THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 4

Final Examination — 2013/2014

CMU 2220/ CME 4220 — Concepts in Chemistry

(3 hours)

26th November 2014 (Wednesday) 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)	=	$6.023\times10^{23}\ mol^{-1}$
Faraday constant (F)	=	$96,500\ C\ mol^{-1}$
Planck constant (h)	=	$6.63\times10^{-34}\ J\ s$
Velocity of light (c)	=	$3.0\times10^{8}\ m\ s^{-1}$
Standard atmospheric pressure	=	$10^{5}\ Pa\left(N\,m^{-2}\right)$
Protonic charge (e)	=	$1.602177\times10^{-19}\ C$
π	=	3.14159
$Log_e(X)$	=	$2.303\ Log_{10}(X)$

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

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

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

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

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

Part A:

(i) Define the following as applied in studying conductivity of electrolytes in solution.

(α) Conductivity of a solution

(β) Ionic mobility

(γ) Transport number of an ionic species in a solution.

(ii) Explain why the ionic mobility of an ion in aqueous medium is highest at infinite dilution.

(iii) Calculate the total charge on 1.2 mole of CO_3^{2-}.

(40 marks)

Part B:

A strong electrolyte, AB, dissociates in aqueous medium as $AB(s) \rightarrow A^{3+}(aq) + B^{3-}(aq)$. The ionic mobilities $\left(\text{in units of } m^2\ V^{-1}s^{-1}\right)$ of $A^{3+}(aq)$ and $B^{3-}(aq)$ in a 0.2 mol dm^{-3} solution of AB at 25°C are 55.0×10^{-9} and 79.0×10^{-9}, respectively.

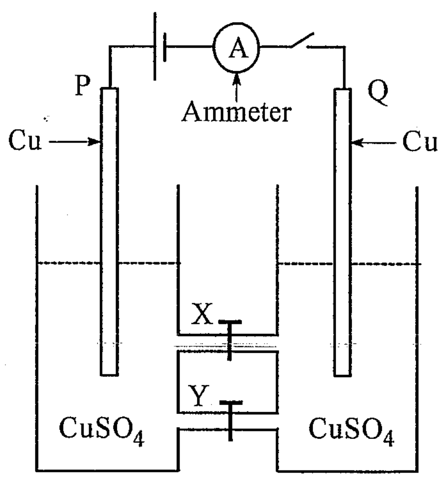
(i) Write down the relationship between the molar conductivity of AB and the molar conductivities of $A^{3+}(aq)$ and $B^{3-}(aq)$, and identify all the parameters in it.

(ii) Write down the relationship between the molar conductivity of an ionic species and its ionic mobility, and identify all the parameters in it.

(iii) Calculate the molar conductivity of AB in the above mentioned solution.

(40 marks)

(b) A student electrolysed aqueous solutions of copper sulphate using two copper electrodes using the apparatus shown in the figure. The left and right hand chambers are connected with glass tubes X and Y, fitted with taps so that the electric current through each of the tubes can be stopped by closing each of them. During the electrolysis experiment, (both taps opened) he maintained a constant ammeter reading of 2.1 A for 20 s. [Relative atomic mass of copper is 63.5]



(i) Giving reasons, state whether the ammeter reading would have increased, decreased or remained the same if the tap in tube Y were closed during this experiment without making any other changes in the apparatus.

(ii) Giving reasons identify the electrode (P or Q) which lost mass during the experiment.

(iii) Calculate the increase in mass of the cathode during the experiment.

[Question 1 is continued in the next page]

(iv) At a particular moment during the experiment (with both taps opened) the student determined the electric current through tube X to be 1.3 A. Calculate the rate of flow of copper ions (in mol s^{-1}) in tube Y at that moment if the transport number of copper ions (in tube Y) is 0.6.

(60 marks)

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

Part A:

(i) Write down three factors that determine the height of a peak in the absorption spectrum (absorbance versus frequency) of a chemical species in solution obtained using a double beam spectrometer.

(ii) Calculate the number of photons crossing a unit area in unit time in a monochromatic beam of electromagnetic radiation of frequency 1.0×10^{14} Hz and intensity, $5.0 \times 10^{-2}\ \text{W m}^{-2}$.

(iii) Briefly describe the role of the monochromator and why it is needed in an absorption spectrometer.

(30 marks)

Part B:

(i) Define the following processes.

(α) Stimulated absorption.

(β) Stimulated emission

(γ) Spontaneous emission.

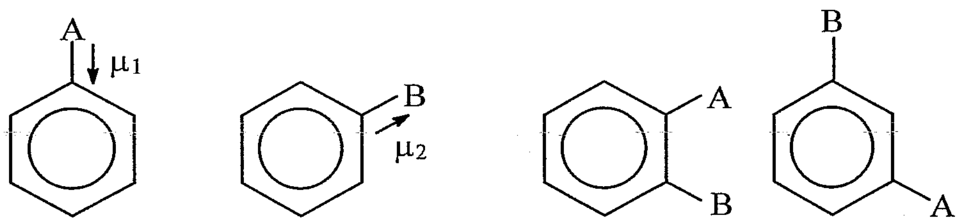
(ii) Briefly describe what is meant by the following.

(α) Doppler Broadening

(β) Lifetime Broadening (or Uncertainty Broadening).

(30 marks)

(b) Consider the substituted benzene molecules, (α), (β), (γ) and (δ), shown in the following diagram where A and B are two organic functional groups.



(α) (β) (γ) (δ)

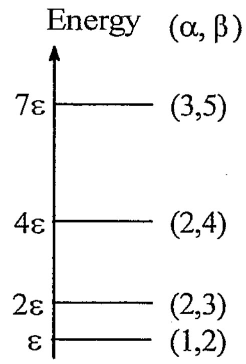
The dipole moments, μ_1 and μ_2, of molecules (α) and (β) are 0.40 D and 1.57 D, respectively. They are in the directions shown in the diagram. Estimate the dipole moments of molecules (γ) and (δ).

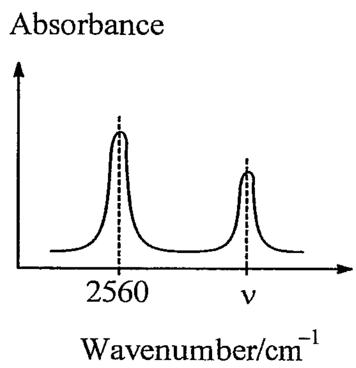
$$\left[\text{Sin}\left(30^0\right) = \text{Cos}\left(60^0\right) = 0.5; \quad \text{Sin}\left(60^0\right) = \text{Cos}\left(30^0\right) = \sqrt{3}/2\right]$$

(30 marks)

[Question 2 is continued in the next page]

(c) Consider a molecule, Q, having only 4 energy levels denoted by two quantum numbers, (α, β). Following figure shows the values of (α, β) and the energies of these four levels (i.e. $\varepsilon, 2\varepsilon, 4\varepsilon$ and 7ε). Here, $\varepsilon\,(>0)$ is the energy of the ground state. The selection rules in the absorption spectroscopy of Q are $\Delta\alpha = +1$ and $\Delta\beta = +2$. The observed absorption spectrum is also schematically represented in the figure.





(i) Giving reasons state the maximum number of lines that may be observed in the absorption spectrum of Q.

(ii) Calculate the following, in units of cm^{-1}.

(α) The ground state energy, ε, of the molecule.

(β) The position, ν, of the second line in the spectrum shown above.

(40 marks)

3. (a) A student observed that four consecutive absorption lines in the microwave spectrum of the gaseous diatomic molecule, AB, appear at wavenumbers $75.624\ cm^{-1}$, $100.832\ cm^{-1}$, $126.04\ cm^{-1}$ and $151.248\ cm^{-1}$.

(i) Using the above wavenumbers show that AB behaves as a rigid rotor.

(ii) Assign each of the above absorption lines to a particular rotational transition in AB.

(iii) Calculate the equilibrium bond length of AB.
[Relative atomic masses: A = 26.980; B = 1.00]

(50 marks)

(b) (i) (α) Write down the relationship between Gibbs free energy and Chemical Potential, (μ_i).

(β) Deduce the expression for the temperature coefficient of chemical potential at constant pressure, $\left(\frac{\partial \mu_i}{\partial T}\right)_{P, n_j}$, in a closed system.

(15 marks)

[Question 3 is continued in the next page]

(ii) The partial molar volumes of ethanol and water in a solution containing 5.0 mol of water and 1.05 mol of ethanol are $17.839\ cm^3$ and $55.10\ cm^3$ respectively. Calculate the excess partial molar volume if density of ethanol is $0.7893\ kg\ dm^{-3}$ and water is $1.0000\ kg\ dm^{-3}$

(35 marks)

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

Part A:

(a) Write down thermodynamically deducible expressions for the following;

(i) The enthalpy change at one temperature if the enthalpy change at another temperature is known.

(ii) The Gibbs free energy of a process at one temperature if the Gibbs free energy change at another temperature is known

(20 marks)

(b) (i) Write down the integrated form of the Clausius-Clapeyron equation and identify all the terms in it.
Indicate clearly the conditions under which this equation is applicable.

(ii) The temperature dependence of the vapour pressure of the solid and liquid forms of a given compound "A" are given below;

Solid A $$\log_{10}\left(\frac{P}{\text{torr}}\right) = 10 - \frac{2000}{T/K}$$

Liquid A $$\log_{10}\left(\frac{P}{\text{torr}}\right) = 6 - \frac{1500}{T/K}$$

Deduce the temperature corresponding to the triple point of "A".

State any assumptions you make.

(50 marks)

(c) (i) Give the definition of Helmholtz free energy.

(ii) Five moles of an ideal gas is compressed from a pressure of 1 atm to 6 atm at $27^{o}C$. Calculate the change in Helmholtz free energy, ΔA.

(30 marks)

Part B:

(a) State clearly under what conditions and/or to what types of systems, the following thermodynamic expressions can be applied.

(i) $\Delta G = \Delta H - T\Delta S$.

(ii) $\Delta T = K_{1000}\ m$

(iii) $\Delta S = n\,C_{v,m} \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right)$

(12 marks)

[Question 4 is continued in the next page]

(b) Write down the mathematical form of the second law of thermodynamics for a spontaneous process and an equilibrium process, based on the
(i) entropy change that takes place in an experimental system.
(ii) entropy change in the universe.
(iii) Gibbs free energy criteria.

(18 marks)

(c) The molar heat capacity of oxygen gas at constant pressure is given by the expression, $\bar{C}_P/(\mathrm{J\,K^{-1}\,mol^{-1}}) = 25.723 + 12.979\times10^{-3}T - 38.618\times10^{-7}T^2$.
Assume that oxygen gas behaves as an ideal gas. Calculate the change in entropy when two moles of oxygen gas undergo a change of temperature from $27^\circ C$ to $227^\circ C$ followed by an expansion from $2\ dm^3$ to $8\ dm^3$.

(30 marks)

(d) (i) Starting from the first law of thermodynamics, derive the fundamental equation $dG = VdP - SdT$ for a reversible process in a closed system.
(ii) Write down the Maxwell relationship that can be derived using the above equation.

(40 marks)

5. (a) (i) 20.00 ml of a liquid A [relative molar mass 96 and density $1.2\times10^3\ g\ dm^{-3}$] 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) Derive the following expression for total pressure (P_T) with respect to an ideal mixture formed by two liquids, A and B; identify, clearly, the symbols in this expression.

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

(16 marks)

(b) 78.0 g of Benzene (B) is mixed with 184.0 g of toluene (T) to form an ideal binary mixture. At $60^\circ C$, the vapour pressure of pure B and T, respectively, are 50 and 20 kPa.
(i) Calculate the pressure at which this mixture begins to boil?
(ii) Calculate the mole fraction of B in the vapour phase of the above mixture at $60^\circ C$?

(16 marks)

(c) The phase diagram for Mg-Cu at constant pressure shows that two compounds are formed: $MgCu_2$ which melts at $800^\circ C$ and Mg_2Cu which melts at $600^\circ C$. The melting point of Cu and Mg are $1100^\circ C$ and $650^\circ C$ respectively. The three eutectics are at 20 % $(700^\circ C)$, 55% $(550^\circ C)$, and 80% $(400^\circ C)$, where the composition is given in terms of mole % of Mg.
(i) Construct a clearly labeled phase diagram, identifying the relevant regions in terms of the phases present.

[Question 5 is continued in the next page]

(ii) Sketch a cooling curve corresponding to a melt of composition 50 mole % of Mg. Illustrate the meaning of the term "Break" and "Halt" with reference to the cooling curve you have drawn.

(38 marks)

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

Part A:

(i) Define the following:

(α) The term "Upper Critical Temperature- UCT" for a pair of partially miscible liquids.

(β) An Azeotrope with respect to a binary liquid mixture.

(ii) Identify the Upper Critical Temperature and the Azeotrope with sketches of the appropriate curve/phase diagrams.

(iii) When 60.0 g each of two partially miscible liquids A and B are mixed at $27^{\circ}C$, two layers with 25% of A and 75% of A (by mass) in each layer are formed. Calculate the mass of A in each layer (all relevant steps **must** be shown).

(30 marks)

Part B:

(i) Considering two fully immiscible liquids, A and B, **write down** the mathematical expression for the ratio of the masses of the two components W_A/W_B obtained on steam distillation in terms of their molar masses $(M_A \text{ and } M_B)$ and pure vapor pressures $\left(P_A^0 \text{ and } P_B^0\right)$ respectively.

(ii) It is reported that the boiling point of the immiscible liquid system naphthalene–water is $98^{\circ}C$ at a pressure of 98 kPa. The vapour pressure of pure water at this temperature is 94 kPa, Calculate the mass percent of naphthalene in the distillate. [Molecular formula of napthalene – $C_{10}H_8$; C = 12.0 ; H =1.0].

(iii) What do you understand by the term "positive deviation from Raoults Law? Illustrate with a relevant graph.

(30 marks)

6. (a) (i) Consider the following mechanism, which is used to describe the decomposition of a gaseous molecule, A.

$$A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + A$$

$$A^* \xrightarrow{k_2} \text{Products}$$

Write down the rate expression for the rate of formation of A^*, $\dfrac{d[A^*]}{dt}$.

[Question 6 is continued in the next page]

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

Derive the expression, $[A]=[A_o]e^{-k_1 t}$ where $[A]$ is the concentration of A at time t and $[A_o]$ is the initial concentration of A.

(22 marks)

(b) (i) **Write down** the exponential form of the Arhennious Equation and identify, clearly, all the symbols used.

(ii) **Write down** the corresponding logarithmic form of the above equation and indicate the condition under which this equation can represent a straight line.

(18 marks)

(c) The following values were reported from an experiment that involved application of Arhennious equation.

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

(i) Carry out an **appropriate tabulation** of data required to plot a suitable graph.

(ii) Assuming that a linear relationship exists under the assumed conditions, calculate the gradient and intercept using any two data points.

(36 marks)

(d) A reaction of the form $A \rightarrow P$, is suspected to be either first order or second order. In order to verify and confirm the order of this reaction, a student carried out an experiment and reported the following values.

Half life $(t_{1/2}) \times 10^{-2}/\text{s}$	Initial Concentration $a/(\text{mol dm}^{-3})$
53.8	3.0
81.0	2.0
161.7	1.0

(i) Is this a first order or second order reaction? With the aid of relevant mathematical expressions for both cases, clearly explain your choice.

(ii) Determine the rate constant of this reaction.

(24 marks)

The End