

CHM 3400 – Fundamentals of Physical Chemistry  
Second Hour Exam

There are five problems on the exam. Do all of the problems. Show your work

$$R = 0.08206 \text{ L}\cdot\text{atm}/\text{mole}\cdot\text{K}$$

$$N_A = 6.022 \times 10^{23}$$

$$R = 0.08314 \text{ L}\cdot\text{bar}/\text{mole}\cdot\text{K}$$

$$1 \text{ L}\cdot\text{atm} = 101.3 \text{ J}$$

$$R = 8.314 \text{ J}/\text{mole}\cdot\text{K}$$

$$1 \text{ atm} = 1.013 \text{ bar} = 1.013 \times 10^5 \text{ N}/\text{m}^2$$

$$F = 96485 \text{ C}/\text{mol}$$

$$1 \text{ atm} = 760 \text{ torr}$$

$$(1 \text{ volt})\cdot(1 \text{ Coulomb}) = 1 \text{ Joule}$$

Two phase diagrams are given below. The one on the left is for a pure chemical substance, (substance C), and is used in problem 1. The one on the right is for a mixture of two volatile liquids (A and B), and is used in problem 2.

1. (18 points) This question deals with pure chemical substance C, whose phase diagram is the left side diagram below.

a) For pure substance C give the temperature corresponding to i.) the normal melting point for the substance, ii.) the normal boiling point for the substance, and iii.) the normal sublimation point for the substance. If one or more of these points does not exist, briefly explain why the point does not exist.

b) Points A and B on the phase diagram for pure substance C have the following location

A:  $p = 1.71 \text{ atm}$ ,  $T = 120.0 \text{ }^\circ\text{C}$

B:  $p = 4.54 \text{ atm}$ ,  $T = 140.0 \text{ }^\circ\text{C}$

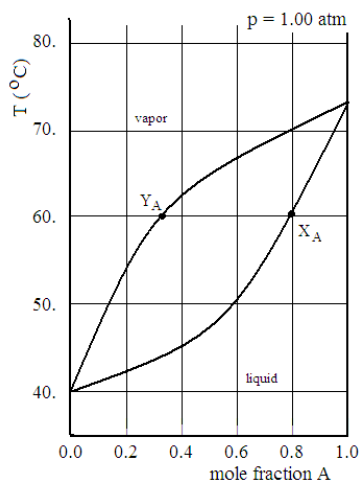
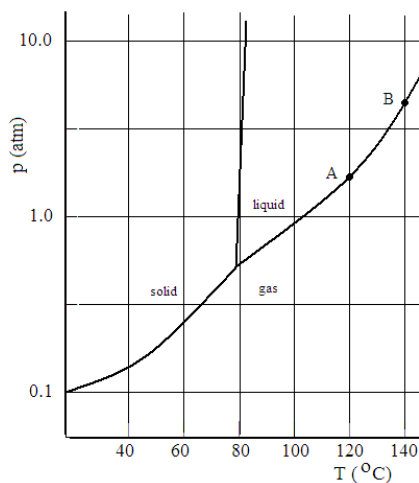
Based on this data find  $\Delta H_{\text{vap}}$ , the enthalpy of vaporization for substance C.

2. (20 points) This question deals with the mixture of volatile liquids A and B, whose phase diagram is the right side diagram below. Note that at  $T = 60. \text{ }^\circ\text{C}$  the mole fractions of A in the liquid and vapor phases are  $X_A = 0.795$  and  $Y_A = 0.330$

a) What are  $T_A^\circ$  and  $T_B^\circ$ , the normal boiling point temperatures for liquids A and B?

b) For a closed system with  $Z_A = 0.60$  and  $T = 60. \text{ }^\circ\text{C}$  which will be larger - the total number of moles of liquid in the system, or the total number of moles of vapor in the system? Briefly justify your answer.

c) Assuming that A and B form an ideal solution, find the value for  $p_A^*$ , the vapor pressure of pure A, at  $T = 60.0 \text{ }^\circ\text{C}$ ? Give your answer in units of atm.



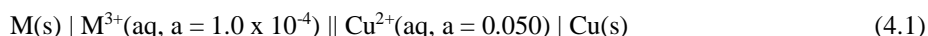
3. (14 points) A common method for providing nourishment to someone following surgery is the use of a 5% solution of glucose in water, injected intravenously directly into the blood stream. Such a solution contains 5.00 g glucose ( $M = 180.2 \text{ g/mol}$ ) per 100.0 mL solution. Since the solution is approximately isotonic (same osmotic pressure) with blood plasma, use of a solution at this concentration of glucose does no damage to red blood cells or other cells in the blood stream.

Find the osmotic pressure of a 5% glucose solution in water at  $T = 37.^\circ\text{C}$ . Give your final answer in units of atm.

Standard half-cell reduction potentials for several substances are given below (at  $T = 25.0^\circ\text{C}$ ) and may be of use in doing problem 4.

Reaction	$E^\circ$ (v)	Reaction	$E^\circ$ (v)
$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu}(\text{s})$	+ 0.34 v	$2 \text{H}_2\text{O}(\ell) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$	- 0.83 v
$2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g})$	0.00 v		

4. (24 points) Consider the following galvanic cell



where M represents some unspecified rare earth metal, and the activities of  $\text{M}^{3+}$  and  $\text{Cu}^{2+}$  ions are as specified in the cell diagram. The cell potential for the given conditions for this galvanic cell, measured at  $T = 25.0^\circ\text{C}$ , is  $E_{\text{cell}} = 0.143 \text{ v}$ .

a) What are the half-cell oxidation reaction, the half-cell reduction reaction, and the net cell reaction for the above galvanic cell?

b) What is the numerical value for  $\Delta G_{\text{cell}}$ , the free energy change, for the above galvanic cell?

c) What is the value for  $E^\circ(\text{M}^{3+}, \text{M})$ , the standard half-cell reduction potential at  $T = 25.0^\circ\text{C}$ , for the process



5. (24 points) Iron pentacarbonyl ( $\text{Fe}(\text{CO})_5$ ) is an inorganic compound used as the starting material in the preparation of additional inorganic iron compounds, many of which are themselves used in synthetic organic chemistry. It is prepared by the reaction



The reaction is slow at room temperature, and so is normally carried out at high temperature and pressure. Because of this, the equilibrium properties of the compound must be inferred from thermochemical data.

a) Give the expression for the equilibrium constant for the above reaction in terms of reactant and product activities.

b) Give the expression for the equilibrium constant for the above reaction assuming ideal behavior of the reactants and products.

Using the data given below (at  $T = 298. \text{ K}$ ), find the following:

c) The numerical value for the equilibrium constant at  $T = 298. \text{ K}$ .

d) The numerical value for the equilibrium constant at  $T = 500. \text{ K}$ .

Substance	$\Delta H^\circ_f$ (kJ/mol)	$\Delta G^\circ_f$ (kJ/mol)	$S^\circ$ (J/mol·K)
$\text{CO}(\text{g})$	- 110.53	- 137.17	197.67
$\text{Fe}(\text{s})$	0.0	0.0	27.28
$\text{Fe}(\text{CO})_5(\text{g})$	- 733.9	- 697.3	445.2

Solutions.

- 1) a) Based on the phase diagram

$$T_{\text{fus}}^{\circ} = 79. \text{ }^{\circ}\text{C} \quad T_{\text{vap}}^{\circ} = 105. \text{ }^{\circ}\text{C}$$

There is no normal sublimation point, because there is no place where the solid/gas boundary intersects the line corresponding to  $p = 1.0 \text{ atm}$ .

- b) We know the vapor pressure at two different temperatures, and so we can use the relationship

$$\ln(p_2/p_1) = -(\Delta H_{\text{vap}}/R) \{ (1/T_2) - (1/T_1) \}$$

$$\Delta H_{\text{vap}} = - \frac{R \ln(p_2/p_1)}{\{ (1/T_2) - (1/T_1) \}} = - \frac{(8.314 \text{ J/mol K}) \ln(4.54/1.71)}{\{ (1/413.2 \text{ K}) - (1/393.2 \text{ K}) \}} = 65.9 \text{ kJ/mol}$$

- 2) a) Based on the phase diagram

$$T_A^{\circ} = 73. \text{ }^{\circ}\text{C} \quad T_B^{\circ} = 40. \text{ }^{\circ}\text{C}$$

b) The lever from  $Z_A = 0.60$  to the liquid is shorter than the lever to the vapor, and so by the lever rule there is a larger number of moles of liquid than moles of gas. A calculation based on the mathematical formulation of the lever rule is in agreement with this qualitative result but is not required in the problem.

$$\begin{array}{ll} \text{c) } p_A = X_A p_A^* & \text{(Raoult's law; applies for ideal solutions)} \\ p_A = Y_A p_{\text{tot}} & \text{(Dalton's law of partial pressures)} \end{array}$$

$$\text{So } X_A p_A^* = Y_A p_{\text{tot}}$$

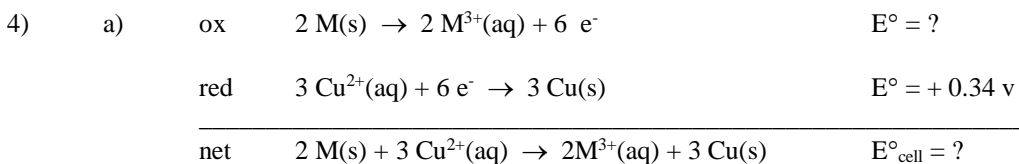
$$p_A^* = (Y_A/X_A) p_{\text{tot}} = (0.330/0.795) (1.00 \text{ atm}) = 0.415 \text{ atm}$$

- 3) We first find the number of moles of glucose

$$n = 5.00 \text{ g } \frac{1 \text{ mol}}{180.2 \text{ g}} = 0.02775 \text{ mol}$$

$$\text{The concentration of glucose is then } [\text{glu}] = \frac{0.02775 \text{ mol}}{0.100 \text{ L}} = 0.2775 \text{ mol/L}$$

$$\begin{aligned} \text{Therefore } \Pi &= [\text{glu}]RT = (0.2775 \text{ mol/L})(0.08206 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(310. \text{ K}) \\ &= 7.06 \text{ atm} \end{aligned}$$



$$\text{b) } \Delta G = -vFE_{\text{cell}} = -6(96485. \text{ C/mol})(0.143 \text{ v}) = -82.8 \text{ kJ/mol}$$

c) To proceed we first need to find  $E^\circ_{\text{cell}}$ , the standard state cell potential.

$$E_{\text{cell}} = E^\circ_{\text{cell}} - (RT/vF) \ln Q$$

so  $E^\circ_{\text{cell}} = E_{\text{cell}} + (RT/vF) \ln Q$

$$Q = \frac{(a_{\text{M}^{3+}})^2 (a_{\text{Cu}})^3}{(a_{\text{Cu}^{2+}})^3 (a_{\text{M}})^2} = \frac{(1.0 \times 10^{-4})^2 (1)^3}{(0.050)^3 (1)^2} = 8.0 \times 10^{-5}$$

and so  $E^\circ_{\text{cell}} = 0.143 \text{ v} + \frac{(8.314 \text{ J/mol}\cdot\text{K})(298. \text{ K})}{(6)(96485. \text{ C/mol})} \ln(8.0 \times 10^{-5})$

$$= 0.143 \text{ v} + (-0.0404 \text{ v}) = 0.103 \text{ v}$$

But  $E^\circ_{\text{cell}} = E^\circ_{\text{ox}} + E^\circ_{\text{red}}$

$$E^\circ_{\text{ox}} = E^\circ_{\text{cell}} - E^\circ_{\text{red}} = 0.103 \text{ v} - 0.34 \text{ v} = -0.237 \text{ v}$$

Therefore  $E^\circ_{\text{red}}(\text{M}^{3+}, \text{M}) = -E^\circ_{\text{ox}} = +0.237 \text{ v}$

5) a)  $K = \frac{(a_{\text{Fe}(\text{CO})_5})}{(a_{\text{Fe}}) (a_{\text{CO}})^5}$  where K is given in terms of activities

b)  $K = \frac{(p_{\text{Fe}(\text{CO})_5})}{(p_{\text{CO}})^5}$  where we have assumed ideal behavior, and division by standard pressure (1.00 bar) is implied

To do the last two parts of the problem it is useful to first find  $\Delta G^\circ_{\text{rxn}}$  and  $\Delta H^\circ_{\text{rxn}}$

$$\Delta G^\circ_{\text{rxn}} = [(\Delta G^\circ_{\text{f}}(\text{Fe}(\text{CO})_5(\text{g})))] - [(\Delta G^\circ_{\text{f}}(\text{Fe}(\text{s})) + 5(\Delta G^\circ_{\text{f}}(\text{CO}(\text{g})))]$$

$$= [(-697.3)] - [(0.0) + 5(-137.17)] = -11.45 \text{ kJ/mol}$$

$$\Delta H^\circ_{\text{rxn}} = [(\Delta H^\circ_{\text{f}}(\text{Fe}(\text{CO})_5(\text{g})))] - [(\Delta H^\circ_{\text{f}}(\text{Fe}(\text{s})) + 5(\Delta H^\circ_{\text{f}}(\text{CO}(\text{g})))]$$

$$= [(-733.9)] - [(0.0) + 5(-110.53)] = -181.2 \text{ kJ/mol}$$

c)  $\ln K = -\frac{\Delta G^\circ_{\text{rxn}}}{RT} = -\frac{(-11450. \text{ J/mol})}{(8.314 \text{ J/mol}\cdot\text{K})(298. \text{ K})} = 4.62$

$$K = e^{4.62} = 102.$$

d)  $\ln(K_2/K_1) = -(\Delta H^\circ_{\text{rxn}}/R) \{ (1/T_2) - (1/T_1) \}$

$$= -[(-181200. \text{ J/mol})/8.314 \text{ J/mol}\cdot\text{K}] [(1/500. \text{ K}) - (1/298. \text{ K})]$$

$$= -29.55$$

So  $(K_2/K_1) = e^{-29.55} = 1.47 \times 10^{-13}$

$$K_2 = K_1 (1.47 \times 10^{-13}) = (102.)(1.47 \times 10^{-13}) = 1.5 \times 10^{-11}$$