UNIVERSITY OF TORONTO
FACULTY OF APPLIED SCIENCE AND ENGINEERING

FINAL EXAMINATIONS, DECEMBER 1999

CHE 112F - PHYSICAL CHEMISTRY

Examiners: C.E. Chaffey, P.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

$1 atm = 1.01325 \times 10^5$ Pa $= 1.01325$ bar $= 760$ Torr $R = 8.314$ J mol^{-1}K^{-1}
$T = \theta + 273.15$ $N_A = 6.02214 \times 10^{23}$ mol^{-1}
1 *mole of ideal gas at STP occupies* 22.414 L

Molar masses: H=1.008   O=16.00   C=12.01   Fe=55.85   Ni=58.70

1.   At 25°C the vapour pressures of pure ethanol and pure methanol are 26.7 kPa and 53.3 kPa, respectively. These two liquids are completely miscible and form ideal solutions. At 25°C a certain mixture of 50.0 moles (total) of these two liquids generates an equilibrium vapour which contains 70.0% by volume of methanol.

(a) Calculate (i) the mole fraction of methanol in the liquid phase, and (ii) the total equilibrium vapour pressure above the solution.   [7 marks]

(b) What would the mole fraction of methanol in the vapour phase be if air at a partial pressure of 100 kPa also were present above the solution?   [5 marks]

(c) Given that 0.0040 moles of O_2 and 0.0010 moles of N_2 dissolve from the air into the ethanol-methanol liquid mixture, calculate the Henry's law constant for oxygen in this solution. You may assume that the partial pressure of air is still 100 kPa and that its molar composition is 20.0% O_2 and 80.0% N_2.   [5 marks]

2.   An aqueous solution at 25°C and initially at pH ≈ 1, contains 0.70 g Fe^{2+} per litre as $Fe_2(SO_4)_3$ and 5.80 g Ni^{2+} per litre as $NiSO_4$. A nickel producing company in Ontario wants to separate nickel from iron by a hydroxide precipitation process in which a strong base such as NaOH is slowly added to the solution.

For parts (a), (b), and (c) you may assume that the activity of each species is the same as its molarity, and that the volume of the solution stays constant.

(a) At what pH will the iron just start to precipitate from solution as solid Fe(OH), if the solubility product for $Fe(OH)_3$ at 25°C is $K_{sp} = 2.0 \times 10^{-39}$? The self-dissociation constant for water at 25°C is $K_w = 1.00 \times 10^{-14}$.   [4 marks]

(b) At what pH will nickel start to precipitate from solution as Ni(OH), if the solubility product for $Ni(OH)_2$ at 25°C is $K_{sp} = 6.5 \times 10^{-18}$?   [4 marks]

(c) What will be the concentration of iron remaining in the solution just before the nickel starts to precipitate?   [4 marks]

(d) If activity coefficient corrections were taken into account, would the value of the pH reported for part (a) be higher, lower, or the same as the value obtained by neglecting such corrections? Be sure to explain your reasoning.   [4 marks]

3.   A strong, rigid, thermally insulated tank has a fixed volume of 6.00 L. Initially it contains 70.0 moles of ethylene gas (C_2H_4) at 30.0°C. Then a valve is opened and 10.0 moles of ethylene flows out of the tank, leaving behind 60.0 moles of the gas. The final uniform temperature of the ethylene remaining in the tank is 13.0°C.

(a) Assuming that ethylene behaves as an ideal gas, calculate ΔP, the change in the pressure of the gas in the tank as a result of this process.   [7 marks]

(b) Suggest a reason why the value obtained in part (a) will not be accurate. [3 marks]

(c) What would the change in pressure be if, instead of obeying the ideal gas law, the gas

obeyed the *van der Waals* equation of state; namely, $\left[P + a\left(\dfrac{n^2}{V^2}\right) \right](V - nb) = nRT$?

For ethylene gas, a = 0.462 Pa m^6 mol^{-2}, and b = 5.83 x 10^{-5} m^3 mol^{-1}. [7 marks]

4.   Gaseous propanol-2 (C_3H_3O) can react *endothermically* at high temperatures in the presence of a catalyst to produce propanal gas (C_3H_3O) and hydrogen gas (H_2) according to the following reaction:

$$C_3H_3O_{(g)} \rightarrow C_3H_3O_{(g)} + H_{2(g)}$$

(a) Pure hot propanol-2 at a certain elevated temperature is introduced into an evacuated constant volume reaction vessel, which contains an appropriate catalyst. At this temperature, the equilibrium constant for the above reaction has a value of K = 1.72. The initial pressure of the hot propanol-2 (before it begins to react) is 75.0 kPa. After the reaction has stopped and the system has attained equilibrium, what are the partial pressures of the
(i) propanol-2? (ii) propanal?   [10 marks]

(b) Answer each of the following questions in two or three sentences, giving your reasons:
Does the fraction of the initial propanol-2 that reacts increase, decrease, or stay the same, when

(i) the initial pressure is increased? (ii) the temperature is increased?   [6 marks]

5.   Calculate ΔS for each of the following processes, in J K^{-1}; (data are provided at the end of the question):

(a) A 400 mL cup of hot tea cools from 80.0°C to 25.0°C at one atm pressure. [4 marks]

(b) One mole of an ideal gas expands isothermally at 25.0°C from an initial pressure of 10.0 atm to a final pressure of 1.00 atm.   [4 marks]

(c) One mole of saturated steam at one atm pressure and 100.0°C condenses to liquid water at 100.0°C and one aim pressure.   [4 marks]

(d) One mole of liquid water is formed from Hydrogen gas and oxygen gas at 25.0°C and one atm pressure. (The maximum amount of non-expansion work—"other" work—that this process can deliver is equivalent to lifting a 1000 kg mass through a vertical displacement of 24.17m in the gravitational field.)   [6 marks]

Data: $\bar{c}_p$ for tea = 4.18 J g^{-1} K^{-1}; density of tea = 1.00 g mL^{-1}; specific enthalpy of vaporization for water at 100°C and one atm pressure = 2257 J g^{-1}; enthalpy of combustion of hydrogen to form liquid water at 25°C and one atm pressure = -285.83 kJ mol^{-1}; acceleration due to gravity = 9.81 m s^{-2}.

6. (a) At 298.15 K, ethylcyclohexane (C_8H_{16}) can be formed by the hydrogenation of ethylbenzene (C_8H_{10}), with a standard enthalpy change -202 kJ mol^{-1}. Given that at 298.15 K the standard enthalpy of combustion of C_8H_{16} to water vapour and carbon dioxide gas is -5181 kJ mol^{-1}, and that the enthalpies of formation of water vapour and carbon dioxide gas are -244 kJ mol^{-1} and -394 kJ mol^{-1}, respectively, calculate the standard enthalpy of formation of ethylbenzene at 298.15 K. Report the answer in kJ mol^{-1}.

[10 marks]

(b) At its normal melting point of 80.55°C, the enthalpy of fusion of solid naphthalene ($C_{10}H_8$) is 150.6 J g^{-1}. Calculate the change in the melting point when the pressure is increased by one atm. The density of solid naphthalene is 1.146 g cm^{-1}, and that of liquid naphthalene is 0.981 g cm^{-1}.   [6 marks]

[Total = 100 marks]