Det Kgl. Danske Videnskabernes Selskab.
Mathematisk-fysiske Meddelelser. **XII**, 7.

ON THE USE OF OSMOTIC PRESSURE IN CHEMICAL THERMODYNAMICS

THE SOLUBILITY CURVE OF SLIGHTLY SOLUBLE SUBSTANCES

BY

J. N. BRØNSTED

KØBENHAVN
LEVIN & MUNKSGAARD
1933

Printed in Denmark.
Bianco Lunos Bogtrykkeri A/S.

(Contribution from the Physical Chemical Institute of the University of Copenhagen.)

The concept of osmotic pressure has played a very important role in the development of the classical theory of dilute solutions. However, the van't Hoff law that the osmotic pressure, as regards the effect of volume and temperature changes, follows the same formula as a perfect gas has foreshadowed a similarity between solutions and gases which actually is of a rather doubtful nature. The distinction between gases and solutions becomes particularly marked in those phenomena which involve variation of temperature. Disregarding the presence of a solvent, as one is tempted to do in view of the supposed parallelism in properties of gases and dilute solutions, in many such cases leads to erroneous results.

The character and magnitude of such errors may be illustrated by considering the calculation of the temperature coefficient of the solubility of a slightly soluble substance on the basis of the second law of thermodynamics. This calculation leads to the well known equation:

$$Q = RT^2 \frac{d\ln s}{dT} \qquad (1)$$

where Q is the ordinary calorimetric heat of solution and s the solubility. The actual sense of this equation, however, is doubtful. The ambiguity arises from the fact that

s, according to the derivation, may designate either weight or volume molality. While at constant temperature and pressure the difference between the two concentration scales disappears at infinite dilution, the temperature gradients of the solubilities retain a finite difference regardless of the absolute value of the solubility.

The first derivation of Equation (1) was given by Le Chatelier[1]. He utilized the vapour pressure curves of the pure solvent and the saturated solution:

$$\lambda_0 = RT^2 \frac{dln\, p_0}{dT}$$

and:

$$\lambda = RT^2 \frac{dln\, p}{dT}$$

respectively, from which:

$$\lambda_0 - \lambda = x\,Q = RT^2 \frac{dln\left(\frac{p_0}{p}\right)}{dT}$$

where x is the solubility expressed as mol fraction. Introducing here the law of Wüllner-Raoult:

$$ln\frac{p_0}{p} = \frac{p_0 - p}{p_0} = x$$

one gets:

$$x\,Q = RT^2 \frac{dx}{dT}$$

or:

$$Q = RT^2 \frac{dln\, x}{dT}.$$

Since the solubility changes have been derived here for constant pressure the correct form of this equation would be:

[1] Le Chatelier, Compt. rend. **100** 50 (1885).

$$Q_p = RT^2 \left(\frac{\partial \ln x}{\partial T}\right)_p. \qquad (2)$$

Another derivation has been given by VAN'T HOFF[1] who based his conclusions upon the similarity between solutions and gases. Considering the process of dissolution as being quite analogous to the process of evaporation, the formula for the evaporation of a liquid:

$$\lambda = RT^2 \frac{d\ln p}{dT}$$

where λ is the ordinary reversible heat of evaporation and p the vapour pressure, is directly applicable to the case of dissolution of a sparingly soluble substance, when for λ is put the reversible heat of dissolution q, and for p the osmotic pressure P. The formula is meant to apply under ordinary conditions i. e. at constant pressure and should be written therefore

$$q_p = RT^2 \left(\frac{\partial \ln P}{\partial T}\right)_p. \qquad (3)$$

Introducing here $P = RTc$, where c is volume concentration, Equation (3) easily changes into:

$$Q_p = RT^2 \left(\frac{\partial \ln c}{\partial T}\right)_p. \qquad (4)$$

On much the same basis Iw. SCHRÖDER[2] has used a reversible cycle to deduce a solubility equation. This author, however, identifies the heat absorption in the

[1] VAN'T HOFF, Arch. Néerl. **20** 239 (1886), Vorlesungen über theoretische und physikalische Chemie, I. 28 (1898).

[2] Iw. SCHRÖDER, Z. phys. Chem. **11** 449 (1893).

reversible dissolution process with the heat of dissolution of the solute in its saturated solution, and thus arrives at the equation:

$$Q_p = RT^2 \left(\frac{\partial \ln P}{\partial T} \right)_p$$

which is decidedly erroneous. Only on introduction of a second error by putting:

$$\frac{d \ln P}{dT} = \frac{d \ln x}{dT}$$

does the formula (2) of Le Chatelier follow.

In another paper by Deventer and van de Stadt[1], in which the analogy between the vapour and solubility equilibrium has been particularly emphasized, a general equation has been set up for the case of concentrated solutions, by means of which they adduce a formula for a dilute solution identical with the formula (4) of van't Hoff.

Comparison of Equation (2) of Le Chatelier and Equation (4) of van't Hoff, however, shows a distinct disagreement between the two equations, since x and c vary differently with varying temperature. The relation between the two concentration terms at great dilution is:

$$x = V_2 c \qquad (5)$$

where V_2 is the molal volume of the pure solvent. The difference calculated by means of (2) and (4) is therefore:

$$\Delta Q = RT^2 \left(\frac{\partial \ln V_2}{\partial T} \right)_p$$

[1] Deventer and van de Stadt. Z. phys. Chem. **9** 43 (1892).

which is determined merely by the coefficient of expansion of the solvent and does not vanish with vanishing concentration of the saturated solution.

The most direct way of determining the solubility formula is on the basis of the thermodynamic functions. For the change of thermodynamic potential F_1 of one mole of the solid one can write:

$$dF_1 = \left(\frac{\partial F_1}{\partial p}\right)_T dp + \left(\frac{\partial F_1}{\partial T}\right)_p dT$$

and for one mole of the dissolved substance:

$$d\bar{F}_1 = \left(\frac{\partial \bar{F}_1}{\partial p}\right)_{T,x} dp + \left(\frac{\partial \bar{F}_1}{\partial T}\right)_{p,x} dT + \left(\frac{\partial \bar{F}_1}{\partial x}\right)_{T,p} dx.$$

For the state of saturation $F_1 = \bar{F}_1$ and $dF_1 = d\bar{F}_1$ Hence at constant pressure:

$$\left(\frac{\partial \bar{F}_1}{\partial T}\right)_{p,x} - \left(\frac{\partial F_1}{\partial T}\right)_p + \left(\frac{\partial \bar{F}_1}{\partial x}\right)_{T,p} \left(\frac{\partial x}{\partial T}\right)_p = 0$$

or since:

$$\left(\frac{\partial F_1}{\partial T}\right)_p = \frac{F_1 - H_1}{T},$$

$$\left(\frac{\partial \bar{F}_1}{\partial T}\right)_{p,x} = \frac{\bar{F}_1 - \bar{H}_1}{T}$$

and

$$\left(\frac{\partial \bar{F}_1}{\partial x}\right)_{T,p} = \frac{RT}{x}$$

where H is the heat function:

$$\bar{H}_1 - H_1 = RT^2 \left(\frac{\partial \ln x}{\partial T}\right)_p \qquad (6)$$

$\bar{H}_1 - H_1$ is the heat absorbed when one mole of the solid dissolves in the solvent at constant pressure, and is identical with the quantity Q_p in Equation (2).

In a quite analogous way using the Helmholtz free energy instead of the thermodynamic potential one obtains:

$$\bar{E}_1 - E_1 = RT^2 \left(\frac{\partial \ln x}{\partial T}\right)_v \qquad (7)$$

where E means energy and $\bar{E}_1 - E_1$ equals the quantity Q_v in Equation (10). It is shown below that (6) and (7) are identical.

The strict method employing thermodynamical functions thus leads to the same formula as derived by Le Chatelier, and consequently the derivation of the van't Hoff formula by means of the osmotic pressure must be subject to some correction. Nevertheless this formula is the one generally adopted in text books of physical chemistry and the customary proof presented is based on the same doubtful analogy between gases and solutions. Various authors, mostly Americans, who have treated the problem of equilibrium from the standpoint of the thermodynamic functions give the correct formula and the correct derivation[1]. So far as the author is aware, however, the distinction between the two equations has never been subject to any discussion, and the reasons for their diversity therefore still seem obscure.

In order to point out the kind of error involved in the application of osmotic pressure for deriving the solubility

[1] E. W. Washburn. Principles of Physical Chemistry, p. 210 (1921). Lewis and Randall. Thermodynamics, p. 228 (1923). The derivation of the solubility formula (6) given above is essentially that of Lewis and Randall.

curve it is necessary to re-examine the fundamental application of the second law. For that purpose we shall consider the following reversible cycle.

1. At constant external pressure p and constant temperature T one mol of the slightly soluble substance K_1 is allowed to pass into solution into n_2 mols of the solvent K_2, the reversibility of the process being secured by the application of a semipermeable piston. The heat absorbed in this isothermal process is q. If the molecular volume of K_1 in the solution is V_1 and P the osmotic pressure the work done is PV_1.

2. The system is heated from T to $T+dT$ at constant external pressure p and constant volume of the solute V_1. Due to rise in temperature and change in solubility the osmotic pressure increases to $P+dP$. The volume:

$$dV = n_2 \left(\frac{\partial V_2}{\partial T}\right)_p dT$$

passes from solution through the semipermeable piston.

3. The piston is lowered through the volume V_1 on application of the work $V_1 (P+dP)$. One mol of the solid solute falls out.

4. The temperature of the system is lowered to T.

Application of the second law to this reversible cycle gives:

$$q = TV_1 \left(\frac{\partial P}{\partial T}\right)_p$$

and introducing $V_1 = \frac{1}{c}$ and $P = RTc$ Equation (4) immediately follows.

In this derivation q has been taken as the ordinary reversible heat solution at constant external pressure. This,

however, is not permissible. When the solute goes into solution the corresponding amount of solvent of the initial pressure p of the surroundings is brought under the osmotic pressure P, the total pressure of the solution formed being $p+P$. While the work, necessary to compress the solution vanishes as the solubility converges towards zero and therefore needs no consideration, the heat of compression, just as the volume change, keeps a finite value even at infinite dilution. The heat absorption due to the compression of the volume V_1 we shall call q_2. This heat is included in q.

To calculate its value we apply again the second law which gives:

$$dq_2 = T \frac{dv\,dp}{dT}$$

where:

$$dv = \left(\frac{\partial v}{\partial p}\right)_T dp$$

and:

$$dp = \left(\frac{\partial p}{\partial T}\right)_v dT.$$

Hence:

$$dq_2 = T \left(\frac{\partial v}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_v dp.$$

Introducing:

$$\left(\frac{\partial v}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_p = -1$$

and:

$$v = n_2 V_2$$

and integrating we get:

$$q_2 = -T \left(\frac{\partial v}{\partial T}\right)_p \Delta p \qquad (8)$$

or

$$q_2 = -T n_2 \left(\frac{\partial V_2}{\partial T}\right)_p P.$$

Inserting $V_1 = n_2 V_2$ and $PV_1 = RT$ this equation transforms into:

$$q_2 = -RT^2 \left(\frac{\partial \ln V_2}{\partial T} \right)_p .$$

From this equation we learn that for a molal volume V_1 of a dilute solution the heat of compression caused by the exposure of the solution to its own osmotic pressure is constant, regardless of the concentration of the solution, depending merely upon the temperature expansion coefficient of the solvent.

The heat absorption q entering in Equation (3) therefore does not equal the ordinary reversible heat of solution, but is the sum of this heat and the heat absorption due to the compression of the solution. Retaining the symbol Q_p for the ordinary heat of solution at constant pressure, Equation (4) should therefore be written as follows:

$$Q_p - RT^2 \left(\frac{\partial \ln V_2}{\partial T} \right)_p = RT^2 \left(\frac{\partial \ln c}{\partial T} \right)_p .$$

Introducing here Equation (5), we finally obtain:

$$Q_p = RT^2 \left(\frac{\partial \ln x}{\partial T} \right)_p \qquad (9)$$

which obviously is in full conformity with the correct Le Chatelier Equation (2).

The reversible cycle, fundamental to the solubility equation, however, may be carried out in simpler ways than in the above van't Hoff procedure, in which the system after formation of the solution on heating separates part of the solvent in a pure state. The method may be the one of constant pressure or constant volume of the

total system. For the simplification of these calculations it should be noted that, without sacrificing any accuracy in consideration of the reversible cycle, for small solubilities one is permitted to disregard the work done by or against the constant pressure of the surroundings, as well as the volume change on dissolution of the solute, the work of compression of the solution when exposed to the osmotic pressure, and the effect of this pressure upon the solubility.

When all operations of the reversible cycle are carried out in such a way that the initial and final pressure in all operations is constant $= p$ the reversible heat absorption is q_p. The work done by this cycle, however, in this case does not equal $V_1 dP$ but is given by:

$$dA = (P + dP)\,(V_1 + dV_1) - PV_1$$

where:

$$dP = \left(\frac{\partial P}{\partial T}\right)_p dT = RT\left(\frac{\partial c}{\partial T}\right)_p dT + Rc\,dT$$

and

$$dV_1 = n_2\left(\frac{\partial V_2}{\partial T}\right)_p dT.$$

Hence:

$$q_p = TPn_2\left(\frac{\partial V_2}{\partial T}\right)_p + RT^2\left(\frac{\partial \ln c}{\partial T}\right)_p + RT$$

or:

$$Q_p = RT^2\left(\frac{\partial \ln x}{\partial T}\right)_p$$

which is identical with (2).

On the other hand performing all operations at constant volume the reversible heat absorption is q_v and the work done by the cycle simply:

$$dA = V_1\,dP.$$

Hence:

$$q_v = TV_1 \left(\frac{\partial P}{\partial T}\right)_v$$

and:

$$Q_v = RT^2 \left(\frac{\partial \ln c}{\partial T}\right)_v.$$

At constant volume, however, $d\ln c = d\ln x$ and therefore:

$$Q_v = RT^2 \left(\frac{\partial \ln x}{\partial T}\right)_v. \qquad (10)$$

This is identical with Equation (7). To show its identity with (2) we must find the relation between Q_v and Q_p and between:

$$\left(\frac{\partial \ln x}{\partial T}\right)_p \quad \text{and} \quad \left(\frac{\partial \ln x}{\partial T}\right)_v.$$

The difference between Q_p and Q_v equals the heat absorption which occurs when a solution of K_1 in $n_2 K_2$, formed at constant volume from its components initially of the pressure p, expands reversibly to reach the pressure p.

This heat of expansion in accordance with Equation (8) is:

$$q_2 = -T \left(\frac{\partial v}{\partial T}\right)_p \Delta p$$

where Δp is the increase in pressure accompanying the increase in volume Δv. This expansion is actually the volume increase of the dissolution process at constant pressure p.

Introduction of:

$$\Delta V = \left(\frac{\partial v}{\partial p}\right)_T \Delta p$$

gives:

$$q_2 = -T\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial v}\right)_T \Delta V$$

or:

$$q_2 = T\left(\frac{\partial p}{\partial T}\right)_v \Delta V.$$

Hence:

$$Q_p = Q_v + T\left(\frac{\partial p}{\partial T}\right)_v \Delta V. \qquad (11)$$

In order to determine the difference between $\left(\frac{\partial \ln x}{\partial T}\right)_p$ and $\left(\frac{\partial \ln x}{\partial T}\right)_v$ we use the thermodynamic equations:

$$\left(\frac{\partial \ln x}{\partial T}\right)_p = \left(\frac{\partial \ln x}{\partial T}\right)_v - \left(\frac{\partial \ln x}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_v$$

and

$$\left(\frac{\partial \ln x}{\partial p}\right)_T = -\frac{\Delta V}{RT}.$$

We then obtain:

$$RT^2\left(\frac{\partial \ln x}{\partial T}\right)_p = RT^2\left(\frac{\partial \ln x}{\partial T}\right)_v + T\left(\frac{\partial p}{\partial T}\right)_v \Delta V. \qquad (12)$$

When finally in Equation (10) we insert the value of Q_v from (11) and the value of $RT^2\left(\frac{\partial \ln x}{\partial T}\right)_v$ from (12) the identy of (10) and (2) becomes obvious.

The correctness of (10) also appears from its identity with Equation (7), since the difference $\overline{E}_1 - E_1$ at constant volume equals the heat of solution Q_v.

All the various methods by which the solubility coefficient is computable from the second law of thermodynamics then unite in showing that the original formula of LE CHATELIER is correct, whereas the formula of VAN'T HOFF is characterized by an inaccuracy due to lack of observance of the distinction between a liquid and a gaseous system. The difference between the two formulae is expressed by the member:

$$RT^2\left(\frac{\partial \ln V_2}{\partial T}\right)_p$$

which merely depends upon the thermal coefficient of expansion of the solvent.

We realise from these results that the osmotic pressure, when used with circumspection, is applicable as a basis for thermodynamic calculations also in such cases where the simple analogy between gases and solutions is no longer tenable. The method, however, is more cumbrous and more open to errors than that of the thermodynamic functions.

In solvents such as water, where at ordinary temperature the coefficient of expansion is small, the correction is insignificant. For many other solvents with a high coefficient of expansion the error on the other hand may assume an appreciable value. For benzene, for instance, the value of the above member at ordinary temperature amounts to about 200 calories. In the neighbourhood of the critical point, where the solvent expands very steeply with temperature Equation (4) is no longer even approximately true.

The correction holds similarly to solutions of solids and gases. Particularly for the last mentioned systems the correction is of importance, since in many cases the solubilities of gases in liquids vary but slightly with temperature, and the determination of states in which the dissolution takes place with no change in energy for such systems is of a special interest.

Forelagt paa Mødet den 5. Maj 1933.
Færdig fra Trykkeriet den 23. Juni 1933.