00177

THE OPENUNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 4

Final Examination — 2017/2018

CMU 2220/ CME 4220— Concepts in Chemistry

(3 hours)

8th April 2019 (Monday) 9.30 a.m. — 12.30 p.m.

- There are six (06) questions and nine (09) 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)	=	$8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}$
Avogadro constant (N_A)	=	$6.023\times10^{23}\ \mathrm{mol^{-1}}$
Faraday constant (F)	=	$96,500\ \mathrm{C\,mol^{-1}}$
Planck constant (h)	=	$6.63\times10^{-34}\ \mathrm{J\,s}$
Velocity of light (c)	=	$3.0\times10^{8}\ \mathrm{m\,s^{-1}}$
Standard pressure	=	$10^5\ \mathrm{Pa}\left(\mathrm{N\,m^{-2}}\right)$ = 1 bar
Protonic charge (e)	=	$1.602177\times10^{-19}\ \mathrm{C}$
π	=	3.14159
$\mathrm{Log}_e(X)$	=	$2.303\ \mathrm{Log}_{10}(X)$

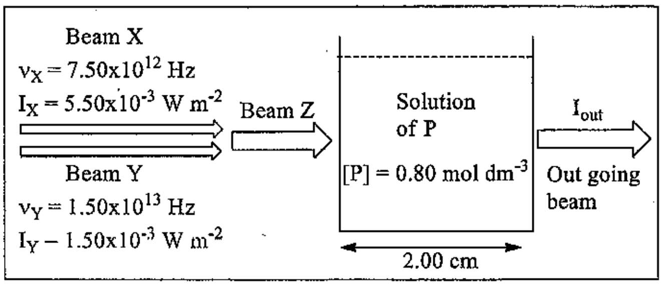
Some equations used in chemistry are given below using standard notation.

$\log(\gamma_\pm) = -A Z_+ |Z_-| \sqrt{I}$, $\quad E_J = BJ(J+1)$, $\quad \bar{B} = \dfrac{h}{8\pi^2 \mu R^2 c}$, $\quad \bar{\nu} = 2\bar{B}(J+1)$,

$\rho = \dfrac{I}{h\nu c}$, $\quad u = \dfrac{xa\kappa}{Q}$ $\quad \lambda_B = u_B|Z_B|F$, $\quad v_B = u_B E$, $\quad j = \kappa E$ $\quad A = \varepsilon C l$,

$j_B = v_B c_B |Z_B| F$, $\quad \Lambda_Y = \dfrac{\kappa_Y}{C_Y}$, $\quad \lambda_B = \dfrac{\kappa_B}{c_B}$, $\quad \kappa_B = u_B c_B |Z_B| F$.

1. (a) A student merged two (parallel) beams, X and Y, of electromagnetic radiation to obtain a (parallel) beam Z. She passed Z through a sample of an aqueous solution of a salt, P, and measured the intensity, I_{out}, of the outgoing beam. See the figure.



The frequencies of the radiation in beams X and Y were 7.50×10^{12} Hz and 1.50×10^{13} Hz, respectively. The intensities of them were 5.50×10^{-3} W m^{-2} and 1.50×10^{-3} W m^{-2}, respectively. Concentration of P was 0.80 mol dm^{-3}. The path length of the cell used was 2.00 cm. Molar extinction coefficient of P at radiation frequency 7.50×10^{12} Hz, is 0.50 mol^{-1} dm^3 cm^{-1}.

It is known that P absorbs only the photons with frequency 7.50×10^{12} Hz. None of the other chemicals in the sample absorbed photons from beam Z.

(i) Write down the relationship between intensity of a monochromatic beam of radiation and number density of photons in it and identify all the terms in it.

(ii) Write down Beer-Lambert law and identify all the terms in it.

(iii) Calculate the number density of photons in beam Z.

(iv) Calculate the intensity, I_{out}, of the outgoing beam.

(50 marks)

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

Part A:

(i) Define the following terms as applied in molecular spectroscopy

(α) Gross selection rule

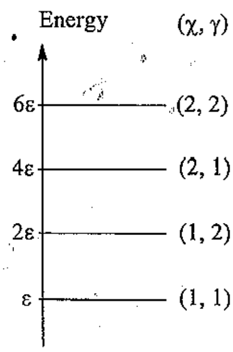
(β) Specific selection rule.

(γ) Stimulated emission.

(δ) Life time broadening.

(20 marks)

(ii) A (hypothetical) molecule has only four energy levels at energies, ε, 2ε, 4ε and 6ε. They are labelled by two quantum numbers, (χ, γ). The energies and the values of quantum numbers are shown in the figure. The specific selection rules in absorption spectroscopy of the molecule are $\Delta\chi = +1$ and $\Delta\gamma = \pm 1$.



(α) Deduce the maximum number of lines that can appear in the absorption spectrum of the molecule.
Indicate the corresponding energy level transition/s in standard form (as $(\chi_1, \gamma_1) \rightarrow (\chi_2, \gamma_2)$).

(β) Calculate the frequencies of the lines that can appear in the absorption spectrum if $\varepsilon = 2.1 \times 10^{-21}$ J.

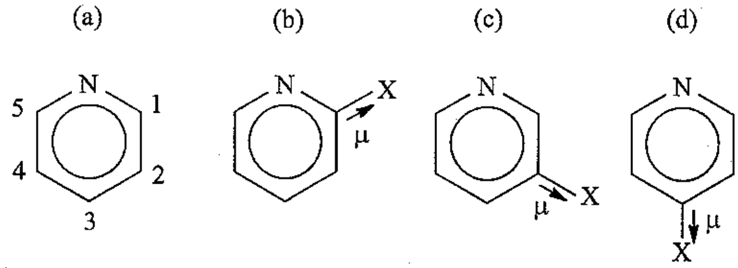
(30 marks)

Part B:

(i) State the importance of the *transition dipole moment* in molecular spectroscopy.

(10 marks)

(ii) 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 figures (b), (c) and (d). Assume that $C-C-X$ and $N-C-X$ bond angles in (b), (c) and (d) to be $120°$.

$$\left[\cos(60°)=\frac{1}{2},\ \ \sin(60°)=\frac{\sqrt{3}}{2},\ \ \cos(120°)=-\frac{1}{2},\ \ \sin(120°)=\frac{\sqrt{3}}{2}\right]$$

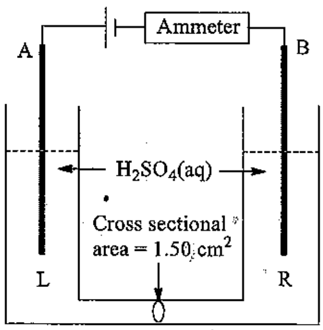
(α) Draw the structure shown in figure (a) and indicate the direction of the dipole moment of pyridine on it.

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

(40 marks)

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

(a) A student electrolysed an aqueous solution of H_2SO_4 using two carbon electrodes, A and B. The apparatus had two chambers, L and R, which are connected by a tube having a cross sectional area of $1.50\ cm^2$; see the figure. The electric current measured by the ammeter was $3.00\ A$ and remained constant throughout the experiment. The transport number of H^+ was 0.60. The concentration of H_2SO_4 was $0.80\ mol\ dm^{-3}$. Conductivity of the H_2SO_4 solution was $0.060\ S\,m^{-1}$.



(i) Giving reasons state the direction of the electric field within the connecting tube.

(ii) Giving reasons state the electric current in the connecting tube.

(iii) Calculate the following quantities within the connecting tube.

(α) Electric field strength.

(β) Current carried by H^+.

(γ) Rate of flow of H^+ in $mol\ s^{-1}$.

(50 marks)

(b) Consider a solution of the acidic salt, MHA of concentration $0.60\ \text{mol dm}^{-3}$. The salt dissociates fully according to $MHA \rightarrow M^{+} + HA^{-}$. However, HA^{-} dissociates only partially according to $HA^{-} \rightleftharpoons H^{+} + A^{2-}$. The degree of dissociation of HA^{-} in the solution is 0.50. In this solution the ionic mobilities, of H^{+}, M^{+}, HA^{-} and A^{2-}, in units of $m^2\ V^{-1}\ s^{-1}$, are 3.00×10^{-7}, 4.80×10^{-8}, 4.20×10^{-8} and 7.80×10^{-8}, respectively.

(i) Write down the relationship between the conductivity of MHA, κ_{MHA} and the conductivities of H^{+}, M^{+}, HA^{-} and A^{2-} (i.e. κ_{H^+}, κ_{M^+}, κ_{HA^-} and $\kappa_{A^{2-}}$).

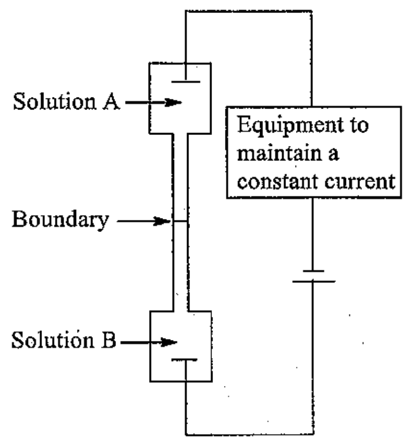
(ii) Write down the relationship between conductivity due to an ionic species and its ionic mobility and identify all the terms in it.

(iii) Write down the relationship between the molar conductivity of an electrolyte and its conductivity.

(iv) Calculate the molar conductivity of MHA in the solution.

(50 marks)

(c) The set up used by a student in measuring the ionic mobility of an ion, X^{2-}, in a $0.0200\ \text{mol dm}^{-3}$ aqueous solution of MX, at 25^0C, is shown in the figure. He used a solution of MY_2 as the following solution. For a current held constant at $1.600\ \text{mA}$, it was found that the boundary moved $0.100\ \text{m}$ in $3500\ \text{s}$, in the tube of average cross sectional area $1.200\times10^{-5}\ \text{m}^2$. The conductivity of the MX solution, at 25^0C, is $0.2400\ \text{S m}^{-1}$.



(i) Giving reasons identify solutions A and B.

(ii) Giving reasons state which solution, out of the solutions of MX and MY_2, has the higher density.

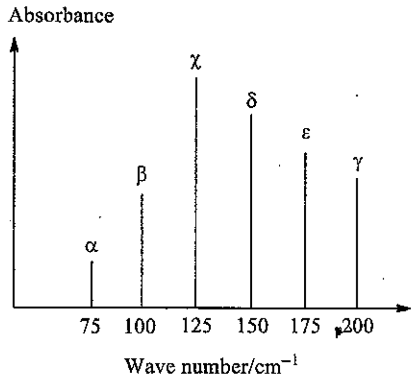
(iii) Giving reasons state which ion, out of X^{2-} and Y^{-}, has the higher ionic mobility.

(iv) Write down the equation used in calculating the ionic mobility in moving boundary experiment and identify all the parameters in it.

(v) Calculate the ionic mobility of X^{2-} in the solution of MX.

(50 marks)

3. (a) Part of the microwave spectrum of a rigid diatomic molecule, AB, obtained by a student, is shown in the figure. The reduced mass of AB is 1.614×10^{-27} kg.



(i) Starting with the expression for rotational energy levels of a rigid diatomic molecule and the section rule in microwave spectroscopy, derive $\bar{\nu} = 2\bar{B}(J+1)$.

(ii) Giving reasons state the rotational transition that creates line α in this spectrum.

(iii) Calculate the bond length of AB.

(50 marks)

(b) (i) State what is meant by univariant phase transformation. Give examples of the four common univariant phase transformations.

(ii) Write down the characteristic features of univariant systems

(iii) Write down the mathematical expression for entropy change in a univariant phase transformation.

(iv) Deduce the value of Gibbs free energy change for univariant phase transformation.

(24 marks)

(c) The temperature dependence of the vapour pressure of solid and liquid forms of a given compound X are given as follows;

For solid $\log_{10}(P/\text{torr}) = 12 - \dfrac{2500}{T/K}$

For liquid $\log_{10}(P/\text{torr}) = 6 - \dfrac{1800}{T/K}$

(i) What do you understand by the term "triple point of X"?

(ii) Deduce the temperature corresponding to the triple point of X.

(26 marks)

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

Part A:

(a) (i) Starting from the first and second laws of thermodynamics, derive the fundamental equation $dG = V\,dP - S\,dT$ for a reversible process in a closed system where no work other than PV work occurs.

(ii) Write down the Maxwell relationship that can be derived using the above equation.

(30 marks)

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

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

(20 marks)

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

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

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

(iii) $\Delta S = n\, C_{v,m} \ln(T) + n R \ln(V)$

(iv) $\Delta G = 0$

(20 marks)

(d) 1000 moles of a monatomic ideal gas $\left(C_{p,m} = 5R/2\right)$ are heated from $27°C$ to $327°C$ at constant pressure. Calculate ΔH and ΔS for this process.

(30 marks)

Part B:

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

(i) $\Delta A < 0$

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

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

(iv) $\ln(P) = -\Delta H / RT$ + constant

(20 marks)

(b) 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)

(c) The variation of the equilibrium constant K_{eq} of a reaction at a temperature T is given by the equation $\ln(K_{eq}) = 9.45 - \dfrac{490}{T/K}$. Calculate ΔG^0, ΔS^0 and ΔH^0 for this reaction at $60°C$.

(36 marks)

(d) 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.

(24 marks)

5. (a) The hydrolysis reaction between methyl acetate (an ester) and sodium hydroxide is found to be first order with respect to each of the reactants and, the rate constant (k) for this reaction is reported to be $1.0\times10^{-4}\ mol^{-1}\,m^3\,min^{-1}$ at 300 K.

(i) Determine the value of the rate constant in the units of $mol^{-1}\,dm^3\,s^{-1}$.

(ii) Given that $kt = \frac{x}{a(a-x)}$ is the integrated form of the rate equation, determine the time taken for concentration to reduce to $0.40\ mol\,dm^{-3}$ at 300 K if the initial concentration is $0.75\ mol\,dm^{-3}$.

(12 marks)

(b) It was reported that the rate constant [at $25^\circ C$] of a certain reaction doubled on increasing the temperature by $10^\circ C$. Apply the Arrhenius equation and calculate the value of the activation energy of this reaction.
What assumption/s do you make in this calculation?

(24 marks)

(c) $$\underset{A}{cis-MX_2Y_2^+} \rightleftharpoons \underset{B}{trans-MX_2Y_2^+}$$

The cis and trans forms of the complex $MX_2Y_2^+$ are said to exist in equilibrium as shown by the above reversible equation. The values for the rate constants, k_1 and k_2, (the respective rate constants in the forward and reverse directions), reported at $25^\circ C$, are $k_1 = 5.0\times10^{-6}\ min^{-1}$ and $k_2 = 4.0\times10^{-5}\ min^{-1}$.
An experiment commenced with the cis form of the above complex whose initial concentration, a, was $0.075\ mol\,dm^{-3}$. The equilibrium concentration of the trans isomer is symbolized by x_e. Considering this equilibrium to be first order in both directions,

(i) write down the expression for the equilibrium constant and hence derive an expression for $\frac{k_1}{k_2}$ in terms of the **equilibrium concentrations** of **A** and **B.**

(ii) determine the equilibrium concentration of the trans isomer.

(20 marks)

(d) Consider the following reaction scheme

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

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

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

$$2RCO \xrightarrow{k_4} RCOCOR$$

Applying the steady state approximation for the radical, R^*, show that the concentration of R^* can be expressed as $\left[R^*\right] = \frac{k_3[RCO] + k_1[RCHO]}{k_2[RCHO]}$.

(14 marks)

(e) (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./$^\circ C$	27	37	47	57	67
$k\times10^3/min^{-1}$	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)

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

(i) Extensive variable

(ii) Positive deviation from Raoults Law

(12 marks)

(b) Liquid A and liquid B form a fully miscible binary system at all compositions. At standard atmospheric pressure, liquid A and liquid B form a constant boiling mixture with the composition given by X_A [the mole fraction of A] equal to 0.6.

(i) Assuming the boiling point of A to be greater than that of B, sketch a clearly labelled temperature versus composition phase diagram.

(ii) If an equimolar mixture of A and B is subject to fractional distillation, discuss / explain briefly the outcome when compared with that of an ideal, binary solution.

(24 marks)

(c) The phase diagram for Mg-Cu at constant pressure shows that two compounds are formed: $MgCu_2$ and Mg_2Cu with congruent melting points of $800^\circ C$ and $600^\circ C$ respectively. The melting point of Cu is $1100^\circ C$ and that of Mg is $650^\circ C$.
The three eutectic compositions and temperatures are given below.

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) What is meant by a congruent melting point?

(ii) Why is a eutectic point considered as invariant?

(iii) Sketch a clearly labelled phase diagram based on the information given above; identify the relevant regions in terms of the phases present.

(iv) Sketch a cooling curve for the melt of composition corresponding to the compound $MgCu_2$. Illustrate the meaning of the term "Halt" with reference to the cooling curve you have drawn and the expected phase changes. Why is there no "Break" in this cooling curve?

(34 marks)

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

Part A:

(i) Sketch a clearly labelled solubility curve for a pair of partially miscible liquids that shows a "Lower Critical Temperature" (LCT).

(08 marks)

(ii) 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 weight of A in each layer (all relevant steps must be shown)

(12 marks)

(iii) It is reported that Cinnamaldehyde (B.Pt $246^{\circ}C$) is the aldehyde that gives cinnamon its flavor and odour and that the essential oil of cinnamon bark is about 90% cinnamaldehyde. Steam distillation is used to obtain nearly pure cinnamaldehyde.

What is the advantage in carrying out steam distillation in the above case?

(10 marks)

Part B:

117.0 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 $50\,kPa$ and $20\,kPa$. [Relative atomic masses: C = 12; H = 1]

(i) Write down the mathematical expression that defines Raoults law and identify all the symbols in it.

(ii) Derive an expression for the total pressure using Raoults law (in the form of a liner equation) for the above ideal binary mixture in terms of saturated vapour pressures and the mole fraction of benzene in the liquid phase (at a given temperature). Identify the variables, the gradient, and intercept in the expression that you derived.

(iii) Calculate the pressure at which this mixture begins to boil.

(iv) Calculate the mole fraction of benzene in the vapour phase.

(30 marks)

The END