

- please answer all 5 questions in the spaces provided
- this is a 1-hour test (but you have 2 hours to write it!)
- a calculator and the equation sheets provided may be used
- all questions are of equal value
- no books or notes are allowed
- no marks for unreadable answers

1. a) 7.85 grams of a compound of formula Sulfamic acid $\text{H}_3\text{NO}_3\text{S}$ (molecular weight 98.1 g mol^{-1}) is dissolved in 400.0 grams of water (18.0 g mol^{-1}). The freezing point depression of the solution is 0.56 K . $K = 0.10 \text{ at } 25^\circ\text{C}$

Is the compound a nonelectrolyte? Or is it an electrolyte? Justify your answer using the freezing point data. Be specific! (Assume the solution is ideal, and use $K_f = 1.86 \text{ K kg mol}^{-1}$.)

compound molality $m = \frac{(7.85 / 98.1) \text{ mol}}{0.400 \text{ kg H}_2\text{O}} = 0.200 \text{ mol kg}^{-1}$

if the compound is a nonelectrolyte, expect $\Delta T = K_f (0.200 \frac{\text{mol}}{\text{kg}})$
 $\Delta T = 1.86(0.200) = 0.37 \text{ K}$

if it's a 1:1 electrolyte (like NaCl), expect $\Delta T = 2K_f(0.200) = 0.74 \text{ K}$

The measured ΔT is $> 0.37 \text{ K}$, $< 0.74 \text{ K} \Rightarrow$ must be a weak (incompletely) dissociate electrolyte

b) The vapor pressure of water over an aqueous sucrose solution is 23.581 Torr at 25°C . At this temperature the vapor pressure of pure water is 23.753 Torr .

i) Why is it a good approximation to assume that the Raoult's-law activity coefficient of water is unity ($\gamma_{\text{H}_2\text{O(RL)}} = 1$) for this solution?

$P_{\text{H}_2\text{O}} \approx P_{\text{H}_2\text{O}}^*$ "Almost" pure water. $\left(X_{\text{H}_2\text{O}} = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2\text{O}}^*} = \frac{23.581}{23.753} = 0.99276 \approx 1 \right)$
 $\gamma_{\text{H}_2\text{O(RL)}} \rightarrow 1$ as $X_{\text{H}_2\text{O}} \rightarrow 1$

ii) Calculate the molality of sucrose (342.3 g mol^{-1}) in the solution.

sucrose mole fraction $X_{\text{sucrose}} = 1 - X_{\text{H}_2\text{O}} = 0.00724$

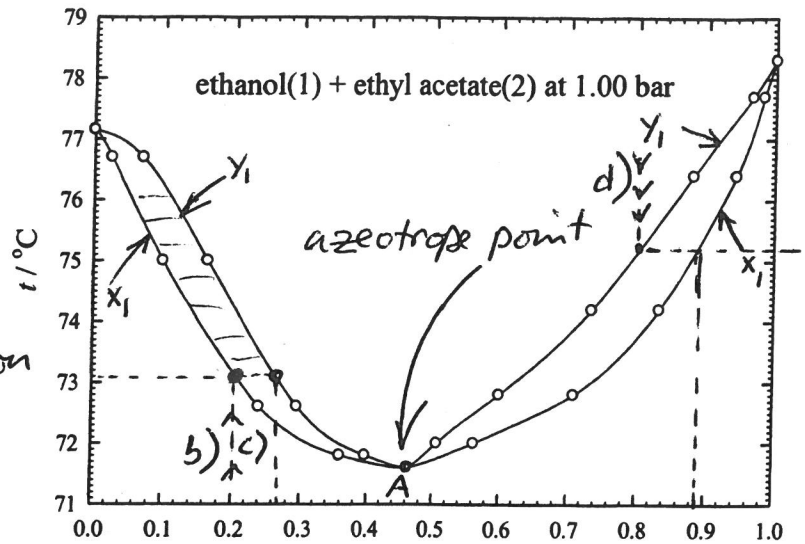
$\left(\begin{matrix} 0.00724 \text{ moles sucrose} \\ + \\ 0.99276 \text{ moles water} \end{matrix} \right) \Rightarrow \frac{0.00724 \text{ mol sucrose}}{(0.99276 \text{ mol H}_2\text{O}) \left(\frac{0.0180 \text{ kg}}{\text{mol H}_2\text{O}} \right)} = 0.405 \frac{\text{mol}}{\text{kg}}$

iii) Calculate the osmotic pressure of the solution. Use $18.0 \text{ cm}^3 \text{ mol}^{-1}$ for the molar volume of water.

from equation sheet $\pi = - \frac{RT}{V_{\text{H}_2\text{O}}^*} \ln X_{\text{H}_2\text{O}}$

$\pi = - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{18.0 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}} \ln 0.99276 = 1.00 \times 10^6 \text{ Pa} = 10.0 \text{ bar}$

2. Use the boiling point diagram plotted below to answer this question.



a) Explain how this diagram illustrates azeotropic behavior. Be specific! **point A**

liquid ethanol(1)
ethyl acetate (2)
mixtures of composition
 $x_1 = 0.46$ are in
equilibrium with
vapor of the same

composition $y_1 = 0.46$,
where fractional distillation produces no change in composition

b) One of your classmates claims that the vapor in equilibrium with a solution is always richer in the more volatile component than the liquid. Use the diagram to prove that he or she is wrong!

from the diagram: ethyl acetate(2) is more volatile than ethanol(1)
(b.p. 77.2 °C) (78.3 °C)

but at $x_1 < 0.46$ (azeotrope composition), tie lines show that $y_1 > x_1$ vapor richer in ethanol! **See diagram**

c) Give the boiling point of a liquid ethanol + ethyl acetate mixture consisting of 0.40 moles of ethanol and 1.60 moles of ethyl acetate at 1.00 bar. Also give the composition of the vapor.

$$x_1 = \frac{0.40}{0.40 + 1.60} = 0.20 \text{ (liquid)}$$

73.1 °C boiling temperature

$$y_1 \approx 0.27 \text{ (vapor)}$$

(richer in ethanol, the less volatile component!)

See diagram

d) A vapor mixture consisting of 1.60 moles of ethanol and 0.40 moles of ethyl acetate is cooled at a total pressure of 1.00 bar. Give the dewpoint (the temperature at which the first liquid forms) and the composition of the first liquid.

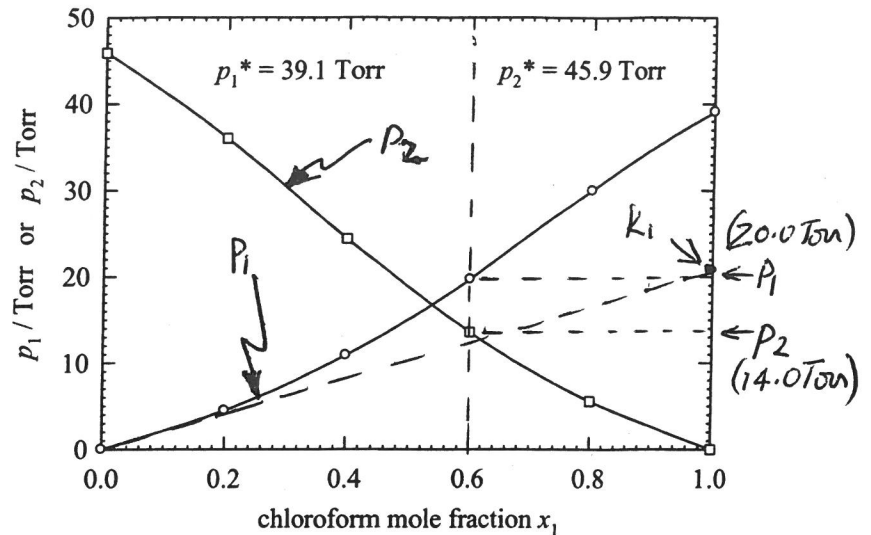
$$y_1 = \frac{n_1}{n_1 + n_2} = \frac{1.60}{1.60 + 0.40} = 0.80 \text{ (vapor)}$$

first liquid at 75.2 °C with $x_1 = 0.89$

See diagram

3.

Use the plotted vapor pressures of liquid chloroform(1) + acetone(2) mixtures at 35 °C to answer this question.



a) Calculate the Raoult's-law activity coefficient of chloroform (γ_{1RL}) at $x_1 = 0.600$

$$\gamma_{1RL} = \frac{P_1(\text{actual})}{P_1(\text{Raoult's Law})} = \frac{P_1}{x_1 p_1^*} = \frac{20.0 \text{ Torr}}{(0.600)39.1 \text{ Torr}} = 0.85$$

(see diagram for reaching the P_1 value)

b) Calculate the Raoult's-law activity coefficient of acetone (γ_{2RL}) at $x_1 = 0.600 \Rightarrow x_2 = 0.400$

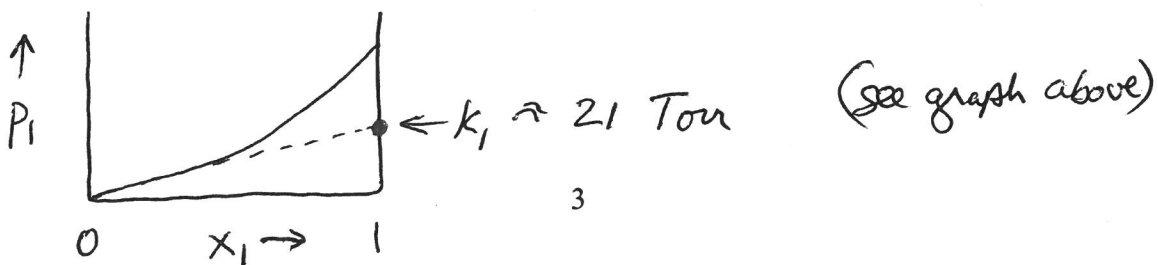
$$\gamma_{2RL} = \frac{P_2}{x_2 p_2^*} = \frac{14.0 \text{ Torr}}{(0.400)45.9 \text{ Torr}} = 0.76$$

$35^\circ\text{C} \rightarrow 308.15\text{K}$

c) Calculate ΔG for mixing 0.600 moles of pure liquid chloroform and 0.400 moles of pure liquid acetone at 35 °C. (Do not assume ideal solutions.) ← replace x_1, x_2 with $\gamma_1 x_1, \gamma_2 x_2$

$$\begin{aligned} \Delta G_{\text{mix}} &= n_1 RT \ln(\gamma_1 x_1) + n_2 RT \ln(\gamma_2 x_2) \\ &= \underbrace{n_1 RT \ln x_1}_{\text{ideal}} + \underbrace{n_1 RT \ln \gamma_1}_{\text{nonideal}} + \underbrace{n_2 RT \ln x_2}_{\text{ideal}} + \underbrace{n_2 RT \ln \gamma_2}_{\text{nonideal}} \\ &= (8.314)(308.15)[0.600 \ln 0.600 + 0.400 \ln 0.400] \\ &\quad + 8.314(308.15)[0.600 \ln 0.85 + 0.400 \ln 0.76] \\ &= \underbrace{-1724 \text{ J}}_{\text{(ideal)}} - \underbrace{531 \text{ J}}_{\text{(nonideal)}} = -2255 \text{ J} \end{aligned}$$

d) Use the graph to estimate the Henry's law constant for chloroform.



4. a) For solid BaCl₂ in equilibrium with an aqueous BaCl₂ solution at 1.00 bar. Give:

$$C \text{ (the number of components)} = 2 \quad (\text{BaCl}_2 \text{ and H}_2\text{O})$$

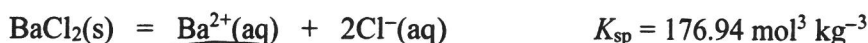
$$P \text{ (the number of phases)} = 2 \quad (\text{solid BaCl}_2 \text{ and aqueous sol. n})$$

$$F \text{ (the degrees of freedom)} = C + 2 - P - 1 \quad (\text{pressure is fixed, one less degree of freedom})$$

$$= 2 + 2 - 2 - 1$$

$$= 1 \quad (\text{e.g., temperature can be varied})$$

b) At 25 °C the equilibrium constant K_{sp} for dissolving solid BaCl₂ in water is



and the solubility of the salt is $1.779 \text{ mol kg}^{-1}$ For an aqueous solution of BaCl₂ in equilibrium with solid BaCl₂ at 25 °C (i.e., a saturated solution), calculate:

i) the barium chloride activity (a_{BaCl_2})

at equilibrium:

$$K_{sp} = a_{\text{Ba}^{2+}(\text{aq})} [a_{\text{Cl}^{-}(\text{aq})}]^2$$

$$= a_{\text{BaCl}_2(\text{aq})}$$

$$= 176.94 \text{ mol}^3 \text{ kg}^{-3}$$

ii) the mean ionic activity coefficient (γ_{\pm}) of barium chloride

$$K_{sp} = a_{\text{Ba}^{2+}(\text{aq})} [a_{\text{Cl}^{-}(\text{aq})}]^2 = (\gamma_{+} m_{\text{Ba}^{2+}}) (\gamma_{-} m_{\text{Cl}^{-}})^2$$

$$K_{sp} = (\gamma_{+} m) (\gamma_{-} 2m)^2 = \gamma_{+} \gamma_{-}^2 4m^3 = \gamma_{\pm}^3 4m^3$$

$$\gamma_{\pm} = \left(\frac{K_{sp}}{4m^3} \right)^{1/3} = \left[\frac{176.94}{4(1.779)^3} \right]^{1/3} = 1.988$$

c) According to the Third Law of Thermodynamics, the absolute entropies of substances are always zero (for perfect crystals at $T = 0 \text{ K}$) or positive ($T > 0$).

But according to material covered in Chapter 10, the entropies of aqueous ions can be negative!

For example $S_m^{\circ}(\text{OH}^{-}, \text{aq}) = -10.75 \text{ J K}^{-1} \text{ mol}^{-1}$

Explain this apparent discrepancy. Is the Third Law wrong? No!

relative to
 $S_m^{\circ}(\text{H}^{+}(\text{aq})) = 0$
 arbitrary zero!

By convention, single-ion entropies (and other single-ion thermodynamic properties) are tabulated relative to zero values arbitrarily chosen for $\text{H}^{+}(\text{aq})$ at standard state.
(they are not absolute Third-Law entropies)

For, example $S_m^{\circ}(\text{OH}^{-}, \text{aq}) = -10.75 \text{ J K}^{-1} \text{ mol}^{-1}$ means the standard molar entropy of $\text{OH}^{-}(\text{aq})$ is $10.75 \text{ J K}^{-1} \text{ mol}^{-1}$ lower than the absolute entropy of $\text{H}^{+}(\text{aq})$

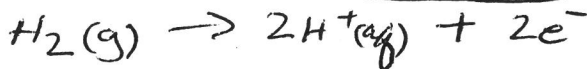
5. This question refers to the reversible electrochemical cell



Data: $E^\circ = 1.3604 \text{ V}$ at 25.0°C

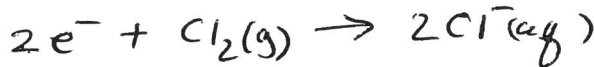
a) Write the

anode reaction:
(oxidation, L)

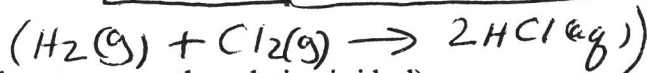
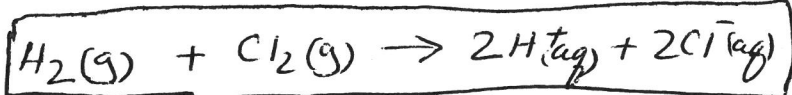


$n = 2$

cathode reaction:
(reduction, R)



overall cell reaction:



Nernst equation (do not assume the solution is ideal):

$$E = E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{RT}{2F} \ln \left(\frac{a_{H^+(aq)}^2 a_{Cl^-(aq)}^2}{a_{H_2(g)} a_{Cl_2(g)}} \right)$$

$$= E^\circ - \frac{RT}{2F} \ln \left[\frac{(\gamma_+ m)^2 (\gamma_- m)^2}{(1 \text{ bar}) (1 \text{ bar})} \right] = E^\circ - \frac{RT}{2F} \ln (\gamma_{\pm}^4 m^4)$$

b) The mean ionic activity coefficient of 5.00 mol kg^{-1} aqueous HCl is $\gamma_{\pm} = 2.38$ at 25.0°C . Calculate the cell voltage E at this temperature.

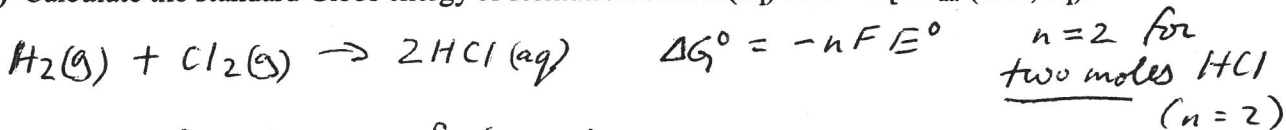
$$E = E^\circ - \frac{RT}{2F} \ln (\gamma_{\pm}^4 m^4) = E^\circ - \frac{RT}{2F} 4 \ln (\gamma_{\pm} m)$$

$$= E^\circ - \frac{2RT}{F} \ln (\gamma_{\pm} m) = 1.3604 \text{ V} - \frac{2(8.314)(298.15)}{96485} \ln (2.38)(5.00)$$

$$= 1.3604 \text{ V} - 0.1272 \text{ V}$$

$$E = 1.2331 \text{ V}$$

c) Calculate the standard Gibbs energy of formation of HCl(aq) at 25°C [$\Delta G_{fm}^\circ(\text{HCl}, \text{aq})$].



for one mole HCl: $\Delta G_{fm}^\circ(\text{HCl}, \text{aq}) = -FE^\circ$
 $(n=1) \quad = -(96485)(1.3604) = -131200 \frac{\text{J}}{\text{mol}}$

d) The values of $\Delta G_{fm}^\circ(\text{HCl}, \text{aq})$ and $\Delta G_{fm}^\circ(\text{Cl}^-, \text{aq})$ are identical. Why?

$$\Delta G_{fm}^\circ(\text{HCl}, \text{aq}) = \Delta G_{fm}^\circ(H^+(aq)) + \Delta G_{fm}^\circ(Cl^-, \text{aq})$$

$\Delta G_{fm}^\circ(H^+(aq)) = 0$ (zero by definition)

$$= \Delta G_{fm}^\circ(Cl^-, \text{aq})$$

- Q1
- Q2
- Q3
- Q4
- Q5

