in the above series.

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[22] See the definition of osmotic pressure, p. 478.

Osmotic Pressure and Freezing-point Lowering (P = *const.*).—The problem may be stated thus: How does the osmotic pressure of a solution change with the temperature at which the solution is in equilibrium with the pure solid solvent? The arrangement of the engine is as follows:

Chamber **E**: Filled with a solution in equilibrium with an excess of pure solid solvent and therefore at the temperature of its freezing point, T_F. The mol fraction of the solvent in the solution is N_A. The pure liquid solvent (in cylinder **B**) in equilibrium with the solution is under the osmotic pressure Π.

Chamber **E′**: Exactly as chamber **E** except the mol fraction of the solvent is $N_A + dN_A$, the freezing point $T_F + dT_F$ and the osmotic pressure $\Pi + d\Pi$.

$d\Pi$ in this instance is given by the expression

$$d\Pi = (\partial\Pi/\partial T)_N(\partial T_F/\partial N_A)_P dN_A + (\partial\Pi/\partial N_A)_T dN_A. \qquad (80)$$

To operate the engine allow one mol of solid solvent to melt in chamber **E′** and remove the resulting liquid osmotically with piston **BB′**. The reverse operation occurs in chamber **E′**. The work done by piston **BB′** is $-Vd\Pi$. The heat absorbed at the higher temperature (*i. e.*, from reservoir **R′**) is the molecular heat of fusion (L_F) of the solid solvent, under the pressure P, to form liquid solvent under the pressure $p - \Pi$. We have therefore by the Second Law

$$-Vd\Pi = L_F dT_F/T_F, \qquad (81)$$

or

$$(\partial\Pi/\partial T_F) = -L_F/VT_F. \qquad (82)$$

In this equation we can put $T_F = T_0 - \Delta t_F$, and obtain

$$d\Pi = L_F d(\Delta t_F)/V(T_0 - \Delta t_F), \qquad (83)$$

where Δt_F is the freezing-point lowering in centigrade degrees and T_0 is the freezing point of the pure solvent on the absolute scale.

In order to integrate we need only express V and L_F as functions of Δt_F. V may be expressed by the equation

$$V = V_0 + a\Delta t_F + b(\Delta t_F)^2 + \ldots\ldots \qquad (84)$$

where V_0 is the molecular volume when $\Delta t_F = 0$ and $\Pi = 0$, and a, b, etc., are constants whose numerical values can be computed from the coefficients of compressibility and thermal expansion of the liquid solvent and from approximate values of Π for different values of Δt_F up to the limit desired. For L_F the first law of thermodynamics gives us the general relation,

$$L_F = L_{F_0} + \Delta C_{P_0}\Delta t_F + {}^1/_2\alpha\Delta t_F^2 + {}^1/_3\beta\Delta t_F^3 + \ldots \qquad (85)$$

In this equation L_{F_0} is the molecular heat of fusion of the pure solvent at its freezing point T_0, ΔC_{P_0} is the attendant *decrease* in the heat capacity of the system and α, β, etc., are constants expressing the dependence of ΔC_P upon the temperature.[23]

Substituting equations (84) and (85) in equation (83) and integrating so as to obtain Π as a series function in Δt_F, we obtain the relation

$$\Pi = \frac{L_{F_\circ}}{V_\circ T_\circ}\Bigg[\Delta t_F + {}^1/_2\left(\frac{V_\circ - aT_\circ}{V_\circ T_\circ} - \frac{\Delta C_{P_\circ}}{L_{F_\circ}}\right)\Delta t_F^2 + {}^1/_3\left(\frac{(V_\circ - aT_\circ)^2}{V_\circ^2 T_\circ^2} - \right.$$
$$\left.\frac{\Delta C_{P_\circ}(V_\circ - aT_\circ)}{L_{F_\circ} V_\circ T_\circ} + \frac{a - bT_\circ}{V_\circ T_\circ} + \frac{{}^1/_2\alpha}{L_{F_\circ}}\right)\Delta t_F^3 + {}^1/_4\left(\frac{(V_\circ - aT_\circ)^3}{V_\circ^3 T_\circ^3} - \right.$$
$$\frac{\Delta C_{P_\circ}(V_\circ - aT_\circ)^2}{L_{F_\circ} V_\circ^2 T_\circ^2} + \frac{(a - bT)(V_\circ - aT)}{V_\circ^2 T_\circ^2} + \frac{{}^1/_2\alpha}{L_{F_\circ} V_\circ T_\circ} +$$
$$\left.\frac{(V_\circ - aT_\circ)(a - bT_\circ)}{V_\circ^2 T_\circ^2} - \frac{\Delta C_{P_\circ}(a - bT_\circ)}{L_{F_\circ} V_\circ T_\circ} + \frac{b}{V_\circ T_\circ} - \frac{{}^1/_2\beta}{L_{F_\circ}}\right)\Delta^{4}_{F}\Bigg] \quad (86)$$

This apparently cumbersome equation becomes quite simple when we consider a concrete case, owing to the fact that many of the terms in the parentheses are negligible. Let us consider a water solution, for example, and suppose Δt_F to be known with an accuracy of 0.1 per cent. For this case equation (86) becomes

$$\Pi = 12.06(\Delta t_F - 1.78.10^{-3}\Delta t_F^2 - 2.5.10^{-6}\Delta t_F^3) \text{ atmospheres.} \quad (87)$$

This equation can be used for values of Δt_F as high as 100° without introducing an error of more than a few tenths of one per cent.[24]

Osmotic Pressure and Boiling-point Raising (*P = const.*).—The problem may be stated as follows: How does the osmotic pressure change with the temperature at which the partial vapor pressure of the solvent from the solution is equal to the external pressure upon the solution?

The arrangement of the engine is as follows:

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[23] In the case of water, for example, we have for its molecular heat capacity at constant pressure, $C_P = C_{P_0} + at + bt^2 + \ldots.$ and for ice $C'_P = C'_{P_0} + a't + b't^2 + \ldots.$ Subtracting the first equation from the second and putting

$$C'_P - C_P = \Delta C_P,\ a' - a = \alpha, \text{ and } b' - b = \beta,$$

we obtain

$$\Delta C_P = \Delta C_{P_0} + \alpha t + \beta t^2 + \ldots$$

Combining this with the purely thermodynamic equation,

$$dL_F/dt = -dL_F/d(\Delta t_F) = -\Delta C_P,$$

and integrating, we obtain equation (85).

Strictly speaking, another term should be added to this expression to include the heat of compression of the liquid solvent from P to $P - \Pi$, since the operation of the engine produces liquid solvent at the latter pressure. In most cases this heat effect will be entirely negligible in comparison with the heat of fusion and this assumption is made in equation (85).

[24] The values of the constants for water are: L_{F_0} = 59.309 liter atmospheres, ΔC_{P_0} = 0.363 liter atmosphere per degree, $V_\circ$ = 0.01801 liter, a = 0.000014 liter; α, β, and b are negligible. For examples illustrating the application of equation (87) see Lewis, THIS JOURNAL, **30**, 671 (1908).

Chamber **E**: Filled with a solution under the pressure P at its boiling point,[25] T_B. The mol fraction of the solvent is N_A and its partial vapor pressure, acting against piston **A**, is p ($= P$). The pure liquid solvent in cylinder **B** is under the osmotic pressure Π.

Chamber **E′**: Exactly as chamber **E** except that the mol fraction of the solvent is $N_A + dN_A$, the temperature (B. P.) is $T_B + dT_B$ and the osmotic pressure is $\Pi + d\Pi$. The vapor pressure is P.

$d\Pi$ in this instance is given by the expression

$$d\Pi = (\partial\Pi/\partial T)_N(\partial T_B/\partial N_A)_P dN_A + (\partial\Pi/\partial N_A)_T dN_A. \qquad (88)$$

To operate the engine, vaporize one mol of solvent from chamber **E′** by means of piston **AA′** and introduce simultaneously one mol of liquid solvent osmotically by means of piston **BB′**. The reverse process occurs in chamber **E**. The only work involved is that done by piston **BB′**, which is $Vd\Pi$. The heat absorbed at the higher temperature is the molecular heat of vaporization (L) of the pure liquid solvent under the pressure $p - \Pi$ to form vapor at the pressure p. We have therefore by the Second Law,

$$Vd\Pi = LdT_B/T_B, \qquad (89)$$

or

$$(\partial\Pi/\partial T_B) = L/VT_B. \qquad (90)$$

In this equation we can put

$$T_B = T_{B_0} + \Delta t_B$$

and obtain

$$d\Pi = Ld(\Delta t_B)/V(T_{B_0} + \Delta t_B), \qquad (91)$$

where Δt_B is the elevation of the boiling point in centigrade degrees and T_{B_0} is the boiling point of the pure solvent on the absolute scale.

The method of integration to be followed for this equation depends largely on the nature of the solvent, the equation of state of the vapor and the magnitude of T_{B_0} as compared with the critical temperature of the pure solvent. If the vapor of the solvent obeys the gas laws and T_{B_0} is considerably lower than the critical temperature, we could adopt a method of integration identical with that employed for the corresponding freezing point equation and would obtain an integrated expression perfectly analogous to equation (86). Consequently it will not be necessary to consider this case in further detail.

Vapor Pressure and Freezing-point Lowering (*P = const.*).—The problem may be stated as follows: How does the vapor pressure of the solvent from a solution vary with the temperature at which the solution is in equilibrium with the pure solid solvent? Now the vapor pressure from the solution and solid solvent are equal when the two are in equi-

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[25] Note that the b. p. is here defined as the temperature at which the partial vapor pressure of the solvent is equal to the total pressure on the solution.

librium, consequently this question is the same as inquiring, How does the vapor pressure of the pure solid solvent vary with the temperature? and this relation has already been derived. It is equation (5) which we may write as follows (using T_F in place of T to indicate that we mean the absolute temperature of the freezing point of the solution):

$$(\partial p/\partial T_{\mathrm{F}})_{\mathrm{P}} = L_{\mathrm{S}}/vT_{\mathrm{F}}. \tag{92}$$

In this equation L_S is the molecular heat of sublimation of the pure solid solvent under the pressure P to form saturated vapor at the pressure p. dp is expressed by the equation

$$dp = (\partial p/\partial T)_N(\partial T_F\partial N_{\mathrm{A}})_P dN_{\mathrm{A}} + (\partial p/\partial N_{\mathrm{A}})_P dN_{\mathrm{A}} \tag{93}$$

Let us integrate equation (92) for aqueous solutions. Assuming the perfect gas law for saturated water vapor below 0°, equation (92) may be written:

$$d\ln p = (L_S/R)dT/\mathrm{T}^2. \tag{94}$$

Owing to the slight difference between the heat capacities of ice and its vapor, L_S will have such a small temperature coefficient that it may be regarded as constant without much error, even for large values of the freezing point lowering, Δt_F. Integrating equation (94) with this assumption we obtain

$$\ln p_0/p = (L_S/RT_0)\Delta t_F/T. \tag{95}$$

In this equation p is the vapor pressure of the solution at the absolute temperature of its freezing point T.

9. Summary and Conclusion.

1. A simplification of the cyclical process method of Carnot has been described, which reduces the cycle of necessary operations to a single step and allows the desired thermodynamic equation to be written down "by inspection." Not only does this result in an increased clearness and certainty as to the exact significance of the quantities appearing in the equation, but it also insures an entirely rigorous result because it is impossible to introduce into the process any assumption except the two laws of thermodynamics.

2. The use of this simplified process (embodied in what has been called the "Perfect Thermodynamic Engine") as the basis for the construction of a simple but entirely rigorous system of thermodynamic chemistry, is illustrated by applying it to the derivation of a number of fundamental relations.

3. The modified process possesses, to a higher degree, all of the advantages of the ordinary cyclical process with none of its disadvantages. The system of equations which it yields possesses all of the rigor of any of the analytic systems of thermodynamics with none of their abstruse conceptions and intricate, involved and long drawn-out derivations. By means of the perfect thermodynamic engine one can pass in a

single step from the Second Law of thermodynamics directly to the differential equation of the desired relation.

4. In connection with the application of the engine to the subject of chemical equilibrium, the following points have been brought out:

(*a*) Contrary to the statement of T. B. Robertson, the Mass Action Law is not an expression of the condition for equilibrium in a system whose equation of state is $p(v - d) = RT$.

(*b*) The derivation of the Law of the Constancy of the Solubility Product for a solute which dissociates in solution does not involve any assumption regarding the nature of the law which regulates the equilibrium between the undissociated molecules and their products of dissociation. Consequently the theoretical basis for the Solubility Product Law in the case of strong electrolytes is not destroyed by the fact that they do not obey the Mass Action Law, as inferred by Stieglitz.

5. It is shown that many of our equations which contain the van't Hoff i, involve an unnecessary number of assumptions and that each equation can be split up into two simpler equations, one involving only the ions, the other only the unionized molecules. The advantage of so doing is illustrated by a consideration of the experimental data of Noyes and Sammet on the solubility of orthonitrobenzoic acid.

URBANA, ILLINOIS, January 15, 1910.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

HETEROGENEOUS EQUILIBRIA BETWEEN AQUEOUS AND METALLIC SOLUTIONS: THE INTERACTION OF MIXED SALT SOLUTIONS AND LIQUID AMALGAMS (FIRST PAPER).

A STUDY OF THE REACTION, $KHg_m + Na^{\cdot} \rightleftarrows K^{\cdot} + NaHg_n + (m-n)\ Hg$.

BY GEORGE MCPHAIL SMITH.

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It has previously been shown[1] that the alkali metals exist, in liquid mercurial solution, in the form of compounds of the general formula $MeHg_n$, containing only one atom of the amalgamated metal to the molecule. It has also been shown that a mixed solution, containing the chlorides of sodium and potassium, reacts readily with either sodium or potassium amalgam, with the rapid establishment of an equilibrium. The same has been found to be the case with sodium and rubidium, and sodium and caesium amalgams, when treated with the corresponding mixed solutions.[2]

The present paper is the outcome of a more detailed study of the first

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[1] Ueber die relative Beständigkeit bzw. die Konstitution der verdünnten Amalgame der Alkali-bzw. Erdalkalimetalle. G. McP. Smith, *Z. anorg. Chem.*, **58**, 381 (1908).

[2] *Loc. cit.*