00420

THE OPENUNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 4

Final Examination — 2015/2016

CMU 2220/ CME 4220— Concepts in Chemistry

(3 hours)

18th January 2017 (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.

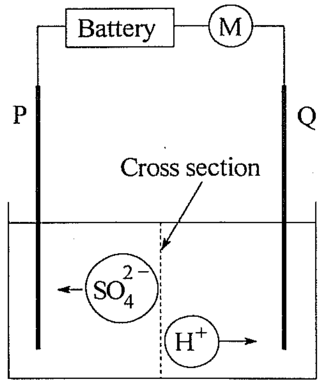
$\log(\gamma_{\pm}) = -A Z_+ |Z_-| \sqrt{I}$, $E_J = BJ(J+1)$, $N_j = N_i\left(\frac{g_j}{g_i}\right)\exp\left(-\frac{E_j - E_i}{kT}\right)$, $\bar{\nu} = 2\bar{B}(J+1)$

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

$j_B = v_B c_B |Z_B| F$ $\Lambda_Y = \frac{\kappa_Y}{C_Y}$ $\lambda_B = \frac{\kappa_B}{c_B}$ $\mu^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos(\theta)$

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

(a) A student electrolysed a dilute solution of sulphuric acid using two platinum rods, P and Q, a battery and an ammeter, M, for 500 s (see the figure). The ammeter reading remained constant at 2.3 A throughout the experiment. The direction of movement of the sulphate and hydrogen ions during the experiment are shown in the figure. The transport numbers of the sulphate and hydrogen ions in this solution are 0.4 and 0.6, respectively.



(i) Giving reasons state the magnitude of the current through the solution.

(ii) Calculate the (positive) charge delivered by the battery during the experiment.

(iii) Calculate the charge carried by each of the ions, sulphate and hydrogen, through a cross section of the solution between P and Q.

(iv) Giving reasons identify the anode and cathode out of P and Q.

(v) Write down the anode and cathode reactions.

(50 marks)

(b) A student prepared a solution by dissolving 0.25 mol of sodium chloride in one litre of 0.75 mol dm^{-3} aqueous acetic acid in solution. The degree of dissociation of acetic acid in this solution is 0.5. The molar conductivities of $Na^+(aq)$, $Cl^-(aq)$, $H^+(aq)$ and $CH_3COO^-(aq)$, in units of $S\ m^2\ mol^{-1}$, are , 45.0×10^{-4}, 70.0×10^{-4}, 345.0×10^{-4} and 35.0×10^{-4}, respectively.

(i) Write down the relationship between the conductivity and molar conductivity of an ionic species in a solution and identify all the parameters in it.

(ii) Calculate the molar conductivity of acetic acid the above mentioned solution.

(iii) Calculate the conductivity of the above mentioned solution.
State assumption/s, if any, you make in this calculation.

(50 marks)

(c) Calcium fluoride (CaF_2) is a sparingly soluble salt which behaves as a strong electrolyte in aqueous medium. At $25^\circ C$ the conductivity due to CaF_2 in a saturated solution is $4.67\times10^{-3}\ S\ m^{-1}$. At $25^\circ C$ the limiting molar conductivities of $Ca^{2+}(aq)$ and $F^-(aq)$, in units of $S\ m^2\ mol^{-1}$, are 118.0×10^{-4} and 55.0×10^{-4}, respectively.

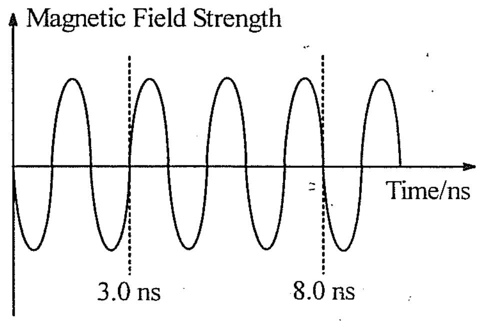
(i) Write down the relationship between the solubility product of CaF_2 and the concentrations of $Ca^{2+}(aq)$ and $F^-(aq)$ in a saturated solution of CaF_2 and identify all the parameters in it.

(ii) Write down a relationship between the molar conductivity of CaF_2 and conductivity in a solution, and identify all the parameters in it.

(iii) Calculate the solubility product of CaF_2 at $25^\circ C$.
State assumption/s, if any, you make in this calculation.

(50 marks)

2. (a) The number density of photons in a beam of monochromatic electromagnetic radiation is $4.5\times10^{20}\ m^{-3}$. The variation (in time) of the magnetic field strength of the radiation in the beam is shown in the figure. As shown, the magnetic field strength is zero at 3.0 and 8.0 nanoseconds.



(i) Write down a relationship between the number density of photons in a beam and its intensity.
Identify all the parameters in it.

(ii) Calculate the intensity of the above mentioned beam of radiation.

(25 marks)

(b) A student was given two aqueous solutions, P and Q, of a pure compound X. He filled three identical cells with P, Q and distilled water used in preparing P and Q. Then he measured the absorbance of P and Q using a double beam absorption spectrometer (with monochromatic radiation of frequency ν, known to be absorbed by X) to be 0.3 and 0.7 respectively.

(i) Which solution out of P and Q has a higher concentration of X?
Briefly explain your answer.

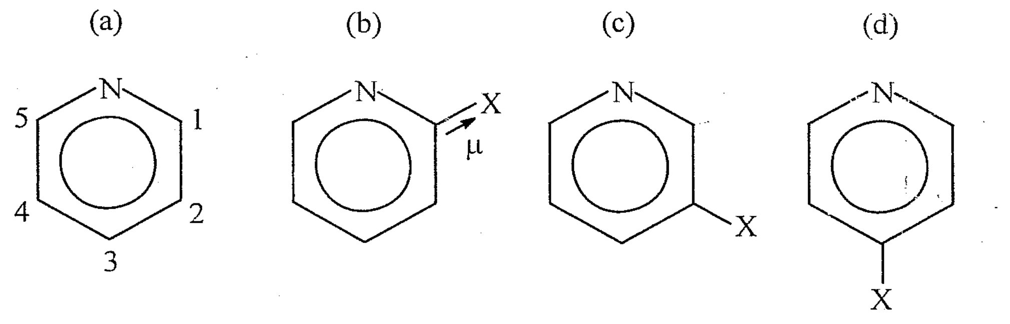
(ii) What will be the absorbance reading on the double beam spectrometer if the cell with Q is placed where the sample is placed and the cell with P is placed where the cell with distilled water is placed?
Briefly explain your answer.

(25 marks)

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

Part A:

Dipole moment of a pyridine molecule is 2.2 D and is on the line passing through the nitrogen nucleus and the carbon nucleus numbered as 3 in figure (a) below.



In addition to the dipole moment of pyridine, a dipole moment is created by X when attached to pyridine (where X is a functional group). This additional dipole moment, μ, (created by X) is 1.2 D and is along the C-X bond in the direction shown in figure (b). Assume that $C-C-X$ and $N-C-X$ bond angles in (b), (c) and (d) to be 120°. $\left[\cos(60^\circ)=\frac{1}{2},\ \sin(60^\circ)=\frac{\sqrt{3}}{2},\ \cos(120^\circ)=-\frac{1}{2},\ \sin(120^\circ)=\frac{\sqrt{3}}{2}\right]$

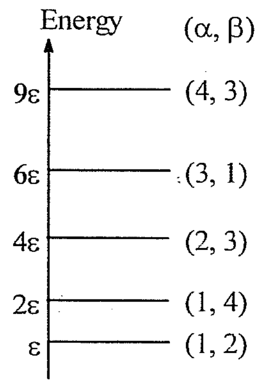
(i) Draw the structure shown in figure (a) on your answer sheet and indicate direction of the dipole moment of pyridine on it.

(ii) Calculate the dipole moment of molecules shown in figures (b), (c) and (d).

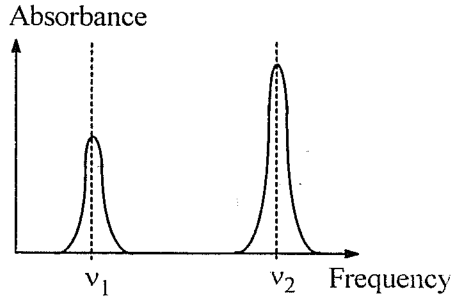
(50 marks)

Part B:

Consider a molecule having only five energy levels which are identified by two quantum numbers, (α, β), which are indicated in figure (a) below. The selection rules in absorption spectroscopy of the molecule are $\Delta\alpha = 0, \pm1$ and $\Delta\beta = \pm2$. The **full** absorption spectrum of this molecule is shown in figure (b).



(a)



(b)

(i) According to the selection rules, the **maximum** number of lines one may observe in the absorption spectrum of a sample of these molecules is three. Indicate them, in the usual form, using the quantum numbers of the upper and lower energy levels involved. $\left[\text{i.e. } (\alpha_1, \beta_1) \rightarrow (\alpha_2, \beta_2)\right]$

(ii) Giving reasons, determine the possible sets of values, i.e. (ν_1, ν_2), of the absorption frequencies, ν_1 and ν_2, in terms of ε.

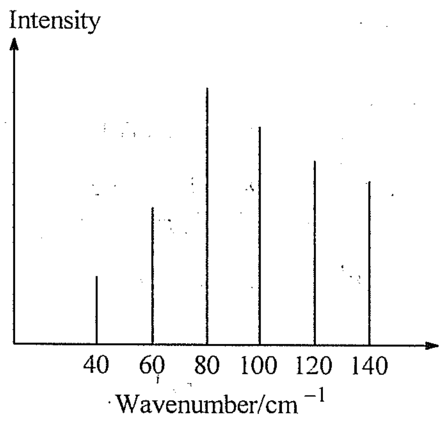
(50 marks)

3. (a) Part of the microwave spectrum of a diatomic molecule, XY, recorded by a student, is shown in the figure. The relative atomic masses of X and Y are 1.0 and 35.0, respectively.

(i) Deduce whether XY behaves as a rigid rotor or non-rigid rotor.

(ii) Write down the relationship between the rotational constant (in wave number units) of XY and its bond length. Identify all the parameters in it.

(iii) Calculate the bond length of XY.



(50 marks)

[Question 3 is continued in the next page]

(b) (i) Consider a two component **open** system containing n_1 moles of component 1 and n_2 moles of component 2. The pressure of the system is P, Volume V and temperature T.

(α) If the infinitesimal change, dG, in free energy G of the system can be written as,

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2} dP + \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2} dT + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2} dn_1 + \mathbf{Y}$$

Write down an appropriate expression for the quantity **"Y"** in the above equation.

(β) Deduce the relevant expression for dG if it was a **closed** system.

(γ) The quantity $\left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2}$ which appears in the above equation is given two names in thermodynamics. Write down these two names.

(δ) Indicate whether the quantity given in (γ) is an intensive or extensive thermodynamic property.

(20 marks)

(ii) (α) State what is meant by a colligative property and give <u>four</u> common types of colligative properties.

(β) Identify the symbols used in the following equation (related to colligative properties).

$$\Delta T = \frac{RT_0^2}{\Delta H_m} y.$$

(iii) Pure benzene freezes at $5.4°C$ and a solution of 0.2g of a compound A in 7.8g of benzene freezes at $4.4°C$. The enthalpy of fusion of benzene is $8.314\ kJ\ mol^{-1}$. (Relative atomic masses: H = 1, C = 12, O = 16). Calculate the apparent relative molecular mass of compound A.

(30 marks)

4. Answer either **<u>Part A</u>** OR **<u>Part B</u>** (but **NOT** both).

<u>Part A:</u>

(a) The Clapeyron equation is given as, $\frac{dP}{dT} = \frac{\Delta H}{T\,\Delta V}$.

(i) To what type of systems and under which conditions will the Clapeyron equation apply.

(ii) Using the Clapeyron equation, derive the Clausius-Clapeyron equation. State the assumptions used in deriving this equation.

(iii) An organic compound has a vapour pressure of 10 kPa at 200K and 100 kPa at 400K. Calculate the molar enthalpy change of vaporisation of the compound.

(50 marks)

[Question 4 is continued in the next page]

(b) Given the two fundamental thermodynamic equations, $dG = V\,dP - S\,dT$ and $dA = -P\,dV - S\,dT$.

(i) Write down the corresponding Maxwell relationships.

(ii) Derive the volume and temperature coefficients of A at constant temperature and volume respectively.

(20 marks)

(c) (i) Complete the Gibbs-Helmholtz equation written in the form, $\left[\dfrac{\partial\left(\Delta G^0/T\right)}{\partial T}\right]_P$.

(ii) Deduce the variation of equilibrium constant K with temperature using Gibbs-Helmholtz equation.

(30 marks)

Part B:

(a) Derive the fundamental thermodynamic equation, $dA = -P\,dV - S\,dT$ starting from the first law of thermodynamics. Indicate the conditions applicable in deriving this equation.

(30 marks)

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

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

(20 marks)

(c) The partial molar volumes of ethanol and water are $56\ cm^3\ mol^{-1}$ and $18\ cm^3\ mol^{-1}$ respectively. Calculate the total volume of a mixture of 50 g of ethanol and 50 g water at $25^\circ C$. (Relative atomic masses: C= 12, H = 1, O = 16)

(30 marks)

(d) The equilibrium constant for the reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ at $25^\circ C$ is 5.8×10^5. For this reaction, calculate,

(i) the Gibbs free energy change at equilibrium and

(ii) the standard Gibbs free energy change.

(20 marks)

5. (a) A kinetic experiment was carried out and the following data were reported with respect to a reaction of the form, $A \rightarrow P$.

temp/$^\circ C$	27	37
$k \times 10^5 / mol^{-1}\ dm^3\ s^{-1}$	1.00	2.50

(i) Write down the logarithmic form of the Arhennious Equation that relates rate constant (k) to the activation energy (E_a) and absolute temperature (T/K).

(ii) State the condition/s under which the above expression can be considered as a linear equation.

(iii) **Calculate the** activation energy using the expression in (i).

(24 marks)

[Question 5 is continued in the next page]

(b) The hydrolysis reaction between a certain ester (an alkyl acetate) and sodium hydroxide is found to be first order with respect to each of the reactants and, the rate constant for this reaction is reported to be 2.5×10^{2} mol^{-1} m^{3} s^{-1} at 300 K.

(i) Write down the chemical equation for the above hydrolysis reaction.

(ii) Write down the general rate expression for this reaction, assuming that the initial concentrations of both the reactants are same and equal to "b" mol dm^{-3} and that the concentration of the ester reacted at any time, t, is "x" mol dm^{-3}.

(iii) Hence, derive the integrated form of the above expression.

(32 marks)

(c) In carrying out the kinetic experiment in (b), you have been asked to mix $20.00\ cm^{3}$ of the ester (relative molar mass, 90, density $= 900.0\ kg\ m^{-3}$ at 300 K) with distilled water and $2.0\ mol\ dm^{-3}$ NaOH such that the total volume is $250.0\ cm^{3}$ and, that the concentration of NaOH is equal to that of the ester in the reaction mixture. [Relative atomic masses: Na = 23; H= 1.0; C = 12.0; O = 16.0]

(i) Determine the initial concentration of ester in the reaction mixture.

(ii) Calculate the volume of $2.0\ mol\ dm^{-3}$ NaOH that you are expected to add.

(20 marks)

(d) The decomposition of a gaseous molecule, **A**, is said to be a two-step reaction as shown below.

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

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

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

(ii) Show that $-\dfrac{d[A]}{dt} = \dfrac{k_1[A]^2}{1+\dfrac{k_{-1}}{k_1}[A]}$ under steady state conditions.

(24 marks)

6. (a) What do you understand by the following terms?

(i) Intensive variable.

(ii) Positive deviation from Raoults Law.

(iii) An Azeotrope

(18 marks)

(b) (i) What do you understand by the term "eutectic composition" with respect to a binary system?
Why is an eutectic point considered as invariant?

(ii) Metal A $(M.Pt = 700\ ^{\circ}C)$ and Metal B $(M.Pt = 1200\ ^{\circ}C)$ form two compounds, at elevated temperatures, of formula A_2B and AB_2 with congruent M. Pt's $600^{\circ}C$ and $800^{\circ}C$ respectively.
Sketch a fully labelled phase diagram indicating all relevant regions, curves and points including the possible eutectic/s for the above system

[Question 6 is continued in the next page]

(iii) Sketch a cooling curve corresponding to a melt that represents

(α) an eutectic composition

(β) one of the compounds formed

(γ) any other mixture that **does not** correspond to a compound formed or an eutectic

Apply phase rule to explain the shape of the cooling curves in (α) and (γ)
(You may refer to the phase diagram you have drawn in b (ii) above in this regard)

(52 marks)

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

Part A:

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

(ii) $20.00\ cm^3$ of a liquid A (relative molar mass, 90, density $= 900.0\ kg\ m^{-3}$) is mixed with $25.00\ g$ of a liquid B (relative molar mass = 125) at room temperature. Assuming that this binary system is fully miscible, calculate the mole fraction of A in the solution.

(iii) Considering the above solution to be ideal and that the vapour pressure of pure A and pure B are 90 torr and 45 torr respectively, calculate the total vapour pressure of the mixture at this temperature and the corresponding composition of the vapour at this temperature.
[Assume that the formation of the vapour phase does not alter the composition of the liquid phase.]

(30 marks)

Part B:

(i) Molality is defined as the number of moles of solute per kilogram of solvent. Given that the molality of an aqueous solution of acetic acid is $5.0\ mol\ kg^{-1}$ 5.0, calculate

(α) the mole fraction of water in this solution

(β) the concentration of acetic acid assuming the density of the solution as $1.3\ g\ cm^{-3}$. [Relative atomic masses: C=12.0; O = 16.0; H = 1.0]

(ii) Define the term "Lower Critical Temperature" for a pair of partially miscible liquids, A and B. and, sketch a clearly labelled solubility curve for the above system.

(30 marks)

The End