Relations Between Vapour Pressures and Solubilities

of Hydrates

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Let S denote a non-volatile substance which forms two crystalline hydrates S_m and S_n, respectively with m and n molecules of water per molecule of S (m is different from n, one of them may be zero). p^0 denotes the vapour pressure of pure water, $p_{m,n}$ that of a mixture of S_m and S_n. p_m and p_n indicate the vapour pressures of the saturated solutions of, respectively, S_m and S_n. The activities of S in the same solutions are denoted by a_m and a_n.

When $(n-m)\,dx$ moles of water vapour are transferred, reversibly and isothermally, from pure water to the mixture of crystalline S_m and S_n, dx moles of S_n are produced at the expense of dx moles of S_m. The work gained is

$$dA = (n-m)\ RT \ln \frac{p^0}{p_{m,n}}\, dx \tag{1}$$

The same transformation may be performed in the following way. dx moles of crystalline S_m are dissolved in a saturated solution of S_m and transferred, reversibly and isothermally, from this solution to a saturated solution of S_n. At the same time, $(n-m)\,dx$ moles of water are transferred from pure water to the saturated solution of S_n. By crystallization, dx moles of S_n are obtained. The work gained may be written as follows

$$dA = RT\left[\ln \frac{a_m}{a_n} + m \ln \frac{p_m}{p_n} + (n-m)\ln \frac{p^0}{p_n}\right] dx \tag{2}$$

Combination of this equation with equation 1 leads to

5

$$(n - m) \ln p_{m,\,n} = \ln \frac{a_n}{a_m} + n \ln p_n - m \ln p_m \tag{3}$$

If S is a salt, a_n and a_m are the thermodynamic solubility products of S_n and S_m, that is, the solubility products containing the activities of the ions instead of the concentrations. If c_m and c_n denote the molar concentrations of the two saturated solutions, ν the number of ions produced by the dissociation of one molecule of S, and f_m and f_n the mean activity coefficients of the ions in the two solutions, equation 3 may be written as follows

$$(n - m) \log p_{m,\,n} = \nu \log \frac{c_n f_n}{c_m f_m} + n \log p_n - m \log p_m \tag{4}$$

If the solubilities are sufficiently small one may set $p_n = p_m = p^0$, and obtain

$$(n - m) \log \frac{p_{m,n}}{p^0} = \nu \log \frac{c_n f_n}{c_m f_m} \tag{5}$$

When we apply the Gibbs-Duhem relation to an aqueous solution of S, we obtain

$$x \, \mathrm{d}\ln a + (1 - x) \, \mathrm{d}\ln a_{H_2O} = 0$$

where x denotes the mole fraction and a the activity of S while a_{H_2O} indicates the activity of the water. Owing to the proportionality between a_{H_2O} and the vapour pressure p one obtains from this relation

$$x \, \mathrm{d}\ln a + (1 - x) \, \mathrm{d}\ln p = 0$$

and by integration

$$\ln \frac{a_n}{a_m} = \ln \frac{p_n}{p_m} - \int_{x_m}^{x_n} \frac{\mathrm{d}\ln p}{x} \tag{6}$$

On introducing this expression into equation 3, one obtains

$$(n - m) \ln p_{m,\,n} = (n + 1) \ln p_n - (m + 1) \ln p_m - \int_{x_m}^{x_n} \frac{\mathrm{d}\ln p}{x} \tag{7}$$

An exact solution of the integration in this formula cannot be given since p, in general, is not known as a function of x. If, however, the vapour pressures

of the unstable solutions in the concentration interval from x_m to x_n have been measured, a numerical value of the integral may be computed.

An approximate formula may be deduced from equation 7 when we assume that p, in the interval from x_m to x_n, is a linear function of x

$$p = P (1 - kx) \tag{8}$$

where the constants P and k are given by the expressions

$$P = \frac{x_n p_m - x_m p_n}{x_n - x_m}$$

and

$$k = \frac{p_m - p_n}{x_n p_m - x_m p_n} \tag{9}$$

By means of equation 8, one obtains

$$- \int_{x_m}^{x_n} \frac{d\ln p}{x} = k \int_{x_m}^{x_n} \frac{dx}{x (1 - kx)} = k \ln \frac{x_n}{x_m} - k \ln \frac{p_n}{p_m} \tag{10}$$

On introducing this expression into equation 7, one obtains

$$(n - m) \log p_{m,n} = (n + 1 - k) \log p_n - (m + 1 - k) \log p_m + k \log \frac{x_n}{x_m} \tag{11}$$

By means of this formula, one may calculate an approximate value of the vapour pressure $p_{m,n}$ of the mixture of the crystals S_m and S_n when the solubilities of the two hydrates and the vapour pressures of their saturated solutions have been measured.

Let S_m be the stable hydrate. If x_m, p_m, $p_{m,n}$, and, in addition, the vapour pressures and concentrations of a series of unsaturated solutions $(x < x_m)$ have been measured, but the measurements have not been extended to solutions supersaturated with S_m, approximate values of x_n and of p_n may be found in the following way. The tangent to the experimental vapour pressure curve in the point x_m, p_m is drawn. It is assumed as an approximation that the slope $(- a)$ of this tangent is equal to the slope $(- kP)$ of the straight line represented by equation 8. Hence, one has

$$P = p_m + a x_m \tag{12}$$

$$k = \frac{\alpha}{p_m + \alpha\, x_m} \tag{13}$$

On introducing

$$p_n = P\,(1 - kx_n) \tag{14}$$

into equation 11, and rearranging the terms, one finds

$$(n + 1 - k)\, \log\,(1 - kx_n) + k\, \log x_n = (n - m)\, \log p_{m,n} +$$
$$(m + 1 - k)\, \log p_m + k\, \log x_m - (n + 1 - k)\, \log P \tag{15}$$

By means of this formula, an approximate value of the solubility x_n of the unstable hydrate may be computed. The corresponding vapour pressure may be estimated by means of equation 14.

If only x_m, p_m, and $p_{m,n}$ (but not the vapour pressures of the unsaturated solutions) have been measured, one may, by means of equations 15 and 14, find rather rough approximations to x_n and p_n when one sets

$$\alpha = \frac{p^0 - p_m}{x_m}$$

and, consequently, according to equations 12 and 13

$$P = p^0 \quad \text{and} \quad k = \frac{p^0 - p_m}{p^0\, x_m}$$

We shall now examine the case where one of the hydrates, say the m-hydrate, exists in two crystalline forms, S_m and $S_m{}'$ of which S_m is supposed to be the stable (or more stable) modification. In the following, the symbols referring to the form $S_m{}'$ are dashed. When equation 3 is applied to $S_m{}'$ instead of S_m, one obtains

$$(n - m)\, \ln p_{m,n}{}' = \ln \frac{a_n}{a_m{}'} + n\, \ln p_n - m\, \ln p_m{}'$$

From this equation and equation 3 by subtraction

$$(n - m)\, \ln \frac{p_{m,n}}{p_{m,n}{}'} = \ln \frac{a_m{}'}{a_m} - m\, \ln \frac{p_m}{p_m{}'} \tag{16}$$

By the same procedure one obtains from equations 5 and 7

$$(n - m) \log \frac{p_{m,n}}{p_{m,n}{'}} = \nu \log \frac{c_m{'} f_m{'}}{c_m f_m} \tag{17}$$

and

$$(n - m) \ln \frac{p_{m,n}}{p_{m,n}{'}} = -(m + 1) \ln \frac{p_m}{p_m{'}} - \int_{x_m}^{x_m{'}} \frac{d\ln p}{x} \tag{18}$$

If we assume, as an approximation, that the linear relation 8 is valid in the interval between x_m and $x_m{'}$, we obtain, in analogy with equation 11,

$$(n - m) \log \frac{p_{m,n}}{p_{m,n}{'}} = k \log \frac{x_m{'}}{x_m} - (m + 1 - k) \log \frac{p_m}{p_m{'}} \tag{19}$$

The constant k may be computed from the expression

$$k = \frac{p_m - p_m{'}}{x_m{'} p_m - x_m p_m{'}} \tag{20}$$

If only the vapour pressures of solutions where $x \leqq x_m$ have been measured, approximate values of the constants P and k in equation 9 may be found by means of equations 12 and 13. On introducing

$$p_m{'} = P (1 - k x_m{'}) \tag{21}$$

into equation 19 and rearranging the terms, one obtains

$$(m + 1 - k) \log (1 - k x_m{'}) + k \log x_m{'}$$
$$= (n - m) \log \frac{p_{m,n}}{p_{m,n}{'}} + k \log x_m - (m + 1 - k) \log \frac{p}{p_m} \tag{22}$$

By means of formulae 21 and 22 one may compute approximate values of the vapour pressure and concentration of the solution saturated with the unstable modification $S_m{'}$ when $p_{m,n}$, $p_{m,n}{'}$, and the vapour pressure curve for $x \leqq x_m$ have been determined.

If only $p_{m,n}$, $p_{m,n}{'}$, x_m, and p_m have been determined, we may find very rough approximations to $x_m{'}$ and $p_m{'}$ by means of equations 22 and 21 when we set $P = p^0$ and $k = (p^0 - p_m)/p^0 x_m$.

The following examples will illustrate the application of some of the formulae given above.

1. Calculation of the decomposition pressure $p_{1,2}$ of the unstable dihydrate of calcium oxalate. The solubilities of the mono- and di-hydrate of calcium oxalate in water at 25° C have been measured by the author of this paper [1] who found $c_1 = 4.84 \cdot 10^{-5}$ and $c_2 = 7.65 \cdot 10^{-5}$. By means of the Debye-Hückel limiting law, $-\log f = 0.5 \cdot 2^2 \cdot \sqrt{4c}$, we find $-\log f_1 = 0.028$ and $-\log f_2 = 0.035$. Hence, by equation 5, $p_{1,2} = 2.42\, p^0$. Although the decomposition pressure is 2.42 times the vapour pressure of water the dry dihydrate does not decompose at room temperature. A 9 years old preparation, which had been stored in an ordinary powder glass, was still almost pure dihydrate.

2. Calculation of the decomposition pressure $p_{0,2}$ of potassium fluoride dihydrate. Lannung [2] has measured the concentrations and vapour pressures of aqueous solutions saturated with KF and $KF,2H_2O$ at 18° C. He found $x_0 = 0.272$, $p_0 = 2.8$ mm Hg, $x_2 = 0.201$, $p_2 = 5.2$ mm Hg. By means of equations 9 and 11, one computes: $k = 2.75$, $\log p_{0,2} = 0.292$, and $p_{0,2} = 2.0$ mm Hg. Lannung found by direct measurement $p_{0,2} = 2.1$ mm Hg.

3. Calculation of the solubility of anhydrous sodium bromide. $NaBr,2H_2O$ is stable in contact with its saturated solution below 51° C, above that temperature the stable form is NaBr. Lannung [2] has measured the vapour pressure $p_{0,2}$ of a mixture of the two hydrates and the vapour pressures of solutions of sodium bromide at 18° C. He found $p_{0,2} = 5.15$ mm Hg, and, for the solutions,

x	0.0501	0.0591	0.0727	0.0888	0.1086	0.1353 ($=x_2$)
p (mm Hg)	13.8	13.3	12.7	11.9	10.9	9.35

The slope of the tangent to the vapour pressure curve in the point x_2, p_2 is $a = -58.2$ from which we find, by means of equations 12 and 13, $P = 17.22$ and $k = 3.38$. x_0 may now be computed from formula 15 ($m = 2$, $n = 0$). We find $x_0 = 0.160$. The corresponding vapour pressure is, according to formula 14, $p_0 = 7.9$ mm Hg. The solubility of anhydrous sodium bromide above the transition point 51° C has been determined by several investigators [3]. By extrapolation of the data one finds that the solubility of NaBr at 18° C is 53.0 g NaBr in 100 g saturated solution, or $x_0 = 0.165$.

SUMMARY

The paper gives the deduction of a series of exact or approximate formulae relating the vapour pressure of a mixture of two hydrates of the same substance to the solubilities of the hydrates in water and certain vapour pressure

data for the solutions. Examples illustrating the application of some of the formulae are given.

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REFERENCES

1. Pedersen, K. J., *Kem. Maanedsblad* **21** (1940) 52.
2. Lannung, A., *Z. physik. Chem.* **A 170** (1934) 134.
3. Seidell, A., *Solubilities.* 3rd ed. vol. 1 (1940) p. 1155.