THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 4

Final Examination — 2012/2013

CMU 2220 — Concepts in Chemistry

(3 hours)

11th December 2013 (Wednesday)   9.30 a.m. – 12.30 p.m.

- There are six (06) questions and seven (07) pages (including the first page) in the paper.
- Answer **ALL 06 (six)** questions.
- The use of a non-programmable calculator is permitted
- Mobile phones are not allowed.

Gas constant (R)	=	8.314 J K^{-1} mol^{-1}
Avogadro constant (N_A)	=	6.023×10^{23} mol^{-1}
Faraday constant (F)	=	$96,500$ C mol^{-1}
Planck constant (h)	=	6.63×10^{-34} J s
Velocity of light (c)	=	3.0×10^8 m s^{-1}
Standard atmospheric pressure	=	10^5 $Pa(Nm^{-2})$
Protonic charge (e)	=	1.602177×10^{-19} C
π	=	3.14159
$Log_e(X)$	=	2.303 $Log_{10}(X)$

Some equations used in chemistry are given below using standard notation.

$$\log(\gamma_\pm) = -A Z_+|Z_-|\sqrt{I}, \quad E_J = BJ(J+1), \quad N_j = N_i\left(\frac{g_j}{g_i}\right)\exp\left(-\frac{E_j - E_i}{kT}\right), \quad \bar{v} = 2\bar{B}(J+1)$$

$$\eta = \frac{I}{h\nu}, \quad \bar{B} = \frac{h}{8\pi^2 \mu R^2 c}, \quad \lambda_B = u_B|Z_B|F, \quad v_B = u_B E, \quad \kappa_B = u_B c_B|Z_B|F \quad A = \varepsilon C l$$

$$j_B = v_B c_B|Z_B|F \qquad u_B = \frac{xa\kappa}{Q} \qquad \Lambda_Y = \Lambda_Y^0 - (a + b\Lambda_Y^0)\sqrt{\frac{C_Y}{c^0}}$$

1. (a) (i) Consider a solution of two non-interacting chemical species, A and B. Write down Beer-Lambert law for the above solution and identify all the parameters in it.

   (ii) HIn is a weak acidic indicator which dissociates in aqueous medium as $HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$. A student was asked to determine the concentration equilibrium constant, K_C, of HIn in a given aqueous solution (prepared by dissolving pure HIn in distilled water) at $25^\circ C$ using a spectroscopic method. He realised that he could determine K_C if he could measure the concentrations of HIn(aq) and In^-(aq) in the solution since $K_C = \left[H^+(aq)\right]\left[In^-(aq)\right]/\left[HIn(aq)\right]$. For this purpose he measured the absorbance of a sample of the solution in a cell of path length 1 cm using a double beam spectrometer at two different wavelengths of the incident radiation. He recorded absorbance values of 0.40 and 0.08 at wavelengths 430 nm and 580 nm, respectively. From a book of constants he found the molar extinction coefficients, in units of $dm^3mol^{-1}cm^{-1}$, of HIn(aq) to be 2.00×10^4 and 9.70×10^2 respectively at 430 nm and 580 nm radiation. Similarly for In^-(aq) they were 6.3×10^2 and 7.10×10^3, respectively at 430 nm and 580 nm radiation. Calculate the concentrations of HIn(aq) and In^-(aq) in the solution.

   State any assumptions you make in your calculation.

   (50 marks)

(b) Answer either **Part A** OR **Part B** (but **NOT** both).
Part A:

Often we assume that the rotational and vibrational energy levels of a molecule to be quantised separately (independently). The rotational energy levels, E_J, of a particular diatomic molecule are given by the expression $E_J = 10J(J+1)\,cm^{-1}$ where J = 0, 1, 2, 3, ... For the same molecule the vibrational energy levels, E_υ, are given by $E_\upsilon = 3000(\upsilon + 1/2)\,cm^{-1}$ where $\upsilon = 0, 1, 2, ...$

   (i) Calculate the rotational energy of the first (lowest) three rotational energy levels.

   (ii) Calculate the vibrational energy of the first (lowest) three vibrational energy levels.

   (iii) Calculate the energy of a photon that can bring about the mixed transition, where the rotational energy level change from $J = 1 \rightarrow J = 2$ and the vibrational energy level changes from $\upsilon = 0 \rightarrow \upsilon = 2$.

   (30 marks)

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Part B:

(i) Write down the Boltzmann distribution function and identify all the parameters in it.

(ii) A hypothetical gaseous molecule has only two non-degenerate energy levels with energies 1.0×10^{-21} J and 3.5×10^{-21} J. Calculate the number of molecules in the higher energy level in a sample of 1 mol of these molecules at 500 K.

(30 marks)

(c) A particular diatomic molecule shows line each in the pure vibrational, electronic and rotational spectra at radiation frequencies v_{Vib}, v_{Elec} and v_{Rot}. Giving reasons, arrange the above three frequencies in ascending order of their magnitude. (Which is the smallest, the second smallest and the largest?)

(20 marks)

2. (a) (i) Define the following processes.

(α) Stimulated emission

(β) Stimulated absorption

(γ) Spontaneous emission

(ii) In measuring the absorbance, a student placed a gaseous sample of a diatomic molecule in a spectrometer and switched on the radiation beam of frequency 2.5×10^{14} Hz. The rate of stimulated emission, stimulated absorption and spontaneous emission of photons with in the sample, in units of $mol \, s^{-1}$, were 1.0×10^{-8}, 6.5×10^{-8} and 0.5×10^{-8} respectively.

(α) Calculate the energy in 1 mol of photons of frequency 2.5×10^{14} Hz.

(β) Calculate the rate of absorption of energy by the sample from the radiation beam in $J \, s^{-1}$.

(50 marks)

(b) (i) Write down the relationship that exists between the standard free energy change and the thermodynamic equilibrium constant of a chemical reaction at a thermodynamic temperature and identify all the parameters in it.

(05 marks)

(ii) Write down the relationship that exists between the thermodynamic equilibrium constant K_1 of a chemical reaction at one temperature T_1 and the thermodynamic equilibrium constant K_2 of the same reaction at another temperature T_2.

(05 marks)

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(iii) The vapour pressure of liquid ozone is 166.0 kN m^{-2} at 130 K and 166.6 kN m^{-2} at 150 K. Calculate the standard boiling point of ozone. State the assumptions you make in the calculation.

(40 marks)

3. Answer any **THREE (03)** parts out of (a), (b), (c) and (d).

(a) A student electrolysed a 1 mol dm^{-3} aqueous solution of NaCl using two identical platinum electrodes (which are placed parallel to each other) as shown in the figure. The ammeter reading was 2.5 A and the area of one side of the platinum electrode is 10 cm^2 (same as the cross section shown in the figure). The transport number of sodium ions in this solution was known to be 0.45.
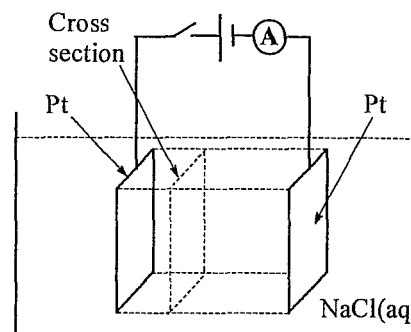
(i) Write down the relationship between the current density of an ionic species in solution and its drift speed and identify all the parameters in it.

(ii) Calculate the drift speed of sodium ions in the above experiment conducted by the student. [Assume that the current in the solution flows within the cell of solution trapped between the platinum plates as indicated by dotted lines in the figure.]

(100/3 marks)

(b) The moving boundary method was applied to a $0.0200 \text{ mol dm}^{-3}$ aqueous NaCl solution at 25^0C using aqueous $CdCl_2$ as the following solution. For a current held constant at 1.600 mA, it was found that the boundary moved 0.100 m in 3453 s, in a tube of average cross sectional area $1.115 \times 10^{-5} \text{ m}^2$. The conductivity of the NaCl solution, at 25^0C and 1 atm, is 0.2313 S m^{-1}. Calculate the ionic mobility of Na^+ at 25^0C and 1 atm, in this solution.

(100/3 marks)

, (c) Mobilities (in $m^2 \text{ V}^{-1} \text{ s}^{-1}$) of Mg^{2+} and Cl^- ions in $0.001 \text{ mol dm}^{-3}$ solution of $MgCl_2$ at 25°C and 1 atm are 55.0×10^{-9} and 79.1×10^{-9} respectively. Calculate the molar conductivity of $MgCl_2$ in this solution if it behaves as a weak electrolyte with a degree of dissociation, $\alpha = 0.9$.

(100/3 marks)

(d) At 25°C the conductivity of conductivity water is $58.0 \times 10^{-7} \text{ S m}^{-1}$. The limiting molar conductivities of hydrogen and hydroxyl ions at 25°C are $0.0350 \times \text{S m}^2 \text{ mol}^{-1}$ and $0.0198 \times \text{S m}^2 \text{ mol}^{-1}$ respectively. Calculate the ionic product of water at 25°C.

(100/3 marks)

1. (a) Starting from the first law of thermodynamics derive $\left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_V$.

(20 marks)

(b) (i) Define chemical potential (μ_i) using a mathematical expression.

(ii) Deduce an expression for the pressure coefficient of chemical potential at constant temperature in a closed system.

(20 marks)

(c) Calculate the total volume of 1 kg of 46% (mass by mass) solution of ethanol in water at $25°C$ given that the partial molar volumes of ethanol and water in this solution are 0.0540 and 0.0175 dm^3mol^{-1} respectively. (Relative molar mass of ethanol is 46 and of water is 18)

(25 marks)

(d) Answer either **Part A** OR **Part B** (but **NOT** both).

Part A:

100 moles of a monatomic ideal gas $\left(C_{V,m} = 3R/2\right)$ in a pressure flask at $27°C$, are expanded adiabatically from $3\,cm^3$ to $4\,cm^3$. Maximum decrease in temperature obtained was $27.4°C$. Calculate the internal energy change and the Helmholtz free energy change accompanying the process at this maximum decrease in temperature. Molar entropy of the gas at $27°C$ is $100\,J\,mol^{-1}\,K^{-1}$.

(35 marks)

Part B:

100 moles of a monatomic ideal gas $(C_{v,m} = 3R/2)$ is heated at constant pressure, from $127°C$ to $427°C$. If the molar entropy of the gas at $127°C$ is $100\,J\,mol^{-1}\,K^{-1}$, calculate the Gibbs free energy that takes place during the heating process.

(35 marks)

5. (a) (i) Write down the symbolical expression for Raoults Law and identify all the symbols in it.

(ii) Derive the following expression for total pressure (P_T) with respect to an ideal mixture formed by two liquids, A and B

$$P_T = x_B\left(P_B^0 - P_A^0\right) + P_A^0$$

(16 marks)

(b) Two liquids, 53.0 g of ethyl benzene and 80.0 g of a compound C, were mixed together to form an ideal binary mixture at room temperature. The vapour pressures of pure ethyl benzene and pure C at this temperature are 45 torr and 30 torr respectively.

(i) Determine the molar mass of C given that the total vapour pressure of the mixture is 40 torr at this temperature? [Relative atomic masses: H=1; C= 12; O=16].

(ii) Calculate the vapour composition corresponding to the above mixture in terms of mole fraction of ethyl benzene.

(30 marks)

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(c) Metal **L** (M.Pt = $450°C$) and Metal **M** (M.Pt = $800°C$) form two compounds, at elevated temperatures, of formula **L$_2$M** with a **congruent melting point** $600°C$ respectively. Two **eutectics** of compositions 0.10, 0.75 (given in terms of the mole fraction of **L**) are formed, with the following M.Pt's: $200°C$ and $350°C$, respectively.
Sketch a fully labeled phase diagram for the above system.

(24 marks)

(d) Answer either **Part A** OR **Part B** (but **NOT** both).

Part A:

(i) When 50.0 g each of two partially miscible liquids A and B are mixed at $27°C$, two layers with 20% of A and 70% of A by weight in each layer are formed. Calculate the weight of A in each layer.

(ii) Assuming that the UCT for the above system is $57°C$, the molar mass of A is 75 g and that of B is 100 g, sketch the solubility curve (the x-axis being the mole fraction of A). Highlight the relevant data points from the information provided and the answers obtained in (ii) above on your sketch.

(30 marks)

Part B:

(i) Give ONE advantage of carrying out steam distillation (instead of normal distillation) to extract oils from Natural Products.

(ii) A chemist carries out steam distillation to separate out a compound A. He obtains a distillate at a temperature of $95°C$ and 760 torr. The ratio of the weight of this compound to the weight of water in the distillate was found to be 0.25. Assuming that water and A are fully immiscible, calculate the molar mass of A given that the saturated vapor pressure of water at $95°C$ is 700 mm Hg.

(30 marks)

6. (a) The following information corresponds to a **second order** reaction of the form A → Products.
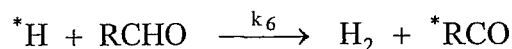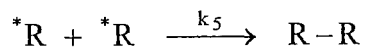Temperature = $27°C$
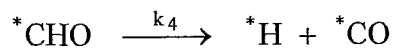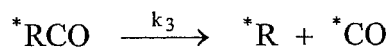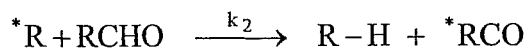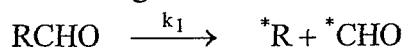Rate constant for the above reaction = 3.0×10^{-2} mol^{-1}m^3 min^{-1}
The initial concentration of A = 1.0×10^2 mol m^{-3}

(i) With the aid of the relevant rate equation (differential), **derive** the corresponding integrated form using the standard symbols.

(ii) Calculate the half − life of this reaction.

(iii) At the same temperature of $27°C$, it is said that the half-life of this reaction could be doubled by reducing the initial concentration to 5.0×10 mol m^{-3}. Explain.

(55 marks)

(b) The hypothetical reaction scheme (mechanism) for the decomposition of an aldehyde RCHO is given below

$$RCHO \xrightarrow{k_1} {}^*R + {}^*CHO$$

$${}^*R + RCHO \xrightarrow{k_2} R-H + {}^*RCO$$

$${}^*RCO \xrightarrow{k_3} {}^*R + {}^*CO$$

$${}^*CHO \xrightarrow{k_4} {}^*H + {}^*CO$$

$${}^*R + {}^*R \xrightarrow{k_5} R-R$$

$${}^*H + RCHO \xrightarrow{k_6} H_2 + {}^*RCO$$

(i) What do you understand by the term "steady state assumption" (SSA) as applied in kinetic studies?

(ii) Identify the initiation step in the above scheme

(iii) Write down the rate equation for the formation of R radical.

(25 marks)

(c) Consider two consecutive irreversible **first order** reactions given by a general equation of the form $A \xrightarrow{k_1} B \xrightarrow{k_2} C$.

Sketch the concentrations (of A, B, C) versus time curves (**one diagram**) in the case where $k_2 >>> k_1$. Explain the shapes of the curves.

(20 marks)

The End