Liquid Structure and Solubility of Sparingly Soluble Salts in Water

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The theoretical formula for the solubility of solids in liquids assuming the solution to be ideal, is applied to aqueous solutions of sparingly soluble salts. The process of dissolution involves chemical reaction between salt and water. The equilibrium constants for a few such reaction equilibria are computed from the coordination numbers of the liquid structure. The results are compared with experimental data on silver halides, lead halides, and Ag_2O .

1. THEORY

When a system is in equilibrium, its free energy is a minimum. For instance, when two phases are in equilibrium with one another, there is no change in the free energy of the entire system, when matter is transferred from one phase to the other. We will apply this principle to the solubility of a sparingly soluble salt in water.

We will consider the process of dissolution as consisting of two steps. In the first step the solid salt is transformed from the solid into the liquid state. In the second step the liquid salt is mixed with the liquid water. We will assume that the mixture is ideal, *i. e.* there is no heat of mixing, and the entropy of mixing is equal to R times the logarithm of the mole fraction X of the salt (Raoult's law). From the fundamental principle

$$\Delta F = 0 \quad (1)$$

we thus obtain

$$\Delta F_m = -T \Delta S_m = -\Delta F_f \quad (2)$$

when m denotes mixing and f fusion.

With Raoult's law

$$\Delta S_m = -R \ln X, \Delta E_m = 0 \quad (3)$$

we have from (2)

$$X = e^{-\frac{\Delta F_f}{RT}} \quad (4)$$

Applying the principle (1) to the process of melting, we find at the melting point T_f

$$\Delta F_f = \Delta E_f - T_f \Delta S_f = 0 \quad (5)$$

Hence,

$$X = e^{-\frac{\Delta E_f}{R} \left(\frac{1}{T} - \frac{1}{T_f} \right)} \quad (6)$$

This is the familiar formula for the solubility of a solid in a liquid on the assumption that the solution is ideal.

Few aqueous solutions are ideal. As a rule the water reacts with the salt. This reaction is accompanied by a free energy of reaction ΔF_e , which must be included in (1). We will write ΔF_e in the form

$$\Delta F_e = \Delta E_e - T \Delta S_e \quad (7)$$

and assume that

$$\Delta S_e = \frac{\Delta E_e}{T_f} + \Delta S_{struct.} \quad (8)$$

Hence,

$$\frac{\Delta F_e}{T} = -\Delta S_{struct.} + \Delta E_e \left(\frac{1}{T} - \frac{1}{T_f} \right) \quad (9)$$

The entropy change $\Delta S_{struct.}$ derives from the structural change involved in the reaction,

$$\Delta S_{struct.} = R \ln W \quad (10)$$

when W denotes the ratio of the numbers of ways in which the two states, before and after the reaction, may be realized.

Including ΔE_e and ΔE_f in the heat of solution ΔE_s of the solid salt we have thus with (1), (6), (9) and (10)

$$X = W e^{-\frac{\Delta E_s}{R} \left(\frac{1}{T} - \frac{1}{T_f} \right)} \quad (11)$$

This formula is valid for a solution such that

$$\Delta S_m = -R \ln X \quad (12)$$

i. e. for a sufficiently dilute solution.

Since there are 55.55 moles of water per litre of pure water, and since the concentration of the water is not appreciably changed by the presence of a sparingly soluble salt in the solution, we may express the solubility in mole/litre instead of mole fraction by rewriting (11) in the form

$$c = 55.55 W e^{-\frac{\Delta E_s}{R} \left(\frac{1}{T} - \frac{1}{T_f} \right)} \quad (13)$$

We will now consider reactions of the types

The equilibrium is characterized by its equilibrium constant

$$K = e^{-\frac{\Delta F_e}{RT}} \quad (16)$$

or with (9)

$$K = W_e^{-\frac{\Delta E_e}{R} \left(\frac{1}{T} - \frac{1}{T_f} \right)} \quad (17)$$

We may therefore calculate K by way of calculating W from the structure of the liquid. Instances of such calculations will be given in section 3.

2. EMPIRICAL RELATIONS

In the following we will apply these formulae to a few cases of sparingly soluble salts. However, before we do so we will consider the experimental data and derive corresponding empirical formulae which we will then interpret by comparing them with the theoretical formulae and by considering the reactions involved. The data employed have been taken from Landolt-Börnstein and from the Handbook of Chemistry and Physics. The values of $-\Delta E_e$ have been taken from those tables ("observed"), from a plot of $\log c = f\left(\frac{1}{T}\right)$ ("from curve"), or computed according to the rule of heats of formation in dilute solution derived elsewhere¹ and from the observed heats of formation in the solid state ("computed").

Tables 1 and 2 give data for silver and lead halides, respectively.

Table 1. Solubility of silver halides.

Salt	AgF	AgCl	AgBr	AgI
$-\Delta E_s$ (computed)	+ 4.3	-15.9	-20.2	-26.5
$-\Delta E_s$ (from Fig. 2)	—	-2×7.79	—	—
c mole/litre at 16°	14	$9.70 \cdot 10^{-6}$	$5.60 \cdot 10^{-7}$	$6.48 \cdot 10^{-9}$
$10 \log c$	$0.146 + 1$	$0.987 - 6$	$0.748 - 7$	$0.812 - 9$
T_f (observed)	708	728	703	830
T_f (from Fig. 1) *	1 410	1 410	1 410	1 410

* T_f is regarded as an empirical constant the significance of which will be discussed in section 4.

Table 2. Solubility of lead halides.

Salt	PbCl ₂	PbBr ₂	PbI ₂
$-\Delta E_s$ (computed)	-6.5	-9.1	-15.2
$-\Delta E_s$ (observed)	-6.55	-10.04	—
$-\Delta E_s$ (from Fig. 3)	-2×3.25	-2×4.58	-3×4.71
T_f (observed)	774	646	675

Fig. 1. $10 \log c = f(-\Delta E_s)$ for silver halides at 16°.

Fig. 1 shows a plot of $10 \log c = f(-\Delta E_s)$ on the observed data of c and the computed values of $-\Delta E_s$. Fig. 2 shows a plot of $10 \log c = f(\frac{1}{T})$ for AgCl. The two curves satisfy the formula

$$c = 0.67 e^{-\frac{\Delta E_s}{2R} (\frac{1}{T} - \frac{1}{T_f})} \quad (18)$$

where $T_f = 1410^\circ \text{K}$.

Fig. 3 shows plots of $10 \log c = f(\frac{1}{T})$ for PbCl_2 , PbBr_2 and PbI_2 . Inserting the values of T_f given in Table 2 we obtain the following formulae

$$\text{PbCl}_2: c = 1.15 e^{-\frac{3.25}{R} (\frac{1}{T} - \frac{1}{T_f})} \quad (19)$$

$$\text{PbBr}_2: c = 1.70 e^{-\frac{4.58}{R} (\frac{1}{T} - \frac{1}{T_f})} \quad (20)$$

$$\text{PbI}_2: c = 0.158 e^{-\frac{4.71}{R} (\frac{1}{T} - \frac{1}{T_f})} \quad (21)$$

Fig. 2. $10 \log c = f \left(\frac{1000}{T} \right)$ for AgCl.

Fig. 3. $10 \log c = f \left(\frac{1000}{T} \right)$ for PbCl_2 (O) and PbBr_2 (x).

$$10 \log c + 1.9 = f \left(\frac{1000}{T} \right) \text{ for } \text{PbI}_2 (+).$$

Fig. 4. $^{10}\log c = f\left(\frac{1000}{T}\right)$ for Ag_2O .

Fig. 4 shows $^{10}\log c = f\left(\frac{1}{T}\right)$ for Ag_2O . The slope of this curve gives $\Delta E_s = 8.2$ for $T < 317^\circ \text{K}$. Inserting $T_f = 1410^\circ \text{K}$ * we obtain from the curve

$$\text{Ag}_2\text{O}: c = 8.7 e^{-\frac{8.2}{R}\left(\frac{1}{T} - \frac{1}{1410}\right)} \quad (22)$$

3. COMPARISON OF THEORETICAL AND EMPIRICAL FORMULAE

A. Solubility of Ag_2O

When a hypothetical liquid Ag_2O is mixed with liquid water, it is built into the structure of the water. Each Ag_2O molecule is surrounded by H_2O molecules and bound to those with $\text{O}-\text{H}-\text{O}$ and $\text{Ag}-\text{O}$ bonds. Fig. 5 illustrates this structure schematically.

The breaking of the $\text{O}-\text{H}-\text{O}$ bond as indicated in Fig. 5 brings about the reaction

The re-formation of the same bond leads to the reaction

We will therefore consider the equilibrium

* This choice of T_f will be discussed in section 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

When the bond is broken, the two OH groups can form new bonds with surrounding H_2O molecules. In pure water each H_2O molecule or OH group is surrounded by 4 neighbors. We will assume this to be the case with the OH groups of $(\text{AgOH})_2$ as well. The number of ways in which new bonds can be formed is thus, 2 for oxygen atom No. 1 and 3 for oxygen atom No. 2. Hence,

$$\frac{1}{W} = 2 \times 3 = 6, \Delta S_{\text{struct.}} = -R \ln 6 \quad (24)$$

and

$$c_{(\text{AgOH})_2} = \frac{55.55}{6} e^{-\frac{\Delta E_s}{R} \left(\frac{1}{T} - \frac{1}{T_f} \right)} = 9.3 e^{-\frac{\Delta E_s}{R} \left(\frac{1}{T} - \frac{1}{T_f} \right)} \quad (25)$$

B. Solubility of silver halides

The equilibrium is

X denoting, F, Cl, Br, or I. The structure is shown in Fig. 6.

This case is considerably more complicated than the previous case. When the two bonds are broken, the AgOH and HX molecules formed may separate. When those separated molecules join so that the Ag and X atoms occupy adjacent lattice sites, they will recombine to form AgX. We have thus to consider two processes: the formation of AgX from AgOH and HX, and the number of ways in which the broken bonds may be reformed.

From the heat of vaporization of HCl in aqueous solution² we know that each HCl molecule is surrounded by 10 H₂O molecules. We will assume that the AgOH molecule occupies two sites and that one AgOH molecule may replace one of those ten H₂O molecules. Around the HCl molecule we may thus consider 11 sites, two of which may be occupied by an AgOH molecule.

The number of pairs of Ag and X atoms per litre of the solution is then³

$$\frac{11}{2} \cdot \frac{c_{\text{AgOH}} \cdot c_{\text{HX}}}{55.55}$$

But this is the number of AgX molecules per litre. Hence,

$$c_{\text{AgX}} = \frac{11}{2} \cdot \frac{c_{\text{AgOH}} \cdot c_{\text{HX}}}{55.55}$$

or

$$c_{\text{AgOH}} \cdot c_{\text{HX}} = \frac{2}{11} \cdot 55.55 \cdot c_{\text{AgX}} \quad (27)$$

We next consider the number of ways in which new bonds can be formed instead of the two broken bonds. There are 10 H₂O molecules with which the Cl atom may form bonds. The number of ways in which the two broken bonds may be reformed is thus $\binom{10}{2} = 45$. The O atom may, again, form 3 new bonds instead of the one broken. For the Ag atom we will assume that it may be surrounded by 10 H₂O molecules, just as is the Cl atom. This assumption is based upon the similarity of the structures of HCl and NaOH in aqueous solution⁴. Hence, the number of ways in which the broken bond may be reformed is 9. The total number of ways in which the broken bonds can be reformed is thus $45 \times 3 \times 9 = 1\,215$ and

$$\frac{1}{W} = 1\,215 \quad (28)$$

Hence, from (27) and (28),

$$c_{\text{AgOH}} = c_{\text{HX}} = \sqrt{2 \frac{55.55}{11 \times 1\,215} \cdot c_{\text{AgX}}} = 0.68 e^{-\frac{\Delta E_s}{2R} \left(\frac{1}{T} - \frac{1}{T_f} \right)} \quad (29)$$

in agreement with (18).

C. Solubility of PbCl₂

We consider the equilibrium

according to Fig. 7.

This case differs from that of AgCl simply by the two Cl atoms and, accordingly, by a factor of 2 in W . Hence,

$$c = 0.68 \times \sqrt{2} e \left[-\frac{\Delta E_s}{2R} \left(\frac{1}{T} - \frac{1}{T_f} \right) - \frac{\Delta E_s}{2R} \left(\frac{1}{T} - \frac{1}{T_f} \right) \right] = 0.96 e \quad (31)$$

The agreement with the empirical formula (19) is not quite so good as in the previous cases. For PbBr_2 we should have the same result (31) which differs from (20) by a factor of 1.8, however. The discrepancy may probably be attributed to complex formations or to an inadequate choice of T_f .

D. Solubility of PbI_2

We consider the equilibrium

according to Fig. 8.

Comparing this case to that of AgCl we find

$$W_{\text{PbI}_2} = W_{\text{AgCl}}^2 \quad (33)$$

and, thus,

$$c_{\text{Pb(OH)}_2} = \sqrt[3]{\frac{55.55}{(2 \frac{55.55}{11 \times 215})^2 c_{\text{PbI}_2}}} = 0.157 c \left[-\frac{\Delta E_s}{3R} \left(\frac{1}{T} - \frac{1}{T_f} \right) \right] \quad (34)$$

in agreement with (21).

4. THE SIGNIFICANCE OF T_f

In deriving the formula (6) for an ideal solution we have disregarded chemical reactions, since otherwise the solution could not have been considered as ideal. The significance of T_f is then the melting point of the solid. However, when reactions occur as illustrated in section 3, the significance of T_f is less obvious, since we have several salts in the solution, *e. g.* AgCl, AgOH, and HCl. The significance of T_f may therefore warrant some comments.

In order to bring all the salts into the liquid state we have to raise the temperature to the highest melting point. Thus, for such a mixture, the solute is the salt with the highest melting point, and the solvent is an aqueous solution of the salts of lower melting points. The significance of T_f is then the melting point of this solute, *i. e.* T_f is the highest melting point among those of the individual salts.

It follows from Fig. 1 that T_f is the same for all the silver halides and about twice as high as the melting points of the halides. We may therefore assume that $T_f = 1410^\circ \text{K}$ is the melting point of the hydroxide, AgOH. There is no reason why the double hydroxide $(\text{AgOH})_2$ should have a different melting

point; in fact, AgOH and $(\text{AgOH})_2$ should be identical in the solid state. Hence, $T_f = 1\,410^\circ\text{K}$ in the case of Ag_2O as well.

For the lead salts PbXOH and $\text{Pb}(\text{OH})_2$ the melting points are not known, nor is T_f the same for all the lead halides. We have therefore arbitrarily taken for T_f the melting points of the halides. In view of the spread of the data as shown by the plots in Fig. 3, it is difficult to say whether the discrepancy between theoretical and empirical formulae is due to an erroneous choice of T_f . It should be pointed out, though, that in order to bring the empirical data in agreement with the theoretical formulae we have to choose lower values of T_f .

5. CONCLUSIONS

The agreement between theoretical and empirical formulae shows that the formula (6), valid for an ideal solution, is applicable to aqueous solutions of sparingly soluble salts, provided due corrections are made for the reactions involved in the process of dissolution. It further shows that the statistical computation of equilibrium constants is possible, provided the coordination numbers of the liquid structure are known.

There is no reason for applying the simple formula (6) to concentrated solutions, *e. g.* the solubility of alkali halides, since those do not follow Raoult's law. Hence, for concentrated solutions, X should be replaced by the actual

value of $e^{-\frac{\Delta F_m}{RT}}$. We will take up this problem in a following publication.

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