

- please answer all 5 questions in the spaces provided
- this is a two-hour test
- a calculator and the equation sheet provided may be used

- all questions are of equal value
- no books or notes are allowed
- no marks for unreadable answers

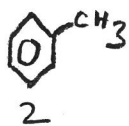
Q1. a) For an ideal liquid solution of volatile components 1 and 2, show the mole fraction of component 1 in the vapor is

$$p_1 = x_1 p_1^* \quad p_2 = x_2 p_2^* \quad (x_2 = 1 - x_1)$$

$$y_1 = \frac{x_1 p_1^*}{x_1 p_1^* + (1 - x_1) p_2^*}$$

$$Y_1 = \frac{n_{1, \text{gas}}}{n_{1, \text{gas}} + n_{2, \text{gas}}} = \frac{\frac{P_1 V}{RT}}{\frac{P_1 V}{RT} + \frac{P_2 V}{RT}} = \frac{P_1}{P_1 + P_2} = \frac{x_1 p_1^*}{x_1 p_1^* + x_2 p_2^*} = \frac{x_1 p_1^*}{x_1 p_1^* + (1 - x_1) p_2^*}$$

b) Explain in molecular terms why benzene and toluene form liquid solutions that are very nearly ideal.



Similar molecular sizes and polarity.  
1-1, 1-2, 2-2 molecular interactions should be nearly identical.

c) Calculate the mole fraction of benzene in the vapor in equilibrium with a liquid solution of benzene(1) + toluene(2) solution of composition  $x_1 = 0.300$  if the respective vapor pressures of pure benzene and pure toluene are 109.3 Torr and 22.30 Torr.

$$Y_1 = \frac{x_1 p_1^*}{x_1 p_1^* + (1 - x_1) p_2^*} = \frac{0.300(109.3 \text{ Torr})}{0.300(109.3 \text{ Torr}) + 0.700(22.30 \text{ Torr})}$$

$(p_1^* = 109.3 \text{ Torr})$   
 $(p_2^* = 22.30 \text{ Torr})$

$$= \frac{32.79}{32.79 + 15.61} = \boxed{0.677}$$

d) Describe how the calculation in c shows the vapor is richer in the more volatile component than the liquid. Name the important purification technique based on this behavior.

$$Y_1 = 0.677$$

(vapor)

$$x_1 = 0.300$$

(liquid)

$$Y_1 > x_1$$

fractional distillation

e) Is the vapor in equilibrium with a liquid mixture of two components always richer in the more volatile component? Explain. **No**

$Y_1 > x_1$  for ideal liquid/vapor equilibrium  
but not necessarily for nonideal liquid/vapor equilibrium.  
At an azeotrope point, for example,  $Y_1 = x_1$ .

Q2. 0.600 moles of pure acetone(1) and 0.400 moles of pure chloroform(2) are mixed at 35 °C to form a liquid solution. The vapor pressures of acetone and chloroform over the solution are  $p_1 = 25.3$  Torr and  $p_2 = 11.7$  Torr. For this solution:

a) Calculate the Raoult's law activity coefficient of acetone. (The vapor pressure of pure liquid acetone is 45.9 Torr at 35 °C)

$$\gamma_{1RL} = \frac{P_1}{x_1 P_1^*} = \frac{25.3 \text{ Torr}}{0.600 (45.9 \text{ Torr})} = \boxed{0.919}$$

b) Calculate the Raoult's law activity coefficient of chloroform. (The vapor pressure of pure liquid chloroform is 39.1 Torr at 35 °C.)

$$\gamma_{2RL} = \frac{P_2}{x_2 P_2^*} = \frac{11.7 \text{ Torr}}{0.400 (39.1 \text{ Torr})} = \boxed{0.748}$$

c) Use the results from a and b to show the acetone + chloroform form nonideal solutions with negative deviations from Raoult's law.  $\rightarrow (P_i < x_i P_i^* \quad (P_i/x_i P_i^*) < 1)$

$$\frac{\text{actual } P_1}{\text{Raoult's law } P_1} = \frac{P_1}{x_1 P_1^*} = \gamma_{1RL} = 0.919 < 1$$

$$\frac{\text{actual } P_2}{\text{Raoult's law } P_2} = \frac{P_2}{x_2 P_2^*} = \gamma_{2RL} = 0.748 < 1$$

d) Explain in terms of molecular interactions why chloroform + acetone form nonideal solutions.

chloroform-acetone attractions are stronger than chloroform-chloroform and acetone-acetone attractions (due to "hydrogen-bonding" dipole-dipole interactions) which makes the solution more stable (lower vapor pressures) than an ideal solution ( $P_1 < x_1 P_1^*$  and  $P_2 < x_2 P_2^*$ )

e) Describe how the equation  $\Delta G_{\text{mix}} = n_1 RT \ln x_1 + n_2 RT \ln x_2$  for the Gibbs energy of mixing of ideal solutions can be modified to calculate  $\Delta G_{\text{mix}}$  for nonideal solutions.

replace  $x_1, x_2$  with activities  $a_1, a_2$  to include nonideal-solution effects.

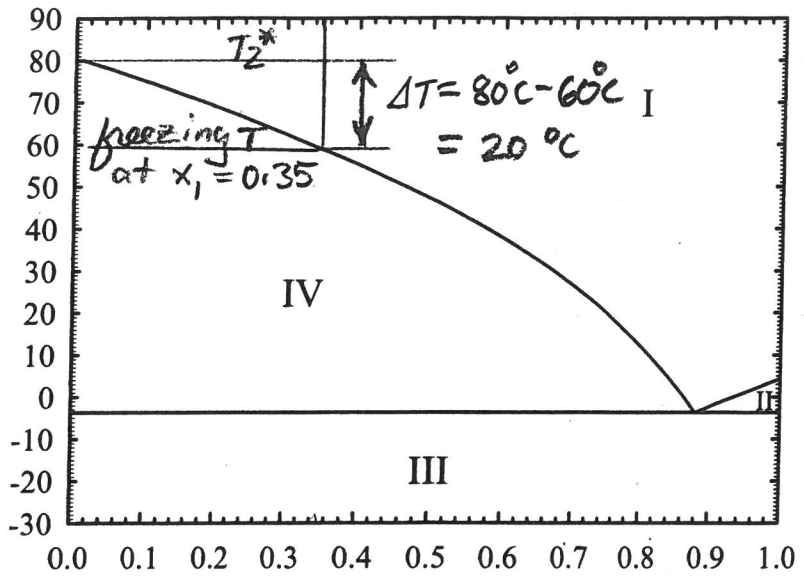
$$a_1 = \gamma_{1RL} x_1 \quad a_2 = \gamma_{2RL} x_2$$

$$\Delta G_{\text{mix}} (\text{nonideal}) = n_1 RT \ln(\gamma_{1RL} x_1) + n_2 RT \ln(\gamma_{2RL} x_2)$$

$$= \boxed{n_1 RT \ln a_1 + n_2 RT \ln a_2}$$

Q3. Use the diagram below to answer this question.

benzene(1) + naphthalene(2) solid-liquid phase diagram at 1 bar



a) Describe the phases present in each of the four regions of the phase diagram.

- I: one-phase liquid solution
- II: liquid solution + solid benzene
- III: solid benzene + solid naphthalene
- IV: liquid solution + solid naphthalene

b) Give the freezing point depression for a solution of composition  $x_1 = 0.35$ .

20 °C (see diagram)  
 $\Delta T = T_2^* - T = 80^\circ\text{C} - 60^\circ\text{C} = 20^\circ\text{C}$

c) Benzene is to be purified by cooling a liquid benzene + naphthalene solution and collecting the benzene crystals that precipitate. Why is it necessary to have a solution with  $x_1 > 0.88$ ?

if  $x_1 < 0.88$ , pure solid naphthalene crystallizes first (not the desired benzene)

d) A liquid benzene + naphthalene solution is in equilibrium with both solid benzene and solid naphthalene at 1 bar.

i) Give the temperature and the composition of the liquid.

-4 °C       $x_1 = 0.88$

ii) Is this an invariant system? Justify your answer.

$F = C + 2 - P = 2 + 2 - 3 = 1$  but pressure is fixed at 1 bar:  $F' = F - 1 = 0$   
yes, invariant system (no degrees of freedom)

Q4. a) Weather reports provide thermodynamic activity data! The **relative humidity** is defined as the partial pressure of water vapor in air divided by the vapor pressure of pure liquid water.

The vapor pressure of pure water is 23.8 Torr at 25 °C. If the relative humidity is 80 % at this temperature, calculate: (80 % = 80 parts per 100 = 0.800)

i) the water activity 
$$a_{\text{water}} = \frac{P_{\text{W}}}{P_{\text{W}}^*} = \boxed{0.80}$$

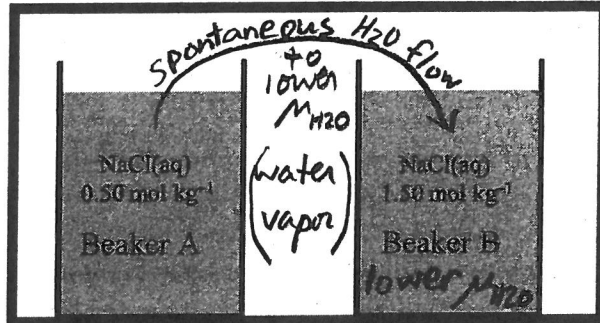
ii) the partial pressure of water

$$P_{\text{W}} = a_{\text{water}} P_{\text{W}}^* = 0.80(23.8 \text{ Torr}) = \boxed{19.0 \text{ Torr}}$$

b) Beaker A containing a 0.50 mol kg<sup>-1</sup> NaCl solution and beaker B containing a 1.5 mol kg<sup>-1</sup> NaCl solution are placed in a sealed chamber, as sketched below.

The level of solution in beaker A is observed to drop. And the level of solution in beaker B is observed to rise. Give a thermodynamic explanation for this mysterious behavior.

Water evaporates from Beaker A and condenses in Beaker B, migrating from a solution of higher water chemical potential to a solution of lower water chemical potential.



NaCl is not volatile: vapor phase permeable only to water!  
**OSMOSE!**

Solution B is more concentrated in NaCl, so the mole fraction of water is lower than in solution A. ( $x_{\text{H}_2\text{O}(B)} < x_{\text{H}_2\text{O}(A)}$ )

$$\mu_{\text{H}_2\text{O}(B)} = \mu_{\text{H}_2\text{O}}^* + RT \ln x_{\text{H}_2\text{O}(B)} < \mu_{\text{H}_2\text{O}(A)}$$

c) Calculate the minimum pressure required to obtain pure water from seawater by reverse osmosis at 25 °C. (hint: this is the osmotic pressure of seawater)

$$c_{\text{Cl}^-} = c_{\text{NaCl}} + 2c_{\text{MgCl}_2} = 0.46 + 2(0.06) = 0.58 \frac{\text{mol}}{\text{L}}$$

Assume seawater is an ideal solution containing 0.46 mol L<sup>-1</sup> NaCl and 0.06 mol L<sup>-1</sup> MgCl<sub>2</sub>.

total ion concentration 
$$c_{\text{tot}} = c_{\text{Na}^+} + c_{\text{Mg}^{2+}} + c_{\text{Cl}^-} = 0.46 + 0.06 + 0.58$$

$$c_{\text{tot}} = 1.10 \frac{\text{mol}}{\text{L}}$$

$$\pi = c_{\text{tot}} RT = (1.10 \text{ mol L}^{-1}) (0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1}) (298.15 \text{ K})$$

$$\pi = \boxed{27.3 \text{ bar}}$$

$$pH = -\log_{10} a_{H^+} = -\log_{10} (\gamma_{H^+} m_{H^+}) = -\log_{10} m_{H^+}$$

Q5. a) Calculate the pH of a 0.0050 mol kg<sup>-1</sup> aqueous HCl solution at 25 °C:

i) assuming the solution is ideal

if ideal,  
 $\gamma_{H^+} = 1$

$$pH(\text{ideal}) = -\log_{10} m_{H^+} = -\log_{10}(0.005)$$

$$= +2.30 \text{ (ideal)}$$

ii) using Debye-Huckel theory  $\rightarrow \ln \gamma_{H^+} = -1.173 \sqrt{I}$

$$I = \frac{z_{H^+}^2 m_{H^+} + z_{Cl^-}^2 m_{Cl^-}}{2} = \frac{0.005 + 0.005}{2} = 0.005 \text{ mol kg}^{-1}$$

$$\ln \gamma_{H^+} = -1.173 \sqrt{0.0050} = -0.0829$$

$$\gamma_{H^+} = e^{-0.0829} = 0.920$$

$$pH = -\log_{10} (\gamma_{H^+} m_{H^+}) = -\log_{10} [(0.920)(0.0050)] = 2.34 \text{ (not ideal)}$$

b) The mean ionic activity coefficient ( $\gamma_{\pm}$ ) of 3.00 mol kg<sup>-1</sup> aqueous CaCl<sub>2</sub> is 1.48 at 25 °C.

Calculate the activity of CaCl<sub>2</sub>.

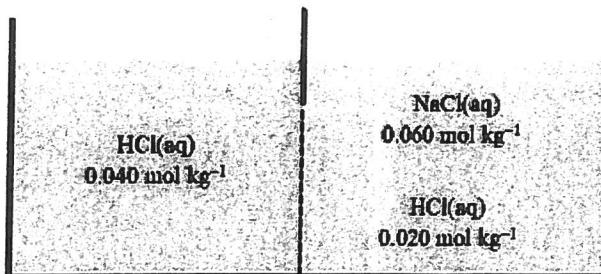
$$a_{CaCl_2} = a_{Ca^{2+}} a_{Cl^-}^2 = (\gamma_{Ca^{2+}} m_{Ca^{2+}}) (\gamma_{Cl^-} m_{Cl^-})^2$$

$$= \gamma_{Ca^{2+}} \gamma_{Cl^-}^2 m_{CaCl_2} (2m_{CaCl_2})^2 = \gamma_{\pm}^3 4m_{CaCl_2}^3 = (1.48)^3 4(3.00)^3 = 350 \frac{\text{mol}^3}{\text{kg}^3}$$

d) A membrane separates a 0.040 mol kg<sup>-1</sup> HCl solution and a solution of 0.020 mol kg<sup>-1</sup> HCl and 0.060 mol kg<sup>-1</sup> NaCl, as sketched below.

The membrane is permeable to H<sup>+</sup> and Cl<sup>-</sup> ions but is impermeable to Na<sup>+</sup> ions.

Assume the solutions are ideal.



i) There is a natural tendency for substances to flow from higher to lower activity to reach chemical equilibrium. Show the activities of HCl in the left and right solutions are identical ( $a_{HCl(L)} = a_{HCl(R)}$ ) and therefore equilibrium has been reached.

$$a_{HCl(L)} = m_{H^+(L)} m_{Cl^-(L)} = (0.040 \frac{\text{mol}}{\text{kg}}) (0.040 \frac{\text{mol}}{\text{kg}}) = 0.0016 \frac{\text{mol}^2}{\text{kg}^2}$$

$$a_{HCl(R)} = m_{H^+(R)} m_{Cl^-(R)} = (0.020 \frac{\text{mol}}{\text{kg}}) (0.080 \frac{\text{mol}}{\text{kg}}) = 0.0016 \frac{\text{mol}^2}{\text{kg}^2}$$

ii) The activity of H<sup>+</sup> ions in the left solution is twice as large as the activity of H<sup>+</sup> ions in the right solution. But H<sup>+</sup> ions do not flow from the left to the right solution. Why?

The membrane potential  $\phi_R - \phi_L = \frac{RT}{z_{H^+} F} \ln \left( \frac{m_{H^+(L)}}{m_{H^+(R)}} \right)$  is positive, raising the total potential (chemical + electrical) of the 0.020 mol kg<sup>-1</sup> H<sup>+</sup> ions and lowering the total potential of the 0.040 mol kg<sup>-1</sup> H<sup>+</sup> ions to give electrochemical equilibrium. (no H<sup>+</sup> flows)

Q1  
 Q2  
 Q3  
 Q4  
 Q5

