



THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 4

Final Examination — 2016/2017

CMU 2220/ CME 4220— Concepts in Chemistry

(3 hours)

13th January 2017 (Saturday)

9.30 a.m. — 12.30 p.m.

- There are six (06) questions and eight (08) 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 pressure	=	10 ⁵ Pa (N m ⁻²) = 1 bar
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.

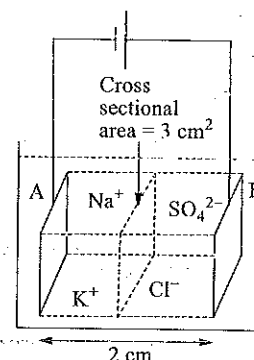
$$\log(\gamma_{\pm}) = -A Z_+ |Z_-| \sqrt{I}, \quad E_J = BJ(J+1), \quad v' = \frac{v}{1 \pm v/c}, \quad \bar{v} = 2\bar{B}(J+1),$$

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

$$j_B = \nu_B c_B |Z_B| F, \quad \Lambda_Y = \frac{\kappa_Y}{C_Y}, \quad \lambda_B = \frac{\kappa_B}{c_B}, \quad \Lambda_Y = \Lambda_Y^0 - (a + b\Lambda_Y^0) \sqrt{\frac{C_Y}{c^0}}$$

1. Answer any **TWO** parts out of (a), (b) and (c).

- (a) A student electrolysed an aqueous solution of NaCl and K_2SO_4 using two equal platinum plates, A and B; see the figure. The electric current was 2.5 A and remained constant throughout the experiment. The plates were kept parallel at a distance of 2 cm from each other. The transport number of Na^+ was 0.2. The concentration of NaCl was 1.5 mol dm^{-3} . Assume that the current flows only within the cell of solution trapped between the plates and its cross sectional area was 3 cm^2 . The potential difference between A and B was 200 V.



- (i) Giving reasons state the direction of the electric field within the cell of solution.
 (ii) What is the electric field strength between the two platinum plates?
 (iii) Calculate the following for the Na^+ ions.
 (α) Current carried.
 (β) Drift speed.
 (γ) Ionic mobility

(50 marks)

- (b) (i) Define the molar conductivity of an electrolyte, Y, in solution.
 (ii) Write down the Onsager limiting law for the molar conductivity of NaCl in a solution and identify all the parameters in it.
 (iii) Write down the relationship between the limiting molar conductivity of an ionic species and its limiting ionic mobility. Identify all the parameters in it.
 (iv) A student prepared a $0.002 \text{ mol dm}^{-3}$ aqueous solution of NaCl at 25°C . Calculate the conductivity of this solution. State assumptions, if any, you make in this calculation.

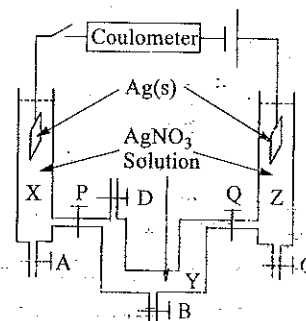
[In standard notation, at 25°C in aqueous medium;

$$u_{Na^+}^0 = 51.9 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1} \text{ and } u_{Cl^-}^0 = 79.1 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$$

In the Onsager limiting law; $a = 0.0606 \text{ S m}^2 \text{ mol}^{-1}$ and $b = 0.230$]

(50 marks)

- (c) A student electrolysed a 0.1 mol dm^{-3} solution of $AgNO_3$ using the apparatus shown in the figure in order to find the transport number of silver ions. The current was passed for 2500 s. After closing the two taps, P and Q, the three chambers, X, Y and Z were drained separately. The silver ion concentrations in these three solutions were determined to be c_X , c_Y and c_Z , respectively. The Coulometer reading for the experiment was 5000 C. The change in the amount of silver ions in chamber X was found to be 0.031 mol.



Assume that only the reduction of silver ions or oxidation of silver occurred at the electrodes and the student has **accurately** determined the transport number of silver ions. [Relative atomic mass: $Ag = 107$]

- (i) What is the value of c_Y ?
- (ii) Giving reasons, state whether each of c_X and c_Z is equal, greater than or smaller than the initial concentration of silver ions, viz. 0.1 mol dm^{-3} .
- (iii) Giving reasons indicate the change in the amount of silver ions in chamber Z.
- (iv) Calculate the transport number of silver ions in the solution. (50 marks)
2. (a) Define the following terms as applied in molecular spectroscopy.
- (i) Absorption spectrum of a chemical species.
- (ii) Number density of photons in a beam of radiation.
- (iii) Transmittance of a sample.
- (iv) Dipole moment. (20 marks)
- (b) (i) Write down an expression for the absorption of radiation by a solution, having two non-interacting chemical species, using Beer-Lambert law. Identify all the parameters in it.
- (ii) A student had to determine the molar extinction coefficient of a chemical species, X, in an aqueous solution at radiation frequency, ν . He was given a double beam spectrometer for this purpose. However, he only had two sample cells, P and Q, which do not absorb radiation at frequency, ν . The path length of P was 1 cm and that of Q was 2 cm. He first adjusted the absorbance reading to zero without keeping the sample or reference in the spectrometer. Then he kept P filled with pure water in the reference chamber and Q filled with the solution in the sample chamber of the spectrometer. The absorbance reading was 2.0. Then he read the absorbance, keeping Q filled with pure water in the reference chamber and P filled with the solution in the sample chamber. The absorbance reading was 1.2. Calculate the molar extinction coefficient of X if its concentration in the solution was 0.05 mol dm^{-3} . (30 marks)
- (c) Answer either **Part A** OR **Part B** (but NOT both).
- Part A:**
- (i) Define the following terms as applied in molecular spectroscopy
- (α) Stimulated absorption
- (β) Stimulated emission
- (γ) Spontaneous emission
- (ii) Giving reasons state the process/es out of the three indicated in part (i) above which tends to decrease the absorbance of a sample of an absorbing chemical species.
- (iii) Consider a sample of a chemical species placed in the beam of radiation of frequency $1.0 \times 10^{12} \text{ Hz}$. It was found that the rates of stimulated absorption, stimulated emission and spontaneous emission in the sample, at frequency $1.0 \times 10^{12} \text{ Hz}$, in units of $\text{mol dm}^{-3} \text{ s}^{-1}$, to be 3.4, 1.2, and 0.9, respectively. Calculate the total rate of absorption of energy from the beam of radiation by the sample in 1 cm^3 . (50 marks)

Part B:

- (i) Briefly describe what is meant by Doppler broadening.
- (ii) Imagine a gaseous sample of molecules placed in a spectrometer at 25°C . Consider the molecules in the sample that moves at the speed $6.0 \times 10^7 \text{ m s}^{-1}$. Calculate the maximum and minimum frequencies (of radiation in the beam in the spectrometer) these molecules can absorb due to Doppler Effect. Assume that the molecule has only two energy levels with a difference, $\Delta E = 6.63 \times 10^{-20} \text{ J}$.
- (50 marks)
3. (a) (i) Giving reasons identify the molecules which can show a microwave spectrum, out of the following.
- (α) HCl (β) CO (γ) CO₂ (δ) HCN
- (ii) Write down the relationship between the rotational constant of a diatomic molecule and its reduced mass and identify all the parameters in it.
- (iii) The rotational constant of a H³⁵Cl molecule is 10.42 cm^{-1} . Calculate the rotational constant of H³⁷Cl. State any assumptions you make in performing the calculation. [Relative atomic masses; H = 1.0, ³⁵Cl = 35.0, ³⁷Cl = 37.0]
- (50 marks)
- (b) Consider the balanced chemical reaction at a temperature T under isobaric conditions; $a\text{A} + b\text{B} \rightarrow c\text{C}$. At a given time t, thereafter but before the system reaches equilibrium, the activities of the components A, B and C are p, q and r respectively. If the standard free energy change for the reaction at temperature T is ΔG° ,
- (i) Write down an expression for the free energy change, ΔG of the reaction under the given conditions.
- (ii) If the equilibrium constant of the reaction is K, under the given conditions, re-write the above expression incorporating K into it.
- (20 marks)
- (c) For a reaction at 500K, $\Delta H^{\circ} = -40 \text{ kJ mol}^{-1}$ while $\Delta S^{\circ} = +100 \text{ J K}^{-1} \text{ mol}^{-1}$. Deduce whether at 500K,
- (i) the reaction will occur spontaneously under standard conditions.
- (ii) the equilibrium constant K increases or decreases with a rise in temperature.
- (iii) The value of K is greater than or less than 1.
- (30 marks)

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

Part A:

(a) Under what conditions, if any, and to what type of system, can the following thermodynamically deducible equations apply.

(i) $\Delta A < 0$

(ii) $\Delta S = \Delta H/T$

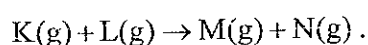
(iii) $dG = V dP - S dT$

(iv) $\Delta T = K_{100} m$

(v) $\ln(P) = -\Delta H/T + \text{constant}$

(15 marks)

(b) Calculate the equilibrium constant (K_p) at 300K, for the given reaction,



The following data are given at 300K;

$$\Delta H^0 = -14.6 \text{ kJ mol}^{-1} \text{ and } \Delta S^0 = -35.9 \text{ J K}^{-1} \text{ mol}^{-1}.$$

(25 marks)

(c) (i) Define Chemical potential (μ) using a mathematical expression.

(ii) Derive the expression for the temperature coefficient of Chemical potential in a

closed system at constant pressure, $\left(\frac{\partial \mu_i}{\partial T}\right)_{P, n_j \neq i}$ using $dG = V dP - S dT$.

(iii) Complete the Gibbs – Helmholtz equation written as, $= -\frac{\Delta H^0}{T^2}$.

(30 marks)

(d) 1000 moles of a monatomic ideal gas ($C_{v,m} = 3R/2$) are heated from 27°C to

327°C at constant pressure. Calculate ΔH and ΔS for this process.

(30 marks)

Part B:

(a) (i) Starting from $G = H - TS$, derive the fundamental thermodynamic equation, $dG = V dP - S dT$, applicable to reversible processes in closed systems where only PV work is possible.

(ii) Write down the Maxwell relationship corresponding to the above fundamental thermodynamic relationship.

(25 marks)

(b) A solution prepared by dissolving 1.0 g of an unknown non-volatile solute in 100.0 g of carbon tetrachloride has a boiling point which is 0.4 K higher than that of pure carbon tetrachloride. Calculate the molar mass of the solute.

(Ebullioscopic constant K_{1000} for carbon tetrachloride = $5.0 \text{ K kg mol}^{-1}$)

(20 marks)

- (c) (i) Write down the mathematical expression that can be written for the variation of the equilibrium constant K_p , with temperature given in the form

$$\left(\frac{\partial \ln(K_p)}{\partial T} \right)_p =$$

- (ii) If the variation of K_p of a reaction at the temperature T is given by the equation,

$$\ln(K_p) = 15.00 - \frac{600}{T}, \text{ calculate } \Delta G^\circ, \Delta H^\circ \text{ and } \Delta S^\circ \text{ for this reaction at } 27^\circ\text{C}.$$

(40 marks)

- (d) Write down the mathematical form of the second law of thermodynamics for spontaneous (irreversible) and equilibrium (reversible) processes,

- (i) in terms of the entropy change that takes place in an experimental system.
 (ii) the entropy change in the universe.

(15 marks)

5. (a) (i) Write down the logarithmic form of the Arrhenius equation. Identify the independent and dependent variables that produce a linear relationship.

- (ii) The following values were reported from an experiment to test the Arrhenius relationship between temperature and rate constant.

Temp./ $^\circ\text{C}$	27	37	47	57	67
$k \times 10^3 / \text{min}^{-1}$	7.5	15.0	20.5	35.0	50.0

Carry out an **appropriate tabulation** of data required to plot a suitable graph in accordance with the expression in (i) above

(30 marks)

- (b) $\text{cis-Cr(en)}_2(\text{OH})_2^+ \rightleftharpoons \text{trans-Cr(en)}_2(\text{OH})_2^+$

This is an example of a reversible reaction where the cis and trans isomers are said to exist in equilibrium. It is known that both the forward and the reverse reactions are first order reactions.

The values for the rate constants, k_1 and k_2 , (the respective rate constants in the forward and reverse directions), reported at 30°C , are $k_1 = 6.0 \times 10^{-4} \text{s}^{-1}$ and $k_2 = 3.0 \times 10^{-3} \text{s}^{-1}$.

- (i) Given that a is the initial concentration of the cis isomer and x is the concentration of this isomer reacted at time, t , write down the mathematical expression for $\frac{dx}{dt}$ (the rate) in the usual manner.

- (ii) Assuming that the concentration of the trans isomer is x_e at equilibrium, show that the equilibrium constant $[K_{\text{equ}}]$ is given by

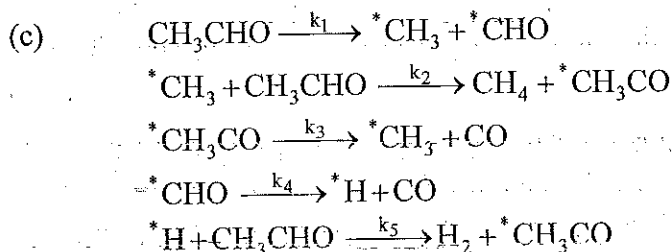
$$K_{\text{equ}} = \frac{k_1}{k_2} = \frac{x_e}{a - x_e}$$

(iii) Commencing an experiment with the cis isomer ($a = 0.10 \text{ mol dm}^{-3}$)

determine the equilibrium concentration of the trans isomer and hence, the time taken for half of the equilibrium amount of the trans isomer to be formed using

the integrated form of the rate equation, $\ln\left(\frac{x_e}{x_e - x}\right) = \left(\frac{k_1 a}{x_e}\right)t$.

(45 marks)



Several reactive intermediates are formed in the steps shown above (Note: each of these steps are elementary reactions with a specific rate constants as given.)

(i) Define the term "Steady State Assumption (SSA)" as applied to such intermediates in kinetic studies

(ii) Write down rate equation for each of the four intermediates

(25 marks)

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

Part A:

(i) Consider two **immiscible** liquids, A and B, in equilibrium with their vapours at a specified temperature. Derive the expression given below that relates the **relative weight** of the two liquids present in the condensate to their molar masses (M_A and M_B) and saturated vapour pressures (P_A^0 and P_B^0) respectively;

$$\frac{W_A}{W_B} = \frac{P_A^0 M_A}{P_B^0 M_B}$$

(ii) A mixture of aniline and water (two immiscible liquids) boils at 98°C . The saturated vapour pressure of aniline and water at this temperature are 42 mm Hg and 718 mm Hg, respectively. Calculate the amount of aniline that can be collected for each 50 g of water by steam distillation

[O=16; N=14; C=12; H=1]

(30 marks)

Part B:

Two liquids, 46.0 g of toluene and 57.0 g of liquid octane, were mixed together to form an ideal binary mixture at room temperature. At this temperature, the vapour pressure of pure toluene is 45 torr and the total vapour pressure of this mixture is 30 torr. [H=1; C=12; O=16].

Assuming that the composition of the liquid phase remains unchanged,

(i) determine the vapour pressure of pure octane at this temperature.

(ii) calculate the vapour composition corresponding to the above mixture in terms of mole fraction of octane.

(30 marks)

- (b) (i) 20.00 cm^3 of a liquid A [relative molar mass 96 and density 1.2 kg dm^{-3}] is mixed with 40.00 g of a liquid B. If the mole fraction of A in this fully miscible system is $1/3$, determine the relative molar mass of B.
- (ii) If 10.0 g of a third compound, C (fully miscible with the other two) of relative molar mass 40.0 is added to the above mixture, determine the mole fraction of B in the new mixture.

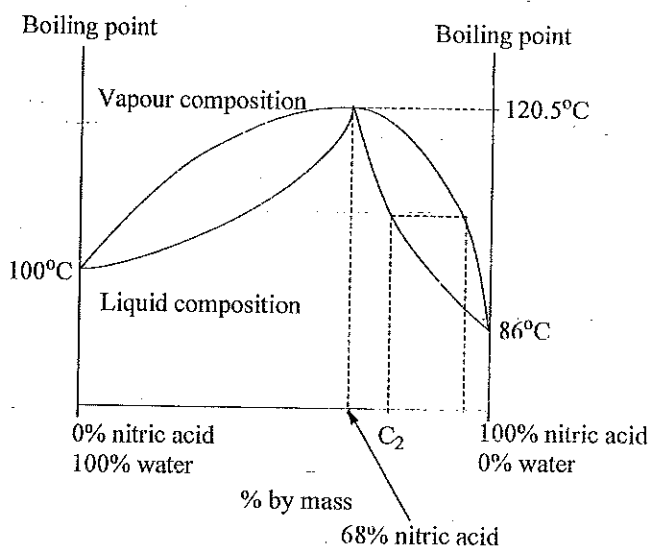
(14 marks)

- (c) Two metals A and B (melting point of A = 1200°C ; melting point of B = 900°C) are said to form a simple eutectic system at elevated temperatures. The eutectic composition corresponds to a melt given by the mole fraction of A equal to $2/3$. The cooling curve corresponding to an equimolar mixture of A and B shows a break at 750°C and a "halt" at 650°C .

- (i) Sketch a fully labelled phase diagram for the above system.
- (ii) Sketch the cooling curve mentioned above; identify the processes, including phase changes, corresponding to each section of the cooling curve.

(32 marks)

- (d) The phase diagram corresponding to the Nitric acid and water system that corresponds to an azeotrope showing negative deviation from ideal behaviour is shown in the figure. The composition of the Azeotropic Mixture is given as 68% Nitric Acid by mass.



- (i) What is meant by "negative deviation" in the above case?
- (ii) Calculate the corresponding mole fraction of Nitric Acid in the Azeotropic Mixture.
- (iii) Briefly outline the process of fractional distillation carried out on a mixture whose composition is indicated as the Azeotropic Mixture C_2 [C = 12; H = 1; N = 14; O = 16]

(24 marks)

The END