00246

THE OPENUNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 4

Final Examination — 2014/2015

CMU 2220/ CME 4220— Concepts in Chemistry

(3 hours)

30th October 2015 (Friday)	9.30 a.m. — 12.30 p.m.

- There are six (06)questions and seven (07) 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)	=	$8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$
Avogadro constant (N_A)	=	$6.023\times10^{23}\ \text{mol}^{-1}$
Faraday constant (F)	=	$96{,}500\ \text{C mol}^{-1}$
Planck constant (h)	=	$6.63\times10^{-34}\ \text{J s}$
Velocity of light (c)	=	$3.0\times10^{8}\ \text{m s}^{-1}$
Standard atmospheric pressure	=	$10^5\ \text{Pa}\left(\text{N m}^{-2}\right)$
Protonic charge (e)	=	$1.602177\times10^{-19}\ \text{C}$
π	=	3.14159
$\text{Log}_e(X)$	=	$2.303\ \text{Log}_{10}(X)$

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

(a) In an experiment a student determined the molar conductivity of an aqueous ammonium hydroxide solution at $25^{\circ}C$ and 1 bar to be $0.0123\ S\,m^2\,mol^{-1}$.

$$\left[\text{At } 25^{\circ}C:\ u^0_{OH^-} = 2.0\times10^{-7}\ m^2\ V^{-1}\ s^{-1} \text{ and } u^0_{NH_4^+} = 7.6\times10^{-8}\ m^2\ V^{-1}\ s^{-1}\right]$$

(i) Write down a relationship between the molar conductivity due to an ionic species in solution and its ionic mobility. Identify all the parameters in the relationship you have written.

(ii) Write down a relationship between the molar conductivity of ammonium hydroxide in solution and its degree of dissociation. Identify all the parameters in the relationship you have written.

(iii) Calculate the degree of dissociation of ammonium hydroxide in the above mentioned solution. State any assumption/s you make.

(50 marks)

(b) A student performed an electrolysis experiment of an alcoholic solution of an electrolyte. The only ions present in the solution were X^{2-} and Y^{3+}. During the experiment he found out that 3.5×10^{-5} mol of X^{2-} passed through a cross section of the solution between the electrodes in 2s. In the same time interval, 2.0×10^{-5} mol of Y^{3+} passed through the same cross section in the opposite direction.

(i) Calculate the total electric current that passed through the cross section.

(ii) Calculate the transport numbers of X^{2-} and Y^{3+}.

(50 marks)

(c) A student prepared a $0.02\ mol\ dm^{-3}$ aqueous solution of $Mg(NO_3)_2$ and labelled it as A. The conductivity of the solution and the transport number of Mg^{2+} in solution A were found to be κ and $t_{Mg^{2+}}$, respectively. In another solution of $Mg(NO_3)_2$ (labelled as B) with some impurities, he found the transport number of Mg^{2+} to be the same as above $\left(\text{i.e. } t_{Mg^{2+}}\right)$. The conductivity of solution B was found to be $1.2\ \kappa$.

(i) Write down a relationship between the conductivity due to an ionic species in solution and its molar concentration. Identify all the parameters in the relationship you have written.

(ii) Write down a relationship between the conductivity due to an ionic species in solution and its transport number in that solution. Identify all the parameters in the relationship you have written.

(iii) Calculate the concentration of Mg^{2+} in the solution B assuming the ionic mobility of Mg^{2+} to be the same in the two solutions, A and B.

(50 marks)

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

Part A:

A student measured the absorbance of a chemical in a solution using a single beam spectrometer at wavelength 10 nm to be 0.5. He observed that the number of photons crossing an area of 2.0 cm^2 within 3 s is 1.25×10^{12} in the beam of radiation. The cross section of the solution (in the sample cell) exposed to the beam of radiation is 1.0 cm^2.

(i) Write down a relationship between the number of photons crossing a unit area of a beam of radiation in unit time and its intensity. Identify all the parameters in it.

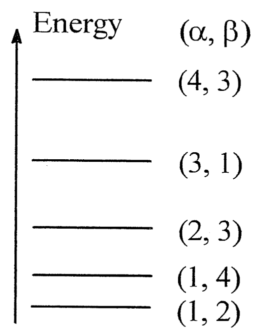
(ii) Calculate the intensity of the radiation beam used in the spectrometer.

(iii) Calculate the rate of absorption of radiation energy by the chemical in the solution in units of J s^{-1}.

(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 the figure to the right. The selection rules in absorption spectroscopy of the molecule are $\Delta\alpha = 0, \pm 1$ and $\Delta\beta = \pm 2$. A student observed only two lines when he recorded the absorption spectrum of a sample of these molecules using a double beam spectrometer.

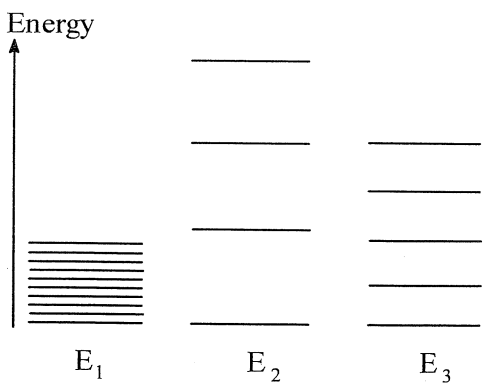


(i) State the **maximum** number of lines one may observe in the absorption spectrum of a sample of these molecules and indicate them, in the usual form, using the quantum numbers of the upper and lower energy levels involved $\left[\text{i.e. } (\alpha_1, \beta_1) \rightarrow (\alpha_2, \beta_2)\right]$

(ii) State **three** (03) possible reasons for the difference between the number of lines the student observed and your answer to part (i) above.

(50 marks)

(b) Pure electronic, pure vibrational and pure rotational energy levels of a molecule are schematically represented in the figure to the right.



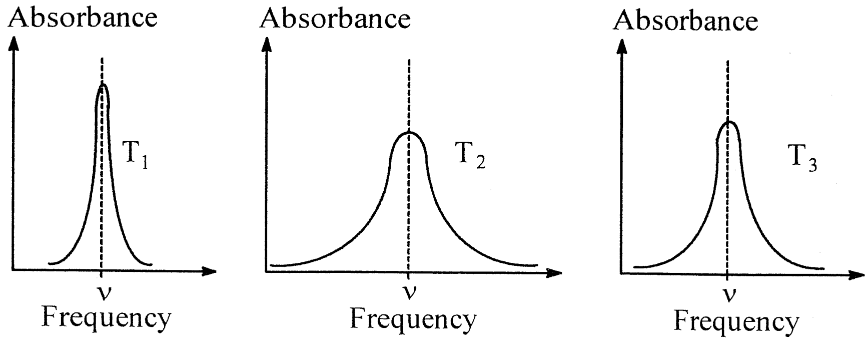
(i) Giving reasons identify the series of energy levels, E_1, E_2 and E_3 as electronic, vibrational and rotational energy levels.

(ii) Using the same energy level diagram, explain which spectroscopy, out of electronic, vibrational and rotational spectroscopy, requires the radiation with photons having the largest wavelength.

(25 marks)

[Question 2 is continued in the next page]

(c) A peak at a particular frequency ν in the absorption spectrum of a molecule recorded (and drawn on the same frequency scale) at three different temperatures, T_1, T_2 and T_3, are shown in the following figure.



(i) State the physical effect, acting on the molecules, that makes the appearance of the above three peaks different.

(ii) Briefly describe how the effect you have indicated in part (i) above brings about the difference in appearance of the peaks in the above figure.

(iii) Giving reasons state the relationship among the temperatures T_1, T_2 and T_3 (i.e. the largest, smallest and the one in between).

(25 marks)

3. (a) The equilibrium bond length of $^{14}N^{16}O$ is 115 pm. Relative atomic masses of $^{14}N = 14$ and $^{16}O = 16$.

(i) Write down the relationship between the rotational constant (in wave number units) of a diatomic molecule and its bond length.
Identify all the parameters in it.

(ii) Write down the relationship between the positions (in wave number units) of the lines in the microwave spectrum of a diatomic molecule and rotational quantum number. Identify all the parameters in it.

(iii) Calculate the rotational constant of $^{14}N^{16}O$.

(iv) Calculate the position of the line due to the transition $J = 3 \rightarrow J = 4$ in the microwave spectrum of $^{14}N^{16}O$.

(50 marks)

(b) (i) Deduce the Maxwell relationship that can be obtained from the thermodynamic expression; $dB = MdY + LdX$ where B, L, M, X and Y are thermodynamic properties.

(ii) Write down (no proof required) the relationship that exists between,

(α) the standard free energy change, ΔG^0, and the equilibrium constant K of a chemical reaction at temperature T.

(β) the equilibrium constant K_1 at one temperature T_1 and the equilibrium constant K_2 at another temperature T_2.

[Question 3 is continued in the next page]

(iii) The equilibrium constant, K_P, for the reaction, $Br_2 \rightarrow Br^* + Br^*$, are 6×10^{-12} Pa at 600 K and 1×10^{-7} Pa at 800 K. Calculate the standard Gibbs free energy change at the two temperatures and the standard enthalpy change for the above reaction.
Write down any assumptions you make.

(50 marks)

4. (a) (i) Write down the mathematical form of the second law of thermodynamics based on the entropy change in an experimental system.

(ii) Give conditions under which ΔS and ΔG can be used as criteria for spontaneity for a process.

(iii) 5 moles of an ideal gas undergoes a reversible isothermal change of volume from 10 dm^3 to 100 dm^3 at 300 K. Calculate the entropy change for this expansion.

(30 marks)

(b) (i) Under what conditions and/or to what type of systems can the following thermodynamically deducible equations apply.

(α) $\Delta A = \Delta U - T\Delta S$

(β) $\Delta T = K_{100}\, m$

(γ) $\Delta S = \dfrac{\Delta H}{T}$

(ii) Complete the Gibbs Helmholtz equation written in the form,

$$\left[\frac{\partial\left(\Delta G^0/T\right)}{\partial T}\right]_P =$$

(20 marks)

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

(ii) At 273 K the enthalpy change of fusion of water is $6.0\ kJ\ mol^{-1}$ and the volume change of fusion is $-1.6\times10^{-6}\ m^3\ mol^{-1}$. Calculate the melting point of ice at a pressure of 1000 atm.

(15 marks)

(d) (i) Define Partial Molar free energy. Write the general expression for partial molar free energy of an i^{th} component in an open system. Is it an extensive or intensive property?

(ii) Derive Gibbs Duhem equation for two components. What is the principle significance of this equation?

(iii) State the third law of thermodynamics.

(35 marks)

5. (a) Following information corresponds to a second order reaction of the form $A \rightarrow$ Products.

Temperature = $27^{\circ}C$

Rate constant for the above reaction = 2.5×10^{-2} $mol^{-1}m^{3}$ min^{-1}

Initial concentration of A = 1.0×10^{-2} mol dm^{-3}

(i) Given $\frac{d[x]}{dt} = k[a\text{-}x]^2$ (where the symbols used have their usual meanings), derive the integrated form of this expression

(ii) Hence, write down the mathematical expression for half life $\left(t_{1/2}\right)$ for this reaction.

(iii) Calculate the half – life of this reaction.

(32 marks)

(b) In carrying out a kinetic experiment involving the hydrolysis reaction between ethyl acetate and sodium hydroxide at 300 K, you have been asked to mix $10.00\ cm^3$ of ethyl acetate (density = $880.0\ kg\ m^{-3}$ at 300 K) with distilled water and $2.0\ mol\ dm^{-3}$ NaOH such that the total volume is $100.00\ cm^3$ and that the concentration of NaOH equals that of ethyl acetate.
[Relative atomic masses: H= 1.0; C = 12.0; O = 16.0]

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

(ii) Calculate the volume of $2.0\ mol\ dm^{-3}$ NaOH added

(iii) Assuming the reaction is first order with respect to each of the reactants, write down the rate equation for this reaction.

(iv) How would you make this a "pseudo first order" reaction with respect to ethyl acetate?

(36 marks)

(c) The reaction scheme (mechanism) for the decomposition of NO_2Cl is given below,

$$NO_2Cl \xrightarrow{k_1} NO_2 + {}^{*}Cl$$

$${}^{*}Cl + NO_2Cl \xrightarrow{k_2} NO_2 + Cl_2$$

(i) Illustrate the meaning of the term "steady state assumption" (SSA) with reference to the above reaction scheme?

(ii) With the aid of the rate equation for the decomposition of NO_2Cl and the Steady State Approximation (SSA), show that

$$-\frac{d[NO_2Cl]}{dt} = 2k_1[NO_2Cl]$$

(22 marks)

[Question 5 is continued in the next page]

(d) Consider the following reversible reaction (first order with respect to each of the reactants)

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C + D$$

where k_1 and k_2 are the rate constants for the forward and reverse reactions respectively. Derive an expression for the equilibrium constant, K, in terms of the rate constants.

(10 marks)

6. (a) What do you understand by the following terms?
   (i) An ideal binary solution
   (ii) An Azeotrope

(16 marks)

(b) Sketch a clearly labelled graph of vapour pressure versus mole fraction to distinguish between an ideal binary solution and a binary solution that shows negative deviation from ideal behaviour.

(20 marks)

(c) At standard atmospheric pressure, nitric acid (boiling point $87^{\circ}C$) and water form a constant boiling mixture (boiling point $122^{\circ}C$) of composition 65 % by mass of nitric acid. This is a fully miscible system at all compositions.

   (i) Calculate the mole fraction of nitric acid corresponding to the constant boiling composition.

   (ii) Sketch and label fully the boiling point/composition diagram (composition in terms of mole fraction of nitric acid) for this system.

   (iii) Fractional distillation of the "constant boiling mixture" does not allow separation of the two components in the mixture. Explain this statement. (Experimental details NOT necessary)

(32 marks)

(d) (i) State **ONE** advantage of carrying out steam distillation (instead of normal distillation)

   (ii) Considering two fully immiscible liquids, A and B, **write down** the mathematical expression (in terms of the standard notations) for the ratio of the masses of the two components A and B, in vapour phase (on distillation) to their molar masses and pure (saturated) vapour pressures.

   (iii) A mixture of Aniline and water boils at $98^{\circ}C$. The vapour pressure of Aniline and water at this temperature are 5.0×10^{3} Pa and 9.5×10^{4} Pa, respectively. On carrying out steam distillation, determine the number of moles of Aniline that is expected to be collected per mole of water.

   [Relative atomic masses: H=1; C= 12; N: 14; O=16].

(32 marks)

The End