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.

The general relation between temperature and the composition of a binary liquid mixture, when the mixture is in equilibrium with pure solid A, is given by Eq. 12.3.6: 

\[
\frac{\partial T}{\partial x_A} \bigg|_{p} = \frac{T^2}{\Delta_{sol,A}H} \tag{12.5.1}
\]

We can replace \(T\) by \(T_{fA}\) to indicate this is the temperature at which the mixture freezes to form solid A. From the expression for the chemical potential of component A in an ideal liquid mixture, \(\mu_A = \mu_A^* + RT\ln x_A\), we have \(\frac{\partial \mu_A}{\partial x_A} = \frac{RT}{x_A}\). With these substitutions, Eq. 12.5.1 becomes

\[
\frac{\partial T_{fA}}{\partial x_A} \bigg|_{p} = \frac{RT_{fA}^2}{x_A \Delta_{sol,A}H} \tag{12.5.2} \quad \text{(ideal liquid mixture)}
\]

Figure 12.4 compares the freezing behavior of benzene predicted by this equation with experimental freezing-point data for mixtures of benzene–toluene and benzene–cyclohexane. Any constituent that forms an ideal liquid mixture with benzene should give freezing points for the formation of solid benzene that fall on the curve in this figure. The agreement is good over a wide range of compositions for benzene–toluene mixtures (open circles), which are known to closely approximate ideal liquid mixtures. The agreement for benzene–cyclohexane mixtures (open triangles), which are not ideal liquid mixtures, is confined to the ideal-dilute region.

The general relation between temperature and the composition of a binary liquid mixture, when the mixture is in equilibrium with pure solid A, is given by Eq. 12.3.6: 

\[
\frac{\partial T}{\partial x_A} \bigg|_{p} = \frac{T^2}{\Delta_{sol,A}H} \tag{12.5.1}
\]

We can replace \(T\) by \(T_{fA}\) to indicate this is the temperature at which the mixture freezes to form solid A. From the expression for the chemical potential of component A in an ideal liquid mixture, \(\mu_A = \mu_A^* + RT\ln x_A\), we have \(\frac{\partial \mu_A}{\partial x_A} = \frac{RT}{x_A}\). With these substitutions, Eq. 12.5.1 becomes

\[
\frac{\partial T_{fA}}{\partial x_A} \bigg|_{p} = \frac{RT_{fA}^2}{x_A \Delta_{sol,A}H} \tag{12.5.2} \quad \text{(ideal liquid mixture)}
\]

Figure 12.4 compares the freezing behavior of benzene predicted by this equation with experimental freezing-point data for mixtures of benzene–toluene and benzene–cyclohexane. Any constituent that forms an ideal liquid mixture with benzene should give freezing points for the formation of solid benzene that fall on the curve in this figure. The agreement is good over a wide range of compositions for benzene–toluene mixtures (open circles), which are known to closely approximate ideal liquid mixtures. The agreement for benzene–cyclohexane mixtures (open triangles), which are not ideal liquid mixtures, is confined to the ideal-dilute region.
If we make the approximation that $\Delta_{sol,A}H$ is constant over the entire range of mixture composition, we can replace it by $\Delta_{fus,A}H$, the molar enthalpy of fusion of pure solid A at its melting point. This approximation allows us to separate the variables in Eq. 12.5.2 and integrate as follows from an arbitrary mixture composition $x'$ at the freezing point $T'$ to pure liquid A at its freezing point $T^*$:

$$
\int_{T'}^{T^*} \frac{dT}{T^2} = \frac{R}{\Delta_{fus,A}H} \int_{x'}^{1} \frac{dx}{x} \tag{12.5.3}
$$

The result, after some rearrangement, is

$$
\ln x = \frac{\Delta_{fus,A}H}{R} \left( \frac{1}{T^*} - \frac{1}{T} \right) \tag{12.5.4}
$$

This equation was used to generate the curves shown in Fig. 12.5. Although the shape of the freezing-point curve ($T$ versus $x_B$) shown in Fig. 12.4 is concave downward, Fig. 12.5 shows this is not always the case. When $\Delta_{fus,A}H/RT^*$ is less than 2, the freezing-point curve at low $x_B$ is concave upward.

### 12.5.2 Solubility of a solid nonelectrolyte

Suppose we find that a solution containing solute B at a particular combination of temperature, pressure, and composition can exist in transfer equilibrium with pure solid B at the same temperature and pressure. This solution is said to be saturated with respect to the solid. We can express the solubility of the solid in the solvent by the value of the mole fraction, concentration, or molality of B in the saturated solution. We can also define solubility as the maximum value of the solute mole fraction, concentration, or molality that can exist in the solution without the possibility of spontaneous precipitation.

This section considers the solubility of a solid nonelectrolyte. For the solution process $B(s) \rightleftharpoons aB(sl)$, the general expression for the thermodynamic equilibrium constant is $K = aB(sl)/aB(solid)$. (In this and other expressions for equilibrium constants in this chapter, activities will be assumed to be for equilibrium states, although not indicated by the "eq" subscripts used in Chap. 11.) The activity of the pure solid is $aB(solid) = G(B|solid)$. Let us use a solute standard state based on mole fraction; then the solute activity is $aB(sl) = GxB(T)/GxB$. From these relations, the solubility expressed as a mole fraction is

$$
x_B = \frac{G(B|solid)K}{GxB(T)g(x,B)} \tag{12.5.5}
$$
If we measure the solubility at the standard pressure, the pressure factors $G(B|sol|)$ and $G(x|B)$ are unity and the solubility is given by $x_B = \frac{K}{\gamma|x|B}$ \tag{12.5.6} \cond{(solubility of solid B, (p=p^st))}

If the pressure is not exactly equal to $(p=p^st)$, but is not very much greater, the values of the pressure factors are close to unity and Eq. 12.5.6 is a good approximation.

We can find the standard molar enthalpy of solution of B from the temperature dependence of the solubility. Combining Eqs. 12.1.12 and 12.5.6, we obtain $\Delta_{sol,B}^H = RT^2 \frac{\ln(c_B/c^st)}{\ln(x_B)} \tag{12.5.7} \cond{(p=p^st)}$

If the solubility $x_B$ increases with increasing temperature, $\Delta_{sol,B}^H$ must be positive and the solution process is endothermic. A decrease of solubility with increasing temperature implies an exothermic solution process. These statements refer to a solid of low solubility; see Sec. 11.9 for a discussion of the general relation between the temperature dependence of solubility and the sign of the molar differential enthalpy of solution at saturation.

For a solute standard state based on molality, we can derive equations like Eqs. 12.5.7 and 12.5.8 with $G(x|B)$ replaced by $G(mb|B)$ and $x_B$ replaced by $(m_B/m^st)$. If we use a solute standard state based on concentration, the expressions become slightly more complicated. The solubility in this case is given by $c_B = \frac{G(B|sol|)Kc^st}{G(c|B)\gamma|c|B}$ \tag{12.5.9}

From Eq. 12.1.11, we obtain, for a nonelectrolyte solid of low solubility, the relation $\Delta_{sol,B}^H = RT^2 \left( \frac{\ln(c_B/c^st)}{\ln(T)} + \alpha A^* \right) \tag{12.5.10} \cond{(p=p^st, \gamma|c|B=1)}$

12.5.3 Ideal solubility of a solid

The ideal solubility of a solid at a given temperature and pressure is the solubility calculated on the assumptions that (1) the liquid is an ideal liquid mixture, and (2) the molar differential enthalpy of solution equals the molar enthalpy of fusion of the solid ($\Delta_{sol,B}^H = \Delta_{fus,B}^H$). These were the assumptions used to derive Eq. 12.5.4 for the freezing-point curve of an ideal liquid mixture. In Eq. 12.5.4, we exchange the constituent labels A and B so that the solid phase is now component B: $\ln x_B = \frac{\Delta_{fus,B}^H}{R} \left( \frac{1}{T^B^*}-\frac{1}{T} \right) \tag{12.5.11} \cond{(ideal solubility of solid B)}$

Here $T^B^*$ is the melting point of solid B.
According to Eq. 12.5.11, the ideal solubility of a solid is independent of the kind of solvent and increases with increasing temperature. For solids with similar molar enthalpies of fusion, the ideal solubility is less at a given temperature the higher is the melting point. This behavior is shown in Fig. 12.6. In order for the experimental solubility of a solid to agree even approximately with the ideal value, the solvent and solute must be chemically similar, and the temperature must be close to the melting point of the solid so that \( \Delta_{\text{sol,B}} H \) is close in value to \( \Delta_{\text{fus,B}} H \).

From the freezing behavior of benzene–toluene mixtures shown by the open circles in Fig. 12.4, we can see that solid benzene has close to ideal solubility in liquid toluene at temperatures not lower than about \( 20 \text{K} \) below the melting point of benzene.

### 12.5.4 Solid compound of mixture components

Binary liquid mixtures are known in which the solid that appears when the mixture is cooled is a compound containing both components in a fixed proportion. This kind of solid is called a **solid compound**, or stoichiometric addition compound. Examples are salt hydrates (salts with fixed numbers of waters of hydration in the formula unit) and certain metal alloys.

The composition of the liquid mixture in this kind of system is variable, whereas the composition of the solid compound is fixed. Suppose the components are A and B, present in the liquid mixture at mole fractions \( x_A \) and \( x_B \), and the solid compound has the formula \( A_{a}B_{b} \). We assume that in the liquid phase the compound is completely dissociated with respect to the components; that is, that no molecules of formula \( A_{a}B_{b} \) exist in the liquid. The reaction equation for the freezing process is

\[
\text{\textit{at}} A(\text{mixt}) + \text{\textit{bt}} B(\text{mixt}) \rightarrow A_{a}B_{b}(s)
\]

When equilibrium exists between the liquid and solid phases, the temperature is the freezing point \( T_{f} \) of the liquid. At equilibrium, the molar reaction Gibbs energy defined by

\[
\Delta_{r} G = \sum_{i} \nu_i \mu_i
\]

is zero: \( \begin{equation}
-a\mu_A + b\mu_B + \mu_{\text{solid}} = 0 \end{equation} \). Here \( \mu_{A} \) and \( \mu_{B} \) refer to chemical potentials in the
liquid mixture, and \(\mu_{\text{solid}}\) refers to the solid compound.

How does the freezing point of the liquid mixture vary with composition? We divide both sides of Eq. 12.5.12 by \(T\) and take differentials: \[ -a \frac{\dif(\mu_A/T)}{\dif T} - b \frac{\dif(\mu_B/T)}{\dif T} + \frac{\dif(\mu_{\text{solid}}/T)}{\dif T} = 0 \] \tag{12.5.13} \cond{\text{(phase equilibrium)}} \end{gather}

The pressure is constant. Then \(\mu_A/T\) and \(\mu_B/T\) are functions of \(T\) and \(x_A\), and \(\mu_{\text{solid}}/T\) is a function only of \(T\). We find expressions for the total differentials of these quantities at constant \(p\) with the help of Eq. 12.1.3: \[ \dif(\mu_A/T) = -\frac{H_A}{T^2} \dif T + \frac{1}{T} \frac{\partial \mu_A}{\partial x_A} \dif x_A \] \[ \dif(\mu_B/T) = -\frac{H_B}{T^2} \dif T + \frac{1}{T} \frac{\partial \mu_B}{\partial x_A} \dif x_A \] \[ \dif(\mu_{\text{solid}}/T) = -\frac{H_{\text{solid}}}{T^2} \dif T \] \tag{12.5.14} \tag{12.5.15} \tag{12.5.16}

When we substitute these expressions in Eq. 12.5.13 and solve for \(\dif T/\dif x_A\), we obtain \[ \frac{\dif T_{f}}{\dif x_A} = \frac{T_{f}}{a H_A + b H_B - H_{\text{solid}}} \left[ a \frac{\partial \mu_A}{\partial x_A} + b \frac{\partial \mu_B}{\partial x_A} \right] \] \tag{12.5.17}

The quantity \((a H_A + b H_B - H_{\text{solid}})\) in the denominator on the right side of Eq. 12.5.17 is \(\Delta_{\text{sol}} H\), the molar differential enthalpy of solution of the solid compound in the liquid mixture. The two partial derivatives on the right side are related through the Gibbs–Duhem equation \((x_A \dif \mu_A + x_B \dif \mu_B = 0)\) (Eq. 9.2.27), which applies to changes at constant \(T\) and \(p\). We rearrange the Gibbs–Duhem equation to \(\dif(\mu_A/T) = -(x_A \dif \mu_A) + (x_B \dif \mu_B)\) and divide by \(\dif x_A\): \[ \dif(\mu_A/T) = -\frac{H_A}{T^2} \dif T + \frac{1}{T} \frac{\partial \mu_A}{\partial x_A} \dif x_A \] \[ \dif(\mu_B/T) = -\frac{H_B}{T^2} \dif T + \frac{1}{T} \frac{\partial \mu_B}{\partial x_A} \dif x_A \] \[ \dif(\mu_{\text{solid}}/T) = -\frac{H_{\text{solid}}}{T^2} \dif T \] \tag{12.5.18}

Making this substitution in Eq. 12.5.17, we obtain the equation \[ \frac{\dif T_{f}}{\dif x_A} = -\frac{H_A}{T_{f}^2} \left[ a \frac{\partial \mu_A}{\partial x_A} + b \frac{\partial \mu_B}{\partial x_A} \right] \] \tag{12.5.19} \tag{12.5.20}

The quantity \((a H_A + b H_B - H_{\text{solid}})\) in the denominator on the right side of Eq. 12.5.17 is \(\Delta_{\text{Delsub}\{\text{sol}\} H}\), the molar differential enthalpy of solution of the solid compound to its melting point to form a liquid mixture of the same composition as the solid. The molar enthalpy change of the fusion process is the molar enthalpy of fusion of the solid compound, \(\Delta_{\text{Delsub}\{\text{fus}\} H}\), a positive quantity. When the liquid has the same composition as the solid, the dissolution and fusion processes are identical; under these conditions, \(\Delta_{\text{Delsub}\{\text{sol}\} H}\) is equal to \(\Delta_{\text{Delsub}\{\text{fus}\} H}\) and is positive.

Equation 12.5.20 shows that the slope of the freezing-point curve, \((\dif x_A)\) versus \((x_A)\), is zero when \((x_A = a/(a+b))\); that is, when the liquid and solid have the same composition. Because \((\dif x_A/T)\) is positive, and \(\Delta_{\text{Delsub}\{\text{sol}\} H}\) at this composition is also positive, we see from the equation that the slope decreases as \((x_A)\) increases. Thus, the freezing-point curve has a maximum at the mixture composition that is the same as the composition of the solid compound. This conclusion applies when both components of the liquid mixture are nonelectrolytes, and also when one component is an electrolyte that dissociates into ions.

Now let us assume the liquid mixture is an ideal liquid mixture of nonelectrolytes in which \(\mu_A\) obeys Raoult’s law for fugacity, \(\mu_A = x_A \mu_A^* + RT \ln x_A\). The partial derivative \(\partial(\mu_A/T)\) then equals \(RT/x_A\), and Eq. 12.5.19 becomes \[ \frac{\dif T_{f}}{\dif x_A} = \frac{RT_{f}^2}{\Delta_{\text{Delsub}\{\text{sol}\} H}} \left[ a \frac{\partial \mu_A}{\partial x_A} + b \frac{\partial \mu_B}{\partial x_A} \right] \] \tag{12.5.21}

By making the approximations that \(\Delta_{\text{Delsub}\{\text{fus}\} H}\) is independent of \(T\) and \(x_A\), and is equal to \(\Delta_{\text{Delsub}\{\text{sol}\} H}\), we can separately the variables and integrate as follows: \[ \int_{T_{f}}^{T_{f}'} \frac{\dif T_{f}}{T_{f}^2} = \frac{RT_{f}^2}{\Delta_{\text{Delsub}\{\text{fus}\} H}} \left[ a \ln \frac{x_A'}{x_A} + b \ln \frac{x_B'}{x_B} \right] \tag{12.5.22} \] The result of the integration is \[ \int_{x_{f}'}^{x_{f}''} \frac{\dif x_A}{T_{f}^2} = \frac{RT_{f}^2}{\Delta_{\text{Delsub}\{\text{fus}\} H}} \left[ a \ln \frac{x_A'}{x_A} + b \ln \frac{x_B'}{x_B} \right] \]
Let \( T'_{\text{f}} \) be the freezing point of a liquid mixture of composition \( x'_A \) and \( x'_B = 1 - x'_A \), and let \( T''_{\text{f}} \) 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.

\[ \text{Figure 12.7} \text{ Solid curve: freezing-point curve of a liquid melt of Zn and Mg that solidifies to the solid compound Zn}_2\text{Mg (Rodney P. Elliot, Constitution of Binary Alloys, First Supplement, McGraw-Hill, New York, 1965, p. 603). The curve maximum (open circle) is at the compound composition } x''_A = 2/3 \text{ and the solid compound melting point } T''_{\text{f}} = 861 \text{K. Dashed curve: calculated using Eq. 12.5.23 with } \Delta_{\text{fus}}H = 15.8 \text{kJ mol}^{-1}. \]

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: \[ \text{M}^{\nu_+}_{(\nu_+)}\text{X}^{\nu_-}_{(\nu_-)}(s) \leftrightarrow \nu_+\text{M}^{z_+}_{(aq)} + \nu_-\text{X}^{z_-}_{(aq)}(aq) \]

Here \( \nu_+ \) and \( \nu_- \) 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 \( B^{(\nu_+)}(s) \leftrightarrow \nu_+B^{(aq)} \), and write the expression for the solubility product as a proper quotient of activities: \begin{equation} K_s = \frac{a_{\nu_+}B}{a_B} \end{equation} From Eq. 10.3.16, we have \( a_{\text{mB}} = g_{(\nu_+)}^\nu(m_+/m_{\text{st}})^{\nu_+}(m_-/m_{\text{st}})^{\nu_-} \). This expression is valid whether or not the ions \( \text{M}^{(z_+)} \) and \( \text{X}^{(z_-)} \) are present in solution in the same ratio as in the solid salt. When we replace \( a_{\text{mB}} \) with this expression, and replace \( a_B \) with
\( \text{(Table 9.5)}, \) we obtain \begin{equation} K_s = \left( \frac{\G \B}{\G \B^*} \right) \g_{\pm}^\nu \left( \frac{m_+}{m^\st} \right)^{\nu_+} \left( \frac{m_-}{m^\st} \right)^{\nu_-} \tag{12.5.25} \end{equation} where \( \nu = \nu_+ + \nu_- \) is the total number of ions per formula unit. \( \g_{\pm} \) 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 \( B^*(s) \rightarrow B(sln) \), will be denoted \( \G \text{subs}(r) \) (the subscript “r” stands for reaction). The value of \( \G \text{subs}(r) \) 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 \begin{gather} \text{Ksubs(s)} = \text{Gsubs(r)} \g_{\pm}^\nu \left( \nu_+^\nu_+ \nu_-^\nu_- \right) \left( \frac{m^\B}{m^\st} \right)^\nu \tag{12.5.26} \text{(no common ion)} \end{gather} We could also have obtained this equation by using the expression of Eq. 10.3.10 for \( \a \text{mbB} \).

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 \( \g_{\pm} \) 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 \( \text{T} \), and \( \G \text{subs}(r) \) depends only on \( \text{T} \) and \( \text{p} \), Eq. 12.5.25 shows that any change in the solution composition at constant \( \text{T} \) and \( \text{p} \) that decreases \( \g_{\pm} \) 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 \begin{gather} \text{Ksubs(s)} = \G \text{subs(r)} \g_{\pm}^\nu \left( \nu_+ m^\B + \nu'_+ m^\C \right)^\nu_+ \left( \nu_- m^\B \right)^\nu_- \left( \nu'_- m^\C \right)^\nu'_- \tag{12.5.27} \text{(common cation)} \end{gather} where \( m^\B \) again is the solubility of the sparingly-soluble salt, and \( m^\C \) is the molality of the second salt. \( \G \text{subs(s)} \) and \( \G \text{subs(r)} \) are constant if \( \text{T} \) and \( \text{p} \) do not change, so any increase in \( m^\C \) at constant \( \text{T} \) and \( \text{p} \) 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 \( K \text{subs(s)} \), we can evaluate the mean ionic activity coefficient \( \g_{\pm} \) 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 \( \G \text{subs(s)} \) by applying Eq. 12.1.12: \begin{equation} \frac{\text{d} \ln \text{Ksubs(s)}}{\text{d} T} = \frac{\text{Delsub(sol,B)}H^\st}{RT^2} \tag{12.5.28} \end{equation} At the standard pressure, \( \text{(Delsub(sol,B)}H^\st) \) is the same as the molar enthalpy of solution at infinite dilution, \( \text{Delsub(sol,B)}H^\infty \).
Contributors

- Howard DeVoe, Associate Professor Emeritus, University of Maryland from Thermodynamics and Chemistry