

12.5: Solid-Liquid Equilibria

A *freezing-point curve* (freezing point as a function of liquid composition) and a *solubility curve* (composition of a solution in equilibrium with a pure solid as a function of temperature) are different ways of describing the same physical situation. Thus, strange as it may sound, the composition x_A of an aqueous solution at the freezing point is the mole fraction solubility of ice in the solution.

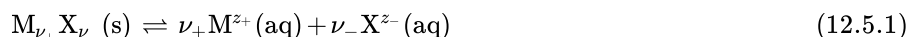
12.5.1 Freezing points of ideal binary liquid mixtures

Section 12.2.1 described the use of freezing-point measurements to determine the solvent chemical potential in a solution of arbitrary composition relative to the chemical potential of the pure solvent. The way in which freezing point varies with solution composition in the limit of infinite dilution was derived in Sec. 12.4.1. Now let us consider the freezing behavior over the entire composition range of an *ideal* liquid mixture.

Let T_f' be the freezing point of a liquid mixture of composition x_A' and $x_B' = 1 - x_A'$, and let T_f'' be the melting point of the solid compound of composition $x_A'' = a/(a+b)$ and $x_B'' = b/(a+b)$. Figure 12.7 shows an example of a molten metal mixture that solidifies to an alloy of fixed composition. The freezing-point curve of this system is closely approximated by Eq. 12.5.23.

12.5.5 Solubility of a solid electrolyte

Consider an equilibrium between a crystalline salt (or other kind of ionic solid) and a solution containing the solvated ions:



Here ν_+ and ν_- are the numbers of cations and anions in the formula unit of the salt, and z_+ and z_- are the charge numbers of these ions. The solution in equilibrium with the solid salt is a saturated solution. The thermodynamic equilibrium constant for this kind of equilibrium is called a **solubility product**, K_s .

We can readily derive a relation between K_s and the molalities of the ions in the saturated solution by treating the dissolved salt as a single solute substance, B. We write the equilibrium in the form $B^*(s) \rightleftharpoons B(\text{sln})$, and write the expression for the solubility product as a proper quotient of activities:

$$K_s = \frac{a_{m,B}}{a_B^*} \quad (12.5.24)$$

From Eq. 10.3.16, we have $a_{m,B} = \Gamma_{m,B} \gamma_{\pm}^{\nu} (m_+/m^\circ)^{\nu_+} (m_-/m^\circ)^{\nu_-}$. This expression is valid whether or not the ions M^{z_+} and X^{z_-} are present in solution in the same ratio as in the solid salt. When we replace $a_{m,B}$ with this expression, and replace a_B^* with Γ_B^* (Table 9.5), we obtain

$$K_s = \left(\frac{\Gamma_{m,B}}{\Gamma_B^*} \right) \gamma_{\pm}^{\nu} \left(\frac{m_+}{m^\circ} \right)^{\nu_+} \left(\frac{m_-}{m^\circ} \right)^{\nu_-} \quad (12.5.25)$$

where $\nu = \nu_+ + \nu_-$ is the total number of ions per formula unit. γ_{\pm} is the mean ionic activity coefficient of the dissolved salt in the saturated solution, and the molalities m_+ and m_- refer to the ions M^{z_+} and X^{z_-} in this solution.

The first factor on the right side of Eq. 12.5.25, the proper quotient of pressure factors for the reaction $B^*(s) \rightarrow B(\text{sln})$, will be denoted Γ_r (the subscript “r” stands for reaction). The value of Γ_r is exactly 1 if the system is at the standard pressure, and is otherwise approximately 1 unless the pressure is very high.

If the aqueous solution is produced by allowing the salt to dissolve in pure water, or in a solution of a second solute containing no ions in common with the salt, then the ion molalities in the saturated solution are $m_+ = \nu_+ m_B$ and $m_- = \nu_- m_B$ where m_B is the solubility of the salt expressed as a molality. Under these conditions, Eq. 12.5.25 becomes

$$K_s = \Gamma_r \gamma_{\pm}^{\nu} (\nu_+^{\nu_+} \nu_-^{\nu_-}) \left(\frac{m_B}{m^\circ} \right)^{\nu} \quad (12.5.26)$$

(no common ion)

We could also have obtained this equation by using the expression of Eq. 10.3.10 for $a_{m,B}$.

If the ionic strength of the saturated salt solution is sufficiently low (i.e., the solubility is sufficiently low), it may be practical to evaluate the solubility product with Eq. 12.5.26 and an estimate of γ_{\pm} from the Debye–Hückel limiting law (see Prob. 12.19). The

most accurate method of measuring a solubility product, however, is through the standard cell potential of an appropriate galvanic cell (Sec. 14.3.3).

Since K_s is a thermodynamic equilibrium constant that depends only on T , and Γ_r depends only on T and p , Eq. 12.5.26 shows that any change in the solution composition at constant T and p that decreases γ_{\pm} must increase the solubility. For example, the solubility of a sparingly-soluble salt increases when a second salt, lacking a common ion, is dissolved in the solution; this is a *salting-in effect*.

Equation 12.5.25 is a general equation that applies even if the solution saturated with one salt contains a second salt with a common ion. For instance, consider the sparingly-soluble salt $M_{\nu_+} X_{\nu_-}$ in transfer equilibrium with a solution containing the more soluble salt $M_{\nu'_+} Y_{\nu'_-}$ at molality m_C . The common ion in this example is the cation M^{z+} . The expression for the solubility product is now

$$K_s = \Gamma_r \gamma_{\pm}^{\nu} (\nu_+ m_B + \nu'_+ m_C)^{\nu_+} (\nu_- m_B)^{\nu_-} / (m^{\circ})^{\nu} \quad (12.5.27)$$

(common cation)

where m_B again is the solubility of the sparingly-soluble salt, and m_C is the molality of the second salt. K_s and Γ_r are constant if T and p do not change, so any increase in m_C at constant T and p must cause a decrease in the solubility m_B . This is called the *common ion effect*.

From the measured solubility of a salt in pure solvent, or in an electrolyte solution with a common cation, and a known value of K_s , we can evaluate the mean ionic activity coefficient γ_{\pm} through Eq. 12.5.26 or 12.5.27. This procedure has the disadvantage of being limited to the value of m_B existing in the saturated solution.

We find the temperature dependence of K_s by applying Eq. 12.1.12:

$$\frac{d \ln K_s}{dT} = \frac{\Delta_{\text{sol},B} H^{\circ}}{RT^2} \quad (12.5.28)$$

At the standard pressure, $\Delta_{\text{sol},B} H^{\circ}$ is the same as the molar enthalpy of solution at infinite dilution, $\Delta_{\text{sol},B} H^{\infty}$.

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