UNIVERSITY OF TORONTO
FACULTY OF APPLIED SCIENCE AND ENGINEERING

FINAL EXAMINATIONS, DECEMBER 2000
CHE 112F - PHYSICAL CHEMISTRY

Examiners: C.E. Chaffey, F.R. Foulkes, V.G. Papangelakis
Time allowed: 2.5 hours

Be sure to PRINT your name on every page!

General Instructions:
1. All calculations are to be made on the special pages supplied, which are to be handed in.
2. One question and solution per page. No marks will be assigned for material on other pages.
3. Use the back of the same page, if necessary.
4. Write all final answers in the rectangular boxes provided.
5. Marks will be deducted for answers not reported with a reasonable number of significant figures.
6. Programmable calculators are not permitted.

Data
1 atm = 1.01325×10^5 Pa = 1.01325 bar   R = 8.314 J mol^{-1} K^{-1} F=96 487 C mol^{-1}
T =θ + 273.15 N_A =6.02214×10^{23} mol^{-1}
1 mole of ideal gas at STP occupies 22.414 L

Data at 298 K, for P° = 1 bar:

Substance	Formula	c_p° J mol^{-1} K^{-1}	s° J K^{-1} mol^{-1}	Δh_f° KJ mol^{-1}	Δg_f° kJ mol^{-1}
Carbon	$C_{(s)}$ (graphite)	8.51	5.74	0	0
Hydrogen	$H_{2(g)}$	28.84	130.68	0	0
Oxygen	$O_{2(g)}$	29.38	205.15	0	0
Ethylene oxide	$C_2H_4O_{(g)}$	47.90	243.01	-52.64	-13.16
Ethanol	$C_2H_5OH_{(g)}$	65.44	282.70	-234.81	-168.20
Ethanol	$C_2H_5OH_{(liq)}$	112.3	165.27	-275.86	-174.25

Additional formulas: $\mathring{E}_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln\left(\frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}\right)$ $\Delta S^\circ = \sum_{\text{Products}} n_i s_i^\circ - \sum_{\text{Reactants}} n_i s_i^\circ$

$\Delta G^\circ = \sum_{\text{Products}} n_i \left(\Delta g_f^\circ\right)_i - \sum_{\text{Reactants}} n_i \left(\Delta g_f^\circ\right)_i$ $\Delta H^\circ = \sum_{\text{Products}} n_i \left(\Delta g_f^\circ\right)_i - \sum_{\text{Reactants}} n_i \left(\Delta g_f^\circ\right)_i$

1. (a) The solubility at 25ºC of barium fluoride (BaF_2) in 0.500 M aqueous HC1 solution is 0.0100 mol L^{-1}. Calculate the solubility product K_{sp} of barium fluoride in water at 25ºC. Note that some of the F^- ions in the above-mentioned HC1 solution will combine with some of the H^+ ions to produce some undissociated hydrofluoric acid (HF), which is a weak acid with an acid dissociation constant at 25ºC of $K_a = 0.0200$. For this problem you may neglect activity coefficient corrections. State and justify any simplifying assumptions you make.

(b) A 500 mL solution of 0.300 M acetic acid (CH_3COOH) is added to 500 mL of 0.100M NaOH solution, both at 25°C. Calculate the final pH of the resulting solution at 25ºC. The acid dissociation constant of aqueous acetic acid at 25°C is $K_a = 1.754 \times 10^{-5}$ For this problem you may neglect activity coefficient corrections, may assume that molarity = molality, and may assume that solution volumes are additive.

Ans: (a) 6.4×10^{-9} (b) 4.45

2. (a) At 0ºC and one atm partial pressure, the solubility in water of oxygen is 48.9 cm^3 L^{-1}. How much oxygen will dissolve in ice water at 0°C that is exposed to the air at 0°C and one atm pressure? Report the O_2 solubility in millimoles per litre (mmol L^{-1}), Air may be considered to be 79.0% by volume nitrogen (N_2) and 21.0% by volume oxygen (O_2).

(b) Elemental sulfur undergoes a phase transition by changing its crystallographic form from rhombic to monoclinic (both solid):

S(rhombic) → S(monoclinic)

The two forms are in equilibrium at 115°C under one atm pressure, whereas the equilibrium temperature is 200°C when the pressure is 100 atm. The enthalpy change of the above phase transformation may be assumed to be constant at +300 J mol^{-1}. Which of the two forms is more dense? Show your reasoning for reaching your conclusion.

Ans: (a) 0.458 mmol L^{-1} (b) Rhombic

3. (a) 60.0 mol of gaseous methane (CH_4) is pumped into an evacuated (empty) rigid vessel. When the temperature of the methane in the vessel is 730°C, its pressure is 6.00 bar. What is the volume of the vessel? Report your answer in m^3.

(b) 60.0 mol of gaseous methane (CH_4) and 60.0 mol of steam are pumped into an evacuated (empty) rigid vessel. The initial temperature of the gas in the vessel is 730°C and the total initial pressure is 12.0 bar. Then the following reaction producing gaseous carbon monoxide and hydrogen proceeds to equilibrium:

$CH_4 + H_2O_{(g)} = CO_{(g)} + 3H_{2(g)}$

The temperature is constant at 730°C, and the volume is constant. At 730°C, the thermodynamic equilibrium constant for this reaction is K = 27.0. What is the equilibrium mole fraction of H_2? Hint: At constant volume and temperature, the partial pressure of each gas is directly proportional to its number of moles.

Ans: (a) 0.8340 m^3 (b) 0.375

4. Ethylene oxide (C_2H_4O) can react with hydrogen gas to produce ethanol (C_2H_5OH):

$C_2H_4O_{(g)} + H_{2(g)} = C_2H_5OH_{(liq)}$

For this reaction producing one mol of liquid ethanol at one bar pressure, calculate:

(a) the molar entropy change, $\Delta S°$ at T=298K, at T = 298 K;
(b) the molar Gibbs free energy change, $\Delta G°$, at T= 298 K;
(c) the molar enthalpy change $\Delta H°$, at T= 340 K, a higher temperature.

Ans: (a) –208.42 J K^{-1} mol^{-1} (b) –161.09 kJ mol^{-1} (c) –221.73 kJ mol^{-1}

5. (a) Consider the following unbalanced redox reaction:

$H_2C_2O_4 + MoO_4^{2-} \xrightarrow{acid} CO_2 + Mo^{3+}$

Using the method of half-reactions:
(i) Determine the balanced oxidation half-reaction;
(ii) Determine the balanced reduction half-reaction; and
(iii) Determine the balanced overall reaction.

Ans: *a*(i) $H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e^-$
(ii) $MoO_4^{2-} + 8H^+ \rightarrow Mo^{3+} + 4H_2O$

(iii) $3H_2C_2O_4 + 2MoO_4^{2-} + 10H^+ \rightarrow 6CO_2 + 2Mo^{3+} + 8H_2O$

(b) For the cell $Cu_{(s)}$ | 0.00100 molal $CuSO_{4(aq)}$ || 0.00100 molal $Cu_2SO_{4(aq)}$ | $Cu_{(s)}$

(i) Write the anode, cathode, and overall cell reaction when $n = 2$.

(ii) Calculate a_{Cu^+} the molal activity of the cuprous ions (Cu^+) in the 0.00100 molal aqueous Cu_2SO_4, solution, using the Debye-Hückel equation for aqueous solutions at 25°C to calculate the cation activity coefficient:

$$\log_{10}\gamma_i = -0.5108 z_i^2 \sqrt{I}$$

You may assume that at the low concentrations involved, molarity = molality, and that all the salts are completely dissociated into ions. (5)

(iii) Calculate the cell voltage at 25°C, taking into account the activities of the cuprous and cupric ions when using the Nernst equation. (5)

(iv) What is the numerical value of the equilibrium constant K at 25°C for the reaction

$2Cu^+_{(aq)} \Longleftrightarrow Cu(s) + Cu^{++}_{(aq)}$ $\quad K = \dfrac{a_{Cu++}}{a^2_{Cu+}}$

Data:

	$E°_{298.15}$ (V vs SHE)
$Cu^+_{(aq)} + e^- \Longleftrightarrow Cu_{(s)}$	$E°_1$? = +0.517 V
$Cu^{++}_{(aq)} + 2e^- \Longleftrightarrow Cu_{(s)}$	$E°_2$; = +0.337 V

Ans: *b*(i)Anode: $Cu \rightarrow Cu^{++} + 2e^-$
Cathode: $2Cu^+ + 2e^- \rightarrow 2Cu$
Cell: $2Cu^+ \rightarrow Cu + Cu^{++}$
(ii) 1.88×10^{-3}; (iii) 0.111V;
(iv)1.22×10^6

[Total Marks 100]