

## Homework 9 key

$$1. P_1 = 120 x_1 e^{0.20 x_2^2 + 0.10 x_2^3}$$

$$P_2 = 140 x_2 e^{0.35 x_1^2 + 0.10 x_1^3}$$

$P_1 \rightarrow x_1 P_1^*$  as  $x_1 \rightarrow 1 / x_2 \rightarrow 0$  and  $P_2 \rightarrow x_2 P_2^*$  as  $x_2 \rightarrow 1$

$$P_1 \rightarrow 120 x_1 \text{ as } x_1 \rightarrow 1 \quad (\text{b/c } e^0 = 1)$$

$$\text{so } P_1^* = 120 \text{ torr}$$

$$P_2 \rightarrow 140 x_2 e^{0.35 x_1^2 - 0.10 x_1^3}$$

$$P_2 \rightarrow 140 x_2 \text{ as } x_2 \rightarrow 1$$

$$P_2^* = 140 \text{ torr}$$

$$P_1 \rightarrow k_{H,1} x_1 \text{ as } x_1 \rightarrow 0 / x_2 \rightarrow 1$$

$$P_1 = 120 x_1 e^{0.20(1)^2 + 0.10(1)^3}$$

$$= 162 x_1 \text{ as } x_1 \rightarrow 0 \quad \text{so } k_{H,1} = 162 \text{ torr}$$

$$P_2 \rightarrow k_{H,2} x_2 \text{ as } x_2 \rightarrow 0 / x_1 \rightarrow 1$$

$$P_2 = 140 x_2 e^{0.35 - 0.10} = 180 x_2 \text{ as } x_2 \rightarrow 0$$

$$k_{H,2} = 180 \text{ torr}$$

2. MS 50... see Excel graph

$$P_1 \rightarrow k_{H,1} x_1 \text{ as } x_1 \rightarrow 0$$

$k_{H, \text{ethanol}}$  is slope as  $x_{\text{ethanol}} \rightarrow 0$

$$\text{slope} = \text{rise/run} \approx 17.65 / 0.1 \approx 176.5 \text{ torr}$$

$k_{H, \text{water}}$  is slope as  $x_{\text{ethanol}} \rightarrow 1$

$$\text{slope} \approx 9.89 / 0.20 \approx 49.5 \text{ torr}$$

MS-51 ... See Excel graph

$$\gamma_i = P_i / x_i P_i^*$$

For ethanol  $P_i^* = 59.2$

Water  $P_i^* = 23.78$

$$\gamma_{\text{ethanol}} = \frac{P_{\text{ethanol}}}{x_{\text{ethanol}}(59.2)}$$

$$\gamma_{\text{water}} = \frac{P_{\text{water}}}{(1 - x_{\text{ethanol}})(23.78)}$$

A pure liquid has an activity of 1. With this data, as the  $x_{\text{ethanol}} \rightarrow 1$ , the activity coefficient for ethanol  $\gamma \rightarrow 1$ . Also when  $x_{\text{ethanol}} \rightarrow 0$ , the activity coefficient for water  $\gamma \rightarrow 1$ . At low concentrations of ethanol  $\gamma_{\text{ethanol}}$  is high.

3. According to Henry's law ...  $p \propto$  concentration  
 or  $P = k_{H,c}$

$$K_{H,c} = P/c = \frac{0.80 \text{ atm}}{5.6 \times 10^{-4} \text{ M}} = 1428.6 \text{ M}^{-1} \text{ atm}$$

$$\text{@ } 4 \text{ atm, } c = P/K_{H,c} = \frac{4 \text{ atm}}{1428.6 \text{ atm/M}} = 0.0028 \text{ M}$$

$$(0.0028 \text{ mol/L})(5 \text{ L}) = 0.014 \text{ mol}$$

$$\text{@ } 0.8 \text{ atm, } c = 5.6 \times 10^{-4} \text{ mol/L}$$

$$(5.6 \times 10^{-4} \text{ mol/L})(5 \text{ L}) = 0.0028 \text{ mol}$$

$$\text{mol } N_2 \text{ expelled} = 0.014 - 0.0028 = 0.0112 \text{ mol}$$

$$M^{\circ} \text{ of } N_2, V = nRT/P = \frac{(0.0112)(0.08206)(310 \text{ K})}{(1 \text{ atm})} = \boxed{0.36 \text{ M}}$$

4.  $p = 1.101 \text{ g/mL}$  of ~~pure glycerol~~ solution  
 in 40% glycerol ...  $(0.4)(1.101 \text{ g/mL}) = 0.4404 \text{ g/mL}$

Molarity (mol/L)

$$(0.4404 \text{ g/mL}) \left( \frac{1 \text{ mol}}{92.093 \text{ g}} \right) \left( \frac{1000 \text{ mL}}{\text{L}} \right) = 4.78 \text{ M}$$

molality

$$\text{g } H_2O \text{ / ml solution ... } (0.6)(1.101 \text{ g/mL}) = 0.6606 \text{ g/mL}$$

$$0.4404 \text{ g glycerol/mL} / 0.6606 \text{ g } H_2O \text{ / mL} = 0.6666 \text{ g glycerol/g } H_2O$$

$$\frac{0.6666 \text{ g glycerol}}{1 \text{ g } H_2O} \cdot \frac{1000 \text{ g } H_2O}{1 \text{ kg } H_2O} \cdot \frac{1 \text{ mol glycerol}}{92.093 \text{ g glycerol}}$$

$$= 7.24 \text{ mol glycerol/kg } H_2O = 7.24 \text{ m}$$

5.  $\text{mole fraction} = \frac{\text{mol glucose}}{\text{mol glucose} + \text{mol H}_2\text{O}}$

$\text{mol glucose} = 0.500 \text{ mol}$

$\text{mol H}_2\text{O} = 1000 \text{ g H}_2\text{O} \cdot \frac{1 \text{ mol}}{18.02 \text{ g}} = 55.49 \text{ mol H}_2\text{O}$

$x_2 = \frac{0.500 \text{ mol glucose}}{0.500 \text{ mol glucose} + 55.49 \text{ mol H}_2\text{O}} = 0.00893$

6.

$C = \frac{\pi}{RT}$

$\pi = 2.06 \text{ torr} \cdot \frac{1 \text{ atm}}{760 \text{ torr}} =$

$C = \frac{\pi}{RT} = \frac{2.06 \text{ torr} \cdot \frac{1 \text{ atm}}{760 \text{ torr}}}{(0.08206 \frac{\text{L atm}}{\text{mol K}})(298 \text{ K})} = 1.11 \times 10^{-4} \text{ M}$

$(1.11 \times 10^{-4} \frac{\text{mol}}{\text{L}})(0.100 \text{ L}) = 1.11 \times 10^{-5} \text{ mol}$

$\text{MW} = \frac{\text{g/mol}}{\text{mol}} = \frac{0.80 \text{ g}}{1.11 \times 10^{-5} \text{ mol}} = 72175 \text{ g/mol}$

7.  $\Delta T_{\text{fus}} = \nu K_f m$

$K_f = 1.86 \text{ K kg/mol} \text{ (pg 1022)}$

$\Delta T_{\text{fus}} = -2.83^\circ\text{C} = 2.83 \text{ K}$

$m = \text{mol HgCl}_2 / \text{kg H}_2\text{O}$

$40.7 \text{ g} \times \frac{1 \text{ mol}}{271.49 \text{ g}} = 0.150 \text{ mol HgCl}_2 \text{ per } 100 \text{ g H}_2\text{O}$

$\frac{0.150 \text{ mol HgCl}_2}{100 \text{ g H}_2\text{O}} \cdot \frac{1000 \text{ g}}{1 \text{ kg}} = 1.50 \text{ m}$

$\nu = \frac{\Delta T_f}{K_f m} = \frac{2.83 \text{ K}}{1.86 \frac{\text{K kg}}{\text{mol}} \cdot 1.50 \frac{\text{mol}}{\text{kg}}} = 1.02$

Since  $\nu \approx 1$ ,  $\text{HgCl}_2$  doesn't dissociate under these conditions and can't conduct electricity.

$$8. \ln \gamma_{\pm} = -1.173 |z_+ z_-| I_c^{1/2}$$

$$I_c = \frac{1}{2} (1^2 \cdot 0.01 + (-1)^2 \cdot 0.01) = 0.010 \text{ M}$$

$$\ln \gamma_{\pm} = -1.173 |1 \cdot -1| (0.01)^{1/2} = -0.1173$$

$$\gamma_{\pm} = 0.889$$

9.

$$I_c (\text{NaCl}) = \frac{1}{2} (1^2 \cdot c + (-1)^2 \cdot c) = c$$

$$I_c (\text{K}_2\text{SO}_4) = \frac{1}{2} (1^2 \cdot 2c + (-2)^2 \cdot c) = 3c$$

$$\text{if } I_c (\text{NaCl}) = 0.315 \text{ mol/L} = c_1$$

$$I_c (\text{K}_2\text{SO}_4) = 0.315 \text{ mol/L} = 3c_2$$

$$c_2 = 0.105 \text{ mol/L}$$

$$10. \Delta T_f = 5.5 - 3.9 = 1.6^\circ\text{C} \Rightarrow 1.6 \text{ K}$$

$$k_f = 5.12 \text{ K} \cdot \text{kg/mol}$$

$$m = \Delta T_f / k_f = 1.6 \text{ K} / 5.12 \text{ K} \cdot \text{kg/mol} = 0.3125 \text{ mol/kg powder benzene}$$

$$\frac{0.3125 \text{ mol powder}}{\text{kg benzene}} \cdot 0.008 \text{ kg} = 0.0025 \text{ mol compound}$$

$$\text{So MW} = \frac{0.0025 \text{ mol}}{0.5 \text{ g}} = 200 \text{ g/mol}$$

Cocaine = 303.4 g/mol so powder is not cocaine

Assumptions: Pure powder, no dissociation of compound, dilute solutions

11.  $K_f$  (benzene) = 5.12 K·kg/mol  
 $\Delta T_f = 2.0^\circ\text{C} \Rightarrow 2.0\text{ K}$

$$\Delta T_f = K_f m$$

$$m = \Delta T_f / K_f = 2.0 / 5.12 = (0.3906 \text{ mol/kg}) (0.08 \text{ kg})$$
$$= 0.0313 \text{ mol}$$

$$3.8 \text{ g} / 0.0313 \text{ mol} = 121.6 \text{ g/mol}$$

$$\text{acetic acid} = 60.05 \text{ g/mol}$$

The structure in benzene must be a dimer of acetic acid MW  $\sim 120.1 \text{ g/mol}$ . Not quite a match due to assumptions in deriving  $\Delta T_f = K_f m$ .