

Chemistry 431  
Problem Set 12  
Fall 2023  
Solutions

1. At  $-5.^\circ\text{C}$  the vapor pressure of ice is 3.012 mm of Hg. whereas the vapor pressure of supercooled liquid water at  $-5.^\circ\text{C}$  is 3.163 mm Hg. Calculate  $\Delta G_m$  for the transition water  $\rightarrow$  ice at  $-5.^\circ\text{C}$ .

**Answer:**

$$\begin{aligned}\Delta G_m &= RT \ln \frac{P_{ice}}{P_{water}} \\ &= (8.3144 \text{ J mol}^{-1}\text{K}^{-1})(268 \text{ K}) \ln \frac{3.012}{3.163} = -109 \text{ J mol}^{-1}\end{aligned}$$

2. Liquid methanol ( $\text{CH}_3\text{OH}$ ) and liquid ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) form an ideal solution. At  $25.0^\circ\text{C}$  the vapor pressures of pure methanol and ethanol are respectively 0.112 bar and 0.061 bar. When 20.0 grams of methanol and 20.0 grams of ethanol are combined in a closed flask at  $25.0^\circ$ , the liquid phase and the vapor phase both contain methanol and ethanol. Calculate the mole fraction of methanol in the vapor phase.

**Answer:**

$$\begin{aligned}n_{\text{methanol}} &= \frac{20 \text{ g}}{32 \text{ g mol}^{-1}} = 0.625 \text{ mol} \\ n_{\text{ethanol}} &= \frac{20 \text{ g}}{46 \text{ g mol}^{-1}} = 0.435 \text{ mol}\end{aligned}$$

In the liquid phase

$$\chi_{\text{methanol}} = \frac{0.625}{0.625 + 0.435} = 0.590 \quad \chi_{\text{ethanol}} = \frac{0.435}{0.435 + 0.625} = 0.410$$

In the vapor phase

$$P_{\text{methanol}} = 0.590(0.112 \text{ bar}) = 0.066 \text{ bar} \quad P_{\text{ethanol}} = 0.410(0.061 \text{ bar}) = 0.025 \text{ bar}$$

Then

$$P_{\text{tot}} = 0.025 \text{ bar} + 0.066 \text{ bar} = 0.091 \text{ bar}$$

and in the vapor phase

$$\chi_{\text{methanol}} = \frac{P_{\text{methanol}}}{P_{\text{tot}}} = \frac{0.066}{0.091} = 0.725$$

3. At 298K water and acetone ( $C_3H_6O$ ) form an ideal solution that obeys Raoult's Law at all compositions, and the vapor pressure of pure acetone is 0.461 bar. 10.0 grams of water are mixed with a mass  $m$  of acetone in a closed container. After equilibrium is reached between the excess liquid mixture and vapor, the total pressure of the vapor is found to be 0.133 bar and the partial pressure of water in the vapor is found to be 0.0240 bar. Ignoring any mass of acetone lost to the vapor, calculate the mass  $m$  of the acetone in the liquid mixture.

**Answer:**

$$n_{H_2O} = \frac{10.0 \text{ g}}{18.0 \text{ g mol}^{-1}} = 0.556 \text{ mol}$$

In the vapor

$$P_{acetone} = P_{tot} - P_{H_2O} = 0.133 \text{ bar} - 0.0240 \text{ bar} = 0.109 \text{ bar}$$

$$P_{acetone} = \chi_{acetone} P_{acetone}^* \quad 0.109 = \chi_{acetone} (0.461) \quad \chi_{acetone} = 0.236$$

$$0.236 = \frac{n_{acetone}}{n_{acetone} + 0.556 \text{ mol}} \quad n_{acetone} = 0.172 \text{ mol}$$

$$m_{acetone} = 0.171 \text{ mol} (58.0 \text{ g mol}^{-1}) = 9.98 \text{ g}$$

4. Benzene boils at 80.10 °C. When 3.0 grams of naphthalene are dissolved in 80.0 grams of benzene, the boiling point is found to be 80.86°C. Determine the enthalpy of vaporization of benzene.

**Answer:**

$$\frac{3.0 \text{ g, naphthalene}}{80 \text{ g, benzene}} \times 1000 \text{ g, benzene} = \frac{37.50 \text{ g, naphthalene}}{1000 \text{ g, benzene}}$$

$$\frac{37.5 \text{ g}}{128 \text{ g mol}^{-1}} = 0.29 \text{ molal}$$

$$\Delta T = \frac{RT^{*2}}{1000\lambda} m$$

$$(80.86 - 80.1) \text{ K} = \frac{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(353.1 \text{ K})^2(0.29 \text{ mol})}{1000 \text{ g } \lambda}$$

$$\lambda = 395.6 \text{ J g}^{-1}$$

5. When 100. grams of chloroform ( $CHCl_3$ ) are mixed with 197. grams of acetone ( $C_3H_6O$ ) at 25.°C, the vapor pressure of the chloroform decreases from 293. mm Hg to 35. mm Hg and the vapor pressure of the acetone decreases from 347. mm Hg to 270. mm Hg. Calculate  $\Delta G$  of mixing for this non-ideal solution.

**Answer:**

$$G_i = n_A \mu_A^* + n_B \mu_B^*$$

$$G_f = n_A \left[ \mu_A^* + RT \ln \frac{P_A}{P_A^*} \right] + n_B \left[ \mu_B^* + RT \ln \frac{P_B}{P_B^*} \right]$$

$$\Delta G = G_f - G_i = n_A RT \ln \frac{P_A}{P_A^*} + n_B RT \ln \frac{P_B}{P_B^*}$$

$$n_A = \frac{100 \text{ g}}{119.5 \text{ g mol}^{-1}} = 0.84 \text{ mol}$$

$$n_B = \frac{197 \text{ g}}{58 \text{ g mol}^{-1}} = 3.40 \text{ mol}$$

$$\Delta G = (8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K}) \left[ (0.84 \text{ mol}) \ln \frac{35}{293} + (3.40 \text{ mol}) \ln \frac{270}{347} \right] = -6536 \text{ J}$$

6. When 10.0 grams of water are mixed with 10.0 grams of methanol ( $\text{CH}_3\text{OH}$ ) isothermally at 300K to form a non ideal solution, the change in the Gibbs free energy is found to be -2250. J. Given the vapor pressures of water and methanol in the mixture are respectively 0.0100 bar and 0.100 bar, and given the vapor pressure of pure water to be 0.0354 bar at 300K, calculate the vapor pressure of pure methanol at 300K.

**Answer:**

$$\Delta G = n_m RT \ln \frac{P_m}{P_m^*} + n_w RT \ln \frac{P_w}{P_w^*}$$

$$n_m = \frac{10 \text{ g}}{32 \text{ g mol}^{-1}} = 0.31 \text{ mol} \quad n_w = \frac{10 \text{ g}}{18 \text{ g mol}^{-1}} = 0.56 \text{ mol}$$

$$-2250 \text{ J} = (8.3144 \text{ J mol}^{-1}\text{K}^{-1})(300 \text{ K}) \left( (0.31 \text{ mol}) \ln \frac{0.100}{P_m^*} + (0.56 \text{ mol}) \ln \frac{0.01}{0.0354} \right)$$

$$P_m^* = 0.19 \text{ bar}$$

7. Liquid benzene ( $\text{C}_6\text{H}_6$ ) and liquid pyridine ( $\text{C}_5\text{H}_5\text{N}$ ) form an ideal solution that obeys Raoult's law at all compositions. At 20.0° 10.0 grams of benzene and 30.3 grams of pyridine are combined in a previously evacuated container, and the sum of the vapor pressures of benzene and pyridine at equilibrium is found to be 0.246 bar. Given the vapor pressure of pure benzene at 20.0° is 0.100 bar, calculate the vapor pressure of pure pyridine at 20.0°C.

**Answer:**

$$n_{\text{benzene}} = \frac{10.0 \text{ g}}{78.1 \text{ g mol}^{-1}} = 0.128 \text{ mol} \quad n_{\text{pyridine}} = \frac{30.3 \text{ g}}{79.1 \text{ g mol}^{-1}} = 0.383 \text{ mol}$$

$$\chi_{\text{benzene}} = \frac{0.128}{0.128 + 0.383} = 0.250 \quad \chi_{\text{pyridine}} = 1 - \chi_{\text{benzene}} = 0.750$$

$$P_{\text{benzene}} = (0.250)(0.100 \text{ bar}) = 0.0250 \text{ bar}$$

$$P_{\text{pyridine}} = P_{\text{tot}} - P_{\text{benzene}} = 0.246 \text{ bar} - 0.0250 \text{ bar} = 0.221 \text{ bar}$$

$$P_{\text{pyridine}} = P_{\text{pyridine}}^* \chi_{\text{pyridine}} \quad 0.221 \text{ bar} = (0.750)P_{\text{pyridine}}^*$$

$$P_{\text{pyridine}}^* = 0.295 \text{ bar}$$

8. At 288 K, the vapor pressure of pure liquid methanol ( $\text{CH}_3\text{OH}$ ) is 0.100 bar and the vapor pressure of pure liquid acetone ( $\text{CH}_3\text{COCH}_3$ ) is 0.230 bar. When 10.0 grams of acetone and 10.0 grams of methanol are combined at 288 K, the change in the Gibbs free energy associated with the formation of the non-ideal mixture is found to be  $\Delta_{\text{mix}}G = -1580$  J. Given the vapor pressure of the acetone for the mixture is 0.074 bar, calculate the total pressure of the vapor phase. Assume all species in the vapor phase obey the ideal-gas law.

**Answer:**

$$\Delta_{\text{mix}}G = n_A RT \ln \frac{P_A}{P_A^*} + n_M RT \ln \frac{P_M}{P_M^*}$$

$$n_A = \frac{10.0 \text{ g}}{58.0 \text{ g mol}^{-1}} = 0.172 \text{ mol} \quad n_M = \frac{10.0 \text{ g}}{32.0 \text{ g mol}^{-1}} = 0.312$$

$$-1580. \text{ J} = (8.3144 \text{ J mol}^{-1}\text{K}^{-1})(288 \text{ K}) \left[ (0.172 \text{ mol}) \ln \frac{0.074 \text{ bar}}{0.230 \text{ bar}} + (0.312 \text{ mol}) \ln \frac{P_M}{0.100 \text{ bar}} \right]$$

$$P_M = 2.25 \times 10^{-2} \text{ bar} \quad P_{\text{tot}} = P_A + P_M = 0.0965 \text{ bar}$$

9. The osmotic pressure of a solution containing 32.6 g  $\text{L}^{-1}$  of a solute was 2.43 atmospheres at 20. $^{\circ}\text{C}$ . Calculate the osmotic pressure of a solution containing 90.1 g  $\text{L}^{-1}$  of the same solute at 0. $^{\circ}\text{C}$ .

**Answer:**

$$\Pi = cRT$$

$$\Pi_2 = (2.43 \text{ atm}) \left( \frac{273}{293} \right) \left( \frac{90.1}{32.6} \right) = 6.2 \text{ atm}$$

10. Naphthalene melts at 80. $^{\circ}\text{C}$  and forms an ideal solution with benzene. The heat of fusion of naphthalene is 148.95 J  $\text{g}^{-1}$ . At what temperature would the solubility be 80. grams of naphthalene per mole of benzene?

**Answer:**

$$n_{\text{benzene}} = 1. \text{ mol} \quad n_{\text{naphthalene}} = \frac{80 \text{ g}}{128 \text{ g mol}^{-1}} = 0.625 \text{ mol}$$

$$\chi_{\text{naphthalene}} = \frac{0.625}{1.625} = 0.385$$

$$0.385 = \exp \left\{ - \frac{(148.95 \text{ J g}^{-1})(128 \text{ g mol}^{-1})}{8.3144 \text{ J mol}^{-1}\text{K}^{-1}} \left( \frac{1}{T} - \frac{1}{353 \text{ K}} \right) \right\}$$

$$T = 308 \text{ K}$$

11. What mass of methanol when dissolved in 10. liters of water will just prevent the formation of ice at -5. $^{\circ}\text{C}$ ? The heat of fusion of ice is 335 J  $\text{g}^{-1}$ .

**Answer:**

$$\Delta T = \frac{RT^{*2}}{1000\lambda} m$$

$$m = \frac{(5 \text{ K})(1000 \text{ g})(335 \text{ J g}^{-1})}{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(273 \text{ K})^2} = 2.7 \text{ molal}$$

2.7 moles in 1 liter or 27 moles in 10 liters. Then

$$(27 \text{ mol})(32 \text{ g mol}^{-1}) = 864 \text{ g}$$

12. The solubility of solid benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ ) in liquid ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) is 4.77 molal at  $25.0^\circ\text{C}$ . Given the normal melting point of benzoic acid is  $122.^\circ\text{C}$  and assuming the solution to be ideal, calculate the enthalpy of fusion of benzoic acid.

**Answer:**

$$n_{\text{ethanol}} = \frac{1000 \text{ g}}{46 \text{ g mol}^{-1}} = 21.74 \text{ mol}$$

$$\chi_{\text{benzoic acid}} = \frac{4.77}{4.77 + 21.74} = 0.18$$

$$\chi = \exp \left\{ -\frac{\Delta H_{m,\text{fus}}}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right) \right\}$$

$$0.18 = \exp \left\{ \frac{-\Delta H_{m,\text{fus}}}{8.3144 \text{ J mol}^{-1}\text{K}^{-1}} \left( \frac{1}{298 \text{ K}} - \frac{1}{395 \text{ K}} \right) \right\}$$

$$\Delta H_{m,\text{fus}} = 17300 \text{ J mol}^{-1}$$

13. When a small quantity of a solute is added to water, the normal freezing point is found to be depressed by  $1.50\text{K}$ . When the same solution is boiled, the normal boiling point is found to be elevated by  $0.413\text{K}$ . Given the enthalpy of fusion of ice is  $6.010 \text{ kJ mol}^{-1}$ , calculate the enthalpy of vaporization of water. Recall that the normal freezing and boiling points of water are respectively  $273\text{K}$  and  $373\text{K}$ .

**Answer:**

$$\Delta T = \frac{RT^{*2}}{\Delta H_{m,\text{fus}}} \chi_s$$

$$1.50 \text{ K} = \frac{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(273. \text{ K})^2}{6010 \text{ J mol}^{-1}} \chi_s \quad \chi_s = 1.45 \times 10^{-2}$$

$$\Delta T = \frac{RT^{*2}}{\Delta H_{m,\text{vap}}} \chi_s$$

$$0.413 \text{ K} = \frac{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(373. \text{ K})^2}{\Delta H_{m,\text{vap}}} (1.45 \times 10^{-2})$$

$$\Delta H_{m,\text{vap}} = 40610 \text{ J mol}^{-1}$$

14. The enthalpies of vaporization and fusion of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) are respectively  $\Delta H_{m,\text{vap}} = 38.6 \text{ kJ mol}^{-1}$  and  $\Delta H_{m,\text{fus}} = 5.02 \text{ kJ mol}^{-1}$  and the normal boiling and freezing points of pure ethanol are respectively  $T_b = 78.4^\circ\text{C}$  and  $T_f = -114.^\circ\text{C}$ . A certain solution of citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ) dissolved in ethanol is found to boil at a temperature of  $81.1^\circ\text{C}$ .

Determine the freezing temperature of the same solution.

**Answer:**

$$\begin{aligned}\Delta T_b &= 81.1 \text{ K} = 78.4 \text{ K} = 2.7 \text{ K} \\ &= \frac{RT^{*2}}{\Delta H_{m,vap}} \chi_s = \frac{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(351.4 \text{ K})^2}{38600 \text{ J mol}^{-1}} \chi_s \quad \chi_s = 0.101 \\ \Delta T_f &= \frac{RT^{*2}}{\Delta H_{m,fus}} \chi_s = \frac{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(159 \text{ K})^2}{5020 \text{ J mol}^{-1}} 0.101 = 4.23 \text{ K} \\ T_f &= -114 \text{ C} - 4.23 \text{ C} = -118.2 \text{ C}\end{aligned}$$

15. In an osmotic pressure apparatus, a dilute aqueous solution shows an osmotic pressure of 1.2 bar at 300K. Given the enthalpy of fusion of water is 6008 J mol<sup>-1</sup>, calculate the freezing point of the solution. You may assume the solution to be sufficiently dilute that the molarity and molality of the solution are numerically identical. Remember that the freezing point of pure water is 273K.

**Answer:**

$$\begin{aligned}c &= \frac{\Pi}{RT} \\ &= \frac{1.2 \text{ bar}}{(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(300 \text{ K})} = 0.0481 \text{ mol L}^{-1} \\ \Delta T &= \frac{RT^{*2}}{1000 \text{ g } \lambda} m \\ &= \frac{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(273 \text{ K})^2}{(1000 \text{ g})(6008 \text{ J mol}^{-1}) \left(\frac{\text{mol}}{18 \text{ g}}\right)} 0.0481 \text{ mol} = 0.0893 \text{ K} \\ T_f &= 273 \text{ K} - 0.0893 \text{ K} = 272.91 \text{ K}\end{aligned}$$

16. When a certain mass of sucrose (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>) is dissolved in 1000. grams of water, the boiling point is found to be elevated by 0.00015K. The same sucrose solution is placed in an osmotic pressure cell at 298K, with pure water on the left and solution on the right. Calculate the height of the sucrose solution on the right side of the cell relative to the height of the pure water on the left. Assume the density of both the solution and pure water are both 1.0 g cm<sup>-3</sup>, the enthalpy of vaporization of water is 2249. J g<sup>-1</sup>, the solution is sufficiently dilute to set the molarity and molality equal, and recall the normal boiling point of water is 373.K.

**Answer:**

$$\begin{aligned}\Delta T &= \frac{RT^{*2}}{1000.\text{g } \lambda_{vap}} m \\ 0.00015 \text{ K} &= \frac{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(373. \text{ K})^2}{(1000.\text{g})(2249. \text{ J g}^{-1})} m\end{aligned}$$

$$m = 2.92 \times 10^{-4} \text{ molal} \sim 2.92 \times 10^{-4} \text{ mol L}^{-1}$$

$$\Pi = cRT = \rho gh \quad h = \frac{cRT}{\rho g}$$

$$h = \frac{(2.92 \times 10^{-4} \text{ mol L}^{-1})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(10^5 \text{ N m}^{-2}\text{bar}^{-1})(298. \text{ K})}{(1.0 \text{ g cm}^{-3})(10^2 \text{ cm/m})^3(\text{kg}/10^3 \text{ g})(9.8 \text{ m s}^{-2})}$$

$$= 0.074 \text{ m}$$

17. When a certain mass of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) is dissolved in 50.0 g of methanol ( $\text{CH}_3\text{OH}$ ), the boiling point of the methanol rises from 64.7 C for pure methanol to 65.1 C in the mixture. In another solution the same mass of glucose is then dissolved in water at 25.0 C to make 1.00 L of solution, and the aqueous solution of glucose is placed in an osmotic pressure cell. The osmotic pressure is measure to be 0.682 bar. Calculate the enthalpy of vaporization of methanol.

**Answer:**

$$c = \frac{\Pi}{RT} = \frac{0.682 \text{ bar}}{(0.083144 \text{ L bar mol}^{-1}\text{K}^{-1})(298. \text{ K})} = 2.75 \times 10^{-2} \text{ mol L}^{-1}$$

$$n_{glucose} = 2.75 \times 10^{-2} \text{ mol} \quad n_{methanol} = \frac{50.0 \text{ g}}{(12.0 + 4.00 + 16.00) \text{ g mol}^{-1}} = 1.56 \text{ mol}$$

$$\chi_{glucose} = \frac{2.75 \times 10^{-2}}{2.75 \times 10^{-2} + 1.56} = 1.73 \times 10^{-2}$$

$$\Delta T = \frac{RT^*2}{\Delta H_{m,vap}} \chi_{glucose}$$

$$(65.1 - 64.7) \text{ K} = \frac{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(337.7 \text{ K})^2}{\Delta H_{m,vap}} (1.73 \times 10^{-2})$$

$$\Delta H_{m,vap} = 41000 \text{ J mol}^{-1}$$