Chapter 18: Ideal Solutions

Calculate the Gibbs energy of mixing for the formation of a solution of 0.500 mol of ethanol with 0.500 mol of ethyl acetate, assuming an ideal solution.

Intermolecular forces in solution have an important impact on chemical reactivity. Solute-solvent interactions shift the position of equilibrium as compared to reactions in the gas phase or reactions involving pure substances. In particular, the unique properties of aqueous solutions are important in biochemistry, medicinal chemistry, biogeoenvironmental chemistry, and oceanography. Solvation is one of the most important areas of physical chemistry that is yet to be adequately characterized by theory from first-principles.

Determining the Gibbs energy of solvation and then the Gibbs energy of a substance in solution is the focus of the next two chapters. The conceptual model of an ideal solution is an important first step in the development of the theory of solvation. The ideal-dilute solution model provides an understanding of **colligative phenomena**, which include vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure. The first step in developing the theory of solutions is to determine how to recast the fundamental equations of thermodynamics into terms appropriate for solutions. The concept of **partial molar properties** is the key new ingredient in finding the Gibbs energy of a substance in solution. Partial molar quantities allow the variation of the intermolecular forces in solution to be easily accounted for in thermodynamic relationships. Our treatment of partial molar effects begins with partial molar volume, since volume changes in solution are easy to visualize.

18.1 Concentration Dependence is Expressed by Partial Molar Properties

Volumes Usually Don't Add in Making Solutions: Mixing 10.00 mL of ethanol and 10.00 mL of water gives a solution of volume 19.20 mL. The temperature also increases by a small amount upon mixing. The volume of the mixture is less than the pure constituents because of favorable interactions between the two substances, which also make formation of the solution exothermic. The molar volume of pure ethanol is 58.46 mL mol^{-1} and of water is 18.07 mL mol^{-1}. The "effective molar volume" of the ethanol in this solution is 55.1 mL mol^{-1} and the "effective molar volume" of water is 17.74 mL mol^{-1}, which are less than the pure molar volumes. The "effective molar volume" is called the **partial molar volume**. The partial molar volume differs from the pure molar volume because of solute-solvent interactions. The partial molar volumes are usually strongly dependent on concentration, Figure 18.1.1a. The partial molar volumes are defined by the derivatives, Figure 18.1.1b:

$$\bar{V}_A \equiv \left(\frac{\partial V}{\partial n_A}\right)_{T,P,n_B} \qquad \bar{V}_B \equiv \left(\frac{\partial V}{\partial n_B}\right)_{T,P,n_A} \qquad 18.1.1$$

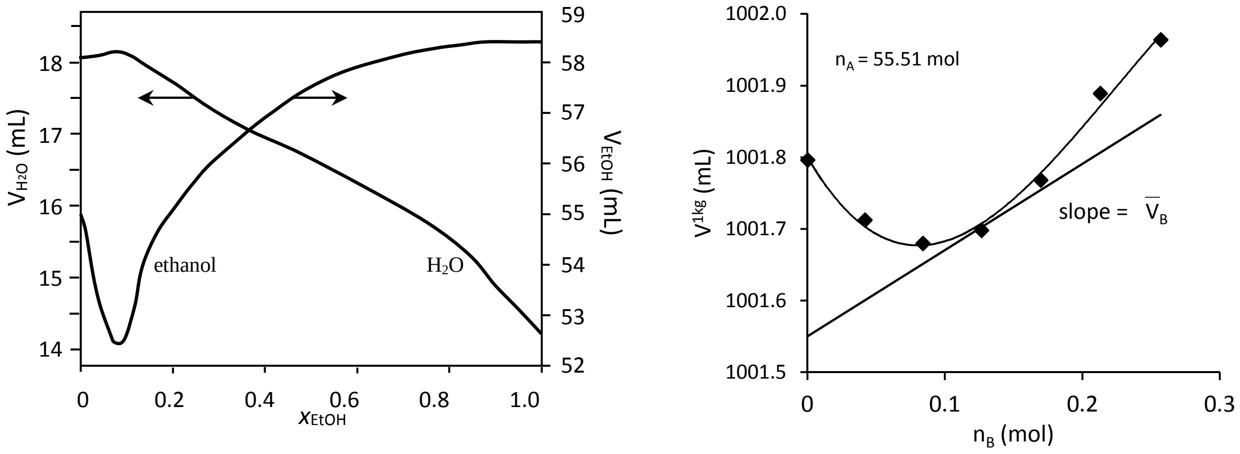
We usually refer to the solvent as constituent A and the solute as constituent B. For pure substances, the partial molar volumes are equal to the pure molar volumes, $\bar{V}_A = V^*_A$ and $\bar{V}_B = V^*_B$. The change in total volume of the solution at constant temperature and pressure is given by:

$$dV = \left(\frac{\partial V}{\partial n_A}\right)_{T,P,n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{T,P,n_A} dn_B = \bar{V}_A\, dn_A + \bar{V}_B\, dn_B \qquad \text{(cst. T\&P)} \qquad 18.1.2$$

To find the total volume of the solution, we integrate this differential at constant composition to give (see Sec. 16.8 and Eq. 16.8.4):

$$V = \bar{V}_A\, n_A + \bar{V}_B\, n_B \qquad \text{(cst. T\&P)} \qquad 18.1.3$$

The total volume of the solution is an additive function of the composition, with the partial molar volumes <u>at the given final concentration</u>. Also note that partial molar volumes are sometimes shown in bold without the “overbar,” $\mathbf{V}_A$ and $\mathbf{V}_B$. How are we to interpret partial molar properties?



(a). (b).

Figure 18.1.1: (a). Partial molar volumes of ethanol and water in solution. (b). The volume of solutions of $MgSO_4$, B, containing 1 kg of water (55.51 mol). The partial molar volume of $MgSO_4$ is the derivative of the volume with respect to the change in moles of $MgSO_4$, keeping the moles of water constant. Note that partial molar volume is negative if the solution shrinks upon addition of solute.

Remember our discussion of the interpretation of derivatives in Sec. 8.4. Correspondingly, Eqs. 18.1.1 can be interpreted in two equivalent ways:

The partial molar volume is the derivative of the volume with respect to the change in moles of the substance, keeping the moles of the other substance in solution constant.

The partial molar volume is the change in volume for adding one mole of substance to so large an amount of solution that the concentration remains unchanged.

We can use the endpoints of the partial molar volume curve for ethanol in Figure 18.1.1a as examples. Consider a swimming pool filled with water. The partial molar volume of ethanol in water at $x_{EtOH} = 0$ is the change in volume when one mole of ethanol is added to the swimming pool, $\bar{V}_{EtOH} = 54.95$ mL mol^{-1}. The change in concentration is negligible because the swimming pool has such a large volume. Now, consider a swimming pool filled with pure ethanol. The partial molar volume of ethanol at $x_{EtOH} = 1$ is the change in volume for adding one mole of ethanol to a swimming pool filled with ethanol, which is just the pure molar volume. Notice in the figure that when the partial molar volume of one constituent increases, the partial molar volume of the other constituent decreases.

The variation of the partial molar volume with concentration results, in large part, from the interaction of the solute and the solvent. Accordingly, we expect that the partial molar volumes of the solute and solvent are related. Consider the total differential of Eq. 18.1.3 for any possible process at constant temperature and pressure; using the product rule gives:

$$dV = \bar{V}_A\, dn_A + n_A\, d\bar{V}_A + \bar{V}_B\, dn_B + n_B\, d\bar{V}_B \qquad \text{(cst. T\&P)} \qquad 18.1.4$$

Both this general expression and Eq. 18.1.2 must be simultaneously satisfied. Subtraction of Eq. 18.1.2 from this last equation shows that the partial molar volumes are related by:

$$0 = n_A\, d\bar{V}_A + n_B\, d\bar{V}_B \qquad \text{(cst. T\&P)} \qquad 18.1.5$$

Eq. 18.1.5 is called a **Gibbs-Duhem relationship**; we will find corresponding relations for each partial molar property. To show that the Gibbs-Duhem relationship allows the calculation of the partial molar property of one constituent in solution from the other, solve the last relationship for $d\bar{V}_B$ to give:

$$d\bar{V}_B = -\frac{n_A}{n_B}\, d\bar{V}_A \qquad \text{(cst. T\&P)} \qquad 18.1.6$$

The mole fractions are defined using $x_A = n_A/n_{tot}$ and $x_B = n_B/n_{tot}$, with $n_{tot} = n_A + n_B$ and $x_A = 1 - x_B$. Dividing the numerator and denominator in Eq. 18.1.6 by n_{tot} gives:

$$d\bar{V}_B = -\frac{n_A/n_{tot}}{n_B/n_{tot}}\, d\bar{V}_A = -\frac{x_A}{x_B}\, d\bar{V}_A = -\frac{x_A}{1 - x_A}\, d\bar{V}_A \qquad \text{(cst. T\&P)} \qquad 18.1.7$$

This form of the Gibbs-Duhem relationship for the volume shows that the derivative of the partial molar volume of the two constituents are opposite in sign; when one increases the other decreases. Integration of this last equation over a range of concentrations allows the calculation of the partial molar volume of one constituent from the other (see below for an example of this process using the chemical potential).

In the laboratory, the partial molar volume of the solute is easily evaluated by measuring the volume or density of a series of solutions of known molality. The molality of the solute is given as $m_B = n_B/w_A$, with w_A the mass of the solvent in kg, Eq. 2.2.4. For a solution containing 1 kg of solvent, $m_B = n_B/1$ kg; the number of moles of solute in the solution is numerically equal to the molality. We can then change variables for the partial molar derivative using the chain rule:

$$\bar{V}_B = \left(\frac{\partial V}{\partial n_B}\right)_{T,P,n_A} = \left(\frac{\partial V}{\partial m_B}\right)_{T,P,n_A}\left(\frac{\partial m_B}{\partial n_B}\right)_{T,P,n_A} = \left(\frac{\partial V^{1kg}}{\partial m_B}\right)_{T,P,n_A}\left(\frac{1}{1\text{ kg}}\right) \qquad \text{(cst. T\&P)} \qquad 18.1.8$$

where V^{1kg} is the volume of a solution that contains 1 kg of solvent. A closely related property, the **apparent molar volume**, is often used in practical circumstances in the laboratory. Consider the volume of a solution as n_B moles of a solute are added to a fixed n_A moles of solvent, Figure 18.1.2. The volume due to the added solute per mole is called the apparent molar volume, ${}^{\phi}V$:

$$^{\phi}V \equiv \frac{V_{solution} - V_{pure\ solvent}}{\text{moles of solute}} = \frac{V - n_A V_A^*}{n_B} \qquad \text{(cst. T\&P)} \qquad 18.1.9$$

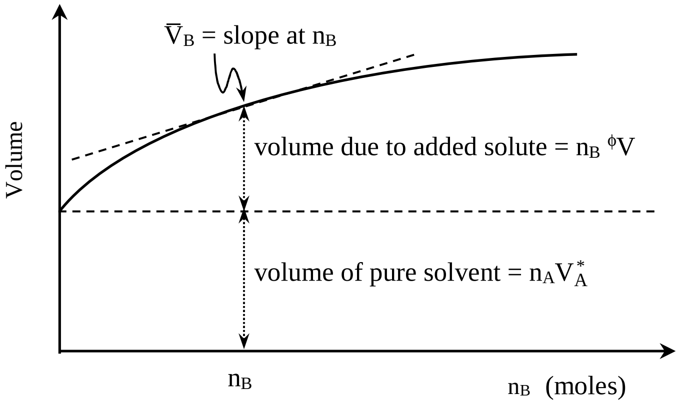


Figure 18.1.2: The total volume of a solution V depends on the volume of the pure solvent and the apparent molar volume of the solute, $^{\phi}V$.

The volume V of the solution at any particular added n_B moles of solute is given by the rearrangement of Eq. 18.1.9:

$$V = n_A V_A^* + n_B\,{}^{\phi}V \qquad \text{and} \qquad \bar{V}_B = {}^{\phi}V + m_B \left(\frac{\partial\,{}^{\phi}V}{\partial m_B}\right)_{T,P,n_A} \qquad \text{(cst. T\&P)} \qquad 18.1.10$$

This first result shows that the apparent molar volume ascribes all of the change in volume of the solution to the solute. The effective volume of the solvent is assumed to be the pure molar volume of the solvent, V_A^*. The apparent molar volume includes the volume of the solute and the change in volume of the solvent caused by the interactions of the solute with the solvent. The partial molar volume, on the other hand, shares the change in volume between the effective volume of the solute and the effective volume of the solvent, both of which vary with concentration. The apparent molar volume is particularly useful in biochemical determinations.

Example 18.1.1: *Partial Molar Volume*

The volume of solution that contains 1 kg of solvent for an aqueous solution of urea at 25°C is given by the following polynomial as function of the molality of urea. The volume is in mL. Determine the partial molar volume of urea and water, and the apparent molar volume of urea for a 0.5000 m solution.

$$V^{1kg} = -1.9934\text{x}10^{-3} m_B^3 + 9.03779\text{x}10^{-2}\, m_B^2 + 44.36388\, m_B + 1002.842$$

Answer: For the partial molar volume of the solute using Eq. 18.1.8 at 0.5000 m gives:

$$\bar{V}_B = \left(\frac{\partial V^{1kg}}{\partial m_B}\right)_{T,P,n_A} kg^{-1} = 3(-1.9934x10^{-3})\, m_B^2 + 2(9.03779x10^{-2})\, m_B + 44.36388$$

$$= 3(-1.9934x10^{-3})(0.5)^2 + 2(9.03779x10^{-2})(0.5) + 44.36388 = 44.4528 \text{ mL mol}^{-1}$$

The total volume at m = 0.5000 m using the given polynomial is V^{1kg} = 1025.046 mL. The partial molar volume of the solvent, water, is given by solving Eq. 18.1.3 for $\bar{V}_A$ with 1 kg of solvent:

$$V^{1kg} = \bar{V}_A\, n_A + \bar{V}_B\, n_B = \bar{V}_A \frac{1000 \text{ g}}{\mathfrak{M}_A} + \bar{V}_B\, m_B \text{ (1 kg)}$$

$$1025.046 \text{ mL} = \bar{V}_A \text{ (55.508 mol)} + 44.4528 \text{ mL mol}^{-1} \text{ (0.5000 mol kg}^{-1}\text{) (1 kg)}$$

$$\bar{V}_A = 18.066 \text{ mL mol}^{-1}$$

The partial molar volume of water at this concentration is almost equal to the pure molar volume at 25°C, $V_A^* = \mathfrak{M}_A/d_{A,pure}$ = 18.0153 g mol^{-1}/0.9970479 g mL^{-1} = 18.069 mL mol^{-1}(Table 2.2.1).

The apparent molar volume is given by Eq. 18.1.9. Using V^{1kg} gives n_A = (1000 g/$\mathfrak{M}_A$) and noting that $V_A^* = \mathfrak{M}_A/d_{A,pure}$ avoids round-off error from the uncertainty in the molar mass of the solvent:

$$^{\phi}V = \frac{V - n_A V_A^*}{n_B} = \frac{V^{1kg} - (1000 \text{ g}/\mathfrak{M}_A)\, V_A^*}{m_B \text{ (1 kg)}} = \frac{V^{1kg} - (1000 \text{ g}/d_{A,pure})}{m_B \text{ (1 kg)}} \qquad \text{(cst. T\&P)} \qquad 18.1.11$$

For urea at 0.5000 m and $d_{A,pure}$ = 0.9970479 g mL^{-1}:

$$= \frac{1025.046 \text{ mL} - 1002.961 \text{ mL}}{0.5000 \text{ mol kg}^{-1} \text{ (1 kg)}} = 44.170 \text{ mL mol}^{-1}$$

The Chemical Potential in Solution is a Partial Molar Quantity: The partial molar volume is just one example of many partial molar properties. For example, the partial molar enthalpy, entropy, and Gibbs energy of a constituent in solution are defined as:

$$\bar{H}_i \equiv \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_j} \qquad \bar{S}_i \equiv \left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_j} \qquad \bar{G}_i \equiv \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} \equiv \mu_i \qquad 18.1.12$$

Comparison of the partial molar Gibbs energy with Eq. 16.6.9 shows the partial molar Gibbs energy is just the chemical potential of the substance. The partial molar properties in Eqs. 18.1.12 are the "chemically effective" enthalpy, entropy, and Gibbs energy of a constituent in solution. The partial molar properties include the effects of the concentration dependent changes in intermolecular interactions. The use of partial molar quantities allows the application of the fundamental equations of thermodynamics to solutions without further changes; for example extending Eq. 18.1.2 for a two constituent solution gives:

$$dH = \bar{H}_A\, dn_A + \bar{H}_B\, dn_B \qquad H = \bar{H}_A\, n_A + \bar{H}_B\, n_B \qquad \text{(cst. T\&P)} \qquad 18.1.13$$

$$dS = \bar{S}_A\, dn_A + \bar{S}_B\, dn_B \qquad S = \bar{S}_A\, n_A + \bar{S}_B\, n_B \qquad \text{(cst. T\&P)} \qquad 18.1.14$$

$$dG = \mu_A\, dn_A + \mu_B\, dn_B \qquad G = \mu_A\, n_A + \mu_B\, n_B \qquad \text{(cst. T\&P)} \qquad 18.1.15$$

$$dG = -S\, dT + V\, dP + \mu_A\, dn_A + \mu_B\, dn_B \qquad 18.1.16$$

In this last equation, $S = -(\partial G/\partial T)_{P,n_A,n_B}$ and $V = (\partial G/\partial P)_{T,n_A,n_B}$ are the total entropy and volume at constant composition for the solution from Eqs. 18.1.14 and 18.1.3. The change in chemical potential for a change in pressure and temperature is given by Maxwell relationships, Eqs. 16.6.15-16.6.18:

$$d\mu_i = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_A,n_B} dT + \left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_A,n_B} dP \qquad \text{(cst. } n_A\&n_B\text{)} \qquad 18.1.17$$

$$d\mu_i = -\,\overline{S}_i\, dT + \overline{V}_i\, dP \qquad \text{(cst. } n_A\&n_B\text{)} \qquad 18.1.18$$

This last expression is the "per mole" solution version of $dG = -\,S\,dT + V\,dP$. The chemical potentials of the solute and solvent are related by the Gibbs-Duhem relationship, derived as in Eq. 18.1.7:

$$0 = n_A\, d\mu_A + n_B\, d\mu_B \qquad \text{giving:} \qquad d\mu_B = -\frac{x_A}{1 - x_A}\, d\mu_A \qquad \text{(cst. T\&P)} \qquad 18.1.19$$

These equations form an exact theoretical foundation for non-ideal gas mixtures, solutions, and chemical equilibria. We now show how to apply these relationships.

The Thermodynamics of Solutions is Based on Chemical Potentials: Consider mixing two constituents to form a solution. For n_A moles of A and n_B moles of B the Gibbs energy of mixing is given by Eq. 16.8.6:

$$\Delta_{mix}G = n_A(\mu_A - \mu_A^*) + n_B(\mu_B - \mu_B^*) \qquad \text{(cst. T\&P)} \quad (16.7.6)18.1.20$$

If A is taken as the solvent and n_B is one mole of solute, the Gibbs energy of mixing is the **Gibbs energy of solvation** at the specified concentration, $\Delta_{sol}G_B(x_B)$. The Gibbs energy of solvation is a sensitive measure of the forces that act in solution. The Gibbs energy of formation for a substance in solution, $\Delta_f G°(x_B)$, is the sum of the Gibbs energy of formation of the pure solid, liquid, or gas and the Gibbs energy of solvation:

$$\Delta_f G°(x_B) = \Delta_f G_B^{\circ}(\text{pure}) + \Delta_{sol}G_B(x_B) \qquad \text{(cst. T\&P)} \qquad 18.1.21$$

To make further progress, we need to determine how the chemical potential varies with concentration for a substance and how we can measure the chemical potential.

18.2 Ideal Solutions Follow Raoult's Law

The first step in understanding solutions is to develop a simple conceptual model of solution behavior, called an ideal solution. A good starting point for this discussion is to consider the mixing of ideal gases, as a point of comparison. Based on the chemical potential of an ideal gas, Eqs. 16.8.10°, we showed that the enthalpy of mixing of ideal gases is zero, the entropy of mixing is independent of the identity of the components, and the Gibbs energy of mixing is purely entropy driven, Eqs. 16.8.17°-16.8.18°. After determining the chemical potential of a constituent in solution we consider mixing of constituents to form a solution.

Partial Vapor Pressure is a Function of Concentration: The chemical potential of a constituent in solution can be determined from its vapor pressure. Consider a pure substance in equilibrium with its pure vapor at vapor pressure, P_A^*, Figure 18.2.1a. The chemical potential of the vapor, assuming ideal gas behavior, is given by Eq. 16.6.20°:

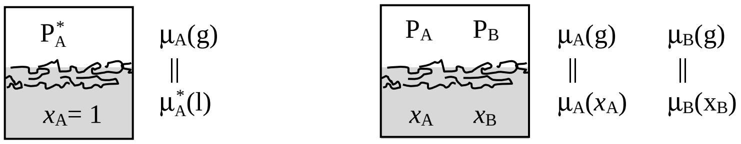
$$\mu_A(g) = \mu_A^\circ(g) + RT \ln P_A^*/P^\circ \qquad \text{(pure)} \qquad 18.2.1^\circ$$

At equilibrium, the pure liquid and its vapor have the same chemical potential:

$$\mu_A^*(l) = \mu_A(g) = \mu_A^\circ(g) + RT \ln P_A^*/P^\circ \qquad \text{(pure)} \qquad 18.2.2^\circ$$

where $\mu_A^*(l)$ is the chemical potential of the pure liquid under its own equilibrium vapor pressure. Now consider a solution with two constituents, A and B, in equilibrium with the vapor above the solution. The equilibrium partial vapor pressures of A and B are P_A and P_B, respectively. The chemical potential of A in the solution, at concentration x_A, is equal to the chemical potential of A in the vapor, Figure 18.2.1b:

$$\mu_A(x_A) = \mu_A(g) = \mu_A^\circ(g) + RT \ln P_A/P^\circ \qquad 18.2.3^\circ$$



(a). pure (b). solution

Figure 18.2.1: (a). A pure liquid under its own equilibrium vapor pressure. (b). A solution under the equilibrium partial vapor pressures P_A and P_B. The partial vapor pressure of a constituent is the "escaping tendency" and is a measure of the chemical potential in solution.

Subtracting Eq. 18.2.2° from Eq. 18.2.3° allows us to compare the chemical potential of the substance in solution to the chemical potential of the pure substance:

$$\mu_A(x_A) - \mu_A^*(l) = RT \ln P_A/P^\circ - RT \ln P_A^*/P^\circ = RT \ln P_A/P_A^* \qquad \text{(cst. T)} \qquad 18.2.4$$

The chemical potential of the pure substance under its pure vapor pressure, P_A^*, can be taken as the reference state, which is the standard state for the solution chemical potential. Adding the pure chemical potential to both sides of Eq. 18.2.4 gives the chemical potential of a substance in solution as:

$$\mu_A(x_A) = \mu_A^*(l) + RT \ln P_A/P_A^* \qquad \text{(cst. T)} \qquad 18.2.5$$

Corresponding equations are written for each constituent in solution. If the vapor phase is not ideal, the partial vapor pressure, P_A, is replaced by the corresponding fugacity, f_A. In summary, at equilibrium, the solution and vapor chemical potentials for each constituent are the same. In turn, the vapor chemical potential is determined by the vapor pressure of the substance. A useful interpretation of Eq. 18.2.5 is that the partial vapor pressure is a direct measure of the chemical potential of a constituent in solution. A large vapor pressure corresponds to a large chemical potential for the substance. For this reason, the equilibrium partial vapor pressure of a substance is called the **escaping tendency**. If the solution environment is unfavorable for a substance, the chemical potential of the substance is large and the vapor pressure is increased because the substance has an increased tendency to escape from the solution and enter the vapor phase. Conversely, favorable solute-solvent interactions stabilize the solution, lower the chemical potential of the substance, and decrease the tendency of the substance to escape into the vapor, lowering the vapor pressure. Our understanding of interactions in solution can now be guided by measurements of the partial vapor pressures above the solution.

Chemical Potentials Depend on Concentration: Consider a range of concentrations for a solution, from very dilute A, $x_A \cong 0$, to pure A, $x_A = 1$. When $x_A = 0$, no A is present and the vapor pressure of A is zero. When $x_A = 1$, the vapor pressure is the pure vapor pressure, P^*_A. Using these limiting values, the simplest possible concentration dependence for the partial vapor pressure of the constituent in solution is the linear relationship:

$$P_A = x_A P^*_A \qquad \text{(ideal solution)} \qquad 18.2.6^*$$

Constituents that follow this relationship are said to be ideal. The expression is called **Raoult's Law.** If all constituents obey Raoult's Law, the solution is an **ideal solution**. The equation numbers for relationships that apply to ideal solutions are shown with a "*." Raoult's Law plays the same role for solutions as the ideal gas law does for gases. However, few solutions are truly ideal. Raoult's Law is never-the-less an excellent point of comparison.

The total vapor pressure above a solution with two ideal constituents is given using Raoult's Law for each constituent:

$$P_{tot} = P_A + P_B = x_A P^*_A + x_B P^*_B \qquad \text{(ideal solution)} \qquad 18.2.7^*$$

The mole fractions are related, since $x_B = 1 - x_A$, and then:

$$P_{tot} = x_A P^*_A + (1 - x_A) P^*_B = (P^*_A - P^*_B)\, x_A + P^*_B \qquad \text{(ideal solution)} \qquad 18.2.8^*$$

Figure 18.2.2 shows the behavior of the vapor pressures for an ideal solution. The partial vapor pressures of the constituents vary linearly with mole fraction according to Raoult's Law, and the total vapor pressure above the solution is also a linear function between the two pure vapor pressures with slope $(P^*_A - P^*_B)$.

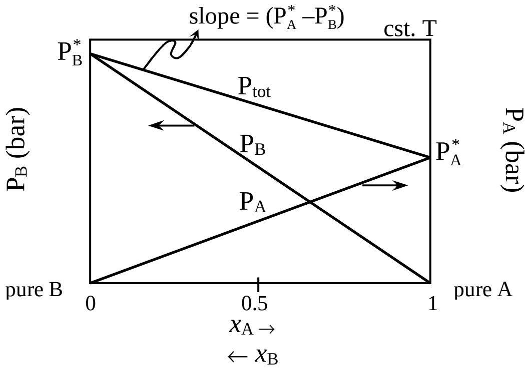


Figure 18.2.2: The total vapor pressure above an ideal solution is a linear function of concentration. Both constituents obey Raoult's Law for an ideal solution. P_A is the partial vapor pressure of A, P_B is the partial vapor pressure of B, and P_{tot} is the total vapor pressure, $P_{tot} = P_A + P_B$.

Most importantly, Raoult's Law allows the determination of the concentration dependence of the chemical potential for a constituent, assuming ideal behavior. Solving Eq. 18.2.6* for the ratio of the partial vapor pressure above the solution to the pure vapor pressure, $P_A/P_A^* = x_A$, and substitution into Eq. 18.2.5 gives:

$$\mu_A(x_A) = \mu_A^*(l) + RT \ln x_A \qquad \text{(ideal solution)} \qquad 18.2.9^*$$

The chemical potential of a constituent in an ideal solution is always less than the pure constituent, since the mole fraction of the solvent is always less than one in a mixture. This ideal solution expression for the chemical potential has a simple interpretation. The concentration dependence of the chemical potential is determined simply by the number of molecules of the substances that make up the solution. The change in chemical potential is purely statistical. The concentration dependence is independent of the identity of the substance. The chemical potential of a constituent in solution is in the same form as the chemical potential of an ideal gas, Eqs. 16.8.10°. We can then conclude that Eqs. 16.8.17°-16.8.18° also hold for ideal solutions, after the substitution of the solution mole fractions, x_i, for the gas phase mole fractions, y_i:

$$\Delta_{mix}S = -\, n_{tot}R \sum_{i=1}^{c} x_i \ln x_i \qquad \text{(ideal solution, cst. T\&P)} \qquad 18.2.10^*$$

$$\Delta_{mix}G = n_{tot}RT \sum_{i=1}^{c} x_i \ln x_i \qquad \text{(ideal solution, cst. T\&P)} \qquad 18.2.11^*$$

The conclusions are: the enthalpy of mixing for an ideal solution is zero, the entropy of mixing is purely statistical, and the Gibbs energy of mixing is entirely entropic, $\Delta_{mix}G = -\,T\,\Delta_{mix}S$, Figure 16.8.2b. However, where an ideal gas mixture has no intermolecular forces, a solution must have strong intermolecular forces; otherwise the condensed phase wouldn't form. For ideal solutions all the intermolecular forces are the same strength; the A–A, B–B, and A–B forces are all equal. Ideal solution behavior has further implications for the thermodynamic forces that are based on the chemical potential.

The pressure derivative of the chemical potential of a constituent in solution is the partial molar volume, Eq. 16.6.16. However, substituting the ideal solution chemical potential from Eq. 18.2.9* gives the result:

$$\bar{V}_A = \left(\frac{\partial \mu_A}{\partial P}\right)_{T,n_A,n_B} = \left(\frac{\partial(\mu_A^* + RT \ln x_A)}{\partial P}\right)_{T,n_A,n_B} = \left(\frac{\partial \mu_A^*}{\partial P}\right)_{T,n_A,n_B} = V_A^* \qquad \text{(ideal)} \qquad 18.2.12^*$$

The mole fraction x_A is a constant because n_A and n_B are constant. The partial molar volume of an ideal constituent is equal to its pure molar volume, $\bar{V}_A = V_A^*$. The consequence is that volumes are additive for ideal constituents. The Gibbs-Helmholtz relationship, Eq 16.3.11, relates the chemical potential to the partial molar enthalpy; substituting in Eq. 18.2.9* gives:

$$-\frac{\bar{H}_A}{T^2} = \left(\frac{\partial(\mu_A/T)}{\partial T}\right)_{P,n_A,n_B} = \left(\frac{\partial(\mu_A^*/T)}{\partial T}\right)_{P,n_A,n_B} + \left(\frac{\partial((RT \ln x_A)/T)}{\partial T}\right)_{P,n_A,n_B} = -\frac{H_A^*}{T^2} \qquad \text{(ideal)}\ 18.2.13^*$$

Again, for an ideal solution, the partial molar enthalpy is equal to the pure molar enthalpy for the constituent, $\bar{H}_A = H_A^*$. The consequence is that the enthalpy of mixing for an ideal solution is zero. These ideal solution results will provide useful simplifications when we consider practical examples. However, we first need to consider the validity of the ideal solution model for real systems.

Example 18.2.1: *Ideal Mixing of Solutions*
Calculate the Gibbs energy of mixing for the formation of a solution of 0.500 mol of ethanol with 0.500 mol of ethyl acetate, assuming an ideal solution at constant pressure and 298.15 K.

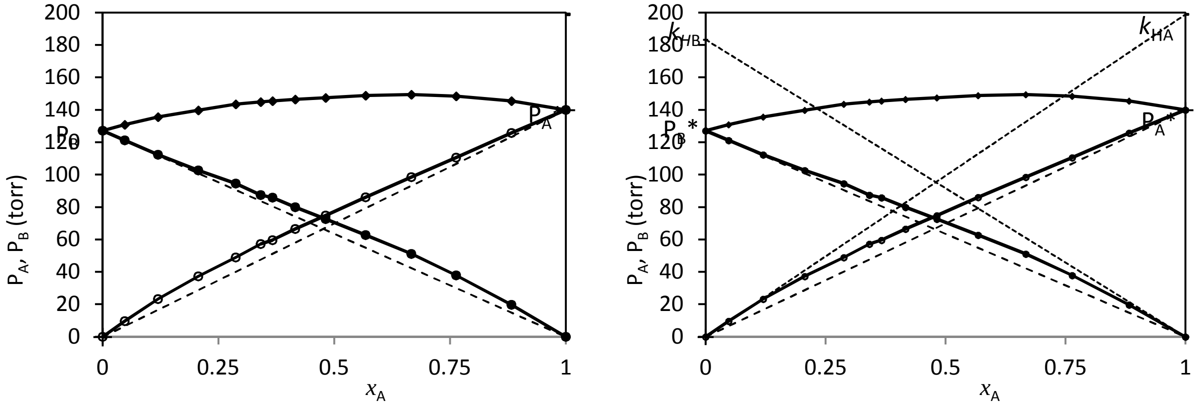
Answer: Using Eq. 18.2.11*, $x_A = x_B = 0.500$, and $n_{tot} = 1.000$ mol:

$$\begin{aligned}\Delta_{mix}G &= n_{tot}RT\,(x_A \ln x_A + x_B \ln x_B)\\ &= 1.00\text{ mol }(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(298.15\text{ K})\,(0.5 \ln 0.5 + 0.5 \ln 0.5)(1\text{ kJ}/1000\text{ J})\\ &= -1.72\text{ kJ}\end{aligned}$$

which is the composition that gives the most favorable Gibbs energy of mixing, Figure 16.8.2b.

18.3 Ideal-Dilute Solutions

The Behavior of the Solute in Dilute Solution is Described by Henry's Law: The vapor pressure diagram for a solution of heptane, A, and 1-bromobutane, B, is shown in Figure 18.3.1a at 50°C.[2]



(a). (b).

Figure 18.3.1: (a). A solution of heptane, A, and 1-bromobutane, B, shows positive deviations from ideality.[2] (Raoult's Law: – – – –) (b). The dilute constituent approaches Henry's Law while the solvent approaches Raoult's Law. (Henry's Law: ----).

Deviations from ideality are judged using the partial vapor pressure, which is the escaping tendency. Solutions with positive deviations from ideality have partial vapor pressures greater than predicted by Raoult's Law. Conversely, solutions with negative deviations from ideality have partial vapor pressures less than predicted by Raoult's Law. Solutions of 1-bromobutane and heptane show positive deviations from Raoult's Law. Positive deviations result when the forces that act in solution are unfavorable compared to the forces in the pure liquids;

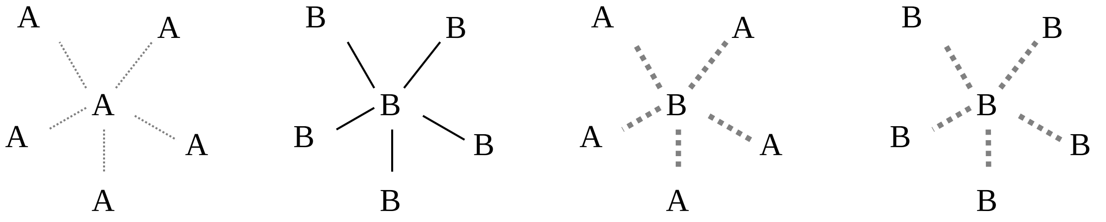
A–B < A–A, B–B. Negative deviations result when the forces that act in solution are favorable compared to the forces in the pure liquids; A–B > A–A, B–B.

Notice that as x_A approaches 1, that heptane's vapor pressure approaches Raoult's Law. As x_B approaches 1, 1-bromobutane's vapor pressure also approaches Raoult's Law. In this sense, Raoult's Law is a limiting law. When $x_A \approx 1$, heptane can be considered as the solvent and the vapor pressure of the solvent follows Raoult's Law, $P_A = x_A\, P^*_A$. When $x_B \approx 1$, 1-bromobutane can be considered as the solvent and the vapor pressure of the solvent, one again, follows Raoult's Law, $P_B = x_B\, P^*_B$. On the other hand, the dilute constituent also approaches linear behavior, but the slope of the vapor pressure curve has a different slope than the Raoult's Law prediction, Figure 18.3.1b. For example, at the right side of the vapor pressure diagram where $x_B \approx 0$, the vapor pressure curve for B approaches a straight line:

$$P_B = k_{H,B}\, x_B \qquad \text{(dilute solute)} \quad 18.3.1^{\dagger}$$

This expression is **Henry's Law,** and $k_{H,B}$ is the **Henry's Law constant** for B acting as the solute in dilute solution. $k_{H,B}$ is the limiting slope of the vapor pressure curve as $x_B \rightarrow 0$. The Henry's Law constant for B is also obtained by extrapolating the dilute solution partial vapor pressure of B to $x_B = 1$, as shown in the figure. Solutions that follow Henry's law for the solute and Raoult's Law for the solvent are called **ideal-dilute solutions**. Henry's Law is also a limiting law; all solutions approach ideal-dilute behavior in the dilute solution limit. The equation numbers for relationships that apply to ideal-dilute solutions are shown with a "†." Similarly, at the left side of the vapor pressure diagram, constituent A can be considered the solute in a dilute solution in B as the solvent, for which Henry's Law is $P_A = x_A\, k_{H,A}$.

Henry's Law constants can be interpreted in light of the forces that act in solution.



(a). pure A (b). pure B (c). dilute solution (d). Henry's Law model

Figure 18.3.2: (a). In pure A, A molecules are surrounded by only A molecules with A–A forces. (b). In pure B, B molecules are surrounded by only B molecules with B–B forces. (c). In dilute solution, B molecules are surrounded by A molecules with A–B forces. (d). The Henry's Law constant is the vapor pressure of B as a hypothetical "pure" substance, but with the A–B forces that act in dilute solution.

$k_{H,B}$ is the dilute solution partial vapor pressure of B extrapolated to $x_B = 1$. The Henry's Law constant for a substance can then be thought of as the vapor pressure the substance would exert if the forces that act in a solution of pure B are replaced by the forces that act in dilute solution, Figure 18.3.2d. Such a model is "hypothetical;" an actual solution with $x_B = 1$ has the vapor pressure, P^*_B. But, thinking of the Henry's Law constant using this hypothetical model provides a useful interpretation of this important quantity. Another way to consider the forces that act in dilute solution is to note that Henry's Law can be rearranged to give an expression that has $k_{H,\mathrm{B}}$ acting as an equilibrium constant for the **desolvation** process:

$$\mathrm{B}\ (x_\mathrm{B}) \overset{k_{H,\mathrm{B}}}{\rightleftarrows} \mathrm{B}\ (\text{gas}, \mathrm{P_B}) \qquad k_{\mathrm{H,B}} = \frac{\mathrm{P_B}}{x_\mathrm{B}} \qquad \text{and} \quad \Delta_{\text{desol}}\mathrm{G}^\circ = -\ \mathrm{RT}\ \ln k_{\mathrm{H,B}} \qquad 18.3.2^\dagger$$

Remember from General Chemistry that standard state reaction Gibbs energies and equilibrium constants are related by $\Delta_\mathrm{r}\mathrm{G}^\circ = -\ \mathrm{RT}\ \ln \mathrm{K_{eq}}$. For the specific process in Eq. 18.3.2†, $\Delta_{\text{desol}}\mathrm{G}^\circ$ is the **Gibbs energy of desolvation** from dilute solution to give the substance in the gas phase. Note that $\Delta_{\text{desol}}\mathrm{G}^\circ = -\ \Delta_{\text{sol}}\mathrm{G}$ for the gas phase of the substance, with $\Delta_{\text{sol}}\mathrm{G}^\circ$ as defined in Eq. 18.1.20. The substance partitions between the solution and the gas phase with the equilibrium ratio $k_{\mathrm{H,B}} = \mathrm{P_B}/x_\mathrm{B}$.

Henry's Law is introduced in General Chemistry texts with reference to gases dissolved in solution. Henry's Law can be thought of as the solubility of a gas at partial pressure $\mathrm{P_B}$ to give a solution at concentration x_B. However, Henry's Law holds for all solutions, with gas, liquid, and solid solutes, in the dilute solution limit. Second only to the chemical potential, Henry's Law is the most fundamental thermodynamic construct that allows the study of intermolecular forces in solution. Henry's Law has many practical consequences. The equilibrium concentration of oxygen in water is determined by Henry's Law, which in turn determines the availability of oxygen for aquatic organisms. Henry's Law constants correlate strongly with the ability of an environmental pollutant to migrate in ground water. Extensive tabulations of aqueous Henry's Law constants have been established for this reason.[3,4] Most importantly, Gibbs energies of desolvation are used to estimate Gibbs energies of formation for substances in solution based on the gas phase results from molecular mechanics and molecular orbital calculations.[5]

Vapor phase and solution phase concentrations in molar terms are often more convenient, instead of the vapor pressure in bars and the mole fraction in solution, Table 18.3.1. The conversion to concentration units is based on $\mathrm{P_B} = \mathrm{c_B}\ \mathrm{RT}$ for the gas phase and Eqs. 2.2.16-2.2.17 for the solution concentration. Henry's Law can be written in alternate units as:[6]

vapor pressure and solution concentration: $\mathrm{P_B} = k_{\mathrm{pc,B}}\ \mathrm{c_B} \qquad \Delta_{\text{desol}}\mathrm{G}^\circ_{\mathrm{pc}} = -\ \mathrm{RT}\ \ln k_{\mathrm{pc,B}} \qquad 18.3.3^\dagger$

$\mathrm{P_B} = k_{\mathrm{pm,B}}\ \mathrm{m_B} \qquad \Delta_{\text{desol}}\mathrm{G}^\circ_{\mathrm{pm}} = -\ \mathrm{RT}\ \ln k_{\mathrm{pm,B}} \qquad 18.3.4^\dagger$

vapor and solution concentrations: $\mathrm{c_B(g)} = k_{\mathrm{cc,B}}\ \mathrm{c_B} \qquad \Delta_{\text{desol}}\mathrm{G}^\circ_{\mathrm{cc}} = -\ \mathrm{RT}\ \ln k_{\mathrm{cc,B}} \qquad 18.3.5^\dagger$

where k_{pc} is the Henry's Law constant for the vapor pressure given as a function of the solution molarity, k_{pm} is the Henry's Law constant for the vapor pressure given as a function of the solution molality, and k_{cc} is the Henry's Law constant for the vapor phase concentration as a function of the solution molarity. Henry's Law holds in the limit of very dilute solutions, for which the conversion from mole fraction to concentration is given by Eqs. 2.2.15-2.216:

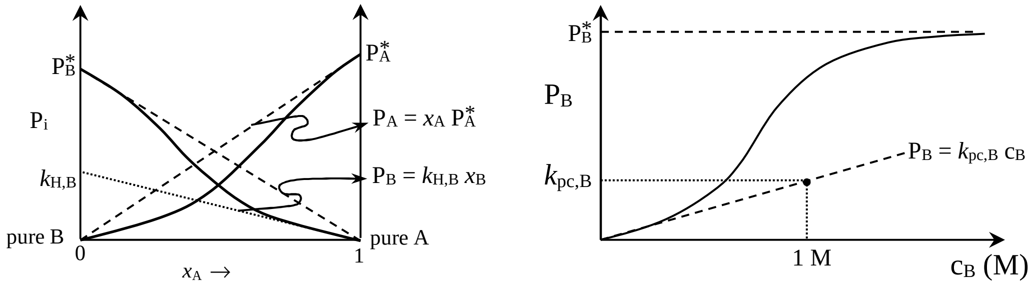
$$k_{\mathrm{pc,B}} = \frac{k_{\mathrm{H,B}}\ (1\ \mathrm{L})}{1000\ \mathrm{mL}\ \mathrm{d_{soln}}/\mathfrak{M}_\mathrm{A}} \qquad k_{\mathrm{pm,B}} = \frac{k_{\mathrm{H,B}}\ (1\ \mathrm{kg})}{1000\ \mathrm{g}/\mathfrak{M}_\mathrm{A}} \qquad k_{\mathrm{cc,B}} = \frac{k_{\mathrm{H,B}}\ (1\ \mathrm{L})}{(1000\ \mathrm{mL}\ \mathrm{d_{soln}}/\mathfrak{M}_\mathrm{A})\mathrm{RT}} \qquad 18.3.6^\dagger$$

In aqueous solution at 25°C, $k_{\mathrm{pc,B}} = k_{\mathrm{H,B}}/55.34\ \mathrm{mol\ L^{-1}}$, $k_{\mathrm{pm,B}} = k_{\mathrm{H,B}}/55.51\ \mathrm{mol\ kg^{-1}}$, and $k_{\mathrm{cc,B}} = \mathrm{k_{H,B}}/(55.34\ \mathrm{RT})$. Graphically, the Henry's Law constant in terms of molarity or molality can also be determined by extrapolating dilute solution behavior to unit concentration on a molarity or molality scale, Figure 18.3.3. The k_{pm} form is in the appropriate units for the calculation of the standard state Gibbs energy of formation of a substance in solution at unit molality from the pure substance Gibbs energies of formation using Eq. 18.1.21. The k_{cc} form is in the appropriate units for the calculation of the Gibbs energy of formation of a substance in solution from molecular mechanics and molecular orbital internal energy calculations, at constant volume.[6]

Table 18.3.1:(DS) Henry's Law constants and Gibbs energies of desolvation. The number in parenthesis is the literature source for that substance and following substances. The literature value is shown in bold. The remaining values are derived using Eqs. 18.3.2†-18.3.6†.*

substance	k_H bar	k_{cc} unitless	k_{pc} bar L mol^{-1}	$\Delta_{desol}G°$ kJ mol^{-1}	$\Delta_{desol}G^{\circ}_{cc}$ kJ mol^{-1}	$\Delta_{desol}G^{\circ}_{pc}$ kJ mol^{-1}
benzene (6)	296.	**0.216**	5.35	-14.11	3.80	-4.16
methyl-*t*-butyl ether	29.6	**0.0216**	0.54	-8.40	9.51	1.55
trichloroethylene (7)	538.	**0.392**	9.72	-15.59	2.32	-5.64
carbon tetrachloride	$1.71\text{x}10^3$	**1.244**	30.84	-18.45	-0.54	-8.50
methane (8)	$\mathbf{4.19x10^4}$	30.5	757.	-26.38	-8.48	-16.43
O_2	$\mathbf{4.40x10^4}$	32.1	795.	-26.50	-8.60	-16.56
CO_2+H_2CO_3 (pure H_2O)	$\mathbf{1.67x10^3}$	1.20	30.2	-18.40	-0.49	-8.45
CO_2+H_2CO_3 (sea H_2O,9)	$1.9\text{x}10^3$	1.38	**34.3**	-18.72	-0.81	-8.77

*The SI units are Pa m^3 mol^{-1}; example: for benzene k_{pc} = 5.35 bar L mol^{-1}(100 Pa bar^{-1} m^3 L^{-1}) = 535. Pa m^3 mol^{-1}.



(a). Mole Fraction (b). Molarity

Figure 18.3.3: The Henry's Law constants and corresponding standard states are extrapolated values at unit concentration. (a). On a mole fraction basis, a Raoult's Law standard state at P^*_A is usually chosen for the solvent and a Henry's Law standard state at $k_{H,B}$ is chosen for the solute. (b). To use molarity, the solute vapor pressure data is replotted versus molarity. The solute standard state is at unit concentration with $P_B = k_{pc,B}(1\text{ M})$.

Example 18.3.1: *Using Henry's Law*

The standard state Gibbs energy of formation of gas phase ethylene is 68.15 kJ mol^{-1} at 25°C. The Henry's Law constant for ethylene in aqueous solution is $k_H = 1.13\text{x}10^4$ bar. Calculate the standard state Gibbs energy of formation of ethylene in water at 25°C assuming molar concentrations.

Answer: The gas phase standard state is P° = 1 bar. The solution standard state concentration is 1 M, if the concentration is expressed in terms of molarity. The units for the Henry's Law constant that correspond to these standard states is $k_{pc,B}$ in bar L mol^{-1}. Using Eqs. 18.3.6†:

$$k_{pc,B} = \frac{k_{H,B}}{55.34 \text{ mol L}^{-1}} = \frac{1.13\text{x}10^{4} \text{ bar}}{55.34 \text{ mol L}^{-1}} = 204.2 \text{ bar L mol}^{-1}$$

The corresponding Gibbs energy of desolvation is given by Eqs. 18.3.3†:

$$\begin{aligned}\Delta_{desol}G^{\circ}_{pc} &= -\,RT \ln k_{pc,B} = -\,8.3145 \text{ J K}^{-1} \text{ mol}^{-1}(298.15 \text{ K})(1 \text{ kJ}/1000 \text{ J}) \ln 204.2 \\ &= -13.19 \text{ kJ mol}^{-1}\end{aligned}$$

Noting that $\Delta_{sol}G° = -\,\Delta_{desol}G^{\circ}_{pc}$ gives the standard state Gibbs energy of formation for aqueous ethylene as, Eq. 18.1.21:

$$\Delta_f G°(aq) = \Delta_f G°(g) + \Delta_{sol}G° = 68.15 \text{ kJ mol}^{-1} + 13.19 \text{ kJ mol}^{-1} = 81.34 \text{ kJ mol}^{-1}$$

Example 18.3.2: *Calculating Henry's Law Constants*
The vapor pressure of 1-bromobutane as a function of concentration in heptane is given by the following power series fit to the experimental data. Calculate the Henry's Law constant.

$$P_{vap} = a\, x_B^{3} + b\, x_B^{2} + c\, x_B$$
with a = 0.0734 ± 0.00514, b = -0.14869 ± 0.0075, c = 0.2445 ± 0.0026 bar

Answer: The slope of the vapor pressure curve is given by the derivative with respect to the mole fraction:

$$\frac{dP_{vap}}{dx_B} = 3\,a\,x_B^{2} + 2\,b\,x_B + c$$

In the dilute solution limit, $x_B \rightarrow 0$ giving $k_{H,B} = (dP_{vap}/dx_B|_{x_B = 0} = c = 0.2445 \pm 0.0026$ bar or 183.4 ± 1.9 torr, Figure 18.3.1b.

Few solutions are ideal for both the solvent and solute. However, all solutions approach ideal-dilute behavior in the dilute solution limit. In dilute solution, we describe the behavior of the solvent using Raoult's Law and the solute using Henry's Law.

Ideal-Dilute Solutions Assume a Raoult's Law Standard State for the Solvent and a Henry's Law Standard State for the Solute: The chemical potential of the solvent in an ideal-dilute solution is given by Eq. 18.2.9*, based on Raoult's Law. The standard state for the solvent is the pure liquid with vapor pressure P^*_A, Figure 18.3.3a, and the standard state chemical potential is given by Eq. 18.2.2°. However, the solute in an ideal-dilute solution isn't accurately described by Eq. 18.2.9*, because the solute follows Henry's Law. The appropriate standard state vapor pressure for the solute is $k_{H,B}$ not P^*_B. Describing the chemical potential of the ideal solute directly in terms of the solute mole fraction requires a change in standard state. Substituting Henry's Law, $P_B = k_{H,B}\, x_B$, into the general equation for the chemical potential, Eq. 18.2.3°, gives for the solute:

$$\mu_B(x_B) = \mu_B^\circ(g) + RT \ln k_{H,B}\, x_B/P^\circ \qquad \text{(dilute solute)} \quad 18.3.7^\dagger$$

$$\mu_B(x_B) = \mu_B^\circ(g) + RT \ln k_{H,B}/P^\circ + RT \ln x_B \qquad \text{(dilute solute)} \quad 18.3.8^\dagger$$

Eq. $18.3.7^\dagger$ can be conveniently written in the same form as Eq. $18.2.9^*$ if we define a new **Henry's Law standard state** for the solute, $\mu_B^\dagger(l)$:

$$\mu_B^\dagger(l) \equiv \mu_B^\circ(g) + RT \ln k_{H,B}/P^\circ \qquad 18.3.9^\dagger$$

Substitution of the Henry's Law standard state into Eq. $18.3.7^\dagger$ gives the chemical potential of the solute in an ideal-dilute solution as:

$$\mu_B(x_B) = \mu_B^\dagger(l) + RT \ln x_B \qquad \text{(ideal dilute solute)} \quad 18.3.10^\dagger$$

To convert from mole fraction based standard states to molarity or molality standard states, we simply express Henry's Law in terms of molarity or molality, Eqs. $18.3.3^\dagger$-$18.3.4^\dagger$:

$$\mu_B = {}^c\mu_B^\circ(l) + RT \ln c_B/c^\circ \quad \text{with} \quad {}^c\mu_B^\circ(l) \equiv \mu_B^\circ(g) + RT \ln k_{pc,B}/P^\circ \quad \text{(ideal dilute)} \quad 18.3.11^\dagger$$

$$\mu_B = {}^m\mu_B^\circ(l) + RT \ln m_B/m^\circ \quad \text{with} \quad {}^m\mu_B^\circ(l) \equiv \mu_B^\circ(g) + RT \ln k_{pm,B}/P^\circ \quad \text{(ideal dilute)} \quad 18.3.12^\dagger$$

where the standard state chemical potentials are ${}^c\mu_B^\circ$ or ${}^m\mu_B^\circ$. The superscripts "c" or "m" indicate that the concentration is expressed as a molarity or molality in defining the standard state.

Keeping the same equation forms for the chemical potential of the solvent and the solute simplifies derivations of solution properties; to change between the solvent and solute, we just switch standard states and x_B, c_B, or m_B for x_A. A Raoult's Law standard state is used for the solvent and a Henry's Law standard state is used for the solute, by convention. This choice of standard states guarantees that when the solvent behaves ideally, the solute also behaves ideally, and Eqs. $18.2.9^*$, $18.3.10^\dagger$-$18.3.12^\dagger$ accurately represent the chemical potentials in the solution. This convention also allows the use of a Raoult's Law standard state for the solvent for any solution, ideal or real. Raoult's Law is the basis for the treatment of distillation and colligative properties.

18.4 Phase Transitions for Binary Mixtures

We begin the discussion of phase transitions in binary systems with liquid-vapor transitions in binary mixtures of two volatile components. The theory of solutions with two volatile components provides an explanation of distillation.

Raoult's Law is Used to Understand Distillation: Distillation is an important method for purifying substances. What level of purity can be obtained using a simple distillation? Raoult's Law provides the underlying theory. Conventional distillations are done at constant pressure, while changing the temperature. However, distillations are also often done at constant temperature, while changing the total pressure. Reduced pressure distillations lower the temperature for the separation, which helps avoid thermal decomposition. We begin our discussion with examples based on reduced pressure distillation, and then we discuss constant pressure distillation. Assume a binary mixture of ideal, volatile components, A and B. We begin by summarizing the relationships that determine the equilibrium state of the system as a function of concentration for ideal solutions:

- In solution—Raoult's Law: $P_A = x_A P_A^*$ $\quad P_B = x_B P_B^*$ (ideal) (18.2.6*)
- In the vapor—Dalton's Law: $P_{tot} = P_A + P_B = x_A P_A^* + x_B P_B^*$ (ideal) (18.2.7*)

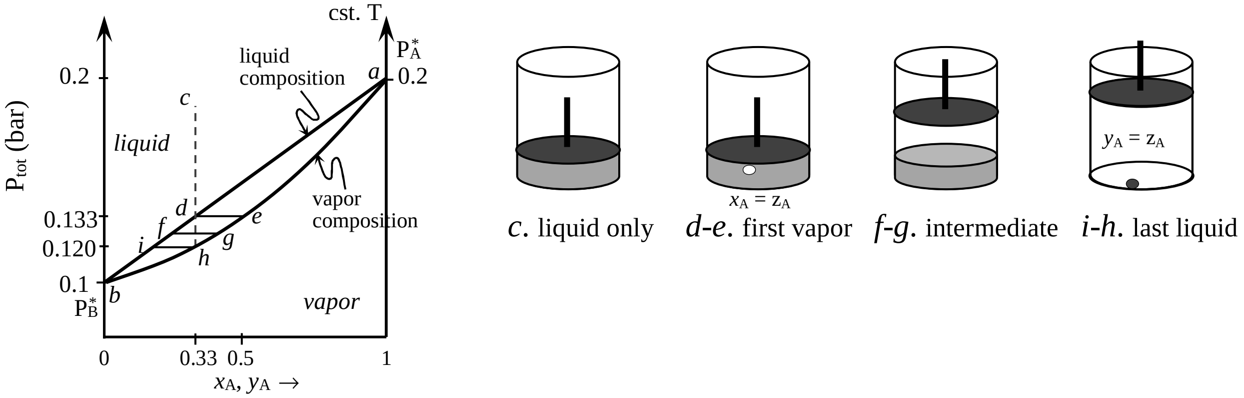
$$P_{tot} = x_A P_A^* + (1 - x_A) P_B^* \qquad \text{(ideal)} \quad (18.2.8^*)$$

$$P_A = y_A\, P_{tot} \quad \text{or} \quad y_A = P_A/P_{tot} \qquad \text{(ideal)} \quad (2.1.10°)$$

$$\text{giving} \quad y_A = \frac{x_A P_A^*}{P_{tot}} = \frac{x_A P_A^*}{x_A P_A^* + (1 - x_A P_A^*)} \qquad \text{(ideal)} \quad 18.4.1^*$$

Consider a constant temperature, reduced pressure distillation with $n_A = 1$ mol and $n_B = 2$ mol. Assume the vapor pressure of pure A is 0.200 bar and the vapor pressure of pure B is 0.100 bar. The system is closed so the overall composition is constant. However, as the distillation proceeds, A and B are transferred from the liquid phase into the vapor phase. Let z_A be the overall composition of the system, including the liquid and the vapor. For this example, $z_A = n_A/n_{tot} = 1/3$. In the phase diagram for the binary mixture, the total vapor pressure above the solution is plotted as a function of the composition of the liquid, x_A, Figure 18.4.1a. The composition axis is also used for the composition of the vapor that is in equilibrium with the solution, y_A. At high pressure only the liquid phase exists, at low pressure only the vapor exists, and for intermediate pressures, two-phases exist in equilibrium. The two-phase region is bounded by the liquid and vapor composition curves. The vapor pressure of pure A is at point *a*, and the vapor pressure of pure B is at point *b*. Pictorial representations of the other labeled states during the distillation are shown in Figure 18.4.1b.

A distillation begins with only the liquid mixture present at high pressure, point *c*. The total pressure is lowered until the **first vapor** appears, at point *d* with $x_A = z_A$, which corresponds to the beginning of the distillation. The composition of the first vapor is richer than the liquid in the more volatile component, point *e*. The line connecting the liquid and vapor compositions at a given total pressure is called a **tie line**. The liquid and vapor compositions at the ends of the tie line are at equilibrium; the chemical potentials of each component are equal in the two phases.



c. liquid only *d-e*. first vapor *f-g*. intermediate *i-h*. last liquid

Figure 18.4.1: (a). Total vapor pressure as a function of the composition of the solution and the vapor for a reduced-pressure, single-plate distillation, assuming ideal solution behavior at constant temperature. (b). The system corresponding to labeled points during the distillation.

As the distillation proceeds, the liquid is depleted of the more volatile component, A. The composition of the remaining liquid has smaller x_A and the tie line moves to the left as the total pressure is decreased, point *f*. The distillation continues as the total pressure is reduced to point *h*. At point *h*, the vapor composition equals the overall system composition, $y_A = z_A$, indicating that all the liquid has been vaporized. The distillation is then complete. The composition of the last remaining drop of liquid is determined by finding the intersection of the tie line with the liquid composition curve, point *i*.

In practical distillations, the vapor is withdrawn and condensed to form the **distillate**. The flask containing the original solution is called the **pot**. The more volatile substance is recovered from the distillate and the less volatile from the pot. This type of distillation is called a **single-plate** distillation, since the vapor is always in equilibrium with the original solution in the pot. In this single-plate distillation, the purest that A may be obtained is from the first vapor at point *e*. As the distillation proceeds, the composition of the vapor has decreased purity for A. The purest that B may be obtained is from the pot for the **last liquid**, point *i*. This example single-plate distillation does not significantly increase the purity of either A in the distillate or B in the pot. Distillations are not an efficient means for purifying substances, unless the pure vapor pressures of the substances are very different. In addition, the energy necessary to do the distillation is roughly the sum of the enthalpies of vaporization for the two substances. The energy necessary to separate ethanol from water is one of the reasons that replacing petroleum with corn-based ethanol as the primary transportation fuel was abandoned in the US in 2009. However, ethanol-gasoline mixtures are useful to build the octane rating.

Example 18.4.1: *First Vapor*

Calculate the total pressure and composition of the first vapor that forms for a solution of 1.00 mol of A and 2.00 mol of B, if the pure vapor pressures are $P_A^* = 0.200$ bar and $P_B^* = 0.100$ bar (point *e* in Figure 18.4.1). Assume an ideal solution.

Answer: The composition of the solution when the first small amount of vapor forms is essentially the bulk composition, $x_A = z_A = 0.333$, $x_B = 0.667$. Using Eq. 18.2.7* for the total equilibrium vapor pressure gives:

$$P_{tot} = x_A P_A^* + x_B P_B^* = 0.333(0.200 \text{ bar}) + 0.667(0.100 \text{ bar}) = 0.133 \text{ bar}$$

The composition of the vapor is given by Dalton's Law, Eq. 2.1.10°, and Raoult's Law for the solution, Eq. 18.2.6*:

$$y_A = P_A/P_{tot} = x_A P_A^*/\ P_{tot} = 0.333(0.200 \text{ bar})/0.133 \text{ bar} = 0.500$$

which is the highest purity for A possible, as recovered by condensing this first vapor. The vapor is richer in the more volatile constituent, A, as expected.

Example 18.4.2: *Last Liquid*

Calculate the total pressure and composition of the last liquid that remains for a solution of 1.00 mol of A and 2.00 mol of B, if the pure vapor pressures are $P_A^* = 0.200$ bar and $P_B^* = 0.100$ bar (point *i* in Figure 18.4.1). Assume an ideal solution.

Answer: The composition of the vapor that is in equilibrium with the last liquid is essentially the bulk composition, $y_A = z_A = 0.333$. Using Eq. 18.4.1*, we can solve for the solution composition that is in equilibrium with the vapor:

$$0.333 = \frac{x_A(0.200 \text{ bar})}{x_A(0.200 \text{ bar}) + (1 - x_A)(0.100 \text{ bar})}$$

Solving for the solution composition gives $x_A = 0.200$, which is the highest purity for B possible, as recovered from the pot from this last drop. We then use Eq. 18.2.8* to find the total pressure for this last liquid:

$$P_{tot} = x_A P_A^* + (1 - x_A)P_B^* = 0.200(0.200 \text{ bar}) + (1 - 0.200)(0.100 \text{ bar}) = 0.120 \text{ bar}$$

The liquid-vapor phase diagram at constant pressure for a binary solution of two-volatile components is a plot of the boiling-point as a function of composition of the solution and the vapor, Figure 18.4.2. To construct the phase diagram, the Clausius-Clapeyron equation, Eq. 17.1.13° or 17.1.14°, is used to find the temperature variation of the vapor pressure of the two pure components. Raoult's Law then allows the phase diagram for liquid-vapor equilibrium at constant pressure to be plotted. The boiling point of the solution is the equilibrium temperature at which the total vapor pressure is equal to the applied pressure. The high temperature phase is the vapor phase, and the low temperature phase is the liquid phase. The endpoints of the solution and vapor composition curves are the pure component boiling points, T_{bA}^* and T_{bB}^*. The next example shows how to construct the phase diagram at constant pressure.

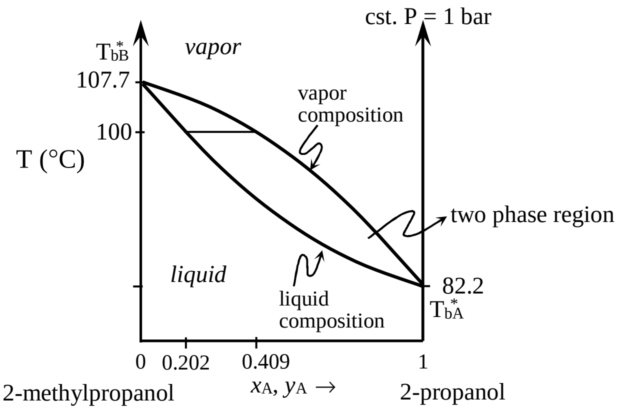


Figure 18.4.2: Liquid-vapor phase diagram at constant pressure for a binary solution of two-volatile components; the boiling-point as a function of composition. Data shown is for 2-propanol and 2-methyl-1-propanol, which form an ideal solution. The tie line joins the solution and vapor compositions that are at equilibrium at the given temperature.

Example 18.4.3: *Boiling point versus composition*

2-Propanol and 2-methylpropanol form an ideal solution. Calculate the composition of the solution and vapor that boils at 100.0°C and an ambient pressure of 1.00 bar. The vapor pressure of pure 2-propanol is 202.3 kPa and the vapor pressure of pure 2-methylpropanol is 74.1 kPa at 100°C.

Answer: The total vapor pressure is equal to the ambient pressure at the boiling point. Let A be 2-propanol. Converting to bar and using Eq. 18.2.8* gives the composition of the solution from:

$$P_{tot} = x_A P_A^* + (1 - x_A)P_B^* = x_A(2.023 \text{ bar}) + (1 - x_A)(0.741 \text{ bar}) = 1.00 \text{ bar}$$

Solving for the solution concentration of A: $x_A = 0.202$.

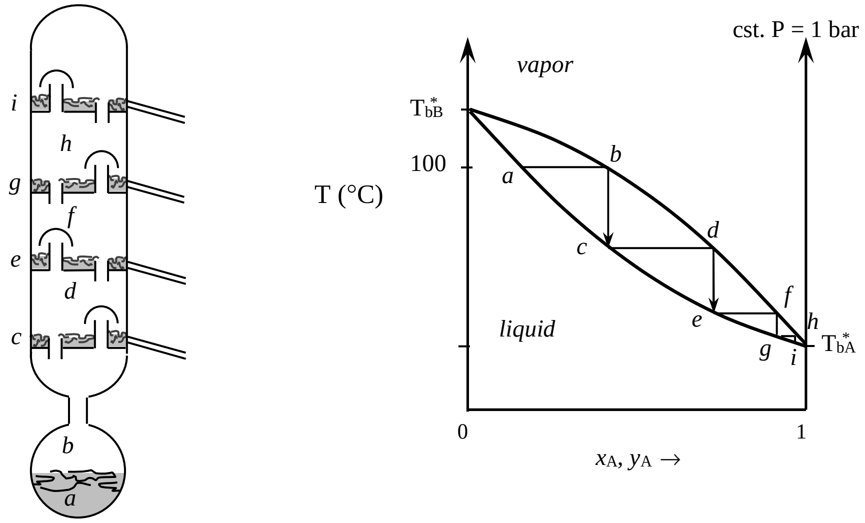
The vapor phase concentration is calculated using Eq. 2.1.10° and Raoult's Law for A, Eq. 18.2.6*:

$$y_A = P_A/P_{tot} = x_A P_A^*/P_{tot} = 0.202(2.023 \text{ bar})/1.00 \text{ bar} = 0.409$$

As a check on this calculation, we note that the vapor is richer in the more volatile component, A, as expected. These points are included in Figure 18.4.2. A tie line is drawn between the solution and vapor compositions that are in equilibrium at the chosen temperature.

This last example only generates two points on the phase diagram. To complete the phase diagram, additional calculations are necessary at a range of boiling points between T_{bA}^* and T_{bB}^*. Liquid-vapor phase diagrams are used to understand constant pressure distillations. Using Example 18.4.3, if the initial pot in the distillation has a composition for A of 0.202 then the first vapor has a composition of 0.409 at 100°C, which is the highest purity for A possible in a single-plate distillation starting from the initial concentration. Once again a single-plate distillation is seen to be an ineffective way to achieve a separation.

Fractional distillations are necessary to achieve effective separations. A bubble-cap distillation column is convenient for describing fractional distillation, Figure 18.4.3a. The initial pot concentration is point *a* in the phase diagram, Figure 18.4.3b. The composition of the vapor above the pot is on the right end of the first tie line, point *b*.



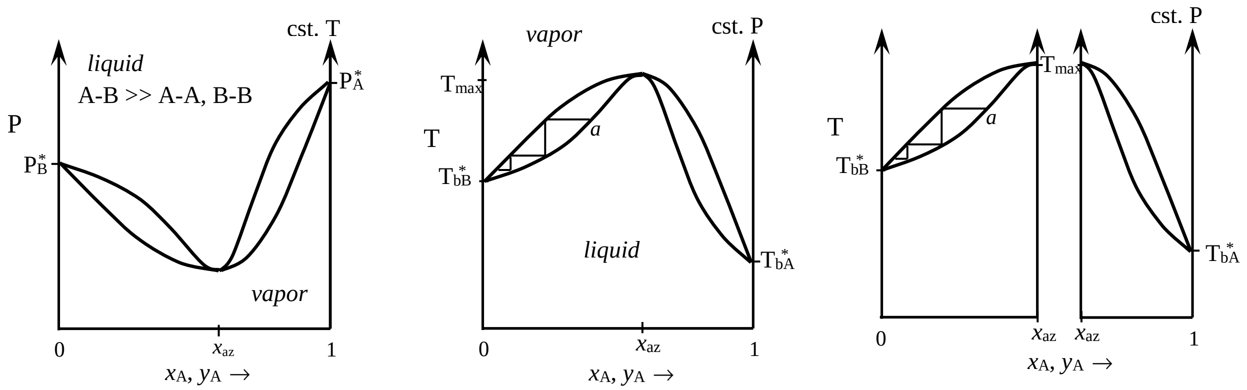
(a). (b).

Figure 18.4.3: (a). A bubble-cap fractional distillation column. (b). A fractional distillation with four theoretical plates. An exhaustive fractional distillation for an ideal solution gives pure A, the more volatile component, in the distillate and pure B in the pot.

During the distillation this vapor condenses onto the first plate, which is at the same concentration as the vapor but on the liquid curve, point *c*. As the temperature rises, the condensate on the first plate at point *c* boils producing vapor with a composition at the end of the second tie line, point *d*. This vapor condenses on the second plate, point *e*. The vapor from the second plate, point *f*, condenses on the third plate, point *g*. This process continues for as many plates as there are in the column. Vapor flows upward from each plate to the next, and excess solution at each plate overflows back to the preceding plate. At each successive plate, the condensate composition becomes richer in the more volatile component. Each successive plate corresponds to equilibrium at the respective temperature as represented by the corresponding tie line. An **exhaustive fraction distillation** is the logical extreme for an infinite number of plates. An exhaustive fractional distillation for an ideal solution gives pure A, the more volatile component, in the distillate. As A is removed in the distillate, the pot becomes richer in B. In an exhaustive fractional distillation, pure B is recovered from the pot.

Each plate can be separately drained by a tap. In the petroleum industry, the different taps produce different products of successively higher boiling range: fuel oil and diesel, 250-350°C; kerosene, 175-325°C; gasoline, 40-205°C; ligroin, 60-100°C. Gaseous nitrogen is separated from liquid oxygen in liquid air by fractional distillation. Bubble cap columns are not used in the laboratory; instead, glass columns are packed with glass spirals or stainless steel ribbons, or are indented to produce greater surface area. In a packed column, the length of column that gives a composition enhancement equivalent to a tie line on the phase diagram is called the **height equivalent of the theoretical plate, HETP**. The length of the column divided by the HTEP gives the number of effective plates for the column. Our predictions so far are based on ideal solution theory. Practical systems often show strong deviations from ideality.

Favorable interactions in solution, A-B >> A-A, B-B, cause large negative deviations from ideality. In extreme cases, negative deviations result in a minimum in the vapor pressure phase diagram and a corresponding maximum in the boiling point phase diagram, Figure 18.4.4ab. On the other hand, very weak interactions in solution cause a maximum in the vapor pressure diagram and a corresponding minimum in the boiling point phase diagram.



(a). (b). (c).

Figure 18.4.4: (a) Vapor pressure phase diagram for a system with strong negative deviations from ideality, giving a maximum boiling azeotrope. (b). Boiling point diagram for a system with a maximum boiling azeotrope. (c). Treat the diagram on either side of the azeotrope as a separate, simple, binary liquid-vapor phase diagram.

The composition that gives the extreme boiling point is called the *azeotropic composition*. An *azeotrope* behaves as if the solution were a pure substance during distillation. The vapor above a solution at the azeotropic composition has the same composition as the solution. Binary azeotropes cannot be purified by distillation. Analyzing a phase diagram that has an azeotrope can be simplified by treating the azeotrope as a hypothetical pure substance and dividing the phase diagram to either side as separate binary systems, Figures 14.4c.

Example 18.4.4: *Azeotropes*

Chloroform and acetone form a maximum boiling azeotrope. Figure 18.4.4 is a schematic representation of the phase diagram, with acetone as component A. Consider distilling a solution with $x_A = 0.33$. What will be recovered in the distillate and pot from an exhaustive fractional distillation?

Answer: Using Figure 18.4.4c, the initial concentration, point *a*, is less than the azeotropic concentration. The tie line extends to lower concentrations for A. An exhaustive fractional distillation gives component B, chloroform, in the distillate and azeotrope in the pot. The maximum concentration of acetone for this distillation is the azeotropic concentration.

Ethanol and water form a minimum boiling azeotrope with a composition of 95.6% ethanol by volume, 89.5 mol% ethanol at 78.1 °C and one atmosphere. The concentration of ethanol from fermentation reaches a maximum of about 15%. Fractional distillation produces azeotrope as the distillate, which is the maximum concentration of ethanol available from distillation of ethanol/water binary mixtures from fermentation. For use in transportation fuels, ethanol must contain less than 0.7% water. The final step in removing water is by dehydration with a zeolite, which is a type of molecular sieve. The dehydration of ethanol by zeolites is very efficient. However, regenerating the zeolite for repeated use is energy intensive, $\Delta_{dehyd}H \approx 86 \text{ kJ mol}^{-1}$.[10] Zeolites are dehydrated under vacuum at elevated temperature.

Colligative Properties are a Function Only of the Concentration of the Solute: A **colligative property** is a property of a solution that depends only on the concentration of the solute and not the chemical properties or specific identity of the solute. The colligative properties include vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure. Independence of the identity of the solute requires that colligative properties are applicable only in the dilute solution limit, so that the solution is approximated as an ideal-dilute solution. The solvent chemical potential is then determined using Raoult's Law, Eq. 18.2.9*. For vapor pressure lowering, boiling point elevation, and osmotic pressure, the colligative properties are restricted to non-volatile solutes, since the experiments all involve equilibrium with the vapor phase. Freezing point depression is a colligative property for volatile and non-volatile solutes. However, freezing point depression is a colligative property only for solutes that are immiscible with the solvent in the solid phase. In other words, the solvent forms a pure solid phase upon freezing with no contamination from the solute.

Vapor pressure lowering is directly expressed by Raoult's Law, $P_A = x_A P_A^*$. The vapor pressure of the solvent in an ideal-dilute solution is less than the pure vapor pressure, since the mole fraction of the solvent is always less than one. The freezing point and boiling point for a solution can be predicted by modifying Figure 17.1.1 for a solution using Raoult's Law as shown in Figure 18.4.5. Assume that the solute is non-volatile and immiscible in the solid solvent. The vapor phase and the solid phase only contain the solvent. Then the chemical potential of the vapor is the chemical potential of the pure solvent vapor, $\mu_A(g) = \mu_A^*(g)$, and the chemical potential of the solid phase is the chemical potential of the pure solid solvent, $\mu_A(s) = \mu_A^*(s)$, both identical to Figure 17.1.1. The chemical potential of the solvent in the solution is decreased compared to the pure solvent, Eq. 18.2.9*. The intersection of the chemical potential curves for the solid and solution phase, where $\mu_A^*(s) = \mu_A(x_A)$, shows that the freezing point is depressed compared to the pure solvent: $T_m < T_m^*$. The intersection of the chemical potential curves for the solution and vapor phase, where $\mu_A(x_A) = \mu_A^*(g)$, shows that the boiling point is elevated compared to the pure solvent: $T_b > T_b^*$. The assumption of Raoult's Law behavior for the solvent allows the quantitative prediction of the boiling point elevation, freezing point depression, and osmotic pressure.

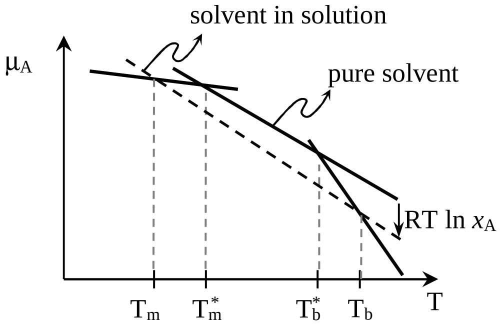


Figure 18.4.5: Only the chemical potential of the solution is lowered by the presence of a solute that is non-volatile and immiscible in the solid solvent. The freezing point of the solution is depressed and the boiling point is elevated. (Compare to Figure 17.1.1.)

The Boiling Point is Elevated for an Ideal-Dilute Solution of a Non-volatile Solute: The boiling point of a solution corresponds to the temperature at which the total vapor pressure is equal to the ambient pressure. The variation of the vapor pressure of a pure substance is given by the Clausius-Clapeyron equation, Eq. 17.1.13° or 17.1.14°, Figure 18.4.6. The total vapor pressure of a solution of a non-volatile solute is just the vapor pressure of the solvent. For an ideal or ideal-dilute solution, the vapor pressure of the solvent is lower than the vapor pressure of the pure solvent, as given by Raoult's Law, so that the temperature of the solution must be increased to reach the boiling point as compared to the pure solvent. At equilibrium, the chemical potentials of the solvent in the vapor and solution are equal, $\mu_A^*(g) = \mu_A(x_A)$. Using Raoult's Law for the solvent, the chemical potential of the solvent in solution is given by Eq. 18.2.9*:

$$\mu_A^*(g) = \mu_A(x_A) = \mu_A^*(l) + RT \ln x_A \qquad \text{(equilibrium, ideal solvent, cst. P)} \qquad 18.4.2^\dagger$$

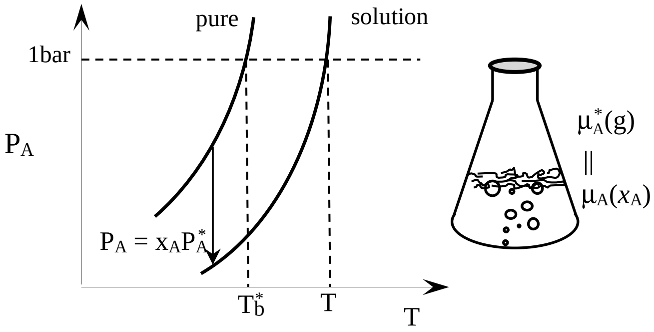


Figure 18.4.6: The vapor pressure of the solvent is decreased in solution, so that the temperature of the solution must be increased to reach the boiling point, as compared to the pure solvent. At equilibrium, the chemical potentials of the solvent in the vapor and solution are equal.

The molar Gibbs energy of vaporization of the pure solvent at temperature T is given by $\Delta_{vap}G_A(T) = \mu_A^*(g) - \mu_A^*(l)$. Solving for the concentration of the solvent that gives the solution boiling point at temperature T using Eq. 18.4.2† gives:

$$\ln x_A = \frac{\mu_A^*(g) - \mu_A^*(x_A)}{RT} = \frac{\Delta_{vap}G_A(T)}{RT} \qquad \text{(ideal solvent, cst. P)} \quad 18.4.3^\dagger$$

For the pure solvent, $x_A = 1$, and the equilibrium temperature is the boiling point of the pure solvent at the ambient pressure, $T = T_b^*$:

$$\ln 1 = \frac{\Delta_{vap}G_A(T_b^*)}{RT_b^*} \qquad \text{(pure solvent, cst. P)} \quad 18.4.4^\dagger$$

We can compare the solution to the pure solvent by subtracting Eq. 18.4.4† from 18.4.3†:

$$\ln \frac{x_A}{1} = \frac{\Delta_{vap}G_A(T)}{RT} - \frac{\Delta_{vap}G_A(T_b^*)}{RT_b^*} \qquad \text{(ideal solvent, cst. P)} \quad 18.4.5^\dagger$$

We can separate enthalpy and entropy effects using $\Delta_{vap}G_A(T) = \Delta_{vap}H_A(T) - T\,\Delta_{vap}S_A(T)$. Being careful to keep track of the specific temperatures for each term gives:

$$\ln x_A = \left(\frac{\Delta_{vap}H_A(T)}{RT} - \frac{\Delta_{vap}S_A(T)}{R}\right) - \left(\frac{\Delta_{vap}H_A(T_b^*)}{RT_b^*} - \frac{\Delta_{vap}S_A(T_b^*)}{R}\right)$$

$$\text{(ideal solvent, cst. P)} \quad 18.4.6^\dagger$$

The change in boiling point is typically only a few degrees. Assuming that $\Delta_{vap}H_A$ and $\Delta_{vap}S_A$ are constant over this small temperature range results in the cancellation of the terms in the entropy:

$$\ln x_A = \frac{\Delta_{vap}H_A(T)}{RT} - \frac{\Delta_{vap}H_A(T_b^*)}{RT_b^*} \qquad \text{(ideal solvent, cst. P\&}\Delta_{vap}S_B^\circ\text{)} \quad 18.4.7^\dagger$$

$$\ln x_A = \frac{\Delta_{vap}H_A}{R}\left(\frac{1}{T} - \frac{1}{T_b^*}\right) \qquad \text{(ideal solvent, cst. P,}\Delta_{vap}H_B^\circ\text{\&}\Delta_{vap}S_B^\circ\text{)} \quad 18.4.8^\dagger$$

where $\Delta_{vap}H_A$ is the average enthalpy of vaporization of the solvent over the temperature range. This last equation shows that the boiling point elevation is independent of the identity of the solute, since only the mole fraction of the solvent is required. The boiling point elevation is defined as $\Delta T \equiv T - T_b^*$:

$$\ln x_A = \frac{\Delta_{vap}H_A}{R}\left(\frac{T_b^* - T}{TT_b^*}\right) = -\frac{\Delta_{vap}H_A}{R}\left(\frac{\Delta T}{TT_b^*}\right) \qquad \text{(ideal solvent, cst. P,}\Delta_{vap}H_B^\circ\&\Delta_{vap}S_B^\circ\text{)} \quad 18.4.9^\dagger$$

For small changes in boiling point, negligible additional error is introduced by approximating $TT_b^* \cong T_b^{*2}$, Eq. 3.5.13-*General Pattern ℘ 4*:

$$\ln x_A = -\left(\frac{\Delta_{vap}H_A}{R\,T_b^{*2}}\right)\Delta T \quad \text{or} \quad \Delta T = -\left(\frac{RT_b^{*2}}{\Delta_{vap}H_A}\right)\ln x_A \qquad \text{(very dilute, cst. P)} \quad 18.4.10^\dagger$$

However, for very dilute solutions, the ln x_A term can be approximated using a Taylor series in the mole fraction of the solute:

$$\ln x_A = \ln(1 - x_B) \cong - x_B + x_B^2 + \ldots \qquad \text{(very dilute)} \quad 18.4.11$$

Keeping only the first term in the Taylor expansion, $\ln x_A = - x_B$, and substitution into Eq. 18.4.9† gives the approximate expressions:

$$x_B \cong \left(\frac{\Delta_{vap}H_A}{R\,T_b^{*2}}\right)\Delta T \quad \text{or} \quad \Delta T \cong \left(\frac{RT_b^{*2}}{\Delta_{vap}H_A}\right) x_B \qquad \text{(very dilute, cst. P)} \quad 18.4.12^\dagger$$

We often express concentration in molality instead of mole fraction. For very dilute solutions, substituting Eq. 2.2.15 for the mole fraction into Eq. 18.4.12† gives the result often introduced in General Chemistry texts:

$$\Delta T \cong \left(\frac{RT_b^{*2}\mathcal{M}_A\,(1\text{ kg})}{1000\text{ g }\Delta_{vap}H_A}\right) m_B \qquad \text{(very dilute, cst. P)} \quad 18.4.13^\dagger$$

$$\text{or} \quad \Delta T \cong K_b\, m_B \quad \text{with } K_b \equiv \left(\frac{RT_b^{*2}\mathcal{M}_A\,(1\text{ kg})}{1000\text{ g }\Delta_{vap}H_A}\right) \qquad \text{(very dilute, cst. P)} \quad 18.4.14^\dagger$$

where K_b is the **molal boiling point elevation constant** or **ebullioscopic constant**, which is extensively tabulated. Note that K_b only depends on the properties of the solvent, as expected for a colligative property. While Eqs. 18.4.14† are commonly used, Eq. 18.4.8† is applicable over a wider concentration range and is the basis for the determination of activities in real solutions. A parallel treatment also applies to freezing point depression.

The Freezing Point is Depressed for an Ideal-Dilute Solution: The freezing point or melting point of a solution is the equilibrium phase transition temperature such that the chemical potentials of the solvent in the pure solid phase and the solution are equal, $\mu_A^*(s) = \mu_A(x_A)$. The equality of the chemical potentials is identical to the case for boiling point elevation except that the pure phase for freezing point depression is the low temperature phase. Then using Raoult's Law for the solvent in solution gives exactly the same results as for boiling point elevation, except for a change in sign:

$$\ln x_A = -\frac{\Delta_{fus}H_A}{R}\left(\frac{1}{T} - \frac{1}{T_m^*}\right) \qquad \text{(ideal solvent, cst. P)} \quad 18.4.15^\dagger$$

$$\ln x_A = -\left(\frac{\Delta_{fus}H_A}{R\,T_m^{*2}}\right)\Delta T \quad \text{or} \quad \Delta T = -\left(\frac{RT_m^{*2}}{\Delta_{fus}H_A}\right)\ln x_A \qquad \text{(very dilute, cst. P)} \quad 18.4.16^\dagger$$

$$x_B \cong \frac{\Delta_{fus}H_A}{R}\left(\frac{\Delta T}{T_m^{*2}}\right) \quad \text{or} \quad \Delta T \cong \left(\frac{RT_m^{*2}}{\Delta_{fus}H_A}\right)x_B \qquad \text{(very dilute, cst. P)} \quad 18.4.17^\dagger$$

$$\Delta T \cong \left(\frac{RT_m^{*2}\mathcal{M}_A\,(1\text{ kg})}{1000\text{ g }\Delta_{fus}H_A}\right)m_B \qquad \text{(very dilute, cst. P)} \quad 18.4.18^\dagger$$

$$\Delta T \cong K_f\,m_B \quad \text{with} \quad K_f \equiv \left(\frac{RT_m^{*2}\mathcal{M}_A\,(1\text{ kg})}{1000\text{ g }\Delta_{fus}H_A}\right) \qquad \text{(very dilute, cst. P)} \quad 18.4.19^\dagger$$

where $\Delta_{fus}H_A$ is the enthalpy of fusion of the solvent, T_m^* is the freezing point of the pure solvent, T is the freezing point of the solution, and the freezing point depression is defined as $\Delta T \equiv T_m^* - T$, which is a positive number. K_f is the **molal freezing point depression constant** or **cryoscopic constant**.

The molality of the solute, m_B, includes all solute species in solution. For colligative phenomena, the identity of the solute is immaterial, so molecular solutes and individual ionic species have the same effect. For strong electrolyte solutions, the molality of the solute and the corresponding mole fraction of the solvent must be modified to account for ionic dissociation, $m_B = \nu\,m$, where ν is the number of ions that result from the dissociation of the strong electrolyte and m is the analytical concentration the solute. For example, for NaCl and $CuSO_4$, $\nu = 2$, while for Na_2SO_4 and $Cu(NO_3)_2$, $\nu = 3$. Ionic solutions show stronger deviations from ideality than molecular solutions, so the concentration range for ideal-dilute behavior is greatly decreased.

Example 18.4.5: *Cooking spaghetti*

Calculate the boiling point elevation and freezing point depression for a solution of 0.500 g of NaCl in 1.000 kg of water. This concentration is comparable to the conditions used in cooking spaghetti. For water, the enthalpy of vaporization is 40.7 kJ mol^{-1} at 100°C and the enthalpy of fusion is 6.01 kJ mol^{-1} at 0°C.

Answer: The molar mass of NaCl is 58.44 g mol^{-1}. The corresponding molality of NaCl is then $m_{NaCl} = 0.500\text{ g}/58.44\text{ g mol}^{-1}/1.000\text{ kg} = 8.56\text{x}10^{-3}$ m. However, since NaCl is a stong electrolyte, $NaCl\ (aq) \rightarrow Na^+ + Cl^-$, the concentration of all solute species in solution is $m_B = 2\,m_{NaCl} = 0.0171$ m. The mole fraction of solute is then given by Eq. 2.2.13 as $x_B = 3.082\text{x}10^{-4}$, giving the mole fraction of water as $x_{H_2O} = 1 - x_B = 0.999692$. The ebullioscopic and cryoscopic constants are, respectively:

$$K_b \equiv \left(\frac{RT_b^{*2}\mathcal{M}_A\,(1\text{ kg})}{1000\text{ g }\Delta_{vap}H_A}\right) = 0.512\text{ mol}^{-1}\text{ kg K} \qquad K_f \equiv \left(\frac{RT_m^{*2}\mathcal{M}_A\,(1\text{ kg})}{1000\text{ g }\Delta_{fus}H_A}\right) = 1.86\text{ mol}^{-1}\text{ kg K}$$

Giving the final results, with different levels of approximation for comparison:

Approximation	Freezing	Boiling
$\Delta T \cong -(RT_{tr}^{*2}/\Delta_{tr}H_A)\ln x_A$	0.03182 K	0.008770 K
$\Delta T \cong (RT_{tr}^{*2}/\Delta_{tr}H_A)\, x_B$	0.03175 K	0.008754 K
$\Delta T \cong K_{tr}\, m_B$	0.03183 K	0.008761 K

The approximation, $\Delta T = -(RT_{tr}^{*2}/\Delta_{tr}H_A)\ln x_A$, agrees with Eqs. 18.4.8† or 18.4.15† to better than four significant figures. (However, even at this low concentration, a 3% deviation from ideality is found. We'll deal with real solutions in the next chapter.) Freezing point depression can be determined with better precision than boiling point elevation, because freezing point depression has a larger magnitude. Adding salt to the water while cooking spaghetti has a negligible effect on the boiling point. Salt is added for flavor, not to change the cooking temperature.

Eq. 18.4.16† is used to determine the purity of samples by differential scanning calorimetry. Purity determinations are routinely used in the pharmaceutical industry for quality control and research. The DSC melting curve of an impure substance is broadened compared to a pure substance, Figure 18.4.7a-b.[11] The mole fraction of the impurity in the final melt is determined by the freezing point depression, ΔT. However, applying Eq. 18.4.16† for a general organic substance, the enthalpy of fusion and the pure melting point are usually not known. The area under the DSC melting curve gives $\Delta_{tr}H_A$ for the substance. A simple extrapolation procedure based on partial areas of the melting curve is used to determine the pure melting point and an accurate value of the freezing point depression, without knowledge of the identity of the impurities.

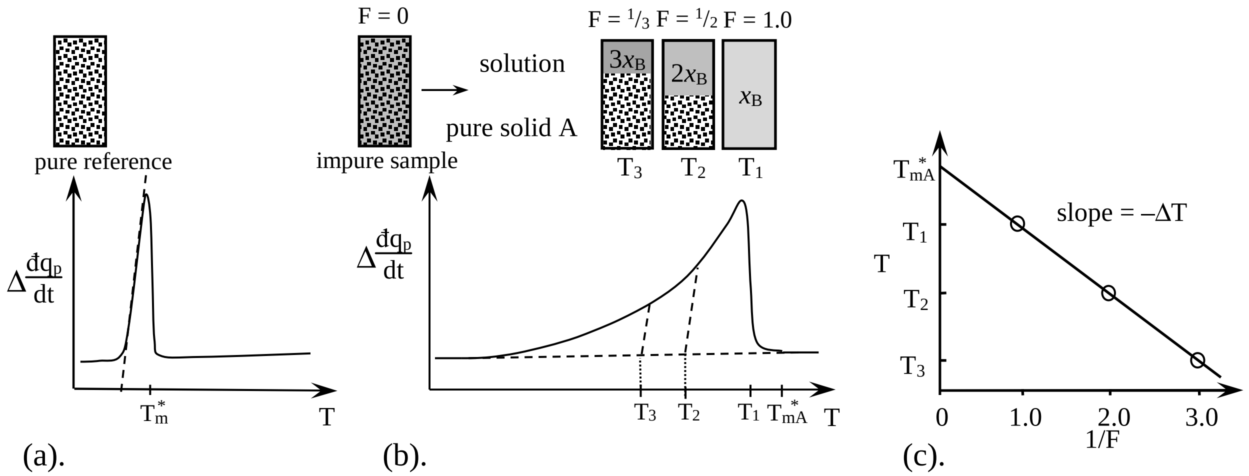


Figure 18.4.7. Freezing point depression solid-immiscible impurities: (a). A pure reference sample gives a narrow melting range. (b). The melting range for an impure sample gives the mole fraction impurity. F is the fraction melted. To correct for slow instrument response, the partial areas are bounded by a line with slope equal to the leading edge of the melting curve for a pure reference compound (- - -). (c). The intermediate melting points extrapolate to give the pure melting point and the slope gives the freezing point depression.

The solution in equilibrium with the solid phase in a melting experiment is called the **melt**. Consider heating an impure solid, A, with impurities that are soluble in the melt but are not soluble in the pure solid substance. At the onset of melting, all impurities dissolve in the initial melt. As the temperature increases, more A melts, which decreases the concentration of the impurities in the melt. As the concentration of the impurities in the melt decreases, the equilibrium melting point of the solution increases. As the last solid melts, the concentration of the impurities in the melt equals the concentration of impurities in the original solid sample, and the final equilibrium melting point gives the freezing point depression, ΔT. The concentration of the impurities in the melt at each stage is inversely proportional to the fraction of the solid that has melted. The DSC melting curve is divided into a sequence of partial areas, each partial area beginning at the onset of melting. The ratio of each of the partial areas to the total area under the melting curve is proportional to the fraction of the solid that has melted, F. If x_B is the concentration of all the impurities in the original sample, the concentration of impurities in the melt is x_B/F. Solving Eq. 18.4.17† for the melting point, $T = T^*_{mA} - (RT^{*2}_m/\Delta_{fus}H_A)\, x_B/F$, a plot of the temperature that corresponds to each partial area versus the inverse of the fraction melted, Figure 18.4.7c, gives an intercept equal to the pure melting point of the solid and slope equal to the freezing point depression, $\Delta T = (RT^{*2}_m/\Delta_{fus}H_A)\, x_B$. Since Eqs. 18.4.16†-8.4.17† are restricted to ideal-dilute solutions, this method is only valid for purities greater than about 98 mol%.

Example 18.4.6: *Purity Determination*

The partial areas and corresponding temperatures from the melting curve for methyl-4-(2,4-dichlorophenoxy)butyrate are given in the table below.[11] The sample mass was 2.2850 mg with a molar mass of 263.12 g mol^{-1}. The partial areas are in arbitrary units, with the total area under the curve, 3302, gives the enthalpy of the transition as 0.2749 J. Calculate the sample purity.

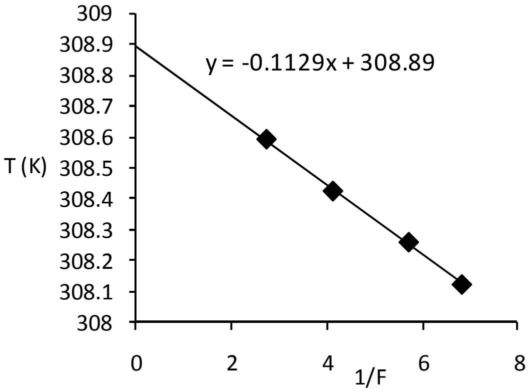
T (K)	308.119	308.256	308.422	308.590
Partial area	483	577	802	1212

Answer: The enthalpy of fusion is determined from the total area under the melting curve on a per mole basis:

$$\Delta_{fus}H_A = \Delta H/n_A = 0.2749 \text{ J } (263.12 \text{ g mol}^{-1}/2.2850\text{x}10^{-3} \text{ g})(1 \text{ kJ}/1000 \text{ J}) = 31.65 \text{ kJ mol}^{-1}$$

A plot of T vs. 1/F gives the intercept as $T^*_{mA} = 308.89 \pm 0.01$ K and ΔT = – slope = 0.1129 ± 0.0025 K^{-1}.

T (K)	Partial Area	F	1/F
308.119	483	0.1463	6.84
308.256	577	0.1747	5.72
308.422	802	0.2429	4.12
308.590	1212	0.3671	2.72
Total	3302		



The mole fraction is given by Eq. 18.4.16†:

$$\ln x_A = \frac{\Delta_{fus}H_A}{R}\left(\frac{\Delta T}{T_m^{*2}}\right) = \frac{31.65\text{x}10^3 \text{J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\left(\frac{0.1129 \text{ K}}{308.89 \text{ K}}\right) = 4.504\text{x}10^{-3} \qquad x_A = 0.9955$$

The sample purity is 99.55 mol%.

In summary, the plot of the freezing point of an ideal solvent as a function of composition using Eq. 18.4.16† approaches linear behavior in the dilute solution limit, $x_A \rightarrow 1$, Figure 18.4.8. The limiting linear behavior is given by Eq. 18.4.17† with slope = $RT_{mA}^{*2}/\Delta_{fus}H_A$. For moderately concentrated solutions, the freezing point depression is greater than the linear prediction. In general, the colligative properties become linear as solutions approach the dilute solution limit, where Eqs. 18.4.12†- 18.4.14† and 18.4.17†- 18.4.19† are applicable.

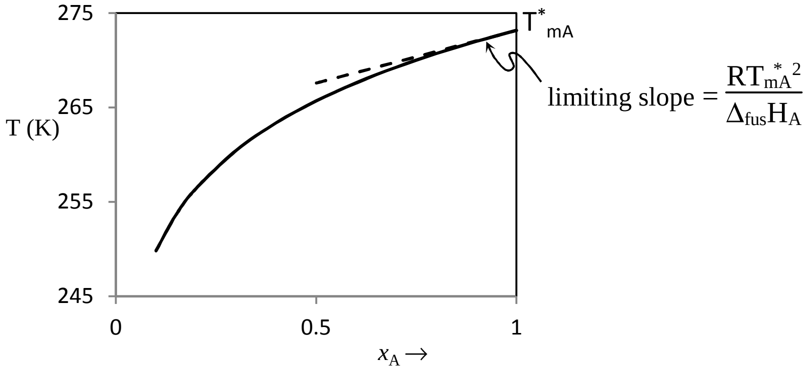


Figure 18.4.8: Freezing point of an ideal solvent as a function of composition. The dilute solution limit, $x_A \rightarrow 1$, gives linear behavior, Eqs. 18.4.17†- 18.4.19†.

Osmotic Pressure Results from Equilibrium across a Semi-Permeable Membrane: Red blood cells burst when suspended in pure water. Cellular membranes are selectively permeable; they allow water to pass but not some solutes. The larger chemical potential of the pure water outside the cells compared to the water in the cytoplasm of the cells causes a transfer of water into the red blood cells, increasing the pressure inside the cells by osmosis until the cell membranes burst. Osmotic pressure is a general phenomenon of semi-permeable membrane systems and is an important property in the laboratory, in biological systems, and especially in medicine. Consider a membrane that is permeable to solvent, but not to a given solute, Figure 18.4.9. The membrane separates two compartments, one containing pure solvent and one containing a solution of a solute that is not transported through the membrane. The concentration of the solvent in the solution is x_A. Assume that the solution is sufficiently dilute to be considered an ideal or an ideal-dilute solution. The chemical potential of the solvent in the solution is less than the pure solvent; $\mu_A(x_A) = \mu_A^*(l) + RT \ln x_A$. The solvent flows across the membrane from the region of high chemical potential of the pure solvent to the region of low chemical potential in the solution. The transfer causes an increase in the volume of the solution, generating a hydrostatic head that gives an increase in pressure, ΔP. The pressure increase is determined by the difference in height of the solution compared to the pure solvent, h, and the density of the solution: $\Delta P = dgh$, Eq. 1.3.2.

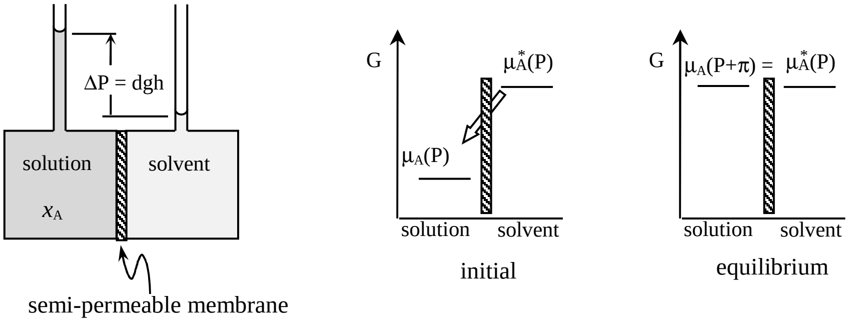


Figure 18.4.9: Osmotic pressure is established by the equalization of the chemical potential of the solvent across a semi-permeable membrane. Solvent flows from the region of high chemical potential to the region of low chemical potential.

At equilibrium, the pressure increase is the osmotic pressure, $\Delta P_{eq} = \pi$. The equilibrium osmotic pressure is established when the chemical potential of the solvent is equalized between the solution and the pure solvent:

$$\mu_A(x_A,P+\pi) = \mu^*_A(l,P) \qquad \text{(equilibrium)} \quad 18.4.20$$

To calculate the osmotic pressure, we need to take into account the effects of concentration and pressure on the chemical potential. The chemical potential of a constituent in solution at a pressure of P + ΔP is given by integrating Eq. 18.1.18 with dT = 0:[12]

$$\mu_i(x_i,P+\Delta P) = \mu_i(x_i,P) + \int_P^{P+\Delta P} \bar{V}_i \, dP \qquad \text{(cst. T)} \quad 18.4.21$$

where $\mu_i(x_i,P)$ is the chemical potential in solution at ambient pressure, P. For moderate changes in pressure, the partial molar volume of the solvent is constant and the integral is $\Delta P\bar{V}_i$:

$$\mu_i(x_i,P+\Delta P) = \mu_i(x_i,P) + \Delta P\bar{V}_i \qquad \text{(cst. T, small } \Delta P) \quad 18.4.22$$

The ideal concentration dependence of the chemical potential from Eqs. 18.2.9* and 18.3.10† are then substituted for the solution chemical potentials at ambient pressure giving for the solvent and solute, respectively:[12]

$$\mu_A(x_A,P+\Delta P) = \mu^*_A(l,P) + RT \ln x_A + \Delta P\bar{V}_A \qquad \text{(ideal solvent, cst. T)} \quad 18.4.23^\dagger$$

$$\mu_B(x_B,P+\Delta P) = \mu^\dagger_B(l,P) + RT \ln x_B + \Delta P\bar{V}_B \qquad \text{(solute, ideal-dilute, cst. T)} \quad 18.4.24^\dagger$$

where we use a Raoult's Law standard state for the solvent, A, and a Henry's Law standard state for the solute, B. These expressions for the Gibbs energy in solution are centrally important for applications in bioenergetics.[12] We will extend these equations for use with real solutions in the next chapter.

For the determination of osmotic pressure at equilibrium, $\Delta P_{eq} = \pi$, the chemical potentials of the solvent in the two compartments are equal. Using Eq. 18.4.20 for the left side of Eq. 18.4.23† gives:

$$\mu_A^*(l,P) = \mu_A^*(l,P) + RT \ln x_A + \pi\bar{V}_A \qquad \text{(equilibrium, ideal-dilute, cst. T)} \quad 18.4.25^\dagger$$

Cancelling the pure liquid standard state from both sides of the last equation and solving for the osmotic pressure term gives:

$$\pi\,\bar{V}_A = -\,RT \ln x_A \qquad \text{(ideal-dilute, cst. T)} \quad 18.4.26^\dagger$$

This result is called the **van't Hoff equation**. For very dilute solutions, this last equation can be simplified further and related directly to the solute concentration, x_B. As before, note that $x_A = 1 - x_B$, and that we can expand the logarithm in a Taylor series, Table 1.5.3, keeping only the leading term to give $\ln(1 - x_B) \cong -\,x_B$. In addition, using Eq. 18.2.12, the partial molar volume of an ideal constituent is equal to the pure molar volume: $\bar{V}_A = V_A^*$. Substituting these approximations into Eq. 18.4.26† gives:

$$\pi\,V_A^* \cong x_B\,RT \qquad \text{(ideal-dilute, cst. T)} \quad 18.4.27^\dagger$$

In addition, for very dilute solutions, the mole fraction of the solute can be approximated as:

$$x_B = \frac{n_B}{n_A + n_B} \cong \frac{n_B}{n_A} \qquad \text{(ideal-dilute, cst. T)} \quad 18.4.28^\dagger$$

Substitution of this approximation gives $\pi\,V_A^* = n_B/n_A\,RT$. Multiplying both sides of this equation by n_A gives:

$$\pi\,V \cong n_B\,RT \qquad \text{with } V \cong n_A V_A^* \qquad \text{(ideal-dilute, cst. T)} \quad 18.4.29^\dagger$$

where the volume of the pure solvent, $n_A V_A^*$, is approximately equal to the volume of the solution, V. The resemblance of this last equation to the ideal gas law is notable, however, the similarity is not theoretically significant. Further, the concentration of the solute is given by $c_B = n_B/V$ so the van't Hoff equation can be written as:

$$\pi \cong c_B\,RT \qquad \text{(ideal-dilute, cst. T)} \quad 18.4.30^\dagger$$

For strong electrolytes, $c_B = \nu\,c$, with c the analytical concentration. Eqs. 18.4.29† and 18.4.30† are given in General Chemistry texts. However, Eq. 18.4.26† is applicable over a wider concentration range. Eq. 18.4.26† also clearly shows that in the dilute solution limit the osmotic pressure is independent of the identity of the solute, as are all colligative properties. The application of this theory for the reverse process, **reverse osmosis**, plays an important role in water purification.

Application of a pressure greater than the equilibrium osmotic pressure to the solution compartment in Figure 18.4.9 causes the chemical potential of the solution to exceed the pure solvent, which reverses the direction of solvent flow. Solvent is transferred from the solution to the pure solvent. This reverse osmosis process is used in laboratory water systems and other water purification applications, because it is more energy efficient than distillation. Reverse osmosis is, however, still very energy intensive. Reverse osmosis is also used in the food industry, for example in the production of maple syrup. Most importantly, reverse osmosis is used in desalination for the production of potable water, water for agricultural uses, and for environmental remediation. Safe drinking water and water suitable for agriculture is in critically-short supply in many parts of the world.[13] The World Bank has predicted that clean water will be the most critical natural resource issue in the near future.[14] Water shortages have been identified as causes of civil unrest and large scale human migrations in Africa. Even in the United States for example, the Salt River in Arizona no longer flows in its natural channel because it has been pumped dry. The Colorado and Rio Grande would similarly dry up, were it not for treaty obligations with Mexico. The only water that reaches Mexico in the Colorado River is agricultural waste water. A large-scale reverse osmosis plant on the Colorado in Yuma, AZ, was designed for treatment of agricultural run-off for injection back into the river channel. The research need in this area is the development of high permeability, mechanically robust, semi-permeable membranes or alternative purification methods.

Example 18.4.7: *Osmotic Pressure*

Plot the chemical potential of water in 0.01000 M sucrose as a function of applied pressure, ΔP, and hydrostatic head, h, at 25°C. Reference the chemical potential to the pure solvent, $\mu_A(x_A,P+\Delta P) - \mu_A^*(l,P)$. The density of the solution is 0.99836 g mL^{-1}.

Answer: This solution is sufficiently ideal so that the partial molar volume may be replaced by the pure molar volume of the solvent, $\bar{V}_A = V_A^* = 18.069$ mL mol^{-1}. Using Eq. 2.2.16, the mole fraction of 0.01000 M sucrose is $x_B = 1.8103\text{x}10^{-4}$. The mole fraction of water is then $x_A = 0.999819$. Using Eq. 18.4.23†, the difference between the chemical potential of the solvent in solution and the pure solvent is:

$$\begin{aligned}\mu_A(x_A,P+\Delta P) - \mu_A^*(l,P) &= RT \ln x_A + \Delta P V_A^* \\ &= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}(298.15 \text{ K}) \ln(0.999819) \\ &\quad + \Delta P(18.069 \text{ mL mol}^{-1})(1 \text{ m}^3/1\text{x}10^6 \text{ mL})(1\text{x}10^5 \text{ Pa/1bar})\end{aligned}$$

At ΔP = 0, the chemical potential difference between the solution and the pure solvent is $\mu_A(x_A,P+\Delta P) - \mu_A^*(l,P) = -0.4488$ J mol^{-1}. At $\Delta P = \pi$ the difference is zero, since the system is at equilibrium, Figure 18.4.10.

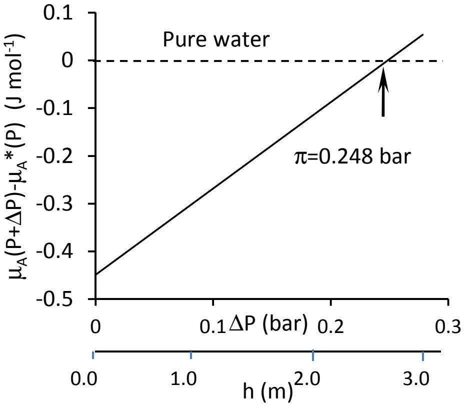


Figure 18.4.10: The solvent chemical potential as a function of applied pressure for a 0.01000 M sucrose solution. The chemical potential difference between the solution and the pure solvent is zero at ΔP = π, the equilibrium osmotic pressure.

The osmotic pressure, assuming ideal behavior, Eq. 18.4.26†, is:

$$\pi = -(RT \ln x_A)/V_A^*$$
$$= -0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1} (298.15 \text{ K}) (\ln 0.999819)/(0.018069 \text{ L mol}^{-1}) = 0.2483 \text{ bar}$$

In comparison, the approximation using Eq. 18.4.30† gives $\pi = c_B RT = 0.2479$ bar, which is sufficient for three-significant figure accuracy at this low concentration. The height of the column of solution necessary to develop the equilibrium osmotic pressure is given by $\Delta P = dgh$:

$$h = \Delta P/(dg) = 0.2483 \text{ bar}/(998.36 \text{ kg m}^{-3}\ 9.80665 \text{ m s}^{-2}) (1\text{x}10^5 \text{ Pa/1bar}) = 2.537 \text{ m}$$

A convenient equation for the chemical potential of the solvent in solution can be obtained by substituting Eq. 18.4.26† into Eq. 18.4.23†:[12]

$$\mu_A(x_A,P+\Delta P) = \mu_A^*(l,P) + (\Delta P - \pi)\bar{V}_A \qquad (\text{cst. T}\&\bar{V}_A) \qquad 18.4.31$$

This last result shows the plot in Figure 18.4.10 has a slope given by the partial molar volume of the solvent and an intercept of $(-\pi\bar{V}_A)$. Eq. 18.4.31 is not restricted to ideal-dilute solutions, if the exact osmotic pressure is used.

Example 18.4.8: *Osmotic Pressure and Chemical Potential*
A 0.01000 M aqueous sucrose solution and pure water are separated by a membrane that is impermeable to sucrose and permeable to water, at 25°C and 1 bar. Calculate the chemical potential of the water and the sucrose at equilibrium. The density of the solution is 0.99836 g mL^{-1}and the partial molar volume of sucrose is $\bar{V}_B = 211.52$ mL mol^{-1}.

Answer: The osmotic pressure of this system is calculated in the last example: with $x_B = 1.8103\text{x}10^{-4}$, $\pi = 0.2483$ bar. At equilibrium the chemical potential of the water in the solution is equal to the chemical potential of pure water, $\mu_A(x_A,P+\pi) = \mu_A^*(l,P)$. For the solute, Eq. 18.4.24†gives the chemical potential at equilibrium with $\Delta P = \pi$:

$$\mu_B(x_B,P+\pi) = \mu_B^\dagger(l,P) + RT \ln x_B + \pi\bar{V}_B$$
$$= \mu_B^\dagger(l,P) + 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}(298.15 \text{ K}) \ln 1.8103\text{x}10^{-4}$$
$$+ 0.2483 \text{ bar}(211.52 \text{ mL mol}^{-1})(1\text{x}10^5\text{Pa/1bar})(1 \text{ m}^3/1\text{x}10^6 \text{ mL})$$
$$= \mu_B^\dagger(l,P) + (-2.16\text{x}10^4 \text{ J mol}^{-1}) + 5.25 \text{ J mol}^{-1}$$

The concentration dependent term dominates the change in chemical potential for the solute compared to the pure substance. See Problem 6 for the partial molar volume of sucrose.

Phase Diagrams for Binary Solid-Liquid Equilibrium: The theory of freezing point depression can also be used to construct the phase diagram for binary solid-liquid equilibrium, Figure 18.4.11. Consider a binary solution at constant pressure with constituents that are immiscible in the solid phase; both A and B freeze out of solution as pure solids. The phase diagram is a plot of the freezing point of the solution as a function of composition. A plot of the freezing point of a solution based on Eq. 18.4.16† is shown in Figure 18.4.8 and is replotted on the right side of the phase diagram for $x_A \rightarrow 1$. On the right side of the phase diagram, A acts as the solvent and B is the solute. However, on the left side of the phase diagram, as $x_B \rightarrow 1$, B acts as the solvent and A is the solute. Switching the roles of the solvent and solute in Eq. 18.4.16† and plotting the freezing point as a function of $x_B = 1 - x_A$ gives the left side of the phase diagram. The freezing point curve for A, acting as the solvent, intersects the temperature axis at the pure melting point of A, T^*_{mA}. The corresponding two-phase region is for the equilibrium between the solution and pure solid A. The freezing point curve for B, acting as the solvent, intersects at the pure melting point of B, T^*_{mB}. The corresponding two-phase region is for the equilibrium between the solution and pure solid B. The phase diagram can be used to answer a useful question. Consider adding a solute to a solvent to lower the freezing point. Can the freezing point of the solution be decreased to an arbitrary value, or is there a minimum freezing point? The point where the two freezing point curves meet on the phase diagram is the minimum freezing point. The minimum freezing point is called the **eutectic temperature**, T_E. The mole fraction at the eutectic temperature is the **eutectic composition**, x_E. Below the eutectic temperature, only pure solid A and pure solid B exist. Solder for electronics applications is a eutectic mixture of tin and lead with a eutectic temperature of 183°C at 63% by mass Sn.

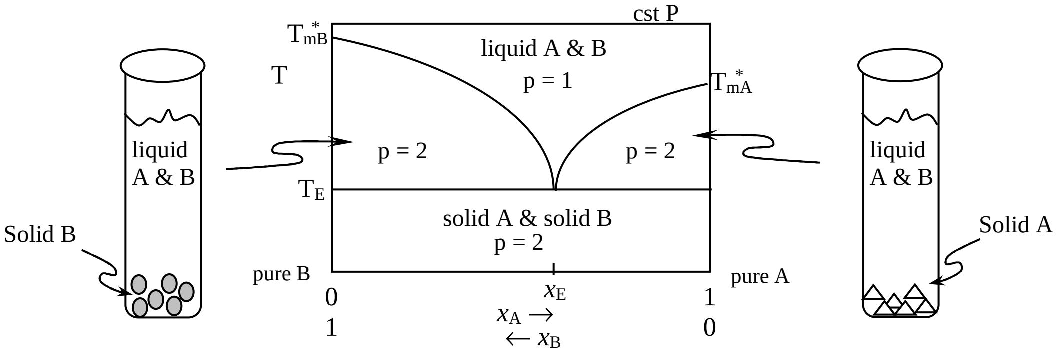


Figure 18.4.11: Binary solid-liquid phase diagram plots the freezing point of the solution as a function of composition. On the left side of the diagram, B acts as the solvent and A is the dilute solute. On the right side of the diagram, A acts as the solvent and B is the dilute solute. This example assumes complete solid-immiscibility.

The number of homogeneous phases present is the variable, p. At high temperature, only the solution phase exists, p = 1. At low temperature, only pure solid A and pure solid B exist, p = 2. At intermediate temperatures the solution and either pure solid A or pure solid B can be at equilibrium, p = 2. The phase diagram can be experimentally constructed by determining cooling curves for a series of initial concentrations, Figure 18.4.12. Consider a solution with a composition greater than the eutectic composition and at high temperature, point *a*. The solution cools rapidly until pure solid A begins to crystallize out of solution, point *b*. The corresponding temperature is the freezing point of the solution. The slope of the cooling curve is moderated because the freezing of the solid from solution is exothermic. As pure solid A crystallizes from solution, the solution concentration becomes richer in B and the solution concentration moves to the left on the phase diagram. The increasing solute concentration lowers the melting point of the solution, so the equilibrium temperature decreases and the system follows the equilibrium freezing point curve to the left. The solution concentration continues to be enriched in B and the freezing point continues to drop until the composition reaches the eutectic composition, point *c*.

At the eutectic point, pure solid B begins to crystallize from solution along with pure solid A. The temperature remains constant at the eutectic temperature, T_E, until all the solution has frozen, point *d*. At that point only pure solid A and pure solid B are present, which cool rapidly, since no exothermic phase changes remain.

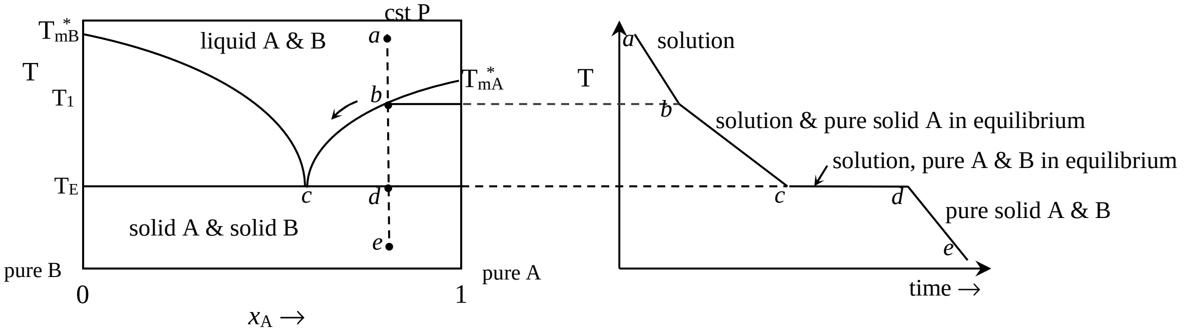
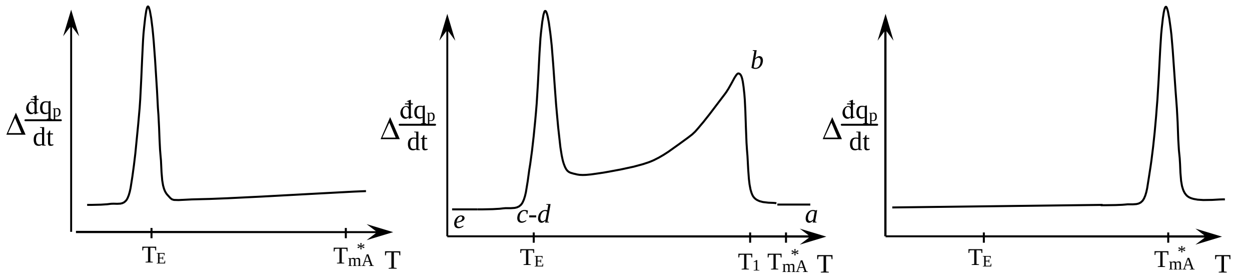


Figure 18.4.12: Cooling curve for a binary solid-liquid system. The first change in slope occurs at *b*, the freezing point of the solution, T_1. The second change in slope occurs at the eutectic temperature, the minimum melting point, point *c*. The last change in slope occurs when all the solution has frozen into pure solid A and pure solid B, point *d*.



(a). Eutectic composition (b). $x_A > x_E$ (c). Pure A

Figure 18.4.13: DSC heating curves (a). at the eutectic composition, (b). for the same composition points as in Figure 18.4.12, and (c). for pure A. For the formation of a non-eitectic solution, peaks occur at the eutectic temperature and the melting/freezing point of the solution for the given composition.

Binary solid-liquid phase diagrams can also be conveniently determined using differential scanning calorimetry, DSC, Figure 18.4.13. A pure substance has a sharp melting curve, Figure 18.4.13c. A typical melting curve is shown in Figure 18.4.13b for the same composition points as in Figure 18.4.12. Starting with a solid mixture of the two pure constituents, point *e*, the temperature is raised until the eutectic temperature is reached, point *d*. The sample begins to melt, to produce a solution at the eutectic composition, point *c*. Melting continues until the solid phase is exhausted in the B component. As the temperature rises the sample continues to melt, however, only pure solid A remains. As A melts the solution becomes richer in A, and the solution composition moves to the right. As the solution becomes richer in A the melting point rises until all the remaining A has melted, point *b*. At point *b*, the composition of the solution is the starting composition of the original solid mixture, and the melting point is at the maximum for the given concentration, which is the solution freezing point, T_1. Conversely, a thermogram of a mixture at the eutectic composition exhibits a single sharp melting peak, Figure 18.4.8a.

The phase diagram of a binary system is seldom as simple as in this example. Some binary systems exhibit the phenomenon of compound formation, where a mixture of the two components, generally with a simple stoichiometry, melts as if it were a pure substance. Water and NaCl are an example. The dihydrate of NaCl, $NaCl\cdot 2(H_2O)$, acts like a pure substance at low temperature. The eutectic temperature between pure water ice and $NaCl\cdot 2(H_2O)$ is -21.1°C and the eutectic composition is 23.3 % by mass NaCl in water. In other words the minimum melting point for NaCl solutions is -21.1°C. Solid-liquid phase diagrams are a central focus of materials science and geochemistry.

Boiling Point Elevation is Used in Making Hard Candy: The colligative properties have wide-ranging applications in many practical circumstances. One application of boiling-point elevation is the production of candy. In making candy, sugar solutions are boiled to decrease the water content. As the sugar content of the solution increases the boiling point increases, Table 18.4.1. However, sugar solutions are probably not ideal, in part due to impurities.[15] Candy thermometers are common kitchen utensils. Other applications of freezing point depression include spreading salts on roads and walkways to remove ice. Propylene glycol is used for airplane de-icing and ethylene glycol is used for automobile cooling system anti-freeze.

Table 18.4.1: The stages of candy production as monitored by boiling point elevation.

Stage	Temperature	mass % sugar
Thread	110-112°C	80%
Soft-ball	112-115°C	85%
Firm-ball	118-120°C	87%
Hard-ball	121-130°C	92%
Soft-crack	132-143°C	95%
Hard-crack	146-154°C	99%
sucrose(s)[15]	186°C	>99.9%

Solutions that exhibit the same osmotic pressure are **isotonic**. For example, isotonic solutions are used in intravenous rehydration therapy and in tissue culture growth-media. The medical conditions hyponatremia and hypernatremia correspond to a deficiency or excess of electrolytes in blood plasma, respectively. Extreme hyponatremia leads to congestive heart failure. Osmometry is crucial in clinical settings. All the colligative property methods are interchangeable. For a given solution concentration, osmotic pressure provides the largest magnitude effect and therefore is the most precise. However, equilibrium is established slowly in osmotic pressure determinations. Most commercial osmometers are based on freezing point depression, although vapor pressure osmometers are also common. Over 100,000 freezing point osmometry determinations are performed per day, world-wide, making freezing point depression the most common thermochemical measurement. For accurate work, including medical and pharmaceutical applications, the effects of solution non-idealities need to be included.

18.5 The Gibbs Phase Rule Determines the Number of Independent Variables

At Equilibrium the Chemical Potential of each Component is "Everywhere Equal": Binary liquid-vapor and solid-liquid phase diagrams show that two phases can exist at equilibrium only over a narrow range of temperatures and pressures, Figures 18.4.1, 18.4.2, and 18.4.11. Three phases coexist at equilibrium at the triple point of a pure substance and at the eutectic temperature for a binary mixture. What are the general conditions for equilibrium when multiple phases and components are present? Gibbs developed a general procedure for counting the number of independent variables that is called the **Gibbs Phase Rule**. The number of independent intensive variables is the number of **thermodynamic degrees of freedom** or the **variance** and is symbolized by "f." The variance is the number of intensive variables that can be changed independently without disturbing the number of phases in equilibrium. The variance is also the number of independent intensive variables that appear in the expression for the total differential of the Gibbs energy. The number of thermodynamic degrees of freedom and the number of molecular degrees of freedom that we discussed in conjunction with the Equipartition Principle in Sec. 8.4 are different concepts, and should not be confused.

The variance of the system is determined by the number of phases in equilibrium and the number of components. The number of homogeneous phases in equilibrium is denoted by "p." The phases include gas, homogeneous liquid phases, and homogeneous solid phases. The number of components is "c" and is discussed in Sec. 14.2, Eq. 14.2.1. We will develop the Gibbs phase rule using a simple example. Consider binary liquid-vapor equilibrium, Figures 18.4.2 and 18.5.1.

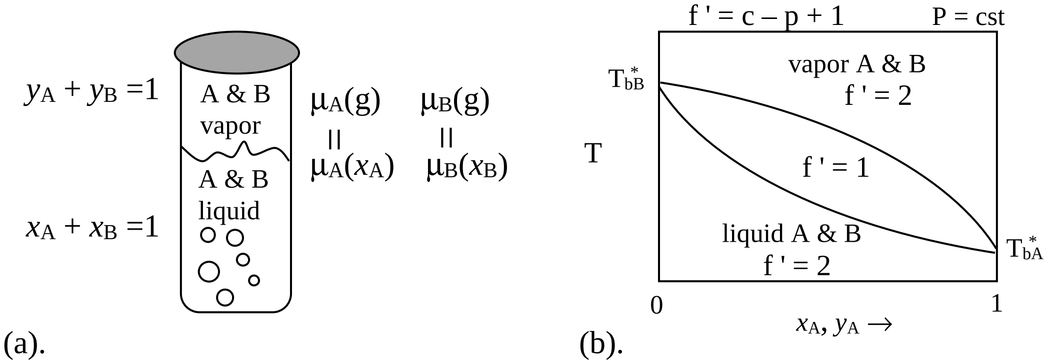


Figure 18.5.1: (a). Two volatile components in a liquid mixture under their equilibrium partial vapor pressures. The chemical potential of each component is equal in each phase at equilibrium. (b). The corresponding phase diagram, at constant pressure, showing the variances at equilibrium.

In general to completely specify all the intensive variables for the system we need to know: T, P, y_A, y_B, x_A, x_B. The total number of intensive variables is given by the number of components multiplied by the number of phases in addition to the overall temperature and pressure:

$$\text{total intensive variables} = c\,p + 2 \qquad \text{(every component in every phase)} \qquad 18.5.1$$

assuming each component can occur in each phase. However, the mole fractions sum to one in each phase:

$$y_A + y_B = 1$$
$$x_A + x_B = 1 \qquad 18.5.2$$

There are p such equations, one for each phase. Each sum of mole fractions decreases the number of independent variables by one. Subtracting the mole fraction constraints from Eq. 18.5.1:

$$\text{total intensive variables} = c\,p + 2 - p \qquad \text{(every component in every phase)} \qquad 18.5.3$$

In addition at equilibrium, the chemical potential of each component is equal in each phase. As we have stressed, the chemical potential is "everywhere equal" at equilibrium:

$$\mu_A(x_A) = \mu_A(g)$$
$$\mu_B(x_B) = \mu_B(g) \qquad \text{(equilibrium)} \qquad 18.5.4$$

For each component, there are (p – 1) equations. For example, for three phases for each component, there are two relationships: $\mu_A(s) = \mu_A(l)$ and $\mu_A(l) = \mu_A(g)$. In general, for c components there are c(p – 1) equations, overall, for the equality of the chemical potential. Subtracting the chemical potential constraints from Eq. 18.5.3 gives the variance:

$$f = \text{independent intensive variables} = c\,p + 2 - p - c(\,p - 1) \qquad \text{(equilibrium)} \qquad 18.5.5$$

Canceling common terms in the last equation gives:[16,17]

$$f = c - p + 2 \qquad \text{(every component in every phase, equilibrium)} \qquad 18.5.6$$

This relationship is the **Gibbs Phase Rule** and is quite general for any number of components in any number of phases. There are two common special cases. When the temperature or pressure is constrained, the variance is given by f ', with:

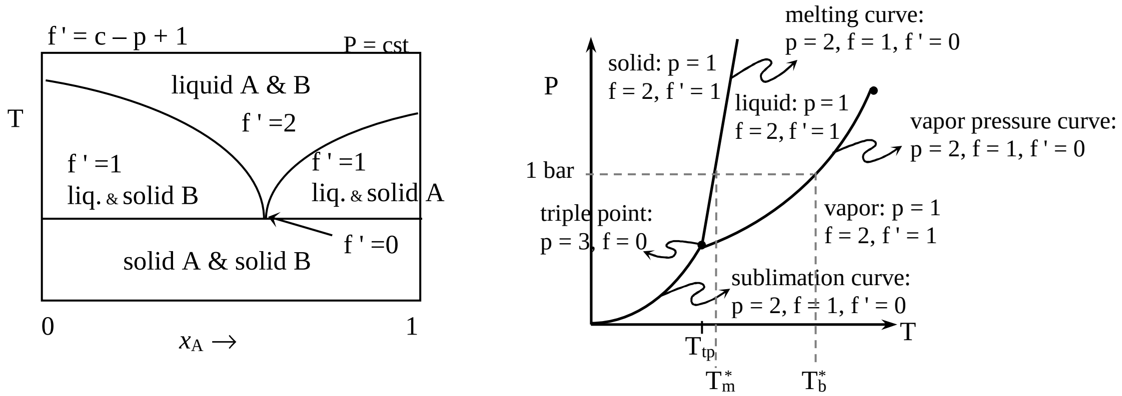
$$f' = c - p + 1 \qquad \text{(every component in every phase, equilibrium, cst. T \underline{or} P)} \qquad 18.5.7$$

If both temperature and pressure are constant, the variance is given by f '', with:

$$f'' = c - p \qquad \text{(every component in every phase, equilibrium, cst. T \underline{\&} P)} \qquad 18.5.8$$

For example, the phase diagram for binary liquid-vapor equilibrium is shown in Figure 18.5.1b. The experiment is done at constant pressure, which decreases the variance by one, f '. At temperatures above the vapor composition curve, only the vapor phase exists. Then p = 1, and the variance is f ' = 2 – 1 + 1 = 2. The system is **bivariant**. The temperature can vary over a wide range for each composition. In the two-phase region, with the liquid and vapor in equilibrium, p = 2 and the variance is f ' = 2 – 2 + 1 = 1. In the two-phase region, choosing a solution composition fixes the boiling point, or conversely choosing a boiling point fixes the composition. Only one variable may be changed independently while the system consists of two phases in equilibrium. The system is **univariant**. At temperatures below the liquid composition curve, only the liquid phase exists and p = 1. At low temperatures the system is bivariant.

Another example is binary solid-liquid equilibrium, Figures 18.4.6 and 18.5.2a, assuming that solid A and B are immiscible. The experiment is again at constant pressure, so we use f '. At high temperatures, only the liquid phase exists, as a solution of A and B. With only one phase, p = 1 and f ' = c – p + 1 = 2 – 1 + 1 = 2. The temperature can vary over a wide range for each composition. In the two-phase regions, with the solid and liquid in equilibrium, $p = 2$ and the variance at constant pressure is $f' = 2 - 2 + 1 = 1$. In the two phase regions, choosing a solution composition fixes the melting point. The system is **univariant**. At the eutectic temperature, the liquid phase and two solid phases co-exist and $p = 3$ giving $f' = 2 - 3 + 1 = 0$. The eutectic temperature is an **invariant** point at constant pressure. The eutectic temperature occurs at one specific composition and one specific temperature at a specified constant pressure.



(a). (b).

Figure 18.5.2: (a). Binary solid-liquid equilibrium, at constant pressure, showing the variances at equilibrium. At the eutectic temperature, liquid, solid A, and solid B are in equilibrium and the system is invariant. (b). The solid-liquid-vapor equilibrium for a pure substance.

Example 18.5.1:
Find the variances for the solid-liquid-vapor phase transitions of a pure substance in general and at constant pressure.

Answer: For a pure substance $c = 1$, Figure 18.5.2b. For a single solid, liquid, or vapor phase alone, $p = 1$ and $f = c - p + 2 = 2$. There are two intensive degrees of freedom. The temperature and pressure of the vapor, for example, can be varied over a wide range subject only to the equation of state: $V_m = RT/P$. If the pressure is constant, $f' = c - p + 1 = 1$, then only the temperature may be changed independently.

The coexistence curves are the melting curve, the vapor pressure curve, and the sublimation curve. Along the coexistence curves, there are two phases in equilibrium, $p = 2$. Then $f = c - p + 2 = 1$: one variable may be changed while maintaining two phases in equilibrium. For example, the temperature may be changed over a wide range, but the vapor pressure is fixed by the chosen temperature to lie along the equilibrium vapor pressure curve. At constant pressure on the coexistence curves, $f' = c - p + 1 = 0$, and the system is invariant. For example, at a constant pressure of 1 bar, the temperature is fixed at the standard melting point and the vapor pressure is fixed at the standard boiling point, if the corresponding phases are in equilibrium.

The Gibbs Phase Rule is a summary of equilibrium chemical potential relationships that guides the interpretation of complex systems. However, the most important application of the Phase Rule is in delineating the functional dependence of the Gibbs energy.

Add One Extensive Independent Variable for Each Phase: Intensive properties are independent of the size of each phase. The Gibbs energy, on the other hand, is an extensive state function. In determining the Gibbs energy of the system we need to take into account the size of each phase. The relative amounts of each component in each phase are then governed by the concentrations, and the system is then completely determined. The total number of independent variables needed to describe the system is called D, for degrees of freedom:

$$D = f + p \qquad 18.5.9$$

D is the number of independent variables that appear in the expression for the total differential of the Gibbs energy.

Example 18.5.2: *Independent Variables for the Gibbs Energy*
A small amount of benzene is added to a separatory funnel containing octanol and water. Octanol and water form two immiscible layers and the solute partitions between the two phases. Find the variance, thermodynamic degrees of freedom, and an expression for dG, at constant temperature and pressure. Include only the liquid phases.

Answer: There are three components, octanol, water, and benzene; c = 3. There are two phases; p = 2. At constant temperature and pressure, f '' = c – p = 1 and D '' = f '' + p = 1 + 2 = 3. There are multiple ways to express the Gibbs energy; but the expression can include only D '' = 3 independent variables. The simplest at constant T and P is written in terms of the total amounts of each component: $dG = \mu_{octanol}\, dn_{octanol} + \mu_{H_2O}\, dn_{H_2O} + \mu_B\, dn_B$. Call the octanol rich phase the (oct) phase and the water rich phase the (aq) phase, then $dn_B = dn_B(oct) + dn_B(aq)$. There are only three independent variables because the distribution of the three components between the two phases is determined by the equivalence of the chemical potentials in the two phases: $\mu_{octanol}(oct) = \mu_{octanol}(aq)$, $\mu_{H_2O}(oct) = \mu_{H_2O}(aq)$, and $\mu_B(oct) = \mu_B(aq)$. For example, for benzene:

$$\mu_B^{\dagger}(org) + RT \ln x_B(oct) = \mu_B^{\dagger}(aq) + RT \ln x_B(aq) \quad \text{or} \quad \ln\left(\frac{x_B(oct)}{x_B(aq)}\right) = \frac{\mu_B^{\dagger}(oct) - \mu_B^{\dagger}(aq)}{RT}$$

The concentrations can alternatively be given as molarities instead of mole fractions.

18.6 Structure-Function Relationships and Solvation

Solvation plays an important role in molecular interactions. Gibbs energies of solvation are commonly used in characterizing substances for structure-activity studies of biological function. Parameters that are used to characterize a substance in structure-activity studies are called **descriptors**. Other common descriptors include dipole moments, molecular mechanics steric energies, molecular volumes, and surface areas. The most commonly used descriptor is **logP**, which characterizes solvation. Log P is the $\log_{10}$ of the octanol/water partition coefficient:

$$P = \frac{c_B(\text{oct})}{c_B(\text{aq})} \qquad 18.6.1$$

The octanol/water partition coefficient is measured by placing the compound under study in a separatory funnel with octanol and water. Octanol and water are immiscible, and the compound partitions between the two phases. The concentration of the compound in the two phases and hence the partition coefficient are a measure of the hydrophobic-hydrophilic character of the compound. The more hydrophobic, the larger are P and logP. LogP is a common descriptor in biological function studies because drugs must often cross membranes. Cell membranes are composed of phospholipids, which have hydrophobic tails that produce a very hydrophobic environment in the middle of the membrane bilayer. Greater hydrophobic character for a drug enhances diffusive transport across membranes.

Log P is directly related to Gibbs energies of desolvation. P is the equilibrium constant for:

$$\text{B (aq)} \rightleftarrows \text{B (oct)} \qquad \Delta_P G^\circ_B = -\,RT \ln P = -\,RT\ 2.303 \log P \qquad 18.6.2$$

and $\Delta_P G^\circ_B$ is the corresponding Gibbs energy change. This system is also introduced in Example 18.5.2, with $\Delta_P G^\circ_B = {}^c\mu^\circ_B(\text{oct}) - {}^c\mu^\circ_B(\text{aq})$ in molar terms. The partitioning can be broken into two separate processes. The first is desolvation from water, which using Eq. 18.3.2† gives:

$$\text{B (aq)} \rightleftarrows \text{B (g)} \qquad \Delta_{desol} G^\circ_B(\text{aq}) = -\,RT \ln k_{pc,B(\text{aq})} \qquad 18.6.3^\dagger$$

where $k_{pc,B(\text{aq})}$ is the Henry's Law constant for substance B in water solution. The second is the desolvation from octanol:

$$\text{B (oct)} \rightleftarrows \text{B (g)} \qquad \Delta_{desol} G^\circ_B(\text{oct}) = -\,RT \ln k_{pc,B(\text{oct})} \qquad 18.6.4^\dagger$$

where $k_{pc,B(\text{octanol})}$ is the Henry's Law constant for substance B in octanol solution. Subtracting Eq. 18.6.4† from Eq. 18.6.3† gives Eq. 18.6.2 with the Gibbs energies related by:

$$\Delta_P G^\circ_B = \Delta_{desol} G^\circ_B(\text{aq}) - \Delta_{desol} G^\circ_B(\text{oct}) \qquad 18.6.5$$

Log P can then be calculated using Eq. 18.6.2. If experimental values for log P are not known, log P can be estimated from Gibbs energies of desolvation.

The key insight of chemistry is the relationship between molecular structure and molecular function. Medicinal chemistry is a particularly rich example of the use of structure-function relationships. **Quantitative Structure Activity Relationships**, **QSAR**, are used to find correlations of biological activity with molecular structure. **Quantitative Structure Property Relationships**, **QSPR**, extend the same idea to chemical property prediction. The relationships are often expressed by a linear equation that relates molecular descriptors, x_{ij}, to the desired biological activity, A_i, for compound i. With q descriptors, the biological activity of the molecule is modeled by the multi-variable linear relationship:

$$A_i = \sum_{j=1}^{q} m_j\, x_{ij} + b \qquad 18.6.6$$

where the m_j and b values are fit coefficients determined using linear least squares curve fitting. An example of a QSAR study is the isonarcotic activity of esters, alcohols, ketones, and ethers with tadpoles, Table 18.7.1. Various organic compounds were added to water with tadpoles. The swimming speed of the tadpoles was observed and the amount of the compound that was necessary to slow the tadpoles was determined, c_i. An effective compound has a low concentration for the production of the desired effect. The activity of the compound is defined to provide a larger activity for a compound with higher efficacy:

$$A_i = \log(1/c_i) \qquad 18.6.7$$

Table 18.7.1: Isonarcotic Activity of Esters, Alcohols, Ketones, and Ethers with Tadpoles.[18]

Compound	log(1/c)	log P
CH_3OH	0.30	-1.27
C_2H_5OH	0.50	-0.75
CH_3COCH_3	0.65	-0.73
$(CH_3)_2CHOH$	0.90	-0.36
$(CH_3)_3COH$	0.90	0.07
$CH_3CH_2CH_2OH$	1.00	-0.23
CH_3COOCH_3	1.10	-0.38
$C_2H_5COCH_3$	1.10	-0.27
$HCOOC_2H_5$	1.20	-0.38
$C_2H_5COC_2H_5$	1.20	0.59
$(CH_3)_2C(C_2H_5)OH$	1.20	0.59
$CH_3(CH_2)_3OH$	1.40	0.29
$(CH_3)_2CHCH_2OH$	1.40	0.16
$CH_3COOC_2H_5$	1.50	0.14
$C_2H_5COC_2H_5$	1.50	0.31
$CH_3(CH_2)_4OH$	1.60	0.81
$CH_3CH_2CH_2COCH_3$	1.70	0.31
$CH_3COOCH_2C_2H_5$	2.00	0.66
$C_2H_5COOC_2H_5$	2.00	0.66
$(CH_3)_2CHCOOC_2H_5$	2.20	1.05

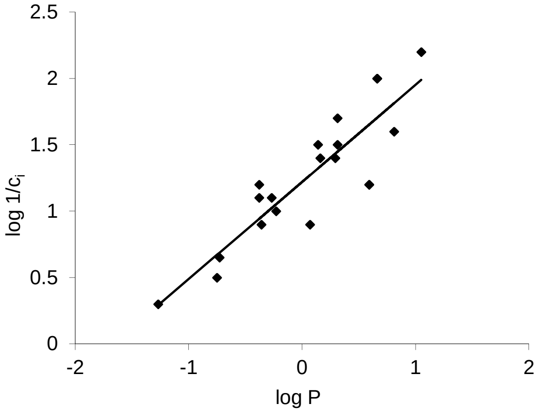


Figure 18.6.1. Isonarcotic Activity of Esters, Alcohols, Ketones, and Ethers with Tadpoles.

After linear least squares regression, Figure 18.6.1, the resulting QSAR equation is:

$$\log(1/c_i) = 0.731 \log P_i + 1.22 \qquad n = 20 \qquad r = 0.881 \qquad 18.6.8$$

The data is reasonably correlated with a regression coefficient of 0.881. In this study only one descriptor is necessary to build an adequate model of the structure-function relationships, but often many descriptors are needed. Solvation, as measured using log P or $\Delta_{desol}G°$, is often a determining factor in correlations of structure with biological activity in medicinal chemistry.

18.7 Summary – Looking Ahead

Partial molar properties enable the fundamental equations of thermodynamics to be easily applied to solutions. For ideal solutions, the partial molar volume is the pure molar volume, the partial molar enthalpy is the pure molar enthalpy, and the Gibbs energy of solution is purely statistically driven. Raoult’s Law and Henry’s Law are the basis for the treatment of ideal and ideal-dilute solutions. The Henry’s Law constant is determined by the solute-solvent intermolecular forces. Raoult’s and Henry’s Law are the basis for the appropriate standard states for components in solution. The standard states are ideal standard states; the values of the standard state properties are determined by extrapolation of the dilute solution environment to unit concentration, giving the ideal limit. The choice of the standard states allows the calculation of the chemical potential of the solvent and solute. At equilibrium the chemical potential of each component is the equal in all phases. The equality of the chemical potential is the basis for understanding phase transitions in multi-component systems. Measurements based on the colligative properties are some of the most commonly made determinations in clinical, industrial, and research laboratories.

The Gibbs phase rule and detailed balance are fundamental principles that govern all chemical phenomena. These two, central generalizations describe the interrelationships between different aspects of chemical reactivity and delineate the boundaries for possible chemical processes. Each principle is a simple statement with wide ranging ramifications.

Most solutions are far from ideal. Experimental methods based on the colligative properties, for example, are independent of the identity of the solute only for very dilute solutions. The properties of real solutions are a function of the <u>activity</u> of the components, rather than the analytical concentration. We introduce the concept of activity in the next chapter. Chemical potentials are then put to use in the study of chemical equilibria in Chapter 20. The theory developed in this chapter allows the prediction of structure-function relationships in solution.

Chapter Summary

1. The partial molar volumes are defined by the derivatives:

$$\bar{V}_A \equiv \left(\frac{\partial V}{\partial n_A}\right)_{T,P,n_B} \qquad \bar{V}_B \equiv \left(\frac{\partial V}{\partial n_B}\right)_{T,P,n_A}$$

2. The total differential of the volume at constant T and P is determined by the partial molar volumes: $dV = \bar{V}_A\, dn_A + \bar{V}_B\, dn_B$
3. Integration of the differential of the volume at constant composition gives the volume of the solution as $V = \bar{V}_A\, n_A + \bar{V}_B\, n_B$.
4. The partial molar volume is the change in volume for adding one mole of substance to so large an amount of solution that the concentration remains unchanged.
5. Gibbs-Duhem relationships give the partial molar property of one constituent in terms of the other. The partial molar volumes and chemical potentials, at constant temperature and pressure, are related by:

$$d\bar{V}_B = -\frac{x_A}{1 - x_A}\, d\bar{V}_A \qquad d\mu_B = -\frac{x_A}{1 - x_A}\, d\mu_A$$

6. V^{1kg} is the volume of a solution that contains 1 kg of solvent. The partial molar volume of the solute is given by:

$$\bar{V}_B = \left(\frac{\partial V}{\partial n_B}\right)_{T,P,n_A} = \left(\frac{\partial V^{1kg}}{\partial m_B}\right)_{T,P,n_A} \left(\frac{1}{1\text{ kg}}\right)$$

7. The apparent molar volume is the volume due to the added solute per mole:

$$^{\phi}V \equiv \frac{V_{\text{solution}} - V_{\text{pure solvent}}}{\text{moles of solute}} = \frac{V - n_A\, V_A^*}{n_B}$$

8. The thermodynamic properties of solutions are functions of the partial molar enthalpy, entropy, and Gibbs energy of the constituents. The partial molar Gibbs energy is the chemical potential. At constant temperature and pressure:

$$dH = \bar{H}_A\, dn_A + \bar{H}_B\, dn_B \qquad H = \bar{H}_A\, n_A + \bar{H}_B\, n_B$$

$dS = \overline{S}_A\, dn_A + \overline{S}_B\, dn_B$ $\qquad\qquad$ $S = \overline{S}_A\, n_A + \overline{S}_B\, n_B$

$dG = \mu_A\, dn_A + \mu_B\, dn_B$ $\qquad\qquad$ $G = \mu_A\, n_A + \mu_B\, n_B$

In general, $dG = -S\, dT + V\, dP + \mu_A\, dn_A + \mu_B\, dn_B$ and $d\mu_i = -\overline{S}_i\, dT + \overline{V}_i\, dP$.

9. For n_A moles of A and n_B moles of B the Gibbs energy of mixing is given by:
   $\Delta_{mix}G = G_2 - G_1 = n_A(\mu_A - \mu_A^*) + n_B(\mu_B - \mu_B^*)$
10. The molar Gibbs energy of mixing of a solute is the Gibbs energy of solvation, $\Delta_{sol}G_B(x_B)$. The Gibbs energy of formation in solution is: $\Delta_f G°(x_B) = \Delta_f G_B^\circ(\text{pure}) + \Delta_{sol}G_B(x_B)$.
11. The Gibbs energy of mixing for ideal solutions is entirely entropic, $\Delta_{mix}G = -T\,\Delta_{mix}S$.
    At constant T and P: $\Delta_{mix}S = -n_{tot}R \sum_{i=1}^{c} x_i \ln x_i$ $\qquad$ $\Delta_{mix}G = n_{tot}RT \sum_{i=1}^{c} x_i \ln x_i$ $\qquad$ $\Delta_{mix}H = 0$
12. The chemical potential of A in solution, at concentration x_A, is equal to the chemical potential of A in the vapor at equilibrium: $\mu_A(x_A) = \mu_A^\circ(g) + RT \ln P_A/P°$.
13. The chemical potential of a constituent is: $\mu_A(x_A) = \mu_A^*(l) + RT \ln P_A/P_A^*$, using the pure liquid standard state, $\mu_A^*(l) = \mu_A^\circ(g) + RT \ln P_A^*/P°$, where P_A^* is the vapor pressure of the pure liquid and P_A is the partial vapor pressure of the substance in equilibrium with the solution.
14. The equilibrium partial vapor pressure of a substance is called the escaping tendency.
15. The partial vapor pressure of a constituent above an ideal solution is given by Raoult's Law: $P_A = x_A\, P_A^*$. If all constituents obey Raoult's Law, the solution is an ideal solution.
16. The equilibrium state for ideal solutions is given by Raoult's and Dalton's Laws:
    - In solution—Raoult's Law: $P_A = x_A P_A^*$ $\qquad$ $P_B = x_B P_B^*$
    - In the vapor—Dalton's Law: $P_{tot} = P_A + P_B = x_A P_A^* + x_B P_B^*$

    $$P_{tot} = x_A P_A^* + (1 - x_A)P_B^*$$

    $$P_A = y_A\, P_{tot} \text{ or } y_A = \frac{P_A}{P_{tot}} = \frac{x_A P_A^*}{P_{tot}} = \frac{x_A P_A^*}{x_A P_A^* + (1 - x_A P_A^*)}$$
17. For an ideal constituent: $\mu_A(x_A) = \mu_A^*(l) + RT \ln x_A$.
18. For an ideal solution, the partial molar volume of a constituent is the pure molar volume, $\overline{V}_A = V_A^*$, the partial molar enthalpy is the pure molar enthalpy, $\overline{H}_A = H_A^*$, and the partial molar entropy is $\overline{S}_A = S_A^* - R \ln x_A$ (see Problems 16 and 17).
19. The solute in dilute solution obeys Henry's Law, $P_B = k_{H,B}\, x_B$, where $k_{H,B}$ is the Henry's Law constant for B. $k_{H,B}$ is the limiting slope of the partial vapor pressure curve as $x_B \rightarrow 0$.
20. Solutions that follow Henry's law for the solute and Raoult's Law for the solvent are called ideal-dilute solutions. Raoult's and Henry's Laws are limiting laws; all solutions approach ideal-dilute behavior in the dilute solution limit, $x_A \rightarrow 1$ and $x_B \rightarrow 0$.
21. The Henry's Law constant, $k_{H,B}$, is the equilibrium constant for the desolvation process:

    $$B\ (x_B) \rightleftarrows B\ (\text{gas}, P_B) \qquad k_{H,B} = P_B/x_B \quad \text{and} \quad \Delta_{desol}G° = -RT \ln k_{H,B}$$

    where $\Delta_{desol}G°$ is the Gibbs energy of desolvation from dilute solution to give the substance in the gas phase; $\Delta_{desol}G° = -\Delta_{sol}G$ for the gas phase of the substance,
22. Henry's Law can be written in concentration units (see Summary Table). Henry's Law in terms of vapor and solution concentrations in molarity: $c_B(g) = k_{cc}\, c_B$ and $\Delta_{desol}G_{cc}^\circ = -RT \ln k_{cc}$ defines the unitless Henry's Law constant, k_{cc}.

23. The chemical potential of a ideal-dilute constituent is: $\mu_B(x_B) = \mu_B^\dagger(l) + RT \ln x_B$, using a Henry's Law standard state, $\mu_B^\dagger(l) \equiv \mu_B^\circ(g) + RT \ln k_{H,B}/P^\circ$.
24. The chemical potential of an ideal-dilute solute can also be expressed is terms of molarity or molality by changing the standard state to unit molarity, ${}^c\mu_B^\circ$, or unit molality, ${}^m\mu_B^\circ$, instead of unit mole fraction, as listed in the Summary Table.
25. Ideal-dilute solutions, by convention, assume a Raoult's Law standard state for the solvent and a Henry's Law standard state for the solute, which guarantees that when the solvent behaves ideally, the solute also behaves ideally.
26. The liquid and vapor compositions at the ends of a tie line are at equilibrium; the chemical potentials of each component are equal in the two phases.
27. The length of a separation column that gives a composition enhancement equivalent to a tie line on the phase diagram is called the height equivalent of the theoretical plate, HETP.
28. An *azeotrope* behaves as if the solution were a pure substance during distillation. The vapor above a solution at the azeotropic composition has the same composition as the solution.
29. A colligative property is a property of dilute solutions that depends only on the concentration of the solute and not the chemical properties or specific identity of the solute.
30. The boiling point elevation and freezing point depression for an ideal-dilute solution at constant pressure, assuming $\Delta_{tr}H_A$ and $\Delta_{tr}S_A$ are constant and the solute is only found in the solution phase, for successively more dilute solutions are:

$$\ln x_A = \frac{\Delta_{vap}H_A}{R}\left(\frac{1}{T} - \frac{1}{T_b^*}\right) \qquad \ln x_A = -\frac{\Delta_{fus}H_A}{R}\left(\frac{1}{T} - \frac{1}{T_m^*}\right)$$

$$\Delta T = -\left(\frac{RT_b^{*2}}{\Delta_{vap}H_A}\right)\ln x_A \qquad \Delta T = -\left(\frac{RT_m^{*2}}{\Delta_{fus}H_A}\right)\ln x_A$$

$$\Delta T \cong \left(\frac{RT_b^{*2}}{\Delta_{vap}H_A}\right) x_B \qquad \Delta T \cong \left(\frac{RT_m^{*2}}{\Delta_{fus}H_A}\right) x_B$$

$$\Delta T \cong K_b\, m_B \qquad K_b \equiv \left(\frac{RT_b^{*2}\mathcal{M}_A\ (1\ \text{kg})}{1000\ \text{g}\ \Delta_{vap}H_A}\right) \qquad \Delta T \cong K_f\, m_B \qquad K_f \equiv \left(\frac{RT_m^{*2}\mathcal{M}_A\ (1\ \text{kg})}{1000\ \text{g}\ \Delta_{fus}H_A}\right)$$

31. For strong electrolytes, for the colligative properties, $m_B = \nu\, m$ or $c_B = \nu\, c$, where ν is the number of ions from the dissociation of the strong electrolyte.
32. The chemical potentials in an ideal-dilute solution at a total pressure of $P + \Delta P$ are:

solvent: $\mu_A(x_A, P+\Delta P) = \mu_A^*(l,P) + RT \ln x_A + \Delta P \bar{V}_A$

$\mu_A(x_A, P+\Delta P) = \mu_A^*(l,P) + (\Delta P - \pi)\bar{V}_A$

solute: $\mu_B(x_B, P+\Delta P) = \mu_B^\dagger(l,P) + RT \ln x_B + \Delta P \bar{V}_B$

where $\bar{V}_A$ and $\bar{V}_B$, the partial molar volumes, are assumed constant over the pressure range.

33. The osmotic pressure with $\mu_A(x_A, P+\pi) = \mu_A^*(l,P)$ for successively more dilute solutions is:

$$\pi\, \bar{V}_A = -RT \ln x_A \qquad \pi\, \bar{V}_A \cong RT\, x_B \qquad \pi\, V \cong x_B\, RT \qquad \pi \cong c_B\, RT$$

34. For solid-liquid equilibrium, the minimum freezing point is called the eutectic temperature and the mole fraction at the eutectic temperature is the eutectic composition.
35. The variance, f, is the number of independent intensive variables at equilibrium. The Gibbs Phase Rule, assuming every component occurs in every phase, is $f = c - p + 2$. At constant T or P, $f' = c - p + 1$, and at constant T and P, $f'' = c - p$.

36. The total number of independent variables needed to describe a system is D = f + p. D is the number of independent variables in the total differential of the Gibbs energy.
37. Log P is a measure of the hydrophobic-hydrophilic character of the compound:

$$\mathrm{B\ (aq)} \rightleftarrows \mathrm{B\ (octanol)} \qquad P = \frac{c_B(\mathrm{octanol})}{c_B(\mathrm{water})} \qquad \Delta_P G^\circ = -RT\ 2.303 \log P$$

with $\Delta_P G^\circ = \Delta_{desol}G^\circ(\mathrm{aq}) - \Delta_{desol}G^\circ(\mathrm{octanol})$.

38. QSAR is used to find correlations of biological activity with molecular structure using linear equations that relate molecular descriptors, x_{ij}, to the desired biological activity, A_i, for compound i:

$$A_i = \sum_{j=1}^{q} m_j\, x_{ij} + b \qquad \text{where the } m_j \text{ and b values are fit coefficients.}$$

Summary Table: Solution Standard States in the Ideal-Dilute Solution limit.

Raoult's Law: Solvent, $x_A = 1$ standard state	Henry's Law: Solute, $x_B = 1$ standard state	Henry's Law: Solute, $m^\circ = 1$ m	Henry's Law: Solute, $c^\circ = 1$ M
$P_A = x_A P_A^*$	$P_B = k_{H,B}\, x_B$	$P_B = k_{pm,B}\, m_B$	$P_B = k_{pc,B}\, c_B$
	$\Delta_{desol}G^\circ = -RT \ln k_{H,B}$	$\Delta_{desol}G^\circ_{pm} = -RT \ln k_{pm,B}$	$\Delta_{desol}G^\circ_{pc} = -RT \ln k_{pc,B}$
		$k_{pm,B} = \dfrac{k_{H,B}\ (1\ \mathrm{kg})}{1000\ \mathrm{g}/\mathcal{M}_A}$	$k_{pc,B} = \dfrac{k_{H,B}\ (1\ \mathrm{L})}{1000\ \mathrm{mL}\ d_{soln}/\mathcal{M}_A}$
		$k_{pm,B} = k_{H,B}/55.51\ \mathrm{mol\ kg^{-1}}$ (*)	$k_{pc,B} = k_{H,B}/55.34\ \mathrm{mol\ L^{-1}}$ (*)
$\mu_A(x_A) = \mu_A^*(l) + RT \ln x_A$	$\mu_B(x_B) = \mu_B^\dagger(l) + RT \ln x_B$	$\mu_B = {}^m\mu_B^\circ(l) + RT \ln m_B/m^\circ$	$\mu_B = {}^c\mu_B^\circ(l) + RT \ln c_B/c^\circ$
$\mu_A^*(l) = \mu_A^\circ(g) + RT \ln P_A^*/P^\circ$	$\mu_B^\dagger(l) \equiv \mu_B^\circ(g) + RT \ln k_{H,B}/P^\circ$	${}^m\mu_B^\circ(l) \equiv \mu_B^\circ(g) + RT \ln k_{pm,B}/P^\circ$	${}^c\mu_B^\circ(l) \equiv \mu_B^\circ(g) + RT \ln k_{pc,B}/P^\circ$
$\mu_A^*(l) = \Delta_f G_A^\circ(\mathrm{pure})$ (°)		${}^m\mu_B^\circ(l) = \Delta_f G_B^\circ(1\ \mathrm{m})$ (°)	${}^c\mu_B^\circ(l) = \Delta_f G_B^\circ(1\ \mathrm{M})$ (°)

(*) Aqueous at 298.15 K (°) Referenced to the pure elements in their standard states.

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Problems: Ideal Solutions

1. The volume of a solution of methanol in water is less than the corresponding sum of the pure components. The solution temperature rises upon mixing. (a). Does this solution show positive or negative deviations from ideality? (b). Are the forces better described as A-B > A-A, B-B or rather A-B < A-A, B-B? (c). Is the vapor pressure of the solution greater than or less than predicted using Raoult's Law? (d). Is the escaping tendency of methanol from the solution greater than or less than that predicted using Raoult's Law? (e). Is the boiling point of the solution greater than or less than predicted using Raoult's Law? (f). Which is larger, the pure vapor pressure of methanol or the Henry's Law constant of methanol in water?

2. A 2.412 m solution of ethanol in water containing 1000.00 g of solvent has a total volume of 1133.08 mL. The partial molar volume of ethanol in this solution is 53.890 mL mol^{-1}. Calculate the partial molar volume of water in this solution.

3. The density of a solution can be accurately determined by measuring the vibration frequency of a U-shaped tube filled with the solution. The volume of a solution containing 1 kg of solvent can be determined from the density of the solution. (a). Show that:

$$V^{1kg} = \frac{n_A\mathfrak{M}_A + n_B\mathfrak{M}_B}{d} = \frac{1000\text{ g} + m_B\,(1\text{ kg})\mathfrak{M}_B}{d}$$

where $\mathfrak{M}_A$ is the molar mass of the solvent, $\mathfrak{M}_B$ is the molar mass of the solute, m_B is the molality of the solute, and d is the density of the solution.
(b). The density of a 5.4266 m solution of ethanol in water is 0.96808 g mL^{-1} at 25°C. The partial molar volume of ethanol in this solution is 54.183 mL mol^{-1}. Calculate the partial molar volume of water in this solution.

4. The relationship between density and the volume of solution that contains 1 kg of solvent is (derived in Problem 3):

$$V^{1kg} = \frac{n_A\mathfrak{M}_A + n_B\mathfrak{M}_B}{d} = \frac{1000\text{ g} + m_B\,(1\text{ kg})\mathfrak{M}_B}{d}$$

The density at 25°C as a function of the concentration of *p*-toluenesulfonic acid in water is given below. The molar mass of *p*-toluenesulfonic acid is 172.205 g mol^{-1}. Calculate the partial molar volumes of *p*-toluenesulfonic acid and water at 2.0000 m at 25°C.[1]

m_B (mol kg^{-1})	0.0000	0.5000	1.0000	2.0000	3.0000	4.0003	4.5005
d (g mL^{-1})	0.99707	1.02159	1.04334	1.07970	1.10846	1.13178	1.14187

5. Prove the relationship for the partial molar volume in Eqs. 18.1.10:

$$\text{Given } V = n_A V_A^* + n_B\,{}^{\phi}V \qquad \text{show that} \quad \bar{V}_B = {}^{\phi}V + m_B\left(\frac{\partial\,{}^{\phi}V}{\partial m_B}\right)_{T,P,n_A}$$

6. The apparent molar volume of sucrose in water is given by the following power series expansion.[2]

$${}^{\phi}V = \bar{V}_B^{\ominus} + RT\,[\,\tfrac{1}{2} A\, m_B + \tfrac{1}{3} B\, m_B^2 + \tfrac{1}{4} C\, m_B^3 + \tfrac{1}{5} D\, m_B^4\,]$$

where $\bar{V}_B^{\ominus}$ is the partial molar volume of the solute at infinite dilution, and A, B, C, and D are constants and R is in units of L atm K^{-1} mol^{-1}. All five coefficients are determined using non-linear least squares curve fitting of experimental data. (a). Find the partial molar volume of the solute as a function of $\bar{V}_B^{\ominus}$, A, B, C, and D. (b). The fit coefficients for sucrose at 25°C are: $\bar{V}_B^{\ominus}$ = 0.21149 L mol^{-1}, A = 1.107×10^{-4} kg mol^{-1} atm^{-1}, B = -1.64×10^{-5} kg^3 mol^{-3} atm^{-1}, C = 1.15×10^{-6} kg^4 mol^{-4} atm^{-1}, and D = 0. Find the partial molar volume of 0.01000 m sucrose at 25°C.

7. Calculate the entropy and Gibbs energy of mixing of 0.80 moles of $H_2O(l)$ and 0.20 moles of ethanol at 298.15 K. Assume an ideal solution.

8. Ethanol from the fermentation of corn or other biomass has been proposed as a replacement for petroleum based transportation fuels. For use in transportation fuels, ethanol must contain less than 0.7% water. Calculate the minimum energy necessary to produce one mole of ethanol, with a concentration of 99.3% ethanol by volume at 25°C, from a fermentation broth containing 15% by volume ethanol. Assume ideal behavior. Compare this minimum separation requirement to the Gibbs energy of combustion of ethanol. The density of ethanol is 0.789 g mL^{-1}.

9. At 50.0°C the vapor pressure of pure hexane and pure heptane are 0.534 bar and 0.188 bar, respectively. The two liquids form nearly an ideal solution. (a) For a solution with a mole fraction of 0.670 heptane, calculate the total vapor pressure and the mole fraction of each component in the vapor phase.[3] (b) The total vapor pressure of a heptane-hexane solution is 0.405 bar. Calculate the mole fraction of heptane in the solution, the partial vapor pressures of each component, and the mole fractions in the vapor phase.

10. At 30.0°C the vapor pressure of pure toluene and pure benzene are 36.7 and 118.2 torr, respectively. The two liquids form a nearly ideal solution. (a) For a solution containing 50.0 mole % of toluene, calculate the total vapor pressure and the mole fraction of each component in the vapor phase. (b) What is the composition of a solution of benzene and toluene that will boil at 30.0°C at a pressure of 50.0 torr?

11. 2-Propanol and 2-methylpropanol form an ideal solution. (a). Calculate the composition of the solution and vapor that boils at 90.0°C and an ambient pressure of 1.00 bar. The standard boiling point of pure 2-propanol is 82.2°C and the enthalpy of vaporization at the standard boiling point is 43.61 kJ mol^{-1}. The standard boiling point of pure 2-methyl-propanol is 107.7°C and the enthalpy of vaporization is 46.26 kJ mol^{-1}. (b). What is the highest purity attainable from a single-plate distillation starting with the composition in Part (a)?

12. The standard state Gibbs energy of formation of methanol in the gas phase at 25°C is -161.96 kJ mol^{-1}. The Henry's Law constant is $k_{pc} = 4.51 \times 10^{-3}$ bar L mol^{-1}. (a). Calculate the standard state Gibbs energy of formation of aqueous methanol at 25°C. (b). Calculate the concentration of methanol in an aqueous solution given an equilibrium vapor pressure for methanol above the solution of 0.0100 bar (1.00 kPa or 7.50 torr).

13. The vapor pressure of heptane in solution with 1-bromobutane is given in the table below, at 50°C.[3] Calculate the Henry's Law constants, k_H, k_{cc}, and k_{pc}, for heptane. The data is plotted in Figure 18.3.1. The density of 1-bromobutane at 25°C is 1.276 g mL^{-1} and the molar mass is 137.02 g mol^{-1}. Assume the density is roughly independent of temperature for this small temperature difference.

x(bromobutane)	0	0.1171	0.2362	0.3329	0.4323	0.5182	0.5836	0.6333
P_{vap}(heptane, torr)	140.0	125.8	110.6	98.4	86.1	74.8	66.4	59.6
x(bromobutane)	0.6588	0.7123	0.7935	0.8805	0.9521	1		
P_{vap}(heptane, torr)	57.3	49	37.2	23.3	9.6	0		

14. The Henry's Law constants, k_H, for O_2 and N_2 in water at 25°C are 4.40×10^4 bar and 8.68×10^4 bar, respectively. Calculate the equilibrium solubility of O_2 and N_2 in water at 25°C in units of molarity and ppm by weight. Find the ratio of O_2 to N_2 in moles. Assume that air is 20.0 mole % O_2 and 80.0 mole % N_2 at a total pressure of 1.00 bar.

15. The Henry's Law constant for CO_2 can be expressed using the concentration of dissolved CO_2, only, or the concentration of CO_2 and carbonic acid:

$$k'_{pc,CO_2} = \frac{P_{CO_2}}{c_{CO_2}} \qquad\qquad k_{pc,CO_2} = \frac{P_{CO_2}}{c_{CO_2} + c_{H_2CO_3}}$$

The equilibrium constant for the dehydration of carbonic acid is about 650:[4]

$$H_2CO_3\ (aq) \rightleftarrows CO_2\ (aq) + H_2O\ (l) \qquad\qquad K = 650$$

The Henry's Law constant for CO_2 in sea water at 25°C is $pk_{pc,CO_2} = -1.53$.[4] Show that $k_{pc,CO_2} \cong k'_{pc,CO_2}$, within experimental error.

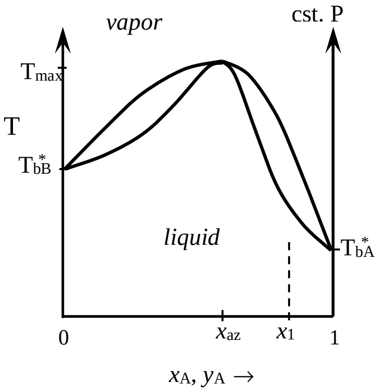
16. Show that the temperature dependence of the chemical potential for an ideal constituent is given by: $(\partial\mu_A/\partial T)_{P,n_A,n_B} = -\overline{S}_A = -S^*_A + R \ln x_A$, where S^*_A is the pure molar entropy of the substance A and the concentration in the solution is x_A.

17. The partial molar entropy of a constituent in an ideal solution, at constant temperature and pressure, is $\overline{S}_i = S^*_i - R \ln x_i$, where S^*_i is the pure molar entropy of the substance i and the concentration of i in the solution is x_i. (See the previous problem for a proof of this equation.) Show that the entropy of mixing of an ideal binary solution is $\Delta_{mix}S = -n_{tot}R\,(x_A \ln x_A + x_B \ln x_B)$ at constant temperature and pressure.

18. Show that the Raoult's Law and Henry's Law standard states for a solute are related by:

$$\mu^{\dagger}_B(l) = \mu^*_B(l) + RT \ln k_{H,B}/P^*_B$$

19. Using the binary liquid-vapor phase diagram shown below, (a). what would be recovered from the distillate and from the pot for an exhaustive fractional distillation, starting with the solution with composition x_1. (b). Does this solution show positive or negative deviations from ideality. Discuss the forces that act in solution as compared to the forces that act in the pure liquids.



20. When 640. mg of naphthalene is dissolved in 40.0 g of chloroform, the boiling point of the solution is 0.455°C higher than that of pure solvent (T^*_A = 61.2°C). Calculate (a) the molal boiling point elevation constant, and (b) the molar enthalpy of vaporization of chloroform.

21. (a). The freezing point depression of a solution of 1.433×10^{-3} g of butanol in 1.000 g of water is 0.035588 K.[5] Calculate the molar mass of butanol. The enthalpy of fusion of water is 6.008 kJ mol^{-1} at 273.15 K. (b). The freezing point depression of a solution of 2.951×10^{-3} g of butanol in 1.000 g of water is 0.07300 K. Calculate the molar mass of butanol again and compare.

22. A sample of benzene has a freezing point of 3.44°C. Calculate the purity of the benzene in mole %. Assume the solution is ideal and the impurities are insoluble in solid benzene. The standard melting point of pure benzene is 5.46°C and the enthalpy of fusion is 10.59 kJ mol^{-1} at the standard melting point.

23. A DSC melting curve was determined for a sample of tetracosane, $C_{24}H_{50}$. The sample weight was 2.21 mg. Partial areas were determined and are reported in the table below, in arbitrary units (as shown schematically in Figure 18.4.7). The total area under the melting curve was 7.351, which corresponds to 0.3919 J. Find the pure melting point, molar enthalpy of fusion, and mol % impurity for the sample. The molar mass of tetracosane is 338.66 g mol^{-1}.

T (K)	322.39	322.44	322.51	322.58
Partial area	1.450	1.669	2.122	2.866

24. Prove that the dependence of the freezing point of a solution on the concentration of the solvent is given by (start with the chemical potentials of the pure solvent and the solution):

$$\ln x_A = -\frac{\Delta_{fus}H_A}{R}\left(\frac{1}{T} - \frac{1}{T_m^*}\right)$$

25. Polyvinyl alcohol is often used in lecture demonstrations to make “slime.” A 4.00% by mass solution of polyvinyl alcohol was placed in an osmometer. The height of the solution above the surface of the pure water at equilibrium was 21.6 cm at 25.0°C. Assume the density of the solution is that of pure water. Calculate the approximate molar mass of the polyvinyl alcohol and the average number of monomers, n, linked in the polymer. [Hint: Polyvinyl alcohol is $CH_3CH(OH)[CH_2CH(OH)]_{n-2}CH_2CH_2OH$, so use $–CH_2CH(OH)-$ for the monomer molar mass.]

26. Osmotic pressure is used to determine the molar mass of polymers. However, Eq. 18.4.30† assumes ideal behavior. For real solutions, Eq. 18.4.30† gives an *effective* molar mass. For careful determinations, the *effective* molar mass of a sample is determined at several concentrations and extrapolated to zero concentration, where Eq. 18.4.30† becomes exact. The osmotic pressure of a sample of polystyrene in toluene was determined at several concentrations at 25°C. Find the molar mass of the polystyrene sample.[6]

C_B (g L^{-1})	2.60	5.16	6.54	9.19
π (Pa)	9.80	32.0	51.0	107.

27. A 0.1000 m aqueous urea solution and pure water are separated by a membrane that is impermeable to urea and permeable to water, at 25°C and 1 bar. Calculate the chemical potential of urea in the solution, relative to the standard state chemical potential, at equilibrium. The density of the solution is 0.99873 g $mL^{-1}$and the data necessary to obtain the partial molar volume of urea is given in Example 18.1.1.

28. Calculate the chemical potential of water in a 0.200 M solution of sucrose at 10.00 bar and 25°C. The partial molar volume of water in this solution is well approximated by the pure molar volume.

29. Starting with the expression for the chemical potential of the solvent in an ideal-dilute solution, prove Eq. 18.4.15†.

30. Consider the solubility of a pure solid, B, in a solvent at temperature T. Assume that the solution is ideal-dilute and at constant pressure. (a). Show that: $\mu_B^*(s) = \mu_B^\dagger(l) + RT \ln x_B$.
(b). The standard state Gibbs energy of solution of the pure solid at temperature T is defined as: $\Delta_{sol}G_B^\circ(T) = \mu_B^\dagger(l) - \mu_B^*(s)$. Show that the solubility of the solute is: $\ln x_B = -\Delta_{sol}G_B^\circ(T)/RT$.
(c). At reference temperature T_o the solubility is x_{Bo}. Show that the temperature dependence of the solubility is given by:

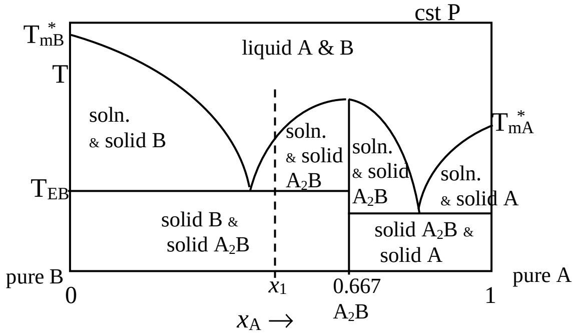
$$\ln \frac{x_B}{x_{Bo}} = -\frac{\Delta_{sol}H_B^\circ}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right) \qquad \text{(ideal-dilute, cst. P)} \qquad \text{P18.29.1}^\dagger$$

31. (a). Show that for small changes in temperature, $\Delta T \equiv T - T_o$, Eq. P18.29.1† reduces to:

$$x_B = x_{Bo} + \left(\frac{\Delta_{sol}H_B^\circ\, x_{Bo}}{RT_o^2}\right)\Delta T$$

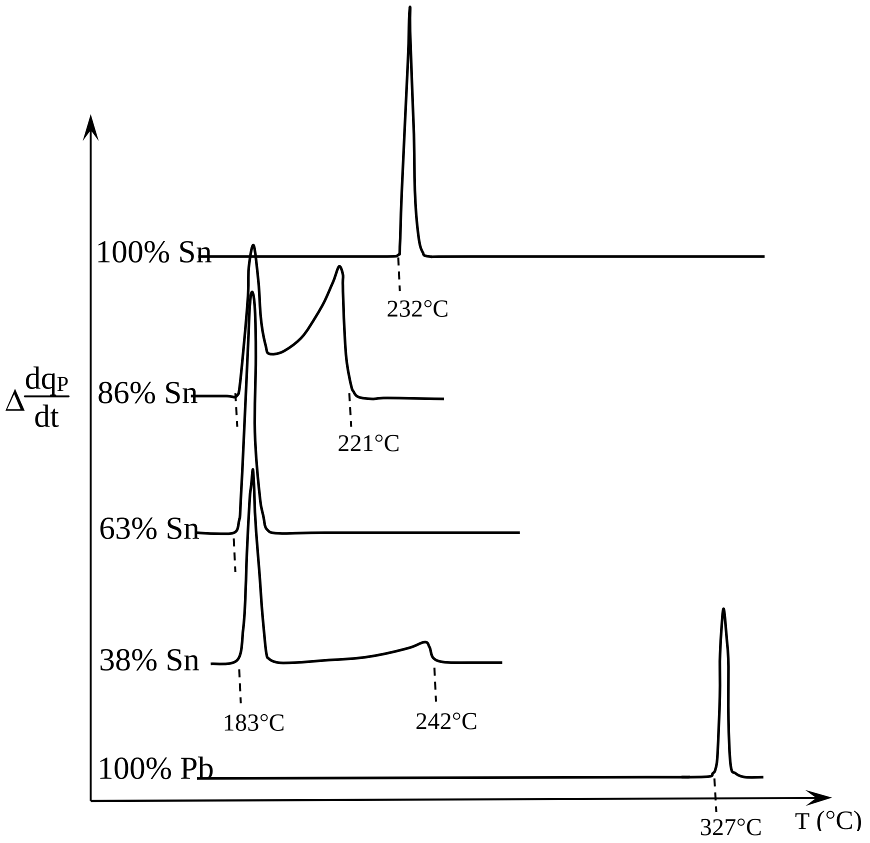
(b). Show that this equation and LeChâtelier's Principle are consistent.

32. Many binary solid-liquid phase diagrams are more complex than Figure 18.4.11. Some systems show the formation of a stable binary **compound** in the solid phase. Compounds typically have simple stoichiometries, such as A_2B, that are stabilized by strong intermolecular forces, like hydrogen bonding, or favorable crystal packing forces. The compound components are not covalently bound, and the compound doesn't exist in the liquid phase. An example of a compound in the phase diagram for NaCl in water is the dehydrate, $NaCl \cdot 2(H_2O)$. The solid-liquid phase diagram for a system with a stable solid-state compound, A_2B, is shown below. Analyzing a phase diagram that shows compound formation can be simplified by treating the compound as a hypothetical pure substance and dividing the phase diagram to either side as separate binary systems. Describe the phase transitions that occur along the cooling curve at the indicated composition, x_1.



33. Relate the changes in the slopes of the segments on the cooling curve, Figure 18.4.12, and the widths of the peaks on the DSC melting curve, Figure 18.4.13, to the variances of the system at constant pressure. Discuss segments b-c and c-d.

34. The following DSC melting thermograms were obtained from a range of starting compositions of Sn and Pb. The compositions are given as % by mass. The baselines of the thermograms are offset for clarity. Sketch the binary solid-liquid phase diagram. Use % by mass Sn as the composition axis, instead of mole fraction; % by mass gives a more convenient plot for this system.[7]



35. Find the variance for a gas in equilibrium with an aqueous solution of the gas. Give an expression for the general differential of the Gibbs energy, the change in Gibbs energy at constant temperature, and the change in Gibbs energy at constant temperature and pressure. Discuss the independent variables.

36. Two partially miscible liquids, A and B, form a two-phase liquid system at equilibrium. One phase is mostly A with a small amount of B and the other phase is mostly B with a small amount of A. Consider only the liquid phases. Give an expression for the general differential of the Gibbs energy, the change in Gibbs energy at constant temperature, and the change in Gibbs energy at constant temperature and pressure. Discuss the independent variables. Most non-polar organic liquids and water are examples of this type of behavior; small amounts of water dissolve in the organic layer and small amounts of organic substance dissolve in the aqueous layer.

37. A system containing three components is univariant. How many phases are present?

38. Show that for a pure substance the largest number of phases that can coexist is three.

39. Determine if the following statements are true or false. If the statement is false, describe the changes that are necessary to make the statement true, if possible. If the statement is true but too restrictive, give the more general statement.

(a). A champagne toast was used to celebrate the final stages of the construction of a transportation tunnel under the Thames River in London, in November 1827.[8] The celebration fell flat because at the higher ambient pressure in the tunnel, the Henry's Law solubility of the CO_2 in the wine increased, making the champagne taste flat. Participants also suffered gastric distress upon regaining ground level. This event is a practical example of Henry's Law.

(b). Soft drinks may be kept from "defizzing" by pumping air into the empty space above the soft drink in a partially filled bottle.

(c). Consider a two-phase region for a binary solid-liquid equilibrium system at constant pressure, with solution in equilibrium with pure solid A, Figure 18.4.12. At a fixed temperature, the solution composition may be any value along the tie line.

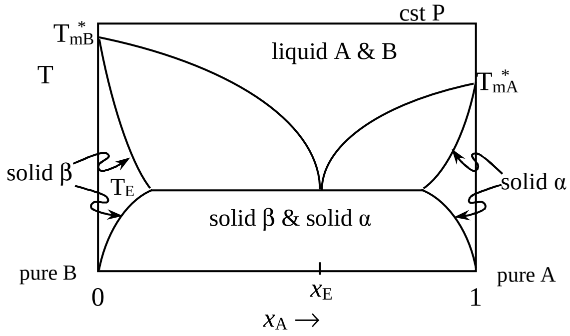
(d). A solution has a minimum freezing point (the eutectic temperature) because at the minimum temperature, the both the solute and the solvent have limited solubility in solution.

(e). The theory of ideal-dilute solutions doesn't take solute-solvent forces into account.

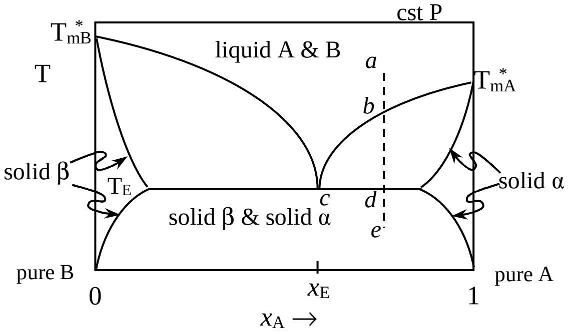
(f). The boiling point is elevated and the freezing point is depressed in a dilute solution of methanol in water.

(g). Two phases cannot be in equilibrium unless all components occur in each phase.

40. For many binary solid-liquid systems, the two solids are partially miscible. The solid phases consist of a phase rich in A with small amounts of B, the α phase, and a phase rich in B with small amounts of A, the β phase. Cooling a solution of A and B, with an initial concentration greater than the eutectic composition, freezes out solid α. Cooling a solution of A and B, with an initial concentration less than the eutectic composition, gives solid β. Below the eutectic temperature, solid β and solid α are in equilibrium. The compositions of the two solid phases depend on temperature. The phase diagram for a binary solid-liquid system with partial miscibility is shown below, at constant pressure. Describe the phases in equilibrium in each part of the phase diagram. Give the variance, f ', for each accessible region of the phase diagram.



41. For many binary solid-liquid systems, the two solids are partially miscible. The solid phases consist of a phase rich in A with small amounts of B, the α phase, and a phase rich in B with small amounts of A, the β phase. Below the eutectic temperature, solid β and solid α are in equilibrium. The compositions of the two solid phases depend on temperature. The phase diagram for a binary solid-liquid system with partial miscibility is shown below, at constant pressure. Describe the phase changes that occur as the solution starting at point *a* is cooled to below the eutectic temperature, point *e*.



42. Consider a binary solid-liquid system with components that are completely immiscible in the solid phase, Figure 18.4.11. Below the eutectic temperature, only pure solid A and pure solid B are present. The general form of the Gibbs Phase Rule, f = c – p + 2, does not apply to this region because the components A and B don't occur in all the phases. Determine the variance in the two-phase solid region below the eutectic temperature for immiscible components.

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