



XC. On the application of the Theory of Chemical Potential to the Thermodynamical Theory of Solutions.—Part I. The general theory of chemical potential in a binary system. Osmotic pressure and vapour-pressure of solutions

S.A. Shorter B.Sc.

To cite this article: S.A. Shorter B.Sc. (1911) XC. On the application of the Theory of Chemical Potential to the Thermodynamical Theory of Solutions.—Part I. The general theory of chemical potential in a binary system. Osmotic pressure and vapour-pressure of solutions , Philosophical Magazine Series 6, 22:132, 933-942, DOI: [10.1080/14786441208637191](https://doi.org/10.1080/14786441208637191)

To link to this article: <http://dx.doi.org/10.1080/14786441208637191>



Published online: 20 Apr 2009.



Submit your article to this journal [↗](#)



Article views: 2



View related articles [↗](#)



Citing articles: 1 View citing articles [↗](#)

2. These slow moving particles can be accelerated at will, the minimum potential difference required to give them a sufficient velocity to affect the plate being about 500 volts per centimetre.

3. There is secondary radiation present as well as primary—both straight lines and their continuations as parabolas are shown on a few of the photographs.

4. The value of e/m is the same for the various carriers as that found by Sir J. J. Thomson in the case of the positive rays formed by the ordinary perforated cathode with high potential discharge.

5. The greater the acceleration the more clearly cut and well defined are the photographs, also the nearer the parabolas extend to the origin.

6. This investigation does not show a negative counter-part to any of the curves.

7. The work thus far has been with residual air only.

In conclusion I wish to express my appreciation to Professor Sir J. J. Thomson for the problem and the main line of attack, also for the facilities of the Cavendish Laboratory that he so kindly placed at my disposal.

August 17, 1911.

XC. *On the Application of the Theory of Chemical Potential to the Thermodynamical Theory of Solutions.* By S. A. SHORTER, B.Sc., Assistant Lecturer in Physics in the University of Leeds.—Part I. *The General Theory of Chemical Potential in a Binary System. Osmotic Pressure and Vapour-Pressure of Solutions**.

GIBBS'S Theory of Chemical Potential † is a very powerful instrument for the solution of many thermodynamical problems. This instrument, however, seems never to have been applied to the solution of many important problems in the Theory of Solutions. Thus many attempts have been made to deduce an expression connecting the osmotic pressure and vapour-pressure of a concentrated solution. Nearly all the expressions which have been deduced are approximate; one well-known expression is quite wrong. In only one case ‡ has an exact expression been deduced connecting the osmotic pressure and vapour-pressure of a

* Communicated by the Author.

† "On the Equilibrium of Heterogeneous Substances," *Collected Works*, vol. i. p. 55.

‡ Porter, Roy. Soc. Proc. A. vol. lxxix. p. 519 (1907).

Phil. Mag. S. 6. Vol. 22. No. 132. Dec. 1911. 3 Q

solution of a single involatile solute. By means of the Theory of Chemical Potential an expression of a very general nature connecting the vapour-pressures of two solutions and the pressures under which they co-exist in osmotic equilibrium, can be deduced with extreme ease, not only in the special case of one involatile solute, but in the general case of any number of involatile solutes. Other problems, such as the conditions of co-existence of a liquid and vapour under different pressures (the effect of pressure on the vapour-pressure), the effect of gravity on a solution, &c., may also be solved in a simple manner by this method. The author proposes to treat these questions in a later communication.

Summary of Notation.

The following are the chief symbols used in this paper :—

M_0 the mass of the solvent S_0 ;

M_1 the mass of the solute S_1 ;

$S = \frac{M_1}{M_0}$ the concentration of the solution ;

W the volume of the solution ;

Π_0 the vapour-pressure of the pure solvent ;

Π the vapour-pressure of the solution ;

$v(s, p, \theta)$ the specific volume of a solution of concentration s at a temperature θ and under a pressure p ;

$v(0, p, \theta)$ the specific volume of the pure solvent ;

$f_0(s, p, \theta)$ the chemical potential of the solvent in a solution of concentration s at a temperature θ and under a pressure p ;

$f_1(s, p, \theta)$ the chemical potential of the solute in the solution ;

$f_0(0, p, \theta)$ the chemical potential of the solvent in the pure liquid state ;

$P_0(s, p, \theta) \equiv \frac{\partial}{\partial p} f_0(s, p, \theta) ;$

$F_0(p, \theta)$ the chemical potential of the solvent in the pure vapour state ;

$V(p, \theta)$ the specific volume of the solvent vapour ;

$\Omega(s, p, \theta)$ the osmotic pressure of a solution of concentration s at a temperature θ , when the pressure on the pure solvent is p .

The symbols v, f_0, P_0 , &c., will sometimes be used alone when there is no doubt as to the particular values of the variables involved.

The Theory of Chemical Potential in a Binary System.

Before considering the applications of the Theory of Chemical Potential, we will give a brief account of Duhem's* development of the theory in a binary system.

If the external generalized forces acting on a system are constant, the condition for equilibrium may be expressed in the following manner:—

Let U denote the internal energy of the system, θ the absolute temperature, ϕ the entropy, and ψ the potential of the external generalized forces (*i. e.* the sum of the products of the forces and the corresponding generalized coordinates), and let

$$\Phi = U - \theta\phi - \psi.$$

The necessary and sufficient condition for equilibrium is that in any virtual isothermal modification of the system

$$\delta\Phi \geq 0.$$

The function Φ is called by Duhem the Total Thermodynamical Potential of the system.

Consider a homogeneous system containing two components, S_0 , which will be called the solvent, and S_1 , which will be called the solute. Let the masses of these components be M_0 and M_1 respectively. Let the volume of the system be W , and suppose it to be subjected to a uniform pressure p . Then we have

$$\Phi = U - \theta\phi + pW.$$

If we consider Φ as a function of M_0 , M_1 , p , θ it will be homogeneous of the first degree in M_0 and M_1 , and can therefore be written in the form

$$\frac{\partial\Phi}{\partial M_0} M_0 + \frac{\partial\Phi}{\partial M_1} M_1.$$

Now $\frac{\partial\Phi}{\partial M_0}$ and $\frac{\partial\Phi}{\partial M_1}$ will be homogeneous functions of M_0 and M_1 of zero degree, and can therefore be written in the forms $f_0(s, p, \theta)$ and $f_1(s, p, \theta)$ respectively, where $s = \frac{M_1}{M_0}$. Since evidently

$$\frac{\partial}{\partial M_1} \frac{\partial\Phi}{\partial M_0} = \frac{\partial}{\partial M_0} \frac{\partial\Phi}{\partial M_1},$$

it can easily be proved that

$$\frac{\partial f_0}{\partial s} = -s \frac{\partial f_1}{\partial s}.$$

* *La Mécanique Chimique*, vol. iii. pp. 1-10.

Consider two homogeneous systems at the same temperature and under the same pressure, the first containing masses M_0 and $M_1 + \delta M_1$ respectively of the components S_0 and S_1 , and the second masses M_0 and $M_1 - \delta M_1$. If these two systems are put into communication we shall have finally a homogeneous system containing masses $2M_0$ and $2M_1$ of the components. This irreversible process of uniform mixing must result in a diminution of the total thermodynamical potential, so that we must have

$$\Phi(2M_0, 2M_1, p, \theta) < \Phi(M_0, M_1 + \delta M_1, p, \theta) + \Phi(M_0, M_1 - \delta M_1, p, \theta).$$

From this we may readily prove the inequalities

$$\frac{\partial}{\partial s} f_1(s, p, \theta) > 0,$$

$$\frac{\partial}{\partial s} f_0(s, p, \theta) < 0.$$

If $v(s, p, \theta)$ denotes the specific volume of the solution we have

$$\frac{\partial \Phi}{\partial p} = (M_0 + M_1)v(s, p, \theta).$$

By differentiating this equation with respect to M_0 and introducing the variable s , we obtain the equation

$$\frac{\partial}{\partial p} f_0(s, p, \theta) = v(s, p, \theta) - s(1+s) \frac{\partial}{\partial s} v(s, p, \theta).$$

The value of $\frac{\partial f_1}{\partial p}$ may be obtained in a similar manner.

The functions $f_0(s, p, \theta)$ and $f_1(s, p, \theta)$ are called the chemical potentials of the components of the system. The importance of the chemical potential lies in the fact that if a system consists of two or more homogeneous parts in equilibrium, the chemical potential of any component must be the same in all parts of the system, so long as the motion of a quantity of that component from one part to the other is a possible virtual modification of the system. This follows from the general condition of equilibrium.

The Effect of a Finite Change of Pressure on the Chemical Potential of the Solvent in the Solution.

In the previous section we have shown that the value of $\frac{\partial}{\partial p} f_0(s, p, \theta)$ can be calculated from simple experimental data.

As this quantity plays a very important part in the subsequent theory, it will be denoted by the special symbol $P_0(s, p, \theta)$. If the volume W of the solution is regarded as a function of M_0 , M_1 , p , and θ , it can be shown that

$$\frac{\partial W}{\partial M_0} = P_0(s, p, \theta).$$

This quantity is evidently positive and of the same order of magnitude as the specific volume of the pure solvent. In cases where the change of volume on solution is small the two quantities are approximately equal.

In the case of a liquid mixture, the changes of pressure involved in the phenomena under consideration cause only a very small change in the density, so that we have approximately

$$f_0(s, p_2, \theta) - f_0(s, p_1, \theta) = (p_2 - p_1)P_0(s, p_1, \theta).$$

If we write

$$P_0(s, p_1 \rightarrow p_2, \theta) = \frac{1}{p_2 - p_1} \int_{p_1}^{p_2} P_0(s, x, \theta) dx,$$

we have the exact equation

$$f_0(s, p_2, \theta) - f_0(s, p_1, \theta) = (p_2 - p_1)P_0(s, p_1 \rightarrow p_2, \theta) \quad . \quad . \quad (1)$$

The quantity $P_0(s, p_1 \rightarrow p_2, \theta)$ may be called the mean value of P_0 between the pressures p_1 and p_2 .

An expression for this mean value may be obtained if we assume that

$$v(s, p, \theta) = v(s, \varpi, \theta) \{1 - \beta(p - \varpi)\}$$

where β is the compressibility of the solution and ϖ any convenient pressure, which in this case we will assume to be atmospheric pressure, since the density measurements necessary for the calculation of P_0 will have been made under atmospheric pressure.

Assuming that $\frac{\partial P_0}{\partial p}$ is independent of the pressure it can readily be shown that

$$P_0(s, p_1 \rightarrow p_2, \theta) = P_0(s, \varpi, \theta) \left\{ 1 - \lambda \left(\frac{p_1 + p_2}{2} - \varpi \right) \right\} \quad (2)$$

where

$$\lambda = \beta - s(1 + s) \frac{v(s, \varpi, \theta)}{P_0(s, \varpi, \theta)} \frac{\partial \beta}{\partial s}.$$

In the special case where $s=0$ the function P_0 becomes equal to the specific volume of the pure solvent, and if we adopt a similar notation for the mean value of this latter quantity we have

$$v(0, p_1 \rightarrow p_2, \theta) = v(0, \varpi, \theta) \left\{ 1 - \beta_0 \left(\frac{p_1 + p_2}{2} - \varpi \right) \right\}. \quad (3)$$

where β_0 is the compressibility of the pure solvent.

The Thermodynamical Theory of Osmotic Pressure.

Consider the pure solvent at a pressure p_0 in equilibrium with the solution at a pressure p , the two being separated by a membrane permeable to the solvent only. The chemical potential of the solvent must have the same value in the solution as it has in the pure liquid state. Hence we have

$$f_0(0, p_0, \theta) = f_0(s, p, \theta).$$

Since the chemical potential of the solvent decreases with increase of concentration, and increases with increase of pressure, p must be greater than p_0 . The difference $p - p_0$ is determined as a function of s, p_0 , and θ by the above equation. We will denote this difference by $\Omega(s, p_0, \theta)$, or by Ω simply, when it is not necessary to specify the particular values of the variables. The above equation may be written in the form.

$$f_0(0, p_0, \theta) = f_0(s, p_0 + \Omega, \theta). \quad (4)$$

The quantity $\Omega(s, p_0, \theta)$ is usually called the osmotic pressure of the solution. This term is rather misleading, since given values of the temperature and concentration do not fix the value of Ω . It is necessary to specify in addition the pure

solvent pressure. The value of $\frac{\partial}{\partial p_0} \Omega(s, p_0, \theta)$ is easily calculated. If an increase δp_0 in the pure solvent pressure causes an increase $\delta \Omega$ in the osmotic pressure, we have

$$f_0(0, p_0 + \delta p_0, \theta) = f_0(s, p_0 + \delta p_0 + \Omega + \delta \Omega, \theta).$$

Hence we have

$$\frac{\partial}{\partial p_0} \Omega(s, p_0, \theta) = \frac{v(0, p_0, \theta)}{P_0(s, p_0, \theta)} - 1.$$

The theory of chemical potential shows clearly that osmotic pressure cannot be regarded as a specific property of the solution. The osmotic pressure is simply the increase of pressure necessary to counteract the lowering effect of the addition of the solute on the chemical potential of the solvent.

The relation between this lowering effect and the compensating pressure increase is shown by the following equation, which may be derived from equation (4) by means of equation (1),

$$f_0(0, p_0, \theta) - f_0(s, p_0, \theta) = \Omega(s, p_0, \theta) P_0(s, p_0 \rightarrow p_0 + \Omega, \theta). \quad (5)$$

The Thermodynamical Theory of Vapour-Pressure.

If the pure liquid solvent and its vapour are in equilibrium, the surface of separation being plane, the pressure of the system is determined as a function of the temperature by the equation

$$f_0(0, \Pi_0, \theta) = F_0(\Pi_0, \theta) \quad . \quad . \quad . \quad . \quad (6)$$

where $F_0(\Pi_0, \theta)$ is the chemical potential of the solvent vapour at a pressure Π_0 and temperature θ .

If the solution and the solvent vapour are similarly in equilibrium, the pressure is determined as a function of the temperature and concentration by the equation

$$f_0(s, \Pi, \theta) = F_0(\Pi, \theta). \quad . \quad . \quad . \quad . \quad (7)$$

If $V(x, \theta)$ denotes the specific volume of the solvent vapour at a pressure x and temperature θ , we have

$$\frac{\partial}{\partial x} F_0(x, \theta) = V(x, \theta).$$

Hence we have, from equations (6) and (7),

$$f_0(0, \Pi_0, \theta) - f_0(s, \Pi_0, \theta) = \int_{\Pi}^{\Pi_0} V(x, \theta) dx - (\Pi_0 - \Pi) P_0(s, \Pi \rightarrow \Pi_0, \theta). \quad . \quad . \quad . \quad . \quad (8)$$

Since $V(x, \theta)$ is always greater than $P_0(s, x, \theta)$, $\Pi_0 - \Pi$ is always positive, *i. e.* the effect of the addition of the solute is to lower the vapour-pressure.

The lowering of the vapour-pressure and the osmotic pressure are both closely related to the lowering of the chemical potential of the solvent. A relation between the two will be deduced in the next section.

The Relation between the Conditions of Osmotic Equilibrium and Vapour-Pressure.

If we suppose that in the case of osmotic equilibrium between the solution and the pure solvent the latter is under

a pressure equal to its own vapour-pressure, equation (5) gives the value of $f_0(0, \Pi_0, \theta) - f_0(s, \Pi_0, \theta)$ in terms of the osmotic pressure. If we equate this to the value given in equation (8) we immediately obtain a relation between this special osmotic pressure and the vapour-pressure. A much more general equation can, however, be deduced without difficulty. Suppose that we have a solution of concentration s under a pressure p in osmotic equilibrium with a solution of concentration s' under a pressure p' . Let Π and Π' be the respective vapour-pressures of the two solutions. A relation between these four pressures may readily be deduced from the three equilibrium equations

$$\begin{aligned} f_0(s, p, \theta) &= f_0(s', p', \theta), \\ f_0(s, \Pi, \theta) &= F_0(\Pi, \theta), \\ f_0(s', \Pi', \theta) &= F_0(\Pi', \theta). \end{aligned}$$

These three equations may be combined so as to form a single equation containing three potential differences, whose values, in terms of quantities which may be measured experimentally, are given by the equations

$$\begin{aligned} f_0(s, p, \theta) - f_0(s, \Pi, \theta) &= (p - \Pi) P_0(s, \Pi \rightarrow p, \theta), \\ f_0(s', p', \theta) - f_0(s', \Pi', \theta) &= (p' - \Pi') P_0(s', \Pi' \rightarrow p', \theta), \\ F_0(\Pi', \theta) - F_0(\Pi, \theta) &= \int_{\Pi}^{\Pi'} V(x, \theta) dx. \end{aligned}$$

On substituting these values in this equation we obtain the equation

$$\int_{\Pi}^{\Pi'} V(x, \theta) dx = (p - \Pi) P_0(s, \Pi \rightarrow p, \theta) - (p' - \Pi') P_0(s', \Pi' \rightarrow p', \theta). \quad \dots \dots (9)$$

This equation (which, of course, is exact) may be regarded as the fundamental equation connecting the vapour-pressures of two solutions and the pressures under which they co-exist in osmotic equilibrium*.

If we suppose that $s > s'$, then $p > p'$; and rearranging the terms of the equation so as to involve directly the difference

* If the concentration of one of the solutions is made equal to zero, and the two terms on the right-hand side of the equation are written in the form of definite integrals, we obtain Porter's result (*loc. cit.*) connecting the osmotic pressure and vapour-pressure of a solution.

of pressure $p-p'$, we obtain the equation

$$p-p' = \frac{\int_{\Pi}^{\Pi'} V(x, \theta) dx}{P_0(s, \Pi \rightarrow p, \theta)} + (p' - \Pi') \left\{ \frac{P_0(s', \Pi' \rightarrow p', \theta)}{P_0(s, \Pi \rightarrow p, \theta)} - 1 \right\} - (\Pi' - \Pi). \quad (10)$$

If we make $s'=0$, the osmotic difference of pressure becomes the so-called osmotic pressure of the solution and the equation becomes

$$\Omega(s, p_0, \theta) = \frac{\int_{\Pi}^{\Pi_0} V(x, \theta) dx}{P_0(s, \Pi \rightarrow p, \theta)} + (p_0 - \Pi_0) \left\{ \frac{v(0, \Pi_0 \rightarrow p_0, \theta)}{P_0(s, \Pi \rightarrow p, \theta)} - 1 \right\} - (\Pi_0 - \Pi). \quad (11)$$

This equation may be put into a form suitable for practical calculation by substitution of the values of $P_0(s, \Pi \rightarrow p, \theta)$ and $v(0, \Pi_0 \rightarrow p_0, \theta)$ given by equations (2) and (3). In this way we obtain the equation

$$\Omega(s, p_0, \theta) = \frac{\int_{\Pi}^{\Pi_0} V(x, \theta) dx}{P_0(s, \varpi, \theta)(1 - \lambda\epsilon)} + (p_0 - \Pi_0) \left\{ \frac{v(0, \varpi, \theta)(1 - \beta_0\epsilon_0)}{P_0(s, \varpi, \theta)(1 - \lambda\epsilon)} - 1 \right\} - (\Pi_0 - \Pi). \quad (12)$$

where

$$\epsilon = \frac{1}{2}(p + \Pi) - \varpi \text{ and } \epsilon_0 = \frac{1}{2}(p_0 + \Pi_0) - \varpi.$$

If we neglect the second and third terms and also the compressibility factor in the first term, we obtain an approximate value Ω_a given by the equation

$$\Omega_a = \frac{\int_{\Pi}^{\Pi_0} V(x, \theta) dx}{P_0(s, \varpi, \theta)}.$$

In general it will be sufficiently accurate to calculate this value first, and then apply two corrections (1) a compressibility correction, equal to $\Omega_a \lambda \{ \frac{1}{2}(p_0 + \Omega_a + \Pi) - \varpi \}$, (2) a pure solvent pressure correction equal to the second term of the above expression with the compressibility factors omitted. Since the ratio of $\Pi_0 - \Pi$ to Ω is of the same order of magnitude as the ratio of the specific volume of the liquid to that of the vapour, the third term is negligible in all ordinary cases.

The Comparison and Tabulation of Experimental Results.

Vapour-pressure and osmotic pressure measurements form two independent methods of investigating the thermodynamical properties of solutions. The simplest method of comparing and tabulating such results is to calculate from the experimental data the lowering of the chemical potential of the solute at some standard pressure (atmospheric or the pure solvent vapour-pressure) *. These calculations may be performed by means of equations (5) and (8). In the case of concentrated solutions it is impossible to measure the ordinary osmotic pressure. A possible way of carrying out the osmotic investigation of such solutions is to measure the equilibrium pressures of successive pairs of a series of solutions of gradually increasing concentration (starting from the pure solvent). If for example in each measurement the weaker solution was under atmospheric pressure, we should have

$$\begin{aligned} f_0(0, \varpi, \theta) - f_0(s_1, \varpi, \theta) &= \Omega_1 P_0(s_1, \varpi \rightarrow \varpi + \Omega_1, \theta), \\ f_0(s_1, \varpi, \theta) - f_0(s_2, \varpi, \theta) &= \Omega_2 P_0(s_2, \varpi \rightarrow \varpi + \Omega_2, \theta), \\ &\vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \\ f_0(s_{n-1}, \varpi, \theta) - f_0(s_n, \varpi, \theta) &= \Omega_n P_0(s_n, \varpi \rightarrow \varpi + \Omega_n, \theta), \end{aligned}$$

where s_1, s_2, \dots, s_n are the successive values of the concentration and $\Omega_1, \Omega_2, \dots, \Omega_n$ are the successive osmotic differences of pressure. The value of $f_0(0, \varpi, \theta) - f_0(s_n, \varpi, \theta)$ may thus be found by adding the quantities on the right-hand sides of the above equations. It is perhaps hardly necessary to remark that the osmotic pressure of the strongest solution is not equal to the sum of the successive osmotic differences of pressure.

The University, Leeds,
June 30th, 1911.

* The fact that the thermodynamic potential is a more suitable magnitude to deal with than the osmotic pressure in the case of concentrated solutions, was pointed out by Duhem several years ago (*La Mécanique Chimique*, vol. iii. p. 70).