

Chapter 18 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?

Answers: (a). Negative deviations; the combined volume is less than the corresponding sum of the pure components. (b). $A-B > A-A, B-B$; the forces are favorable in solution. (c). The partial vapor pressures of each component and the total vapor pressures are less than predicted by Raoult's Law. (d). The escaping tendency is measured by the vapor pressure; the escaping tendency of methanol from the solution is less than predicted by Raoult's Law. (e). Since the vapor pressures are less, the solution must be heated to a higher temperature to have the total vapor pressure of the solution equal to ambient pressure, as compared to the Raoult's Law prediction. (f). $P_B^* > k_{H,B}$, as is diagrammed in Figure 18.3.3a for negative deviations from ideality.

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 $53.890 \text{ mL mol}^{-1}$. Calculate the partial molar volume of water in this solution.

Answer: The number of moles of solute in a solution containing 1000.00 g of solvent is:

$$n_B = m_B (1 \text{ kg})$$

For a 2.412 m solution containing 1000.00 g of solvent, $n_B = 2.412 \text{ mol}$. Using Eq. 18.1.3:

$$V = \bar{V}_A n_A + \bar{V}_B n_B$$

$$1133.08 \text{ mL} = \bar{V}_A 1000.0 \text{ g}/18.0153 \text{ g mol}^{-1} + 53.890 \text{ mL mol}^{-1}(2.412 \text{ mol})$$

$$\bar{V}_A = (1133.08 \text{ mL} - 129.98 \text{ mL})(18.0153 \text{ g mol}^{-1}/1000.0 \text{ g}) = 18.0711 \text{ mL mol}^{-1}$$

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:

$$V^{1\text{kg}} = \frac{n_A \rho_A + n_B \rho_B}{d} = \frac{1000 \text{ g} + m_B (1 \text{ kg}) \rho_B}{d}$$

where \mathcal{M}_A is the molar mass of the solvent, \mathcal{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 $0.96808 \text{ g mL}^{-1}$ at 25°C . The partial molar volume ethanol in this solution is $54.183 \text{ mL mol}^{-1}$. Calculate the partial molar volume of water in this solution.

Answer: (a). The number of moles of solute in a solution containing 1000.00 g of solvent is: $n_B = m_B (1 \text{ kg})$. The total mass of the solution, solute plus solvent, is $n_A \mathcal{M}_A + n_B \mathcal{M}_B$. The volume of the solution is the mass divided by the density:

$$V^{1\text{kg}} = \frac{\text{mass solution}}{\text{density of solution}} = \frac{n_A \mathcal{M}_A + n_B \mathcal{M}_B}{d} = \frac{1000 \text{ g} + m_B (1 \text{ kg}) \mathcal{M}_B}{d}$$

For the particular solution in this problem with $\mathcal{M}_B = 46.06904 \text{ g mol}^{-1}$ for ethanol:

$$V^{1\text{kg}} = \frac{1000.00 \text{ g} + 5.4266 \text{ m} (1 \text{ kg})(46.06904 \text{ g mol}^{-1})}{0.96808 \text{ g mL}^{-1}} = 1291.214 \text{ mL}$$

Using Eq. 18.1.3 to find the partial molar volume of the solvent:

$$V = \bar{V}_A n_A + \bar{V}_B n_B$$

$$1291.214 \text{ mL} = \bar{V}_A 1000.0 \text{ g}/18.0153 \text{ g mol}^{-1} + 54.183 \text{ mL mol}^{-1}(5.4266 \text{ mol})$$

$$\bar{V}_A = (1291.214 \text{ mL} - 294.029 \text{ mL})(18.0153 \text{ g mol}^{-1}/1000.0 \text{ g}) = 17.9646 \text{ mL mol}^{-1}$$

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

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

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 $172.205 \text{ g mol}^{-1}$. Calculate the partial molar volumes of *p*-toluenesulfonic acid and water at 2.0000 m at 25°C .¹

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

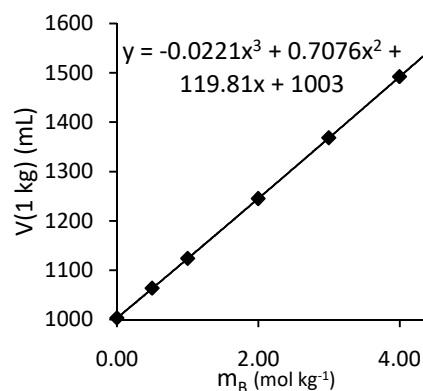
Answer: The plan is to calculate $V^{1\text{kg}}$ for each solution and fit the results to a cubic polynomial in the molality. Then Eq. 18.1.8 is used to find the partial molar volume of the solute and Eq. 18.1.3 is used to find the partial molar volume of the solvent, as in Example 18.1.1.

A spreadsheet was set up to do the calculations. The $V^{1\text{kg}}$ vs. m_B values were fit to a cubic polynomial using the 4-parameter version of the “Non-Linear Least Squares” applet on the textbook Web site or the companion CD. The applet allowed the determination of the uncertainties of the fit parameters. The fit parameters were entered into the spreadsheet and Eq. 18.1.8 was used to calculate the partial molar volumes:

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$$\bar{V}_B = \left(\frac{\partial V}{\partial m_B} \right)_{T,P,n_A} \text{ kg}^{-1} = 3(-0.0221) \text{ m}^2 + 2(0.708) \text{ m} + 119.81 \text{ mL mol}^{-1}$$

	ϱ_A	18.0153	g mol ⁻¹	
	ϱ_B	172.205	g mol ⁻¹	
	a	-0.0221	± 0.0152	
	b	0.708	± 0.1	
	c	119.81	± 0.19	
m_B (mol kg ⁻¹)	d (g mL ⁻¹)	$V^{1\text{kg}}$ (mL)	V_B (mL mol ⁻¹)	V_A (mL mol ⁻¹)
0.0000	0.99707	1002.939	119.810	18.068
0.5000	1.02159	1063.149	120.501	18.068
1.0000	1.04334	1123.512	121.160	18.058
2.0000	1.07970	1245.17	122.377	18.023
3.0000	1.10846	1368.218	123.461	17.976
4.0003	1.13178	1492.226	124.413	17.917
4.5005	1.14187	1554.475	124.840	17.883



The partial molar volumes of the solvent are then calculated using Eq. 18.1.3:

$$V^{1\text{kg}} = \bar{V}_A \frac{1000 \text{ g}}{\varrho_A} + \bar{V}_B m_B (1 \text{ kg})$$

and solving for the partial molar volume of the solvent, for example at 2.000 m:

$$\begin{aligned} \bar{V}_A &= \frac{[V^{1\text{kg}} - \bar{V}_B m_B (1 \text{ kg})] \varrho_A}{1000 \text{ g}} \\ &= \frac{[1245.17 \text{ mL} - 122.377 \text{ mL mol}^{-1} (2.000 \text{ mol kg}^{-1}) (1 \text{ kg})] 18.0153 \text{ g mol}^{-1}}{1000 \text{ g}} \\ &= 18.023 \text{ mL mol}^{-1} \end{aligned}$$

Notice that as the partial molar volume of *p*-toluenesulfonic acid increases that the partial molar volume of water decreases, as required by the Gibbs-Duhem relationship. One caution, however: a cubic curve fit isn't statistically justified with only seven data points. The original literature reference had more data points, but some points were dropped to make the problem more tractable for this homework. Never-the-less, the results here are sufficiently close to the literature values.

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

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

Answer: Using the definition of partial molar volume from Eq. 18.1.8 and the volume in terms of the apparent molar volume gives:

$$\bar{V}_B = \left(\frac{\partial V}{\partial n_B} \right)_{T,P,n_A} = \left(\frac{\partial n_A V_A^*}{\partial n_B} \right)_{T,P,n_A} + \left(\frac{\partial n_B \phi V}{\partial n_B} \right)_{T,P,n_A}$$

The first term is zero because n_A and the pure molar volume of the solvent are constants. Using the product rule for the second term gives:

$$\bar{V}_B = \phi V + n_B \left(\frac{\partial \phi V}{\partial n_B} \right)_{T,P,n_A}$$

We can change the independent variable to molality by using the definition, $m_B = n_B/w_A$, with the mass of solvent, w_A , a constant:

$$\bar{V}_B = \phi V + n_B \left(\frac{\partial \phi V}{\partial m_B} \right)_{T,P,n_A} \left(\frac{\partial m_B}{\partial n_B} \right)_{T,P,n_A} = \phi V + \frac{n_B}{w_A} \left(\frac{\partial \phi V}{\partial m_B} \right)_{T,P,n_A} \left(\frac{\partial n_B}{\partial n_B} \right)_{T,P,n_A}$$

$$\bar{V}_B = \phi V + m_B \left(\frac{\partial \phi V}{\partial m_B} \right)_{T,P,n_A}$$

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

$$\phi V = \bar{V}_B^{\circ} + RT \left[\frac{1}{2} A m_B + \frac{1}{3} B m_B^2 + \frac{1}{4} C m_B^3 + \frac{1}{5} D m_B^4 \right]$$

where \bar{V}_B° 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° , A, B, C, and D. (b). The fit coefficients for sucrose at 25°C are: $\bar{V}_B^{\circ} = 0.21149$ L mol⁻¹, $A = 1.107 \times 10^{-4}$ kg mol⁻¹ atm⁻¹, $B = -1.64 \times 10^{-5}$ kg³ mol⁻³ atm⁻¹, $C = 1.15 \times 10^{-6}$ kg⁴ mol⁻⁴ atm⁻¹, and $D = 0$. Find the partial molar volume of 0.01000 m sucrose at 25°C.

Answer: (a). Using Eqs. 18.1.10 and the given power series expansion of the apparent molar volume, the derivative gives:

$$\begin{aligned} \bar{V}_B &= \phi V + m_B \left(\frac{\partial \phi V}{\partial m_B} \right)_{T,P,n_A} \\ &= \phi V + m_B RT \left[\frac{1}{2} A + \frac{2}{3} B m_B + \frac{3}{4} C m_B^2 + \frac{4}{5} D m_B^3 \right] \end{aligned}$$

Substituting in the power series for ϕV :

$$\begin{aligned} \bar{V}_B &= \bar{V}_B^{\circ} + RT \left[\frac{1}{2} A m_B + \frac{1}{3} B m_B^2 + \frac{1}{4} C m_B^3 + \frac{1}{5} D m_B^4 \right] + RT \left[\frac{1}{2} A m_B + \frac{2}{3} B m_B^2 + \frac{3}{4} C m_B^3 + \frac{4}{5} D m_B^4 \right] \\ \bar{V}_B &= \bar{V}_B^{\circ} + RT \left[A m_B + B m_B^2 + C m_B^3 + D m_B^4 \right] \end{aligned}$$

(b). Using the given fit coefficients and $m_B = 0.0100$ m gives:

$$\begin{aligned} \bar{V}_B &= 0.21149 \text{ L mol}^{-1} + 0.082058 \text{ L atm K}^{-1} \text{ mol}^{-1} (298.15 \text{ K}) \cdot \\ &\quad \left[1.107 \times 10^{-4} (0.01000) + (-1.64 \times 10^{-5}) (0.01000)^2 + 1.15 \times 10^{-6} (0.01000)^3 \right] \text{ atm}^{-1} \\ \bar{V}_B &= 0.21152 \text{ L} = 211.52 \text{ mL} \end{aligned}$$

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This partial molar volume was used in Example 18.4.8. The density of pure sucrose is $d_{\text{pure}} = 1.588 \text{ g mL}^{-1}$. The partial molar volume of sucrose is not far from the pure molar volume, $V_B^* = \mathcal{M}_B/d_{B,\text{pure}} = 342.30 \text{ g mol}^{-1}/1.588 \text{ g mL}^{-1} = 215.5 \text{ mL}$. The pure molar volume could have been used for Example 18.4.8 without excessive error, since the concentration dependent term is so large.

7. Calculate the entropy and Gibbs energy of mixing of 0.80 moles of $\text{H}_2\text{O}(\text{l})$ and 0.20 moles of ethanol at 298.15 K. Assume an ideal solution.

Answer: Using Eqs. 18.2.10° and 18.2.11° or 16.8.16°:

$$\begin{aligned}\Delta_{\text{mix}}S &= -n_{\text{tot}}R \sum_{i=1}^{n_s} x_i \ln x_i = -1.00 \text{ mol}(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})[0.80 \ln 0.80 + 0.20 \ln 0.20] \\ &= 4.16 \text{ J K}^{-1}\end{aligned}$$

$$\Delta_{\text{mix}}G = -T \Delta_{\text{mix}}S = -298.15 \text{ K}(4.16 \text{ J K}^{-1})(1 \text{ kJ}/1000 \text{ J}) = -1.24 \text{ kJ mol}^{-1}$$

8. Ethanol from the fermentation of corn or other sources of biomass has been proposed as a large scale 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} .

Answer: The molar mass of ethanol is 46.07 g mol^{-1} . Assuming a total volume of 100 mL, 15% by volume corresponds to mole amounts: $n_{\text{EtOH}} = 15 \text{ mL}(0.789 \text{ g mL}^{-1})/46.07 \text{ g mol}^{-1} = 0.257 \text{ mol}$ and $n_{\text{H}_2\text{O}} = 85 \text{ mL}(0.9971 \text{ g mL}^{-1})/18.02 \text{ g mol}^{-1} = 4.70 \text{ mol}$. The mole fractions are:

$$x_{\text{EtOH}} = \frac{0.257 \text{ mol}}{4.70 \text{ mol} + 0.257 \text{ mol}} = 0.0518 \quad \text{and} \quad x_{\text{H}_2\text{O}} = 1 - 0.0518 = 0.948$$

After the separation, 100 mL of 99.3% ethanol by volume corresponds to $n_{\text{EtOH}} = 99.3 \text{ mL}(0.789 \text{ g mL}^{-1})/46.07 \text{ g mol}^{-1} = 1.701 \text{ mol}$ and $n_{\text{H}_2\text{O}} = 0.7 \text{ mL}(0.9971 \text{ g mL}^{-1})/18.02 \text{ g mol}^{-1} = 0.039 \text{ mol}$. The mole fractions are:

$$x_{\text{EtOH}} = \frac{1.701 \text{ mol}}{0.039 \text{ mol} + 1.701 \text{ mol}} = 0.978 \quad \text{and} \quad x_{\text{H}_2\text{O}} = 1 - 0.978 = 0.022$$

For the 15% solution, one mole of ethanol is contained in $n_{\text{tot}} = 1 \text{ mol}/x_{\text{EtOH}} = 1/0.0518 = 19.31 \text{ mol}$ of total solution. For the 99.3% solution, one mole of ethanol is contained in $n_{\text{tot}} = 1 \text{ mol}/x_{\text{EtOH}} = 1/0.978 = 1.02 \text{ mol}$ of total solution. The Gibbs energy of mixing, using Eqs. 18.2.10* and 18.2.11*, for the 15% ethanol solution is:

$$\begin{aligned}\Delta_{\text{mix}}S &= -n_{\text{tot}}R \sum_{i=1}^{n_s} x_i \ln x_i \\ &= -19.31 \text{ mol}(8.314 \text{ J K}^{-1} \text{ mol}^{-1})[0.0518 \ln 0.0518 + 0.948 \ln 0.948] \\ &= 32.7 \text{ J K}^{-1}\end{aligned}$$

$$\Delta_{\text{mix}}G = -T \Delta_{\text{mix}}S = -298.15 \text{ K}(32.7 \text{ J K}^{-1})(1 \text{ kJ}/1000 \text{ J}) = -9.76 \text{ kJ} \quad (15 \% \text{ v/v})$$

The Gibbs energy of mixing for the 99.3% ethanol solution is:

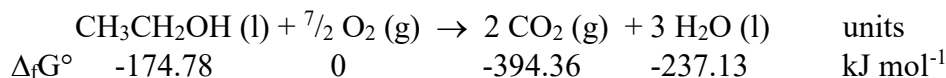
$$\begin{aligned}\Delta_{\text{mix}}S &= -n_{\text{tot}}R \sum_{i=1}^{n_s} x_i \ln x_i \\ &= -1.02 \text{ mol}(8.314 \text{ J K}^{-1} \text{ mol}^{-1})[0.978 \ln 0.978 + 0.022 \ln 0.022] \\ &= 0.897 \text{ J K}^{-1}\end{aligned}$$

$$\Delta_{\text{mix}}G = -T \Delta_{\text{mix}}S = -298.15 \text{ K}(0.897 \text{ J K}^{-1})(1 \text{ kJ}/1000 \text{ J}) = -0.267 \text{ kJ} \quad (99.3 \% \text{ v/v})$$

The Gibbs energy to prepare one mole of ethanol is then the difference:

$$\Delta G = -0.267 \text{ kJ} - (-9.76 \text{ kJ}) = 9.49 \text{ kJ}$$

The molar Gibbs energy of combustion of ethanol is:



$$\Delta_{\text{comb}}G^\circ = [2(-394.36) + 3(-237.13)] - [-174.78] \text{ kJ mol}^{-1} = -1325.33 \text{ kJ mol}^{-1}$$

The ideal minimum Gibbs energy for the separation is a small fraction of the Gibbs energy of combustion, suggesting that biomass conversion to ethanol is an excellent candidate for replacing petroleum. However, distillation and zeolite based drying of ethanol are inefficient processes. All energy inputs need to be considered as well as soil depletion and especially water use. Forest and agricultural waste and hemi-cellulose, a bi-product of the paper industry, are good candidates for conversion to ethanol.

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.

Answer: (a). Use an “X” subscript for hexane and a “P” subscript for heptane: $P_X^* = 0.534 \text{ bar}$, $P_P^* = 0.188 \text{ bar}$, $x_P = 0.670$, $x_X = (1 - x_P) = 0.330$. The total pressure, using Raoult’s law for both components, Eq. 18.2.7*, is:

$$P_{\text{tot}} = x_X P_X^* + x_P P_P^* = 0.330(0.534 \text{ bar}) + 0.670(0.188 \text{ bar}) = 0.302 \text{ bar}$$

Using Dalton’s Law of partial pressures for the vapor phase with, $P_P = y_P P_{\text{tot}}$, Eq. 18.4.1*:

$$y_P = P_P/P_{\text{tot}} = x_P P_P^*/P_{\text{tot}} = 0.670(0.188 \text{ bar})/0.302 \text{ bar} = 0.417$$

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$$\text{and } y_X = 1 - y_P = 1 - 0.417 = 0.583$$

As a check we note that the vapor is richer than the solution in the more volatile component, hexane, as expected. The literature value for the total pressure is 0.293 bar, so the solution shows small negative deviations from ideality.³

(b). This part of the problem works in the opposite direction as in part (a). Using Eq. 18.2.8*, $x_X = (1 - x_P)$, and solving for x_P :

$$P_{\text{tot}} = x_X P_X^* + x_P P_P^* = (1 - x_P) P_X^* + x_P P_P^* = P_X^* + x_P (P_P^* - P_X^*)$$

$$x_P = \frac{P_{\text{tot}} - P_X^*}{P_P^* - P_X^*}$$

and for $P_{\text{tot}} = 0.405$ bar:

$$x_P = \frac{0.405 - 0.534}{0.188 - 0.534} = 0.373 \quad \text{and} \quad x_X = 1 - x_P = 0.627$$

Using Raoult's Law for both components in solution, the partial vapor pressures are:

$$P_X = x_X P_X^* = 0.627(0.534 \text{ bar}) = 0.335 \quad P_P = x_P P_P^* = 0.373(0.188 \text{ bar}) = 0.070$$

As a check on the calculations, we should verify the total pressure as the sum of the partial vapor pressures from the last calculation, $P_{\text{tot}} = P_X + P_P = 0.335 + 0.070 = 0.405$, as given. Finally, using Dalton's Law for each component in the vapor phase, the vapor phase mole fractions are, Eq. 2.1.10°:

$$y_X = P_X/P_{\text{tot}} = 0.335/0.405 = 0.827 \quad \text{and} \quad y_P = 1 - y_X = 0.173$$

As a check we note that the vapor is richer than the solution in the more volatile component, hexane, as expected. The literature value for the mole fraction of heptane in this solution is $x_P = 0.358$ for only a 4% error, caused by the assumption of ideal behavior.³

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?

Answer: (a). Use a "T" subscript for toluene and a "B" subscript for benzene: $P_T^* = 36.7$ torr, $P_B^* = 118.2$ torr, $x_T = 0.500$, $x_B = 0.500$. The total pressure, using Raoult's law for both components, is, Eq. 18.2.7*:

$$P_{\text{tot}} = x_T P_T^* + x_B P_B^* = 0.500(36.7 \text{ torr}) + 0.500(118.2 \text{ torr}) = 77.5 \text{ torr}$$

We use Dalton's law of partial pressures for the vapor phase with, $P_T = y_T P_{\text{tot}}$, Eq. 18.4.1*:

$$y_T = P_T/P_{\text{tot}} = x_T P_T^*/P_{\text{tot}} = 0.500(36.7 \text{ torr})/77.5 \text{ torr} = 0.237$$

$$\text{and } y_B = 1 - y_T = 1 - 0.237 = 0.763$$

As a check, we note that the vapor is richer in the more volatile component, benzene, than the liquid, as expected.

(b). This part of the problem corresponds to a reduced pressure distillation. If the solution is boiling, the vapor pressure is equal to the ambient pressure, $P_{\text{tot}} = 50$ torr:

$$P_{\text{tot}} = x_{\text{T}} P_{\text{T}}^* + x_{\text{B}} P_{\text{B}}^* = 50 \text{ torr}$$

Substituting in the pure vapor pressures and noting that $x_{\text{B}} = 1 - x_{\text{T}}$:

$$P_{\text{tot}} = 50 \text{ torr} = x_{\text{T}}(36.7 \text{ torr}) + (1 - x_{\text{T}})(118.2 \text{ torr})$$

gives $x_{\text{T}} = 0.837$ and $x_{\text{B}} = 1 - x_{\text{T}} = 0.163$

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 $43.61 \text{ kJ mol}^{-1}$. The standard boiling point of pure 2-methyl-propanol is 107.7°C and the enthalpy of vaporization is $46.26 \text{ kJ mol}^{-1}$. (b). What is the highest purity attainable from a single-plate distillation starting with the composition in Part (a)?

Answer: The plan is to use the Clausius-Clapeyron equation to calculate the pure vapor pressures at 90.0°C . Example 18.4.3 then describes the remaining steps to find the corresponding compositions in Figure 18.4.2.

Using Eq. 17.1.14° for 2-propanol, with $T_{\text{b}}^* = 355.4 \text{ K}$ at 1 bar, gives the vapor pressure at 90.0°C , 363.2 K, as:

$$P_2 = P_1 e^{-\frac{\Delta_{\text{tr}}H_{\text{m}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} = 1 \text{ bar } e^{-\frac{43.61 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\left(\frac{1}{363.2 \text{ K}} - \frac{1}{355.4 \text{ K}}\right)} = 1.374 \text{ bar}$$

and for 2-methyl-propanol, with $T_{\text{b}}^* = 380.9 \text{ K}$:

$$P_2 = 1 \text{ bar } e^{-\frac{46.26 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\left(\frac{1}{363.2 \text{ K}} - \frac{1}{380.9 \text{ K}}\right)} = 0.491 \text{ bar}$$

Let A be 2-propanol. Using Eq. 18.2.8* with the total vapor pressure of 1 bar gives the composition of the solution from:

$$P_{\text{tot}} = x_{\text{A}} P_{\text{A}}^* + (1 - x_{\text{A}}) P_{\text{B}}^* = x_{\text{A}}(1.374 \text{ bar}) + (1 - x_{\text{A}})(0.491 \text{ bar}) = 1 \text{ bar}$$

Solving for the solution concentration of A: $x_{\text{A}} = 0.576$.

The vapor phase concentration is calculated using Eq. 18.4.1*:

$$y_{\text{A}} = P_{\text{A}}/P_{\text{tot}} = x_{\text{A}} P_{\text{A}}^*/P_{\text{tot}} = 0.576(1.374 \text{ bar})/1.00 \text{ bar} = 0.791$$

These points are consistent with Figure 18.4.2. (b). For a distillation, if the initial pot concentration is $x_{\text{A}} = 0.576$, the solution boils at 90.0°C in equilibrium with the vapor at $y_{\text{A}} = 0.791$. In other words, starting with $x_{\text{A}} = 0.576$, the highest purity that may be achieved for 2-propanol in a single-plate distillation is 79.1 mol%, but only for the first drop of distillate. Continued distillation produces distillate with lower purity.

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12. The standard state Gibbs energy of formation of methanol in the gas phase at 25°C is $-161.96 \text{ kJ mol}^{-1}$. The Henry's Law constant is $k_{pc} = 4.51 \times 10^{-3} \text{ bar L mol}^{-1}$. (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).

Answer: (a). Follow Example 18.3.1. The small Henry's Law constant shows that methanol is very soluble in water. Methanol-water hydrogen bonds contribute to the stability of the solution. The corresponding Gibbs energy of desolvation is given by Eqs. 18.3.3[†]:

$$\begin{aligned}\Delta_{\text{desol}}G_{pc}^{\circ} &= -RT \ln k_{pc} = -8.3145 \text{ J K}^{-1} \text{ mol}^{-1}(298.15 \text{ K})(1 \text{ kJ}/1000 \text{ J}) \ln 4.51 \times 10^{-3} \\ &= 13.39 \text{ kJ mol}^{-1}\end{aligned}$$

Noting that $\Delta_{\text{sol}}G^{\circ} = -\Delta_{\text{desol}}G_{pc}^{\circ}$ gives the standard state Gibbs energy of formation for aqueous methanol as:

$$\Delta_f G^{\circ}(\text{aq}) = \Delta_f G^{\circ}(\text{g}) + \Delta_{\text{sol}}G^{\circ} = -161.96 \text{ kJ mol}^{-1} + (-13.39 \text{ kJ mol}^{-1}) = -175.35 \text{ kJ mol}^{-1}$$

(b). Using Eq. 18.3.3[†], $P_B = k_{pc} c_B$:

$$c_B = P_B/k_{pc} = 0.0100 \text{ bar}/4.51 \times 10^{-3} \text{ bar L mol}^{-1} = 2.22 \text{ M}$$

The concentration of methanol in water must be quite large, 2.22 M (~7% by weight), to establish a vapor pressure of 0.0100 bar (7.5 torr). This concentration assumes ideal-dilute behavior, and so is a lower limit, since negative deviations from ideality are expected.

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 $137.02 \text{ g mol}^{-1}$. Assume the density is roughly independent of temperature for this small temperature difference.

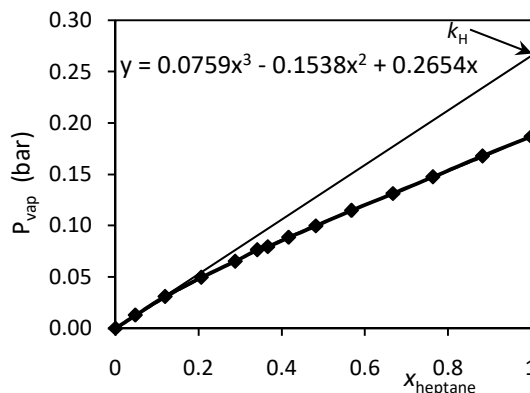
$x(\text{bromobutane})$	0	0.1171	0.2362	0.3329	0.4323	0.5182	0.5836	0.6333
$P_{\text{vap}}(\text{heptane, torr})$	140.0	125.8	110.6	98.4	86.1	74.8	66.4	59.6
$x(\text{bromobutane})$	0.6588	0.7123	0.7935	0.8805	0.9521	1		
$P_{\text{vap}}(\text{heptane, torr})$	57.3	49	37.2	23.3	9.6	0		

Answer: The plan is to fit the vapor pressure data to a cubic polynomial with a constant coefficient of zero, and then follow Example 18.3.2. Alternatively the data could be carefully plotted and then a straight edge used to extrapolate the dilute solution behavior to $x_A = 1$.

The mole fraction of heptane and vapor pressure in bar were calculated using the following spreadsheet and fit to a cubic polynomial using the "Non-linear least Squares Applet," on the textbook Web site or companion CD, $y = a x^3 + b x^2 + c x + d$. The d-parameter was fixed at

zero, since the vapor pressure goes to zero at $x_A = 0$. The Henry's Law constant is the value of the dilute solution line extrapolated to $x_A = 1$. The c-fit coefficient is the Henry's Law constant, $k_{H,A} = c = 0.2654 \pm 0.0038$ bar.

Xbutylbromide	P _{vap} (torr)	Xheptane	P _{vap} (bar)
0	140	1	0.1867
0.1171	125.8	0.8829	0.1677
0.2362	110.6	0.7638	0.1475
0.3329	98.4	0.6671	0.1312
0.4323	86.1	0.5677	0.1148
0.5182	74.8	0.4818	0.0997
0.5836	66.4	0.4164	0.0885
0.6333	59.6	0.3667	0.0795
0.6588	57.3	0.3412	0.0764
0.7123	49	0.2877	0.0653
0.7935	37.2	0.2065	0.0496
0.8805	23.3	0.1195	0.0311
0.9521	9.6	0.0479	0.0128
1	0	0	0



Then substituting Eq. 2.2.16 for the mole fraction into Eq. 18.3.1[†] gives the conversion:

$$P_A = k_{H,A} x_A = k_{H,A} \frac{c_A (1 \text{ L})}{\left(\frac{1000 \text{ mL } d_{\text{soln}}}{\mathcal{N}_A}\right)} = k_{pc,A} c_A \quad \text{with} \quad k_{pc,A} = \frac{k_{H,A} (1 \text{ L})}{\left(\frac{1000 \text{ mL } d_{\text{soln}}}{\mathcal{N}_A}\right)}$$

Assuming the density of the solution is the density of the solvent, 1-bromobutane, gives:

$$k_{pc,A} = \frac{0.2654 \text{ bar } (1 \text{ L})}{\left(\frac{1000 \text{ mL } 1.276 \text{ g mL}^{-1}}{137.02 \text{ g mol}^{-1}}\right)} = \frac{0.2654 \text{ bar L}}{9.313 \text{ mol}} = 0.0285 \text{ bar L mol}^{-1} = 2.85 \text{ Pa m}^3 \text{ mol}^{-1}$$

The unitless Henry's Law constant uses concentration in the gas phase as well as the solution phase:

$$k_{cc,A} = \frac{k_H}{9.313 \text{ mol L}^{-1} RT} = \frac{0.2654 \text{ bar}}{9.313 \text{ mol L}^{-1} (0.083145 \text{ bar L K}^{-1} \text{ mol}^{-1}) (323.15 \text{ K})} = 1.06 \times 10^{-3}$$

The units for R are chosen to cancel the units for k_H .

Note that a "quick and dirty" approach for calculating the Henry's Law constant is to calculate the slope using the data point with the lowest concentration: $k_H \cong 0.0128 \text{ bar}/0.0479 \cong 0.27 \text{ bar}$.

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.

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Answer: The plan is to convert the gas phase mole fractions to partial pressures, convert k_H to k_{pc} , and then find the equilibrium concentrations. The concentrations are then converted to ppm.

Using Dalton's Law for the gas phase gives, $P_{O_2} = y_{O_2} P = 0.20$ bar and $P_{N_2} = y_{N_2} P = 0.80$ bar. We next convert k_H to k_{pc} using Eq. 18.3.6[†]. For O_2 :

$$k_{pc,O_2} = \frac{k_H}{55.34 \text{ mol L}^{-1}} = \frac{4.40 \times 10^4 \text{ bar}}{55.34 \text{ mol L}^{-1}} = 795.1 \text{ bar L mol}^{-1}$$

and $c_{O_2} = P_{O_2}/k_{pc,O_2} = 0.20 \text{ bar}/795.1 \text{ bar L mol}^{-1} = 2.5 \times 10^{-4} \text{ M}$

In ppm, assuming the density of the solution is the density of pure water:

$$\begin{aligned} c_{O_2} &= 2.5 \times 10^{-4} \text{ mol L}^{-1} (1 \text{ L}) (32.0 \text{ g mol}^{-1}) (1 \text{ L}/1000 \text{ mL}) / 0.9971 \text{ g mL}^{-1} (1 \times 10^6 \text{ ppm}) \\ &= 8.0 \text{ ppm} \end{aligned}$$

For N_2 :

$$k_{pc,N_2} = \frac{k_H}{55.34 \text{ mol L}^{-1}} = \frac{8.68 \times 10^4 \text{ bar}}{55.34 \text{ mol L}^{-1}} = 1568. \text{ bar L mol}^{-1}$$

and $c_{N_2} = P_{N_2}/k_{pc,N_2} = 0.80 \text{ bar}/1568. \text{ bar L mol}^{-1} = 5.1 \times 10^{-4} \text{ M}$

$$\begin{aligned} c_{N_2} &= 5.1 \times 10^{-4} \text{ mol L}^{-1} (1 \text{ L}) (28.02 \text{ g mol}^{-1}) (1 \text{ L}/1000 \text{ mL}) / 0.9971 \text{ g mL}^{-1} (1 \times 10^6 \text{ ppm}) \\ &= 14. \text{ ppm} \end{aligned}$$

The mole ratio of oxygen to nitrogen in equilibrium in solution at 25°C is:

$$n_{O_2}/n_{N_2} = 2.5 \times 10^{-4} \text{ M} / 5.1 \times 10^{-4} \text{ M} = 0.49 \approx 1/2$$

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:

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

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



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

Answer: Doing the logarithmic conversion for $p k_{pc,CO_2}$ gives $k_{pc,CO_2} = 0.0295 \pm 0.0007$, or 2.4% error. Equivalently, the result should be expressed with two significant figures: $k_{pc,CO_2} = 0.0295$, which agrees with the normal significant figure rules. The relationship between the two forms of the Henry's Law constant is given by:

$$k'_{pc,CO_2} = k_{pc,CO_2} \left(\frac{c_{CO_2} + c_{H_2CO_3}}{c_{CO_2}} \right)$$

We next need to find $(c_{CO_2} + c_{H_2CO_3})/c_{CO_2}$. The equilibrium expression for the dehydration of carbonic acid is:

$$K = \frac{c_{\text{CO}_2}}{c_{\text{H}_2\text{CO}_3}} \quad \text{and} \quad c_{\text{H}_2\text{CO}_3} = c_{\text{CO}_2}/K \quad \text{giving} \quad \left(\frac{c_{\text{CO}_2} + c_{\text{H}_2\text{CO}_3}}{c_{\text{CO}_2}} \right) = 1 + 1/K$$

Since K is large, $K = 650$, the predominant form for CO_2 in aqueous solution at equilibrium is as dissolved CO_2 , not carbonic acid. The relationship between the two forms of the Henry's Law constant is then:

$$k'_{\text{pc,CO}_2} = k_{\text{pc,CO}_2} (1 + 1/K) = k_{\text{pc,CO}_2} (1 + 1/650) = k_{\text{pc,CO}_2} 1.0015$$

The two constants differ by 0.15%, which is negligible compared to the experimental uncertainty in $k_{\text{H,PC}}$. Note, however, that the total solubility of all carbonate species, $C_T = c_{\text{CO}_2} + c_{\text{H}_2\text{CO}_3} + c_{\text{HCO}_3^-} + c_{\text{CO}_3^{2-}}$, increases with pH and is significantly larger than c_{CO_2} alone near neutral pH (see Section 6.1).

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

Answer: The plan is to use the same reasoning that we used to derive Eq. 18.2.12*, except finding temperature derivative.

The temperature dependence of the chemical potential for a component in solution is given by the partial molar entropy, Eqs. 18.1.17-18.1.18:

$$\left(\frac{\partial\mu_A}{\partial T} \right)_{P,n_A,n_B} = -\bar{S}_A$$

Using Eq. 18.2.9* for the concentration dependence of the chemical potential for an ideal component, $\mu_A(x_A) = \mu_A^* + RT \ln x_A$, and the product rule gives:

$$\begin{aligned} -\bar{S}_A &= \left(\frac{\partial\mu_A}{\partial T} \right)_{P,n_A,n_B} = \left(\frac{\partial(\mu_A^* + RT \ln x_A)}{\partial T} \right)_{P,n_A,n_B} && \text{(ideal)} \\ &= \left(\frac{\partial\mu_A^*}{\partial T} \right)_{P,n_A,n_B} + RT \left(\frac{\partial \ln x_A}{\partial T} \right)_{P,n_A,n_B} + R \ln x_A \left(\frac{\partial T}{\partial T} \right)_{P,n_A,n_B} && \text{(ideal)} \end{aligned}$$

The derivative of $\ln x_A$ is zero because x_A is constant when n_A and n_B are constant:

$$-\bar{S}_A = \left(\frac{\partial\mu_A^*}{\partial T} \right)_{P,n_A,n_B} + R \ln x_A = -S_A^* + R \ln x_A \quad \text{(ideal)}$$

The slope of the chemical potential versus temperature curve is $-S_A^* + R \ln x_A$, as shown in Figure 18.4.5. Or finally, the partial molar entropy of an ideal constituent is:

$$\bar{S}_A = S_A^* - R \ln x_A \quad \text{(ideal)}$$

The entropy of mixing for an ideal solution follows directly from this last equation.

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17. The partial molar entropy of a constituent in an ideal solution, at constant temperature and pressure, is $\bar{S}_i = S_i^* - R \ln x_i$, 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 $\Delta_{\text{mix}}S = -n_{\text{tot}}R (x_A \ln x_A + x_B \ln x_B)$ at constant temperature and pressure.

Answer: The plan is to adapt the derivation for the Gibbs energy of mixing, Eqs. 16.8.6, 16.8.11°-16.8.13°.

Let S_2 be the final entropy for the solution and S_1 be the initial total entropy for the two pure constituents with n_A moles of A with n_B moles of B:

$$\Delta_{\text{mix}}S = S_2 - S_1 = (n_A \bar{S}_A + n_B \bar{S}_B) - (n_A S_A^* + n_B S_B^*) = n_A(\bar{S}_A - S_A^*) + n_B(\bar{S}_B - S_B^*)$$

Using $\bar{S}_A = S_A^* - R \ln x_A$ and $\bar{S}_B = S_B^* - R \ln x_B$ for the two ideal constituents gives:

$$\Delta_{\text{mix}}S = -n_A R \ln x_A - n_B R \ln x_B$$

The pure molar entropy terms cancel. Let $n_{\text{tot}} = n_A + n_B$, with $x_A = n_A/n_{\text{tot}}$ and $x_B = n_B/n_{\text{tot}}$. Dividing and multiplying each term by n_{tot} and factoring out the common factor of $-n_{\text{tot}}R$ gives:

$$\begin{aligned} \Delta_{\text{mix}}S &= -n_{\text{tot}}R \left(\frac{n_A}{n_{\text{tot}}} \ln x_A + \frac{n_B}{n_{\text{tot}}} \ln x_B \right) \\ \Delta_{\text{mix}}S &= -n_{\text{tot}}R (x_A \ln x_A + x_B \ln x_B) \end{aligned} \quad (18.2.10^*)$$

which is the analogous expression to Eq. 16.8.14° for ideal gas mixing.

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

$$\mu_B^\dagger(l) = \mu_B^*(l) + RT \ln k_{H,B}/P_B^*$$

Answer: The definitions of the standard states applied to the solute, B, are:

$$\mu_B^*(l) = \mu_B^\circ(g) + RT \ln P_B^*/P^\circ \quad (\text{Raoult, pure}) \quad (18.2.2^\circ)$$

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

Subtracting Eq. 18.2.2° from Eq. 18.3.9† gives:

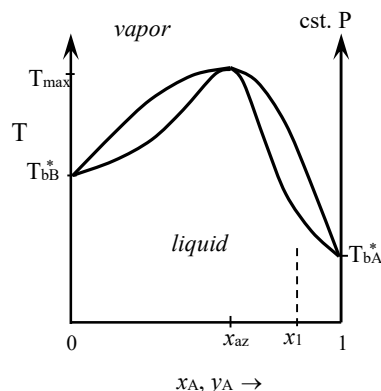
$$\mu_B^\dagger(l) - \mu_B^*(l) = \mu_B^\circ(g) + RT \ln k_{H,B}/P^\circ - \mu_B^\circ(g) - RT \ln P_B^*/P^\circ$$

$$\mu_B^\dagger(l) - \mu_B^*(l) = RT \ln k_{H,B}/P_B^*$$

Adding $\mu_B^*(l)$ to both sides of the last equation gives: $\mu_B^\dagger(l) = \mu_B^*(l) + RT \ln k_{H,B}/P_B^*$.

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.



Answer: (a). Starting from a solution with concentration greater than the azeotropic concentration, the more volatile component (lower boiling point) is pure A. Pure A would be recovered from the distillate and azeotrope would be recovered from the pot.

(b). Deviations from ideality are judged from the perspective of the vapor pressure. This system has a maximum boiling azeotrope; the solution temperature must be increased above the pure boiling points of either pure A or B to attain a vapor pressure equal to the ambient pressure. The azeotrope is harder to vaporize than pure A or pure B. The solution shows strong negative deviations from ideality: $A-B \gg A-A, B-B$.

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 ($T_A^* = 61.2^\circ\text{C}$). Calculate (a) the molal boiling point elevation constant, and (b) the molar enthalpy of vaporization of chloroform.

Answer: The molar mass of naphthalene is $\mathcal{M}_{\text{Naph}} = 128.2 \text{ g mol}^{-1}$ and chloroform is $\mathcal{M}_{\text{chloroform}} = 119.37 \text{ g mol}^{-1}$. This problem is a colligative properties problem with $\Delta T = K_b m_B$. (a). In this equation m_B is the solute molality:

$$m_B = \frac{n_B}{w_{\text{solvent}}} = \frac{0.640 \text{ g} (1 \text{ mol}/128.2 \text{ g mol}^{-1})}{0.0400 \text{ kg}} = 0.1248 \text{ mol kg}^{-1} = 0.1248 \text{ m}$$

Solving for the molal boiling point elevation constant gives:

$$K_b = \frac{\Delta T}{m_B} = \frac{0.455 \text{ K}}{0.1248 \text{ mol kg}^{-1}} = 3.646 \text{ K kg mol}^{-1}$$

(b). The molal boiling point elevation constant is related to the enthalpy of vaporization of the solvent by Eqs. 18.4.14[†]:

$$K_b = \frac{RT_A^{*2} \mathcal{M}_A (1 \text{ kg})}{\Delta_{\text{vap}} H_A^\circ (1000 \text{ g})}$$

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where all the quantities are related to properties of the pure solvent. Solving for the enthalpy change:

$$\begin{aligned}\Delta_{\text{vap}}H_A^\lambda &= \frac{RT_A^{*2} \mathcal{M}_A (1 \text{ kg})}{K_b(1000 \text{ g})} = \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1}(334.4 \text{ K})^2(119.37 \text{ g mol}^{-1})(1 \text{ kg})}{3.646 \text{ K kg mol}^{-1}(1000 \text{ g})} \\ &= 3.044 \times 10^4 \text{ J mol}^{-1} = 30.4 \text{ kJ mol}^{-1}\end{aligned}$$

21. 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 $6.008 \text{ kJ mol}^{-1}$ 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.

Answer: (a). From Eqs. 18.4.19[†], the cryoscopic constant for water is:

$$\begin{aligned}K_f &\equiv \left(\frac{RT_m^{*2} \mathcal{M}_A (1 \text{ kg})}{1000 \text{ g } \Delta_{\text{fus}}H_A} \right) = \left(\frac{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}(273.15 \text{ K})^2(18.0153 \text{ g mol}^{-1})(1 \text{ kg})}{1000 \text{ g } (6.008 \times 10^3 \text{ J mol}^{-1})} \right) \\ &= 1.861 \text{ mol}^{-1} \text{ kg K}\end{aligned}$$

The concentration is given by:

$$\Delta T \cong K_f m_B \quad \text{and} \quad m_B = \Delta T / K_f = 0.035588 \text{ K} / 1.861 \text{ mol}^{-1} \text{ kg K} = 0.019123 \text{ mol kg}^{-1}$$

Then using the given masses, the molality and molar mass of the solute are related by:

$$m_B = \frac{w_B / \mathcal{M}_B}{w_A} = \frac{1.433 \times 10^{-3} \text{ g} / \mathcal{M}_B}{1.000 \text{ g} (1 \text{ kg} / 1000 \text{ g})} \quad \text{giving } \mathcal{M}_B = 74.94 \text{ g mol}^{-1}$$

The literature molar mass of butanol is 74.15 g mol^{-1} .

(b). Repeating the calculations with the more concentrated solution gives:

$$m_B = 0.07300 \text{ K} / 1.861 \text{ mol}^{-1} \text{ kg K} = 0.039226 \text{ mol kg}^{-1}$$

$$m_B = \frac{w_B / \mathcal{M}_B}{w_A} = \frac{2.951 \times 10^{-3} \text{ g} / \mathcal{M}_B}{1.000 \text{ g} (1 \text{ kg} / 1000 \text{ g})} \quad \text{giving } \mathcal{M}_B = 75.23 \text{ g mol}^{-1}$$

For an ideal solution, parts (a) and (b) would give the same result. Butanol-water solutions show small but significant deviations from ideal behavior. The more dilute result is potentially more accurate, since the solution is closer to an ideal solution, but the freezing point depression is less precise since it is a smaller value.

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 $10.59 \text{ kJ mol}^{-1}$ at the standard melting point.

Answer: The plan is to use Eq. 18.4.16[†] with benzene as the solvent. The solution freezing point is 276.59 K, the pure freezing point is 278.61 K, and $\Delta T = (278.61 - 276.59 \text{ K}) = 2.02 \text{ K}$

The freezing point depression is most conveniently given in terms of the mole fraction of the solvent using Eq. 18.4.16[†] with:

$$K' = \left(\frac{\Delta_{\text{fus}}H_A}{R T_m^{*2}} \right) = \left(\frac{10.59 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1} (278.61 \text{ K})^2} \right) = 0.016408 \text{ K}^{-1}$$

$$\ln x_A = K' \Delta T = -0.016408 \text{ K}^{-1} (2.02 \text{ K}) \quad \text{giving } x_A = 0.967$$

The purity is 96.7 mol%. See the next problem for the DSC method that is used when the pure substance standard melting point and enthalpy of fusion are not known.

23. A DSC melting curve was determined for a sample of tetracosane, $\text{C}_{24}\text{H}_{50}$. 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 $338.66 \text{ g mol}^{-1}$.

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

Answer: The plan is to determine $\Delta_{\text{fus}}H_A$ using the total area under the melting curve, sample mass, and molar mass. The fraction of the sample melted, F , is given by the ratio of the partial area to the total area under the melting curve. The pure melting point and freezing point depression are found from a plot of melting point versus $1/F$. Eq. 18.4.16[†] for the freezing point depression gives the mole fraction of the solvent, with tetracosane as the solvent.

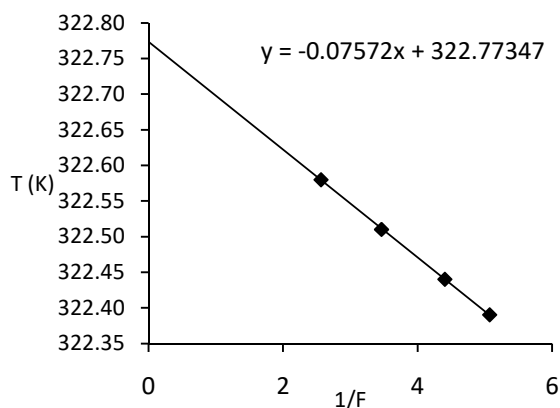
The molar enthalpy of fusion is given by the total area under the melting curve in joules and then converting to the molar quantity:

$$\Delta_{\text{fus}}H_A = \Delta H/n_A = \frac{0.3919 \text{ J} (338.66 \text{ g mol}^{-1})}{2.21 \times 10^{-3} \text{ g}} (1 \text{ kJ}/1000 \text{ J}) = 60.05 \text{ kJ mol}^{-1}$$

The plot was set-up using the following spreadsheet:

total area	7.351			
	part.area	F	1/F	T (K)
	1.45	0.197252	5.069655	322.39
	1.669	0.227044	4.404434	322.44
	2.122	0.288668	3.464185	322.51
	2.866	0.389879	2.564899	322.58

slope	-0.07572	322.7735	intercept
±	0.000537	0.002141	±
r ²	0.9999	0.001017	s(y)
F	19917.64	2	df
SS _{reg}	0.020598	2.07E-06	SS _{resid}



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The intercept is the pure melting point and the slope is the freezing point depression, ΔT , Figure 18.4.7c. The freezing point depression is given directly in terms of the mole fraction of the solvent using Eq. 18.4.16[†] as:

$$\ln x_A = - \left(\frac{\Delta_{\text{fus}}H_A}{R T_m^{*2}} \right) \Delta T$$

with $\left(\frac{\Delta_{\text{fus}}H_A}{R T_m^{*2}} \right) = \left(\frac{60.05 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1} (322.774 \text{ K})^2} \right) = 0.069323 \text{ K}^{-1}$

$$\ln x_A = -0.069323 \text{ K}^{-1} (0.07572 \text{ K}) \quad \text{giving } x_A = 0.9948$$

The purity is 99.48 mol%, using propagation of errors to determine the final number of significant figures.

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):

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

Answer: At equilibrium the chemical potential of the pure solid is equal to the chemical potential of the solvent in solution. Assuming an ideal dilute solution gives $P_A = x_A P_A^*$:

$$\mu_A^*(s) = \mu_A(x_A) = \mu_A^*(l) + RT \ln x_A \quad 1$$

Solving for the logarithm of the concentration:

$$\ln x_A = \frac{\mu_A^*(s) - \mu_A^*(l)}{RT} \quad 2$$

The Gibbs energy of fusion is given by $\Delta_{\text{fus}}G_A = \mu_A^*(l) - \mu_A^*(s)$. For example for aqueous solutions the $\Delta_{\text{fus}}G_A$ corresponds to the transition written as $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)$, with the liquid phase being the “products” and the solid phase the “reactants.” Substitution of $\Delta_{\text{fus}}G_A$ into Eq. 2 gives:

$$\ln x_A = - \frac{\Delta_{\text{fus}}G_A(T)}{RT} \quad (\text{solution}) \quad 3$$

For comparison for a pure solution, $x_A = 1$ and the melting point is the pure solvent melting point, $T = T_m^*$; substitution into Eq. 3 gives for the pure solvent:

$$\ln 1 = - \frac{\Delta_{\text{fus}}G_A(T_m^*)}{RT_m^*} \quad (\text{pure solvent}) \quad 4$$

Subtracting Eq. 4 from Eq. 3:

$$\ln \frac{x_A}{1} = - \frac{\Delta_{\text{fus}}G_A(T)}{RT} + \frac{\Delta_{\text{fus}}G_A(T_m^*)}{RT_m^*} \quad 5$$

Expanding the Gibbs energy in terms of the enthalpy and entropy changes for the phase transition gives:

$$\ln x_A = - \left(\frac{\Delta_{\text{fus}}H_A(T)}{RT} - \frac{\Delta_{\text{fus}}S_A(T)}{R} \right) + \left(\frac{\Delta_{\text{fus}}H_A(T_m^*)}{RT_m^*} - \frac{\Delta_{\text{fus}}S_A(T_m^*)}{R} \right) \quad 6$$

Assuming the temperature change for the phase transition is small, we can assume that $\Delta_{\text{fus}}H_A$ and $\Delta_{\text{fus}}S_A$ are constant over the temperature range and cancelling the entropy terms gives:

$$\ln x_A = - \frac{\Delta_{\text{fus}}H_A(T)}{RT} + \frac{\Delta_{\text{fus}}H_A(T_m^*)}{RT_m^*} = - \frac{\Delta_{\text{fus}}H_A}{R} \left(\frac{1}{T} - \frac{1}{T_m^*} \right) \quad 7$$

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 $\text{CH}_3\text{CH}(\text{OH})[\text{CH}_2\text{CH}(\text{OH})]_{n-2}\text{CH}_2\text{CH}_2\text{OH}$, so use $-\text{CH}_2\text{CH}(\text{OH})-$ for the monomer molar mass.]

Answer: The osmotic pressure is given by Eq. 1.3.2 and $h = 21.6 \text{ cm} = 0.216 \text{ m}$:

$$\begin{aligned} \pi &= dgh = 0.9971 \text{ g mL}^{-1} (1 \text{ kg}/1000 \text{ g}) (1 \times 10^6 \text{ mL}/1 \text{ m}^3) (9.8067 \text{ m s}^{-2}) (0.216 \text{ m}) \\ &= 2.112 \times 10^3 \text{ Pa} = 0.02112 \text{ bar} \end{aligned}$$

Using Eq. 18.4.30[†], since this is such a dilute solution, gives the concentration as:

$$c_B = \pi/RT = \frac{0.02112 \text{ bar}}{0.083145 \text{ bar L mol}^{-1} \text{ K}^{-1} 298.15 \text{ K}} = 8.52 \times 10^{-4} \text{ mol L}^{-1}$$

The solution concentration is used to calculate the molar mass from the definition of molarity:

$$c_B = n_B/V_{\text{soln}} = w_B/\mathcal{M}_B/V_{\text{soln}} \quad \text{or solving for } \mathcal{M}_B: \quad \mathcal{M}_B = w_B/c_B/V_{\text{soln}}$$

were w_B is the mass of solute in a volume of solution, V_{soln} . Assume 100.0 g of solution. The mass of the solute is $w_B = 4.00 \text{ g}$ and the volume of the solution is

$V_{\text{soln}} = w_{\text{soln}}/d_{\text{soln}} = 100.0 \text{ g}/0.9971 \text{ g mL}^{-1} (1 \text{ L}/1000 \text{ mL}) = 0.1003 \text{ L}$ giving:

$$\mathcal{M}_B = w_B/c_B/V_{\text{soln}} = 4.00 \text{ g}/8.52 \times 10^{-4} \text{ mol L}^{-1}/0.1003 \text{ L} = 4.68 \times 10^4 \text{ g mol}^{-1}$$

The monomer weight, $-\text{CH}_2\text{CH}(\text{OH})-$, is 44.06 g mol^{-1} , neglecting the difference in mass between the two ends. The average number of monomers per polymer molecule is then:

$$n = 4.68 \times 10^4 \text{ g mol}^{-1}/44.06 \text{ g mol}^{-1} = 1062. = 1.06 \times 10^3$$

The large molecular mass is not at all unusual for commercial polymers. Even though the solution concentration is quite small, $8.52 \times 10^{-4} \text{ M}$, the osmotic pressure is easily measured to high precision.

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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.

Answer: Eq. 18.4.30[†] was used to determine the effective molar concentration, $c_B = \pi/RT$, and the effective molar mass was determined using the definition of molarity:

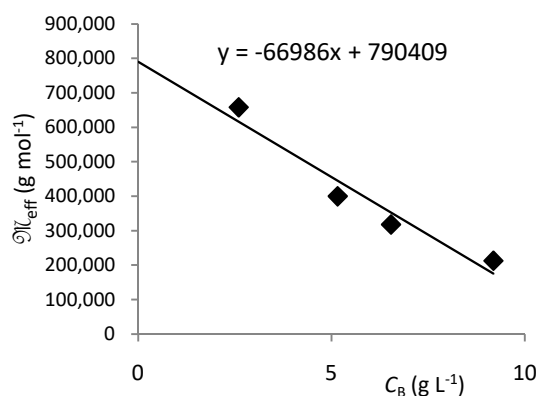
$$c_B = n_B/V_{\text{soln}} = w_B/\mathcal{M}_B/V_{\text{soln}} \quad \text{or solving for } \mathcal{M}_B: \quad \mathcal{M}_B = w_B/c_B/V_{\text{soln}}$$

where w_B is the mass of solute in a volume of solution, V_{soln} . The concentrations in the table are given in g mol⁻¹, C_B . Assume 1.000 L of solution. The mass of the solute is $w_B = C_B(1 \text{ L})$:

$$\mathcal{M}_B = C_B(1 \text{ L})/c_B/1 \text{ L} = C_B/c_B$$

The calculations were implemented in a short spreadsheet:

C_B (g L ⁻¹)	π (Pa)	c_B (mol L ⁻¹)	\mathcal{M}_{eff} (g mol ⁻¹)
2.6	9.8	3.953E-06	6.576E+05
5.16	32	1.291E-05	3.997E+05
6.54	51	2.057E-05	3.179E+05
9.19	107	4.317E-05	2.129E+05



The linear intercept gives the molar mass, $\mathcal{M}_B = 8. \times 10^5 \text{ g mol}^{-1}$. If more data points are available, a non-linear curve fit is appropriate and provides better accuracy.⁶ The large change in effective molar mass with concentration shows significant deviations from ideality, even at these low concentrations.

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 partial molar volume is given in Example 18.1.1.

Answer: Using Eq. 2.2.13, the mole fraction of 0.1000 m urea is $x_B = 1.7983 \times 10^{-3}$. For a dilute solution of a non-electrolyte, the partial molar volume of the solvent is well approximated by the pure molar volume, $V_A^* = \mathcal{M}_A/d_{A,\text{pure}} = 18.069 \text{ mL}$. The osmotic pressure in terms of the mole fraction of solute is given by Eq. 18.4.27[†]:

$$\begin{aligned}\pi &= x_B RT/V_A^* = 1.7983 \times 10^{-3} (0.083145 \text{ bar L K}^{-1} \text{ mol}^{-1}) (298.15 \text{ K}) / 0.018069 \text{ L} \\ &= 2.467 \text{ bar}\end{aligned}$$

For the partial molar volume of the solute using Eq. 18.1.8 at 0.1000 m gives:

$$\begin{aligned}\bar{V}_B &= \left(\frac{\partial V^{1\text{kg}}}{\partial m_B} \right)_{T,P,n_A} \text{ kg}^{-1} = 3(-1.9934 \times 10^{-3}) m_B^2 + 2(9.03779 \times 10^{-2}) m_B + 44.36388 \\ &= 3(-1.9934 \times 10^{-3})(0.1)^2 + 2(9.03779 \times 10^{-2})(0.1) + 44.36388 = 44.382 \text{ mL mol}^{-1}\end{aligned}$$

For the solute, Eq. 18.4.24[†] gives the chemical potential at equilibrium with $\Delta P = \pi$:

$$\begin{aligned}\mu_B(x_B, P+\pi) &= \mu_B^\dagger(l, P) + RT \ln x_B + \pi_B \bar{V}_B \\ &= \mu_B^\dagger(l, P) + 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} (298.15 \text{ K}) \ln 1.7983 \times 10^{-3} \\ &\quad + 2.467 \text{ bar} (44.382 \text{ mL mol}^{-1}) (1 \times 10^5 \text{ Pa/1 bar}) (1 \text{ m}^3/1 \times 10^6 \text{ mL}) \\ &= \mu_B^\dagger(l, P) + (-15.67 \text{ kJ mol}^{-1}) + 0.111 \text{ kJ mol}^{-1}\end{aligned}$$

The concentration dependent term dominates the change in chemical potential for the solute compared to the standard state. On the other hand, for the solvent, which occurs on both sides of the membrane, the concentration dependent term and the osmotic pressure term cancel at equilibrium.

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.

Answer: The plan is to use Eq. 18.4.30[†] to calculate the equilibrium osmotic pressure and then Eq. 18.4.31 to find the chemical potential of the solvent.

The equilibrium osmotic pressure is given by Eq. 18.4.30[†]:

$$\pi = c_B RT = 0.200 \text{ mol L}^{-1} (0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1}) (298.15 \text{ K}) = 4.96 \text{ bar}$$

The partial molar volume of water in this dilute solution is not far from the pure molar volume, $V_A^* = \mathcal{M}_A/d_{A,\text{pure}} = 18.0153 \text{ g mol}^{-1} / 0.997045 \text{ g mL}^{-1} = 18.069 \text{ mL mol}^{-1}$. The chemical potential for water as the solvent is then given by Eq. 18.4.31:

$$\begin{aligned}\mu_A(x_A, P+\Delta P) &= \mu_A^*(l, P) + (\Delta P - \pi) \bar{V}_A \\ &= \mu_A^*(l, P) + (10.00 - 4.96 \text{ bar}) 18.069 \text{ mL mol}^{-1} (1 \times 10^5 \text{ Pa/1 bar}) (1 \text{ m}^3/1 \times 10^6 \text{ mL}) \\ &= \mu_A^*(l, P) + (9.11 \text{ J mol}^{-1})\end{aligned}$$

The chemical potential of pure water is just the Gibbs energy per mole. The standard state Gibbs energy of formation of water is $-237.13 \text{ kJ mol}^{-1}$, so the effect of the pressure is small. However, the difference is not negligible since the 10 bar applied pressure corresponds to a hydrostatic

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head of 102 m and the osmotic pressure corresponds to 51 m. Small differences in chemical potential correspond to large differences in osmotic pressure.

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

Answer: The freezing point or melting point of a solution is the equilibrium phase transition temperature giving $\mu_A(x_A) = \mu_A^*(s)$. Using Raoult's Law for the solvent, the chemical potential of the solvent in solution is given by Eq. 18.2.9^{*}:

$$\mu_A^*(s) = \mu_A(x_A) = \mu_A^*(l) + RT \ln x_A$$

The molar Gibbs energy of fusion of the pure solvent at temperature T is given by $\Delta_{\text{fus}}G_A(T) = \mu_A^*(l) - \mu_A^*(s)$. Solving for the concentration of the solvent that gives the solution freezing point at temperature T gives:

$$\ln x_A = \frac{\mu_A^*(s) - \mu_A^*(l)}{RT} = - \frac{\Delta_{\text{fus}}G_A(T)}{RT}$$

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

$$\ln 1 = - \frac{\Delta_{\text{fus}}G_A(T_m^*)}{RT_m^*}$$

We can compare the solution to the pure solvent by subtracting the last two equations:

$$\ln \frac{x_A}{1} = - \frac{\Delta_{\text{fus}}G_A(T)}{RT} + \frac{\Delta_{\text{fus}}G_A(T_m^*)}{RT_m^*}$$

We can separate enthalpy and entropy effects using $\Delta_{\text{fus}}G_A(T) = \Delta_{\text{fus}}H_A(T) - T \Delta_{\text{fus}}S_A(T)$:

$$\ln x_A = - \left(\frac{\Delta_{\text{fus}}H_A(T)}{RT} - \frac{\Delta_{\text{fus}}S_A(T)}{R} \right) + \left(\frac{\Delta_{\text{fus}}H_A(T_m^*)}{RT_m^*} - \frac{\Delta_{\text{fus}}S_A(T_m^*)}{R} \right)$$

where $\Delta_{\text{fus}}H_A$ is the enthalpy of fusion of the solvent. The change in freezing point is typically only a few degrees. Assuming that $\Delta_{\text{fus}}H_A$ and $\Delta_{\text{fus}}S_A$ are constant over this small temperature range results in the cancellation of the entropy terms:

$$\ln x_A = - \frac{\Delta_{\text{fus}}H_A}{RT} + \frac{\Delta_{\text{fus}}H_A}{RT_m^*}$$

Collecting terms gives exactly the same results as for boiling point elevation, except for a change in sign:

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

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: $\Delta_{\text{sol}}G_B^\circ(T) = \mu_B^\dagger(l) - \mu_B^*(s)$. Show that the solubility of the solute is: $\ln x_B = -\Delta_{\text{sol}}G_B^\circ(T)/RT$. (c). At reference temperature T_o the solubility is x_{B_o} . Show that the temperature dependence of the solubility is given by:

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

Answer: The plan is to set the chemical potential of pure solute B equal to its chemical potential in solution. The steps in the derivation parallel Eqs. 18.4.2[†]-18.4.8[†], but focus on the solute.

(a). At equilibrium, the chemical potential of a solute is equal to the solute's chemical potential in solution, $\mu_B^*(s) = \mu_B(x_B)$. The chemical potential of the solute is given by Eq. 18.3.10[†], assuming an ideal-dilute solution:

$$\mu_B^*(s) = \mu_B(x_B) = \mu_B^\dagger(l) + RT \ln x_B$$

where x_B is the solubility, the concentration that is in equilibrium with the pure solid. The difference in standard states is the standard state Gibbs energy of solution, $\Delta_{\text{sol}}G_B^\circ = \mu_B^\dagger(l) - \mu_B^*(s)$ at temperature T. Solving for the solubility gives:

$$\ln x_B = [\mu_B^*(s) - \mu_B^\dagger(l)]/RT = -\Delta_{\text{sol}}G_B^\circ(T)/RT$$

At reference temperature T_o the solubility is x_{B_o} .

$$\ln x_{B_o} = -\Delta_{\text{sol}}G_B^\circ(T_o)/RT_o$$

The difference in solubilities at T and T_o is then:

$$\ln x_B - \ln x_{B_o} = -\Delta_{\text{sol}}G_B^\circ(T)/RT + \Delta_{\text{sol}}G_B^\circ(T_o)/RT_o$$

The Gibbs energy of solution can be split into enthalpic and entropic terms:

$$\Delta_{\text{sol}}G_B^\circ = \Delta_{\text{sol}}H_B^\circ - T\Delta_{\text{sol}}S_B^\circ$$

$$\ln x_B/x_{B_o} = -\Delta_{\text{sol}}H_B^\circ(T)/RT + \Delta_{\text{sol}}S_B^\circ(T)/R + \Delta_{\text{sol}}H_B^\circ(T_o)/RT_o - \Delta_{\text{sol}}S_B^\circ(T_o)/R$$

Assuming that $\Delta_{\text{sol}}H_B^\circ$ and $\Delta_{\text{sol}}S_B^\circ$ are constant over the temperature range, the entropy terms cancel:

$$\ln \frac{x_B}{x_{B_o}} = -\frac{\Delta_{\text{sol}}H_B^\circ}{R} \left(\frac{1}{T} - \frac{1}{T_o} \right) \quad (\text{ideal-dilute, cst. P, } \Delta_{\text{sol}}H_B^\circ \text{ \& } \Delta_{\text{sol}}S_B^\circ)$$

Solubility is another example of *General Pattern* **¶4: Exponential Temperature Dependence**, $e^{-E/RT}$, and may be rearranged in the same ways.

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

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

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

Answer: The plan is to parallel the approximations in Eqs. 18.4.9[†]-18.4.14[†] and *General Pattern §4*.

(a). Set $\Delta T \equiv T - T_0$. Following *General Pattern §4*, Eq. 3.5.13, for small changes in temperature, $TT_0 \cong T_0^2$. Substitution into Eq. P18.29.1[†] gives:

$$\ln \frac{x_B}{x_{B0}} = - \left(\frac{\Delta_{\text{sol}} H_B^\circ}{R} \right) \left(\frac{T_0 - T}{T T_0} \right) = \left(\frac{\Delta_{\text{sol}} H_B^\circ}{RT_0^2} \right) \Delta T$$

For small changes in temperature, the change in solubility is small and $x_B/x_{B0} \approx 1$. Using the Taylor series approximation, Table 1.5.3, $\ln x \approx x - 1$ near $x_0 \approx 1$ gives:

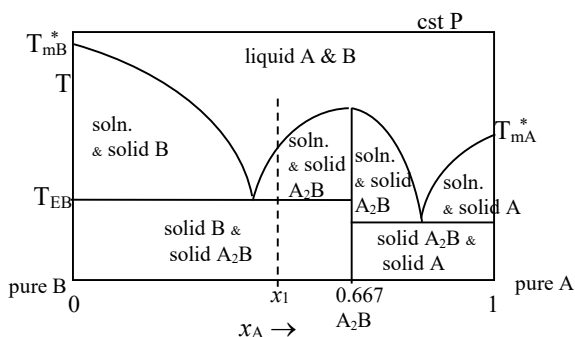
$$\frac{x_B}{x_{B0}} - 1 = \left(\frac{\Delta_{\text{sol}} H_B^\circ}{RT_0^2} \right) \Delta T$$

Solving for x_B :

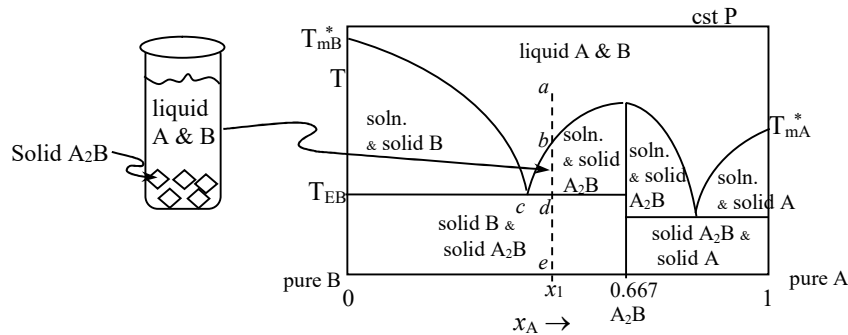
$$x_B = x_{B0} + \left(\frac{\Delta_{\text{sol}} H_B^\circ x_{B0}}{RT_0^2} \right) \Delta T \quad (\text{ideal-dilute, small } \Delta T)$$

(b). If the enthalpy of solution is endothermic, the constant in parentheses is positive and the solubility increases with an increase in temperature. Think of the equilibrium solubility as a chemical reaction, $B(s) \rightleftharpoons B(x_B)$. According to LeChâtelier's Principle, a reaction shifts in the endothermic direction with an increase in temperature. Increasing solubility corresponds to a shift to the right. The last 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, $\text{NaCl} \cdot (\text{H}_2\text{O})_2$. 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 .

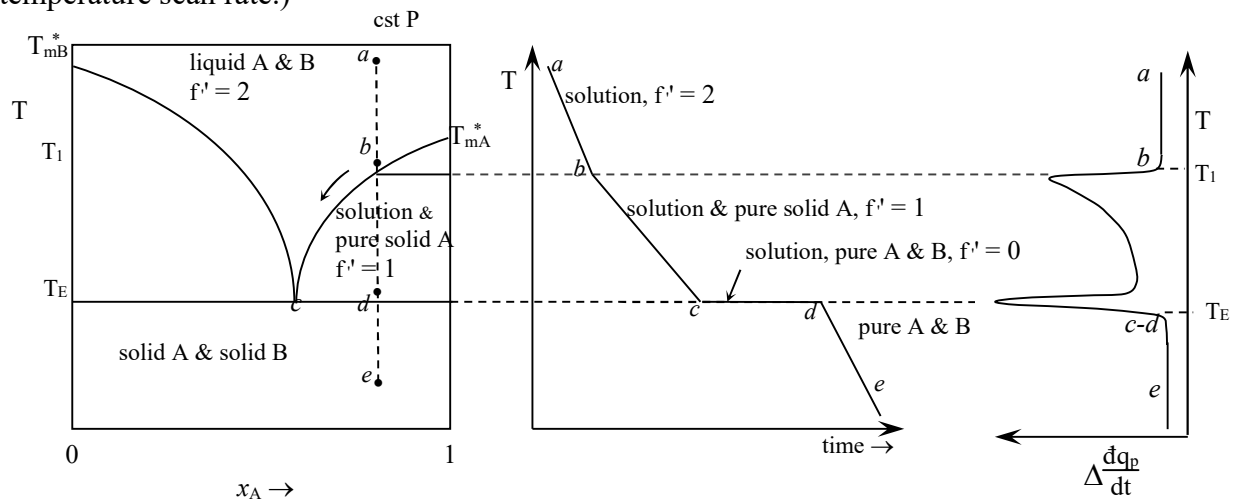


Answer: Start at high temperature, with solution only, point *a*. When the temperature drops to point *b*, solid compound A_2B begins to crystallize out of solution. The solution, which is also called the melt, becomes richer in B and the freezing point decreases. When the temperature drops to the eutectic temperature, between pure B and A_2B , solid A_2B begins to crystallize out of solution. The temperature remains constant until all the solution has solidified. The bulk composition is then at point *d*.

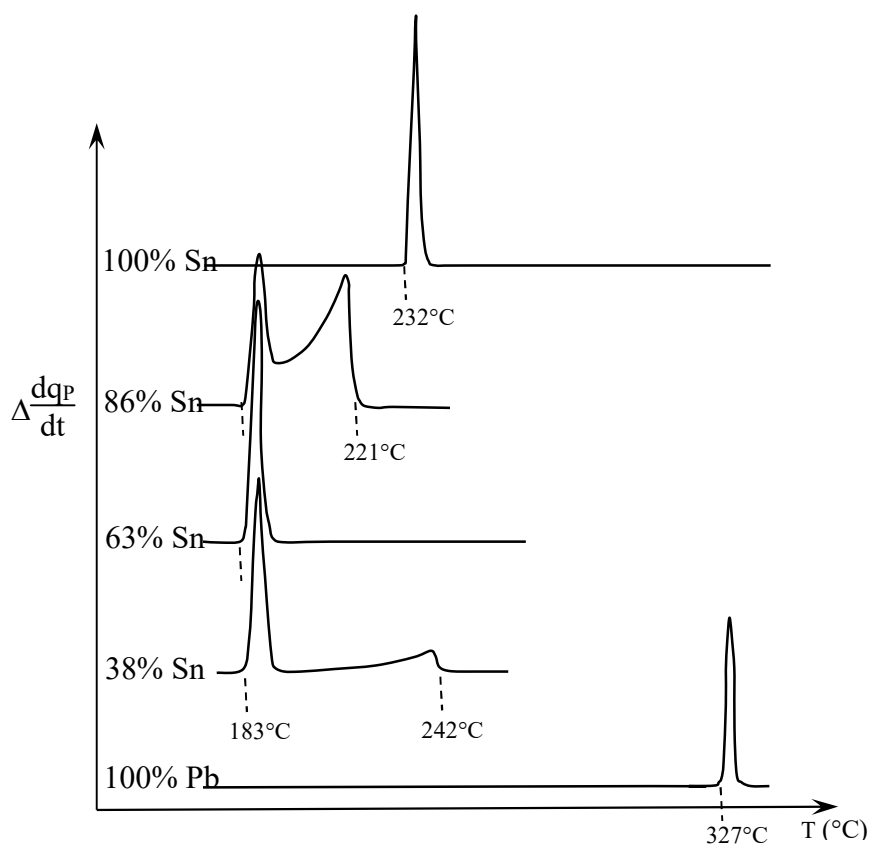


33. Relate the changes in the slopes of the segments on the cooling curve, Figure 18.4.12, and the widths of the peaks on the DSC melting curve, Figure 18.4.13, to the variances of the system at constant pressure. Discuss segments b-c and c-d.

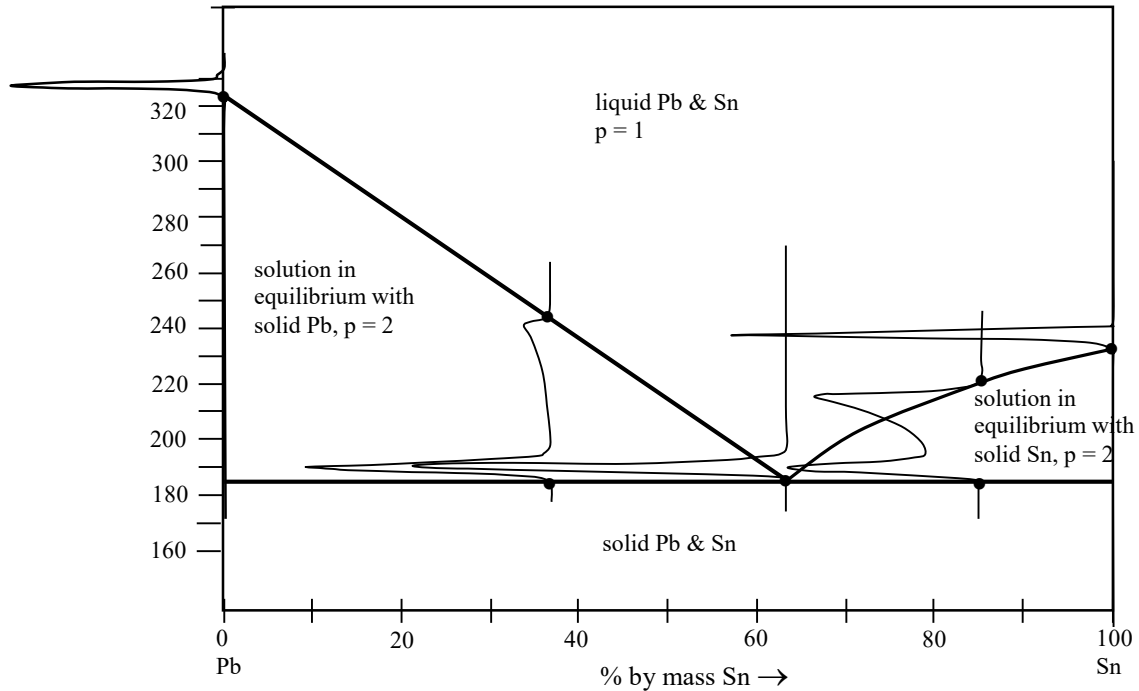
Answer: The corresponding regions and variances are diagrammed, below. For segment b-c the solution is in equilibrium with pure solid A. The variance of the system is $f' = 1$. One intensive variable may be changed independently. For example, for a chosen composition, with freezing point of the solution is fixed. In segment b-c on the cooling curve, the temperature decreases as the solution become richer in B. The freezing point is depressed with increasing concentration of B in the solution. The corresponding melting peak in the DSC melting curve is broad. However, once the solution reaches the eutectic composition, the variance drops to $f' = 0$, there are no independent variables. The temperature must then be fixed at the eutectic temperature. The cooling curve becomes flat at the eutectic temperature and the DSC melting peak at the eutectic temperature is narrow, comparable to the width of the melting peak of a pure substance. (The width of the eutectic melting peak is determined by instrument response times and the temperature scan rate.)



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



Answer: The sharp, low temperature transitions for the mixtures occur at the eutectic temperature. An easy way to think of building the phase diagram is to tilt the thermograms on their sides and replot them along the composition axis. Then connecting the melting temperatures by lines delineates the two-phase regions.



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.

Answer: The two components are H_2O and the gas, $c = 2$. The two phases are the solution and the vapor, $p = 2$. The variances using Eq. 18.5.6 are:

$$\begin{array}{lll} f = c - p + 2 = 2 & \text{at constant } T: & f' = 1 & \text{and at constant } T \text{ \& } P: & f'' = 0 \\ D = c + p = 4 & & D' = 3 & & D'' = 2 \end{array}$$

Call the gas M ; examples include methanol, CH_4 , CHCl_3 , O_2 , and N_2 . The change in Gibbs energy for a general process written in terms of all the possible terms is:

$$dG = -S dT + V dP + \mu_{\text{H}_2\text{O}}(x_{\text{H}_2\text{O}}) dn_{\text{H}_2\text{O},l} + \mu_{\text{H}_2\text{O}}(g) dn_{\text{H}_2\text{O},g} + \mu_M(x_M) dn_{M,l} + \mu_M(g) dn_{M,g} \quad (\text{with 4 independent})$$

The Gibbs Phase Rule points out that since the chemical potentials of each component are equal in the liquid and vapor, in addition to $x_{\text{H}_2\text{O}} + x_M = 1$ and $y_{\text{H}_2\text{O}} + y_M = 1$, there are only two degrees of freedom for the intensive variables. An equivalent way of noting this decrease in variance is that at equilibrium the vapor pressure of water is determined by Raoult's Law and the vapor phase pressure of the dissolved gas is given by Henry's Law. Following the allowed variance and arbitrarily focusing on the solution:

$$\begin{array}{ll} dG = -S dT + V dP + \mu_{\text{H}_2\text{O}}(x_{\text{H}_2\text{O}}) dn_{\text{H}_2\text{O}} + \mu_M(x_M) dn_M & (D = 4) \\ dG = & V dP + \mu_{\text{H}_2\text{O}}(x_{\text{H}_2\text{O}}) dn_{\text{H}_2\text{O}} + \mu_M(x_M) dn_M & (\text{cst. } T: D' = 3) \end{array}$$

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$$dG = \mu_{\text{H}_2\text{O}}(x_{\text{H}_2\text{O}})dn_{\text{H}_2\text{O}} + \mu_{\text{M}}(x_{\text{M}})dn_{\text{M}} \quad (\text{cst. T\&P: } D'' = 2)$$

where $dn_{\text{H}_2\text{O}} = dn_{\text{H}_2\text{O},l} + dn_{\text{H}_2\text{O},g}$ and $dn_{\text{M}} = dn_{\text{M},l} + dn_{\text{M},g}$ (the chemical potential of the components in each phase are equal, so it doesn't matter which phase the components are in for calculating the overall Gibbs energy). The final expression for dG can often be written in various equivalent ways; however, f and D provide a check that you haven't included dependent terms.

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.

Answer: The two components are A and B, $c = 2$. The two phases are the solution rich in A, the α phase, and the solution rich in B, the β phase, so that $p = 2$. The variances are using Eq. 18.5.6:

$$\begin{array}{lll} f = c - p + 2 = 2 & \text{at constant T: } f' = 1 & \text{and at constant T \& P: } f'' = 0 \\ D = c + p = 4 & D' = 3 & D'' = 2 \end{array}$$

The change in Gibbs energy for a general process written in terms of all the possible terms is:

$$dG = -S dT + V dP + \mu_{\text{A}}(x_{\text{A},\alpha}) dn_{\text{A},\alpha} + \mu_{\text{A}}(x_{\text{A},\beta}) dn_{\text{A},\beta} + \mu_{\text{B}}(x_{\text{B},\alpha}) dn_{\text{B},\alpha} + \mu_{\text{B}}(x_{\text{B},\beta}) dn_{\text{B},\beta} \quad (\text{with 4 independent})$$

with $x_{\text{A},\alpha}$ the concentration of A in the alpha phase and $x_{\text{A},\beta}$ the concentration of A in the beta phase. The Gibbs Phase Rule points out that since the chemical potentials of each component are equal in both liquid phases, in addition to $x_{\text{A},\alpha} + x_{\text{B},\alpha} = 1$, and $x_{\text{A},\beta} + x_{\text{B},\beta} = 1$, there are only two degrees of freedom for the intensive variables.

$$\begin{array}{ll} dG = -S dT + V dP + \mu_{\text{A}}(x_{\text{A},\alpha})dn_{\text{A}} + \mu_{\text{B}}(x_{\text{B},\alpha})dn_{\text{B}} & (D = 4) \\ dG = V dP + \mu_{\text{A}}(x_{\text{A},\alpha})dn_{\text{A}} + \mu_{\text{B}}(x_{\text{B},\alpha})dn_{\text{B}} & (\text{cst. T: } D' = 3) \\ dG = \mu_{\text{A}}(x_{\text{A},\alpha})dn_{\text{A}} + \mu_{\text{B}}(x_{\text{B},\alpha})dn_{\text{B}} & (\text{cst. T\&P: } D'' = 2) \end{array}$$

where $dn_{\text{A}} = dn_{\text{A},\alpha} + dn_{\text{A},\beta}$ and $dn_{\text{B}} = dn_{\text{B},\alpha} + dn_{\text{B},\beta}$ are the changes in total moles of A and B in both phases (the chemical potential of the components in each phase are equal, so it doesn't matter which phase the components are in for calculating the overall Gibbs energy). The final expression for dG can often be written in various equivalent ways; however, f and D provide a check that you haven't included dependent terms.

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

Answer: The Gibbs Phase Rule, Eq. 18.5.6, determines the variance. For a univariant system, $f = 1$, and with $c = 3$:

$$\begin{aligned} f &= c - p + 2 \\ 1 &= 3 - p + 2 \end{aligned} \quad \text{giving } p = 4$$

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

Answer: For a pure substance $c = 1$. Since there are no composition variables, the only intensive variables are the temperature and pressure and the variance is $f = 2$. The Gibbs Phase Rule, Eq. 18.5.6, then determines the phases:

$$\begin{aligned} f &= c - p + 2 \\ 2 &= 1 - p + 2 \end{aligned} \quad \text{giving } p = 3$$

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.

Answers: (a). False: Henry's Law, $p_{\text{CO}_2} = k_{\text{H,CO}_2} x_{\text{CO}_2}$, depends on the partial pressure of CO_2 , not the total pressure. The partial pressure of CO_2 at equilibrium in a bottle of champagne is near 6 atm. The partial pressure of CO_2 in ambient air is 0.0003 atm.⁹ The increased ambient pressure at the bottom of the tunnel does not significantly increase the CO_2 partial pressure in the atmosphere, compared to the 6 atm equilibrium partial pressure. Rather, the effect is caused by the kinetics of bubble formation. The kinetics of nucleation and bubble growth as the bubble

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risers in the solution is dependent on total pressure.⁹ The correct statement is: the equilibrium solubility of CO₂ in beverages is essentially independent of total applied pressure of air. However, please see Eq. 17.1.30° for extreme changes in total pressure.

(b). False: pumping air into the empty space in a partially filled bottle increases the total pressure, but the partial pressure of CO₂ remains essentially unchanged. The partial pressure of CO₂ in the atmosphere is negligible in this regard, at 0.0003 atm. Henry's Law, $p_{\text{CO}_2} = k_{\text{H,CO}_2} x_{\text{CO}_2}$, depends on the partial pressure of CO₂, not the total pressure. The increase in total pressure does decrease the rate of bubble nucleation and bubble growth, but the equilibrium is unaffected. In addition, 80% of the transfer of CO₂ into the gas phase is by direct transfer from the surface of the solution (for further information see part (a) and Ref. 9). The correct statement: bottle-top pressure pumps do not prevent “defizzing” of soft drinks at equilibrium.

(c). False: the solution composition is at the solution end of the tie line, on the freezing point coexistence curve. The solid-phase composition is at the solid-phase end of the tie line, which is pure A. The solution composition is fixed at a single value, subject to the system temperature. The corrected statement is: the overall system composition, z_B , may be any value along the tie line.

(d). True: thinking of the system from the perspective of freezing point depression, as the temperature of the solution is lowered, the solvent freezes out of solution. As the solute concentration increases the freezing point is depressed further. However, at some low temperature the solute also crystallizes out of solution, because the solute has limited solubility in the solution. At the eutectic temperature, both solute and solvent crystallize out of solution.

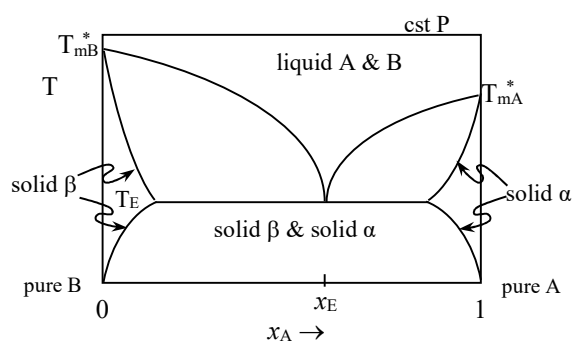
(e). False: The Henry's Law constant is the hypothetical vapor pressure of pure solute, assuming the forces are the same as between the solute and solvent. So, the solute-solvent forces are explicitly accounted for, in the dilute solution limit. Another way of seeing that the solute-solvent forces are carefully accounted for is to note that the Henry's Law constant for the solute is extrapolated from very dilute solution, where the only forces that affect the solute are the solute-solvent forces. Ideal-dilute solution theory does not take into account the concentration dependent changes as the forces shift from the solute-solvent forces in very dilute solution to solute-solute forces in pure solute, as $x_B \rightarrow 1$. The concentration dependent effects are resolved by the definition of activity in the next chapter. The correct statement is: ideal-dilute solution theory accounts for solute-solvent forces in the dilute solution limit, for which the only forces are the solute-solvent interaction.

(f). False/True: The freezing point is depressed in dilute methanol solutions. However, methanol is a volatile solute, so the colligative laws don't apply to the vapor above methanol-water solutions. Instead the binary liquid-vapor phase diagram is applicable, Figure 18.4.2, with water the less volatile component having the higher boiling point. At equilibrium the vapor pressures of methanol and water add, so the boiling point is lower for methanol-water solutions than pure water. The correct statement is: the boiling point is lowered and the freezing point is depressed in a dilute solution of methanol in water.

(g). True with a qualification: if two phases are in contact and a component occurs in one phase but not the other, then a concentration gradient will exist, and the component will diffuse into the other phase. The flux continues until the chemical potential of the component is equal in both phases. However, to be careful a qualification should be added: In the absence of a physical

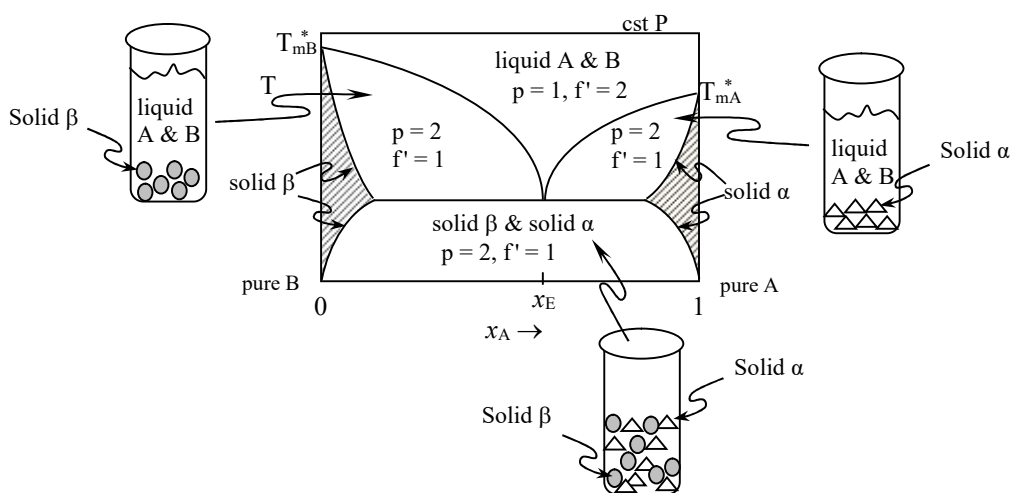
constraint, two phases cannot be in equilibrium unless all components occur in each phase. A semi-permeable membrane is such a constraint.

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.



Answer: The plan is to base the description on Figure 18.5.2a and the Gibbs Phase Rule, Eq. 18.5.6. The experiment is 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.

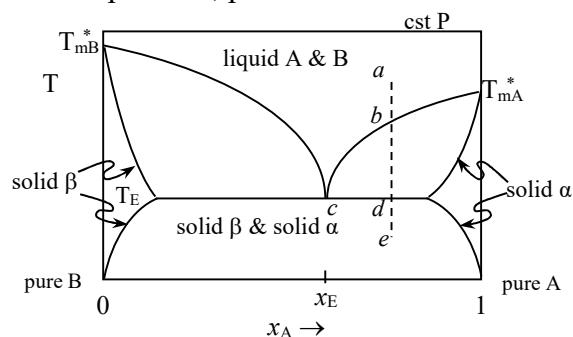


In the solid-liquid two-phase regions, with the solid and liquid in equilibrium, $p = 2$ and the variance at constant pressure is $f' = 2 - 2 + 1 = 1$. On the left side of the phase diagram the

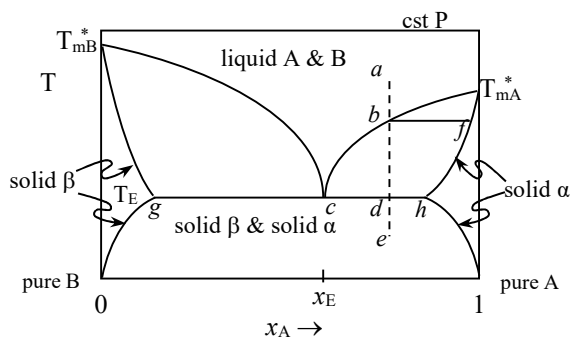
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solution is in equilibrium with the solid rich in B, solid β . On the right side the solution is in equilibrium with the A rich solid, solid α . At the eutectic temperature, the liquid phase, solid β , and solid α co-exist and $p = 3$ giving $f' = 2 - 3 + 1 = 0$. The eutectic temperature is an **invariant** point at constant pressure. Below the eutectic temperature, solid β and solid α are in equilibrium. The specific concentrations for the two solid phases are temperature dependent. The cross-hatched areas are not accessible starting from a homogeneous solution of A and B.

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 .



Answer: Cooling the solution of A and B starting at point a , the first phase change occurs when the temperature reaches the freezing point of the solution, point b . At point b , the solution is in equilibrium with solid α , with the composition given by the right side of the tie line at point f , in the diagram below. As solid α freezes out of solution, the solution composition becomes richer in B; the solution composition moves to the left on the co-existence curve and the freezing point of the solution decreases. The temperature continues to drop until the eutectic temperature is reached, point c . At the eutectic temperature, solid β crystallizes out of solution along with solid α . The temperature remains constant (the eutectic point is an invariant point at constant pressure), until the solution has completely frozen into a heterogeneous mixture of crystallites of solid α and solid β . The compositions of the two solid phases are at the ends of the tie line at the eutectic temperature, points g and h .



Below the eutectic temperature, the combined concentration of the solid phases is equal to the original solution concentration, point *d*, but no single phase has the composition at point *d*. The system continues to cool to point *e*. As the solution cools below the eutectic temperature, the composition of the solid phases at equilibrium change. However, establishing equilibrium is a very slow process in the solid state.

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.

Answer: There are only two intensive variables in the solid two-phase region: T and P. The concentrations are fixed, since the phases are pure. For the solid A phase $x_A = 1$ and for the solid B phase $x_B = 1$. The variance is then $f = 2$, accounting for the temperature and pressure variation. At constant pressure, $f' = 1$, and the system is univariant. Only the temperature may be varied at constant pressure. Please see Problems 39-40 for the more realistic case of partial miscibility.

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