The Open University of Sri Lanka
Faculty of Natural Sciences
B.Sc/ B. Ed Degree Programme

Department	: Chemistry
Level	: 04
Name of the Examination	: Final Examination
Course Code and Title	**: CMU2220 – Concepts in Chemistry**
Academic Year	: 2019/2020
Date	: 18th January 2020 (Saturday)
Time	: 9.30 a.m. – 12.30 p.m.
Duration	: 03 hours

1. Read all instructions carefully before answering the questions.
2. This question paper consists of **06** questions in **09** pages.
3. Answer **ALL 06** questions. All questions carry equal marks.
4. Answer for each question should commence from a new page.
5. Draw fully labelled diagrams where necessary.
6. Having any unauthorized documents/ mobile phones in your possession is a punishable offense.
7. Use blue or black ink to answer the questions.
8. Circle the number of the questions you answered in the front cover of your answer script.
9. Clearly state your index number in **ALL** pages of your answer script.

Some important universal constants are given below, in standard notation.

$R = 8.314\ JK^{-1}\,mol^{-1}$	$N_A = 6.023 \times 10^{23}\ mol^{-1}$	$F = 96{,}500\ C\,mol^{-1}$
$h = 6.63 \times 10^{-34}\ Js$	$c = 3.0 \times 10^{8}\ ms^{-1}$	$P_0 = 10^5\ Pa\left(N\,m^{-2}\right) = 1\ bar$
$e = 1.602177 \times 10^{-19}\ C$	$\pi = 3.14159$	$Log_e(X) = 2.303\ Log_{10}(X)$

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

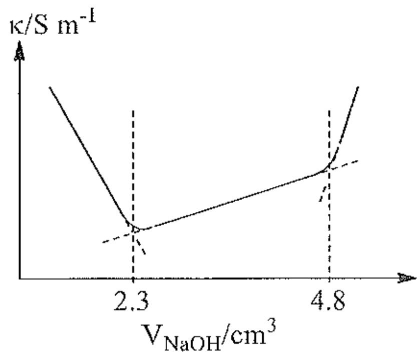
$\log(\gamma_\pm) = -A Z_+ |Z_-| \sqrt{I}$, $E_J = BJ(J+1)$, $J_{max} = \sqrt{\frac{kT}{2hc\bar{B}}} - \frac{1}{2}$, $\bar{\nu} = 2\bar{B}(J+1)$,

$v' = \frac{v}{1 \pm v/c}$, $u = \frac{x a \kappa}{Q}$ $\lambda_B = u_B |Z_B| F$, $v_B = u_B E$, $j = \kappa E$ $A = \varepsilon C l$,

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

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

(a) HA and HB are monobasic acids. HA is a **strong** acid while HB is a **weak** acid (with a very small dissociation constant). Using a standard solution of NaOH, a student performed a conductometric titration in determining the concentrations of HA and HB in a solution containing both acids. The figure shows the conductivity, κ, of the titration mixture versus volume of NaOH graph the student obtained in performing the titration of 25.0 cm^3 of the solution. The concentration of NaOH used was 1.0 mol dm^{-3}.



(i) State the assumption the student has to make in order to determine the concentrations of HA and HB.

(ii) Using the evidence gathered from the graph give a justification for the assumption you make.

(iii) Determine the concentrations of HA and HB in the above mentioned solution.

(50 marks)

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

(α) Conductivity of a solution.

(β) Molar conductivity of a chemical species in solution.

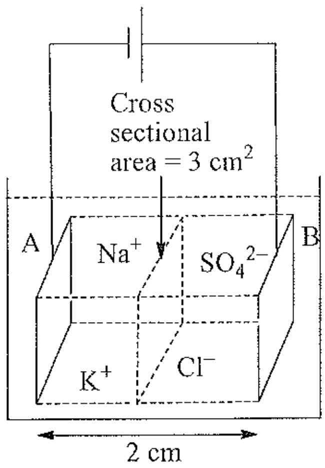
(γ) Transport number of an ionic species in a solution.

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

(iii) Calculate the total charge of sodium ions released to the solution when 1 mol of sodium phosphate (which is a strong electrolyte) is dissolved in $2\ dm^3$ of water.

(50 marks)

(c) 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 concentration of NaCl was $1.5\ mol\ dm^{-3}$. The time taken by an Na^+ ion to travel from A to B was 1000 s. The conductivity of the solution was $0.3\ S\ m^{-1}$. Assume that the current flows only within the cell of solution trapped between the plates and the cross sectional area of it is $3\ cm^2$. The current density is the same throughout the cross section.



(i) Define the ionic mobility of an ion.

(ii) Calculate the ionic mobility of Na^+.

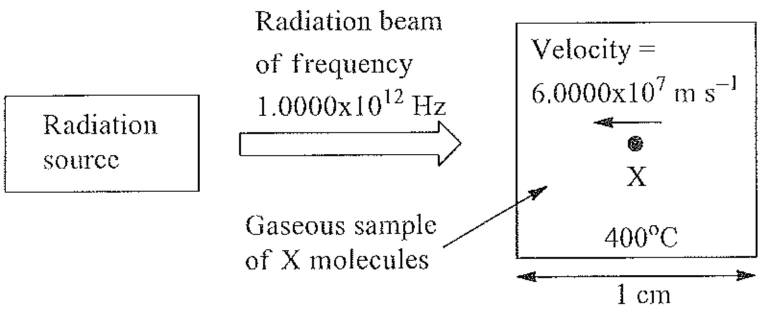
(iii) Calculate the transport number of Na^+.

(50 marks)

2. (a) Briefly describe what is meant by *Doppler broadening* in spectroscopy.

(20 marks)

(b) A molecule X has only two energy levels at $1.0000\times10^{-22}\ J$ and $9.2875\times10^{-22}\ J$. A gaseous sample of X at $400^{\circ}C$ is placed in a (parallel) beam of radiation of frequency $1.0000\times10^{12}\ Hz$ in a sample cell of path length 1 cm. Consider a molecule of X in the sample which is moving directly towards the radiation source at velocity $6.0000\times10^{7}\ ms^{-1}$; see the figure. Showing all the necessary calculations and identifying all the terms in any equation you use, deduce whether the above mentioned molecule can absorb a photon from the beam of radiation.



(30 marks)

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

Part A:

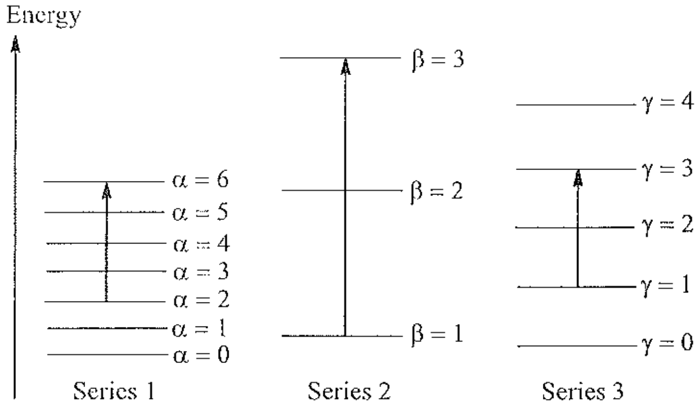
(i) Define the following terms as applied in molecular spectroscopy

(α) Stimulated absorption

(β) Transmittance (of a sample)

(10 marks)

(ii) You learned that the electronic, vibrational and rotational energies of a molecule are quantised separately (independently). In the figure, Series 1, 2 and 3, represent the first few energy levels in each of these energies (NOT in any particular order) of a diatomic molecule. α, β



and γ are the associated quantum numbers. The energy in the series 1, 2 and 3, in units of cm^{-1}, are given by $\bar{E}_1(\alpha) = 20.0\times\alpha(\alpha+1)$, $\bar{E}_2(\beta) = 20000.0\times\beta$ and $\bar{E}_3(\gamma) = 2000.0\times(\gamma+1/2)$, respectively. The parameters α, β and γ correspond to the respective quantum numbers.

(χ) Giving reasons, identify the three series as electronic, rotational and vibrational energies.

(δ) Giving reasons, state the most probable regions of the electromagnetic spectrum where the photons effecting the following transitions are located.

(I) $(\alpha = 0, \beta = 1, \gamma = 3) \rightarrow (\alpha = 0, \beta = 2, \gamma = 4)$

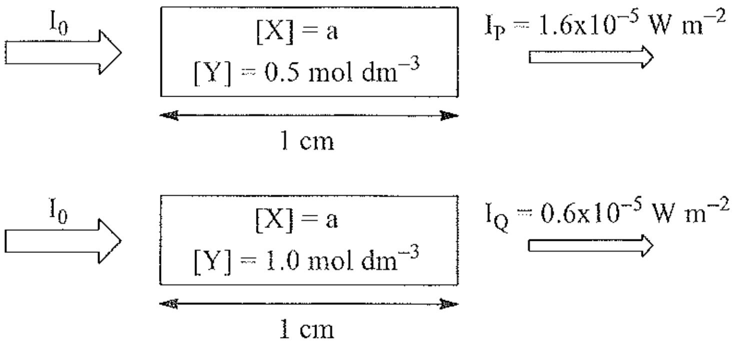
(II) $(\alpha = 0, \beta = 1, \gamma = 3) \rightarrow (\alpha = 1, \beta = 1, \gamma = 3)$

(λ) Calculate the energy required to bring about the mixed transition indicated in the figure, in units of cm^{-1}.

(40 marks)

Part B:

X and Y are two non-interacting chemical species. A student was given two solutions, P and Q, containing X and Y. The concentration of X was the same in P and Q. However, the concentration of Y in P and Q, in units of



mol dm^{-3}, were 0.5 and 1.0, respectively. The student placed samples of P and Q in a beam of monochromatic radiation and measured the intensities of outgoing radiation, I_P and I_Q, to be 1.6×10^{-5} W m^{-2} and 0.6×10^{-5} W m^{-2}, respectively. The student used the same sample cell with a path length of 1 cm. The intensity of the incoming radiation beam was the same for both samples. See the figure.

(i) Write down the Beer-Lambert law for absorbance of a sample of a solution having N number of non-interacting chemical species and identify all the parameters in it.

(ii) Using the equation in part (i) above, show that the absorbance of a sample is the sum of absorbance due to constituent chemicals species in it, when there is no interaction among them.

(iii) Calculate the molar extinction coefficient of Y.

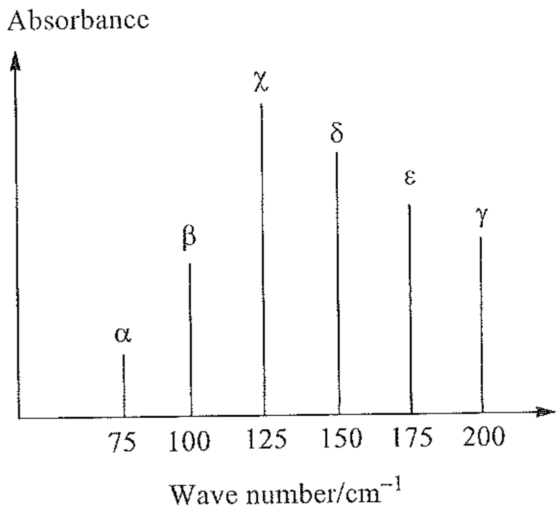
(50 marks)

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) Write down the four fundamental thermodynamic equations that can be applied to a reversible process in a closed system where no work other than PV work occurs.

(ii) Derive the Maxwell relationship using the above equations.

(30 marks)

(c) (i) Give the relationship between μ and G for a multicomponent system at constant T and P.

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

(20 marks)

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

Part A:

(a) (i) Write down the mathematical expression of the Clapeyron equation. Indicate to what type of system and under what conditions it is applicable.

(ii) Deduce the Clausius – Clapeyron equation starting from $\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$, indicating the assumptions made.

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

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

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

Deduce the temperature corresponding to the triple point of "A". State any assumptions you make.

(50 marks)

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

(i) Under what conditions and to what type of system, if any, can the following thermodynamically deducible equations/inequalities apply?

(α) $\Delta G < 0$

(β) $\Delta S = \frac{\Delta H}{T}$

(γ) $dG = V\,dp - S\,dT$

(δ) $\Delta S = n\,C_{V,m}\ln(T) + nR\ln(V)$

(λ) $\Delta T = K_{1000}\,m$

(ii) Calculate the equilibrium constant (K_P) at 300K, for the reaction,

$K(g) + L(g) \rightarrow M(g) + N(g)$.

Following data are given at 300 K:

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

(50 marks)

Part B:

(a) (i) Give the relationship between μ and G for a multicomponent system at constant T and P.

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

(20 marks)

(b) (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 300K. Calculate the change in Helmholtz free energy, ΔA.

(30 marks)

(c) Under what conditions and to what type of system, if any, can the following thermodynamically deducible equations/inequalities apply?

(i) $\Delta A < 0$

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

(iii) $dG = 0$

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

(20 marks)

(d) (i) Write down the relationship between standard Gibbs free energy change and equilibrium constant of a reaction.

(ii) If the variation of K_P of a reaction at the temperature T is given by the equation, $\ln(K_P) = 15.00 - \frac{600}{T/K}$, calculate ΔG^0, ΔH^0 and ΔS^0 for this reaction at $27°C$.

(30 marks)

5. (a) Write down the expression for the Arhennius equation and, clearly identify all the symbols used.

(08 marks)

(b) A bottle of milk stored at $27°C$ sours in **2 days** whilst that stored in a refrigerator at $2°C$ soured in **8 days**. Assuming that the rate of souring (R) is related to the absolute temperature (T/K) and time, t (in days) by the equation, $R = \frac{k}{t}\exp\left(-\frac{5\times10^3}{T}\right)$

determine the value of $\frac{R_1}{R_2}$ where R_1 and R_2 are the rate of souring at $27°C$ and $2°C$, respectively, and k is a constant in the above temperature range.

(18 marks)

(c) Consider a first order elementary reaction of the form $A \rightarrow P$.

(i) Write down the rate equation using the standard symbols and hence, derive the integrated form, expressing time, t, as a function of the amount of A reacted, x $[\text{i.e. } t = f(x)]$.

(ii) A drug is known to be ineffective when it has undergone 30% decomposition. A sample of this drug whose original concentration is given as 500 units/ml was analysed after 20 months; it was found to have a concentration of 420 units/ml. Assuming that this decomposition follows **first order kinetics**, calculate the expiration time of this drug and its half-life.

(32 marks)

(d) Illustrate the meaning of the term Steady State Assumption (SSA) by sketching the rate versus time graph for an intermediate in a chain reaction.

(06 marks)

(e) Consider a consecutive, irreversible first order reaction of the form

$A \xrightarrow{k_1} B \xrightarrow{k_2} C$ where the rate constants, $k_1 \neq k_2 \neq 0$.

Write down the rate equation with respect to the intermediate B.

(06 marks)

(f) 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 for this reaction is reported to be $1.0\times10^{-4}\ \text{mol}^{-1}\ \text{m}^{3}\ \text{min}^{-1}$ at 300 K.

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

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

(iii) In carrying out a kinetic experiment involving the above reaction at 300 K, you have been asked to mix $10.00\ \text{cm}^{3}$ of the ester (density $0.9\ \text{g}\,\text{cm}^{-3}$ at 300 K) with distilled water and NaOH such that the total volume is $100.0\ \text{cm}^{3}$.
Calculate the initial concentration of ester in the reaction mixture.
[Relative atomic masses: H= 1.0; C = 12.0; O = 16.0]

(30 marks)

6. (a) Sketch a clearly labelled **Pressure vs Temperature** phase diagram for water; identify the Triple Point in your diagram.

Apply the phase rule to the Triple Point and determine the number of degrees of freedom

(18 marks)

(b) (i) One (1) dm^{3} of a homogeneous solution consisting of three components, A, B and C, is prepared such that the molar concentrations of B and C are equal to twice that of A. Determine the mole fraction of A.

(ii) 100.0 ml of a mixture of two substances X and Y is prepared such that the concentration is 0.6 M in Y. The mole fraction of X is reported as 1/3. Determine the concentration of X.

(20 marks)

(c) Consider a binary mixture of two liquids A and B which are miscible in all proportions and where the boiling point of A is greater than that of B.

(i) Assuming that A and B form an ideal solution, sketch a **clearly labelled** temperature (boiling point) versus composition phase diagram.

(ii) Assuming that A and B form a non-ideal solution with a boiling point maximum, sketch a **clearly labelled** temperature (boiling point) versus composition phase diagram. The azeotropic composition is given as 35% A (mole percent) with a boiling point of 205°C.

(iii) If an equimolar mixture of A and B, corresponding to the system in (ii) above, is subject to fractional distillation, discuss/explain briefly the outcome when compared with that of a similar process in system (i) above [you may refer to the respective phase diagrams in (i) and (ii)].

(32 marks)

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

Part A:

(i) Write down the mathematical expression that represents Raoults law for an ideal solution and identify clearly the symbols used.

(ii) Two liquids, 53.0 g of ethylbenzene (X) and 84.0 g of a compound Y were mixed together to form an ideal solution at room temperature. The mole fraction of X in this mixture is 0.25. The vapour pressures of pure ethylbenzene is 40 torr and the total vapour pressure of this mixture is 42 torr. With the aid of the relevant laws and mathematical expressions calculate the following.
[Relative atomic masses: H =1.0. C = 12.0; O = 16.0]

(α) The molar mass of Y.

(β) The saturated vapour pressure of Y at this temperature.

(γ) The mole fraction of X in the vapour phase at this temperature.

(30 marks)

Part B:

Two metals A and B (melting point of A being greater than that of B) are said to form a simple eutectic system at elevated temperatures. The eutectic composition is found to be at $X_A = 0.4$ (X_A is the mole fraction of A).

(i) What do you understand by the term "eutectic composition"?

(ii) Sketch a fully labelled phase diagram for the above system.

(iii) The cooling curve corresponding to the melt of the eutectic composition has the shape similar to that of the cooling curves of pure A and B. Sketch the expected shape. Explain the expected shape with reference to the sketch of the cooling curve and the phase rule.

(30 marks)

The END