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On the Misuse of Le Chatelier's Principle for the Prediction of the Temperature Dependence of the Solubility of Salts

In the course of their discussions of Le Chatelier's principle, many textbooks direct attention to the effect of three forms of stress on a system at equilibrium: (1) the addition of either excess reactant or product, (2) changes in the pressure of a gaseous system, and (3) changes in the temperature of the system. The first two forms of stress lead to a shift in the position of the equilibrium, without affecting the magnitude of the equilibrium constant. Changes in the temperature of the system, however, lead to a change in the magnitude of the equilibrium constant as well.

Le Chatelier's principle, as it is commonly expressed, suggests that a stress applied to a system at equilibrium will lead to a shift in the position of the equilibrium which minimizes the effect of that stress. It is therefore often argued that the magnitude of the equilibrium constant for endothermic reactions, in which heat is absorbed from the surroundings,

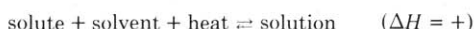


will increase with increasing temperature. Conversely, exothermic reactions, in which heat is liberated,



are characterized by a decrease in the equilibrium constant with increasing temperature.

Numerous authors assume that this concept can be applied to saturated solutions in which a dynamic equilibrium exists between a solid solute and its solution. They suggest that endothermic reactions of the type



will be reflected by an *increase* in solubility with *increasing* temperature. Exothermic reactions



would then be reflected by a *decreased* solubility with *increasing* temperature. Among the examples which are commonly invoked to support this argument are $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$, NaCl and KNO_3 for which the enthalpy of solution is positive, and Na_2SO_4 , Ca(OH)_2 and NaI for which the enthalpy of solution is negative.¹

Unfortunately, we run into several points of confusion when we attempt to apply this hypothesis to the prediction of the temperature dependence of the solubility of inorganic salts. For example, the enthalpies of solution of NaCl and NaI have different signs, as noted above, and yet both salts exhibit an increased solubility with increasing temperature. Furthermore, we know from experience that NaOH evolves heat when dissolved in water ($\Delta H = -$), suggesting that the solubility of NaOH in water should decrease with increasing temperature, and yet the solubility of NaOH increases by roughly a factor of ten between 0° and 100°C . In fact, of the 31 salts of sodium

for which data are available, 14 have *negative* enthalpies of solution, and yet only one, Na_2SO_4 , shows a decreased solubility with increasing temperature.

Careful examination of the available data leads to the conclusion that there is no obvious relationship between the sign of the enthalpy of solution tabulated in the various handbooks and the change in the solubility of inorganic salts with temperature. Some appreciation for the magnitude of this problem can be obtained by examining the enthalpy of solution data for alkali metal and alkaline earth halides given in the table. It is worth noting that each and every one of these salts shows an increased solubility with increasing temperature in the range from 0° – 100°C , regardless of the sign or magnitude of the enthalpy of solution.

Discussion

To understand why this seemingly simple application of a universally accepted principle might fail we must first understand: (1) why Le Chatelier's principle can be applied to the temperature dependence of the equilibrium constant, (2) why small changes in the nature of a salt can lead to changes in both the magnitude and sign of the enthalpy of solution, and (3) why the term enthalpy of solution is intrinsically vague.

Starting from the definition of standard state changes in the Gibbs free energy of a system,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (1)$$

and the relationship between ΔG° and the equilibrium constant, K ,

$$\Delta G^\circ = -RT \ln K \quad (2)$$

we can derive the following equation:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (3)$$

As we can see, the contribution to the equilibrium constant from entropy is temperature independent. Thus, differentiation of $\ln K$ with respect to temperature leads inevitably to the conclusion that the magnitude and sign of ΔH° determine the effect of temperature on the equilibrium constant.

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (4)$$

$$\frac{d(\ln K)}{d(1/T)} = -\frac{\Delta H^\circ}{R} \quad (5)$$

What factors control the sign and magnitude of the enthalpy of solution of a substance? We might start by considering what happens when a solid solute dissolves in a liquid solvent. This process can be formally divided into two thermodynamic steps,



such that the enthalpy of solution (ΔH_{sol}) is the sum of ΔH_1 and ΔH_2 . In this formalism, ΔH_1 corresponds to the enthalpy of fusion of the solute, or the energy associated with the melting of the solid. ΔH_2 is the enthalpy of mixing, the heat liberated or absorbed when the solute and solvent are mixed. An ideal solution, by definition, results from the *athermal*

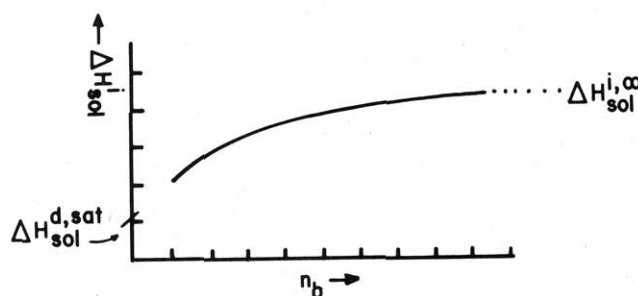
¹ There is some confusion concerning the sign convention for enthalpies of solution. Data are frequently tabulated using the rather unusual convention that positive enthalpies of solution are assigned to salts which liberate energy when dissolved in water, i.e., exothermic dissolution reactions. We have adopted the convention that exothermic processes will be assigned negative enthalpies, and therefore the enthalpy of solution for NaOH at infinite dilution is -10.637 kcal/mole.

Integral Molar Enthalpies of Solution at Infinite Dilution for Alkali and Alkaline Earth Halides^{a,b}

X:	F	Cl	Br	I
M:				
Li	1.059	-8.818	-11.717	-15.1 Kcal/mole
Na	0.213	0.914	-0.200	-1.81
K	-4.244	4.285	4.85	4.93
Rb	-5.80*	4.26	5.285	6.50*
Cs	-8.37*	4.50	6.24	7.46
Mg		-37.03	-43.3	-49.8
Ca	-2.7	-19.23	-24.61	-28.7
Sr	2.10	-11.99	-16.82	-20.66
Ba	1.90	-2.96	-5.61	-10.3*

^a Data taken from Landolt-Börnstein, Group IV, Volume 2, Springer-Verlag, Berlin, 1976, and Selected Values of Chemical Thermodynamic Properties, Circular 500, National Bureau of Standards, 1952.

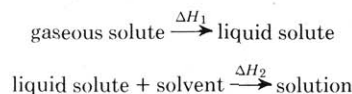
^b Data determined at 25°C unless specified by an *.



An idealized example of the dependence of the integral molar enthalpy of solution, ΔH_{sol}^i , on the ratio of moles of solvent to moles of solute, n_b . ΔH_{sol}^i approaches the limit $\Delta H_{\text{sol}}^{i,\infty}$ at high values of n_b . The intercept on the ordinate of a tangent drawn at any value of n_b yields the differential molar enthalpy of solution, ΔH_{sol}^d . ΔH_{sol}^d approaches the limit $\Delta H_{\text{sol}}^{d,\text{sat}}$ as the value of n_b approaches the point of saturation.

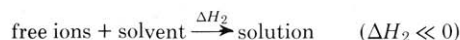
($\Delta H = 0$) mixing of two liquids. Thus, under ideal conditions, ΔH_2 is zero, and the enthalpy of solution is equal to the enthalpy of fusion, ΔH_1 . Since the enthalpy of fusion is invariably positive, solubilities in these ideal solutions should increase with increasing temperature. The most commonly cited example of such a solution results from the dissolution of naphthalene in benzene. However, as has been noted by Lilje and Macomber (1), the tendency of organic compounds dissolved in organic solvents to exhibit an increased solubility with increasing temperature is sufficiently universal that exceptions to this behavior, such as the recrystallization of pyridine hydrobromide from chloroform upon heating, are noteworthy.

An analogous solution is produced when a gas dissolves in a weakly interacting solvent



Once again, the enthalpy of mixing (ΔH_2) is negligible. The first step, however, corresponding to the liquefaction of the gaseous solute, is now exothermic. The enthalpy of solution is therefore negative, and we observe a net decrease in the solubility of most gases with increasing temperature.

Considering the apparent success of this hypothesis at explaining the temperature dependence of the solubility of covalent compounds in weakly interacting solvents, it is somewhat surprising to find that it cannot be applied with similar success to the prediction of the behavior of salts in aqueous solution. We should recognize, however, that solutions formed by dissolving inorganic salts in water are far from ideal. This process is typically considered to be the sum of two steps,



where ΔH_1 is the lattice energy of the salt, and ΔH_2 is the enthalpy of solvation. The lattice energy is invariably strongly endothermic, since it takes considerable energy to rip apart the crystal lattice. The enthalpy of solvation for aqueous solutions is strongly exothermic, however, due to the strong interaction of the charged ions with the polar water molecules. We can now appreciate how fairly subtle changes in the nature of a salt may lead to changes in both the sign and magnitude of the enthalpy of solution. ΔH_{sol} reflects the balance between the lattice energy of the salt and the solvation energy of its ions, and the relative magnitude of these factors thus determines the sign and magnitude of the enthalpy of solution.

We should now turn our attention to the question of why the term enthalpy of solution is inherently vague. In a naive sense we can define the molar enthalpy of solution as the energy either liberated or absorbed when one mole of a solute is dissolved in a given solvent. Unfortunately, the heat given off or absorbed in this process depends upon the quantity of solvent as well, or more precisely, upon the ratio of moles of solvent to moles of solute, n_b , in common notation. There are therefore an infinite number of molar enthalpies of solution for a given solute, and a hypothetical dependence of the molar enthalpy of solution upon the mole ratio n_b is shown in the figure.

The integral molar enthalpy of solution, ΔH_{sol}^i , may be defined as the total heat liberated or absorbed when one mole of solute is dissolved in n_b moles of solvent. ΔH_{sol}^i may therefore be measured at any concentration. The most common measurement, however, is the integral molar enthalpy of solution at infinite dilution, $\Delta H_{\text{sol}}^{i,\infty}$, or the total heat associated with the dissolution of one mole of solute in an infinite amount of solvent. The "heat of solution" tabulated in various reference manuals is actually the integral molar enthalpy of solution at infinite dilution. Unfortunately, there is no intrinsic reason why the sign of $\Delta H_{\text{sol}}^{i,\infty}$ should be related to the temperature dependence of the solubility of a solute.

The temperature dependence of solubility should be related to the differential molar enthalpy of solution, ΔH_{sol}^d , the intercept on the vertical axis in the figure of a tangent at any point on the curve (2). Furthermore, the only value of ΔH_{sol}^d of immediate interest is the differential molar enthalpy of solution at saturation, $\Delta H_{\text{sol}}^{d,\text{sat}}$, since the only question of significance is whether heat is evolved or absorbed as the system approaches equilibrium. Any success at the application of tabulated heat of solution data for simple covalent substances dissolved in weakly interacting solvents must be attributed to the monotonous consistency of the sign of $\Delta H_{\text{sol}}^{i,\infty}$, and therefore perhaps $\Delta H_{\text{sol}}^{d,\text{sat}}$ for these systems.

For ionic substances dissolved in aqueous solution, where the sign of both $\Delta H_{\text{sol}}^{i,\infty}$ and $\Delta H_{\text{sol}}^{d,\text{sat}}$ is less regular, the naive application of $\Delta H_{\text{sol}}^{i,\infty}$ data leads to purely random results, as we suggested above. Mazo and Bernhard (3) have noted previously that whereas the integral molar enthalpy of solution at infinite dilution, $\Delta H_{\text{sol}}^{i,\infty}$, for sodium acetate is -4.140 kcal/mole, the differential molar enthalpy of solution at saturation, $\Delta H_{\text{sol}}^{d,\text{sat}}$, is zero or slightly positive, thereby explaining to their satisfaction the increased solubility of sodium acetate with increasing temperature. There are, however, only a very limited number of compounds for which sufficient data are available to estimate $\Delta H_{\text{sol}}^{d,\text{sat}}$, and this concept is therefore of questionable utility.

We have determined values of $\Delta H_{\text{sol}}^{d,\text{sat}}$ by graphical extrapolation for approximately 20 salts of the alkali and alkaline earth metals (4). For most of the alkali metal halides the extrapolated value of $\Delta H_{\text{sol}}^{d,\text{sat}}$ is effectively zero, or slightly positive, in accord with the observed increase in solubility with increasing temperature. However, the data are not sufficiently well-characterized to allow prediction of the temperature

dependence of solubility with any degree of precision. Furthermore, while the value of $\Delta H_{\text{sol}}^{\text{d}}$ for NaOH becomes progressively less negative as saturation is approached, the extrapolated value of $\Delta H_{\text{sol}}^{\text{d,sat}}$ appears to be on the order of ~ 2 kcal/mole, and it appears that $\Delta H_{\text{sol}}^{\text{d}}$ for NaBr becomes increasingly more negative as saturation is approached. Neither result is in agreement with the observed temperature dependence of the solubility of these salts. Unfortunately, the situation becomes considerably worse when we apply this analysis to salts of the alkaline earth metals. The extrapolated values of $\Delta H_{\text{sol}}^{\text{d,sat}}$ for $\text{Mg}(\text{NO}_3)_2$, MgCl_2 and MgBr_2 range from -20 to -40 kcal/mole. Yet in each case solubility increases with increasing temperature.

It is tempting to offer an explanation for this anomalous behavior, and a number of factors may be involved. (1) Our treatment of equilibria in saturated solutions is notoriously naive. We assume that all of the solute (M_xX_m) dissolved in aqueous solution can be accounted for on the basis of $\text{M}^{m+}(\text{aq})$ and $\text{X}^{x-}(\text{aq})$ ions, neglecting any association between ions or M_xX_m fragments in solution (5). (2) The equilibrium constant of interest represents the ratio of activities not concentrations, and it is well documented that activities in saturated solutions of salts are far from well-behaved. (3) The nature of the substance undergoing dissolution changes with temperature due to changes in the extent of hydration, leading to well documented changes in the magnitude of both the enthalpies of solution and the solubilities. (4) There are certain types of systems which do not obey Le Chatelier's principle under all conditions (6). Open systems, in particular, are subject to violations of this principle (7).

Conclusion

It would appear that application of Le Chatelier's principle and enthalpy of solution data to the prediction of the temperature dependence of the solubility of salts can lead to

wrong answers, even under the most stringent conditions. In the hands of the novice, purely random results are obtained.

Given the desire to generalize the temperature dependence of the solubilities of inorganic salts in aqueous solution, we might suggest that the solubility generally increases with increasing temperature. Over 94% of the salts for which data are tabulated in the Handbook of Chemistry and Physics satisfy this generalization. Purists might then note that over two-thirds of the exceptions to this statement are salts of the following oxyanions: SO_4^{2-} , SeO_4^{2-} , SO_3^{2-} , AsO_4^{3-} and PO_4^{3-} .

Acknowledgment

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