THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 4

Final Examination — 2010/2011

CMU 2220 — Concepts in chemistry

(3 hours)

2nd July 2011 (Saturday) 1.30 p.m — 4.30 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
- Cellular 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.

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

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

1. (a) A particular organic fatty acid, RCOOH, has a molecular weight of $88\ \text{g mol}^{-1}$. When dissolved in water it partially dissociates as $RCOOH \rightleftharpoons RCOO^- + H^+$. What is the charge on 5 ions of $RCOO^-$?

(10 marks)

(b) (i) Write down the mathematical relationship between drift velocity and ionic mobility of an ionic species, and identify all the parameters in it.

(ii) Write down the mathematical relationship between electric field strength and the current density in a solution and identify all the parameters in it.

(iii) Deduce a relationship among the ionic mobility of an ionic species, drift velocity of the same ionic species and the current density in the solution using the mathematical expressions written in parts (i) and (ii) above.

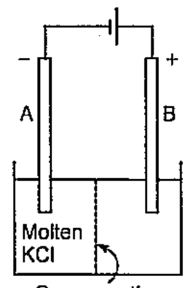
(iv) The moving boundary method was applied to a $0.0200\ \text{mol dm}^{-3}$ aqueous KCl solution at 25^0C using aqueous $CdCl_2$ as the following solution. For a current held constant at $1.600\ \text{mA}$, it was found that the boundary moved $0.110\ \text{m}$ in $3500\ \text{s}$, in a tube of average cross sectional area $1.115 \times 10^{-5}\ \text{m}^2$. The conductivity of the KCl solution, at 25^0C and $1\ \text{atm}$, is $0.2300\ \text{S m}^{-1}$. Calculate the ionic mobility of K^+ at 25^0C, in this solution.

(60 marks)

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

Part A:

Consider the electrolysis process that takes place in the electrolytic cell depicted in the figure to the right. Imagine a cross section of the fluid phase in between the two electrodes which fully divides the molten KCl phase into two which is represented by the dashed line in the figure. The rate of flow of each K^+ and Cl^- ions through this cross section is $1.0 \times 10^{-4}\ \text{mol s}^{-1}$.



Cross section

(i) Calculate the total current passing through this cross section.

(ii) State whether this current flows from A to B or B to A.

(30 marks)

Part B:

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

(ii) The ionic mobilities $\left(\text{in m}^2\ \text{V}^{-1}\ \text{s}^{-1}\right)$ of Mg^{2+} and Cl^- ions in $0.001\ \text{mol dm}^{-3}$ solution of $MgCl_2$ at 25°C and $1\ \text{atm}$ are 55.0×10^{-9} and 79.1×10^{-9} respectively. In this solution $MgCl_2$ behaves as a strong electrolyte.

(α) Write down the relationship between the molar conductivity of $MgCl_2$ and the molar conductivities of Mg^{2+} and Cl^- ions. Identify all the parameters in the expression you have written.

(β) Calculate the molar conductivity of $MgCl_2$ in this solution.

(30 marks)

2. (a) Consider a beam of electromagnetic radiation which was obtained by merging two beams of monochromatic radiation of frequencies 3.5×10^{10} Hz and 5.0×10^{12} Hz. Calculate the energies of the photons in this beam.

(10 marks)

(b) (i) Write down the relationship between the number of photons crossing a unit area in unit time placed perpendicular to a beam of monochromatic radiation and the intensity of the beam, and identify all the parameters in it.

(ii) A student obtained a beam of radiation by merging two laser beams, X and Y, of frequency 2.5×10^{13} Hz and 5.5×10^{14} Hz, respectively. The intensity of the final beam was found to be 3.8×10^{-5} J m^{-2}s^{-1}. Also he found that 75% of the intensity of the final beam was due to radiation of frequency 2.5×10^{13} Hz. Calculate the following.

(α) Intensity of each of the beams X and Y.

(β) Number of photons crossing a unit area in unit time in the final beam.

(30 marks)

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

Part A:

Four consecutive absorption lines in the microwave spectrum of gaseous diatomic molecule, AB, appear at 75.624 cm^{-1}, 100.832 cm^{-1}, 126.04 cm^{-1} and 151.248 cm^{-1}. Relative atomic masses of A and B are 27 and 1 respectively.

(i) Show that AB behaves as a rigid rotor.

(ii) Write down the relationship between the wavenumber of a line in the microwave spectrum and the rotational constant of a diatomic molecule, and identify all the parameters in it.

(iii) Assign each of the above absorption lines to a particular transition.

(iv) Write down the relationship between the rotational constant and the bond length of a diatomic molecule, and identify all the parameters in it.

(v) Calculate the bond length of AB.

(60 marks)

Part B:

(i) Write down the Beer – Lambert law in absorption spectroscopy in the form of a mathematical equation and identify all the parameters in it.

(ii) A 0.03 mol dm^{-3} aqueous solution of $Co(C_2O_4)_3^{3-}$ shows an absorbance of 2.0 when the path length of radiation is 1.0 cm at wavelength 660 μm at 25^{0}C. Calculate the following.

(α) The transmittance of the sample.

(β) Molar absorption coefficient of $Co(C_2O_4)_3^{3-}$ in aqueous solution at 25^{0}C.

(γ) The percentage absorption of radiation of a 0.015 mol dm^{-3} aqueous solution of $Co(C_2O_4)_3^{3-}$ at a path length of 1.0 cm at 25^{0}C.

(60 marks)

3. (a) Sate <u>three</u> factors that determine the value of molar extinction coefficient of a particular chemical compound in solution.

(9 marks)

(b) (i) Write down the Boltzmann distribution function and identify all the parameters in it.

(ii) The ground and the first excited energy levels of a polyatomic molecule have energies 1.00×10^{-23} J and 4.5×10^{-23} J respectively. One mole of such molecules are in the ground level, which is non-degenerate, in a particular sample of these molecules at $25^{\circ}C$. Calculate the number of molecules in the first excited level, which is doubly degenerate, in the same sample at the same temperature.

(41 marks)

(c) 2 mol of $N_2(g)$, assumed to behave ideally, are heated reversibly from 250 to 500 K under isobaric conditions. The molar entropy of the gas at 500K is 160 $J\,K^{-1}\,mol^{-1}$. Calculate q, w, ΔU, ΔH, ΔS and ΔG for the process.

(45 marks)

(d) State the third law of thermodynamics.

(05 marks)

4. (a) A level 4 student reports the following values based on an experiment that he carried out to test the relationship between rate constant and temperature given by the equation $\ln(k) = -m\left(\frac{1}{T}\right) + c$, where k = rate constant, T = absolute temperature and, m and c are constants.

Temp./°C	27	37	47	57	67
$k\times10^4/min^{-1}$	7.5	15.0	20.5	35.0	50.0

Carry out an **appropriate tabulation** of data required to plot a suitable, linear graph.

(25 marks)

(b) For a particular first order reaction of the form $A \rightarrow P$, the initial concentration of A is reduced to half its initial value after 3000 seconds at $27^{\circ}C$.

(i) With the aid of the rate equation (the differential form) for the above reaction, derive the relationship between rate constant and concentration of A at any time, t (the integrated form).

(ii) Calculate the rate constant of the reaction at this temperature

(iii) Calculate the time required (in seconds) for the concentration to be reduced to one quarter of its initial value at this temperature.

(35 marks)

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

(ii) The hypothetical scheme (mechanism) for the decomposition of CH_3CHO is given below along with the respective rate constants.

$$CH_3CHO \xrightarrow{k_1} CH_3 + CHO$$

$$CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3CO$$

$$CH_3CO \xrightarrow{k_3} CH_3 + CO$$

$$2CH_3CO \xrightarrow{k_4} CH_3COCOCH_3$$

(α) Write down the rate equation for the formation of CH_3CO radical.

(β) By applying SSA to the CH_3 radical, show that

$$[CH_3] = \frac{k_3[CH_3CO] + k_1[CH_3CHO]}{k_2[CH_3CHO]}$$

(25 marks)

(d) 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).

Sketch the concentrations (of A, B, C) versus time curve in the case where the values of the two rate constants [k_1 and k_2] are comparable $(k_1 \approx k_2)$. Briefly explain the shape of the curve.

(15 marks)

5. (a) 10.00 ml of a liquid A [relative molar mass 100 and density 900 kg m^{-3}] is mixed with 25.00 g of a liquid B [relative molar mass = 125]. Assuming that this binary system is fully miscible, calculate the mole fraction of A in the solution.

(10 marks)

(b) Two liquids, 23.0 g of methylbenzene and 40.0 g of a compound A (assumed to form an ideal mixture with methylbenzene), were mixed together at room temperature. The vapour pressures of pure methylbenzene and pure A at this temperature are 50 torr and 30 torr respectively. Total vapour pressure of the mixture is 42 torr. With the aid of relevant laws and their mathematical expressions and neglecting the amounts that have gone into the gaseous phase,

(i) Calculate the molar mass of A.

(ii) Calculate the corresponding composition of the vapour at this temperature.

[Relative atomic masses: H =1.0. C = 12.0; O = 16.0]

(30 marks)

(c) Consider an ideal binary mixture of two liquids A and B which are miscible in all proportions.

(i) Sketch a **clearly labeled** temperature (boiling point) versus composition phase diagram for this system assuming that the boiling point of A is greater than that of B.

(ii) A mixture, whose composition is given as X_A [mole fraction of A] = 0.8, is heated up to its boiling point, T_l. Mark this temperature on your sketch and, briefly outline (experimental details not necessary), how you would carry out fractional distillation of the above mixture in order to separate out A and B.

(30 marks)

(d) Answer either <u>Part (i)</u> OR <u>Part (ii)</u> (but NOT both).

(i) A mixture of A and B (where the mole % of A is 35) forms an **azeotrope** with a boiling point at $205^{\circ}C$. This system is said to exhibit **negative deviation from Raoults Law.**

(α) What do you understand by the highlighted (BOLD) terms?

(b) Assuming that the boiling point of pure A is greater than that of pure B, sketch the Temperature versus Composition phase diagram for the above system and label it completely.

(30 marks)

(ii) 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 $X_A = 0.40$ (X_A is the mole fraction of A).

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

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

(30 marks)

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

<u>Part A.</u>

(a) (i) Starting from the first law of Thermodynamics, derive the Gibbs relationship, $dH = T\,dS + V\,dP$, applicable to reversible processes in closed systems where only PV work is possible.

(ii) Write down the Maxwell relationship corresponding to the above Gibbs relationship.

(iii) Write down a mathematical expression for variation of the Gibbs free energy of a reaction with temperature, known as Gibbs – Helmholtz equation.

(45 marks)

(b) Determine whether $Br_2(g)$ will oxidize $H_2S(g)$ according to the equation, $Br_2(g) + H_2S(g) \rightarrow 2HBr(g) + S(s)$. at 298K and one standard atmospheric pressure. The following data are given:

Chemical species	$\Delta G^0_{f,298} / kJ\ mol^{-1}$
$H_2S(g)$	−7.9
$Br_2(g)$	+0.8
$HBr(g)$	−12.8

(30 marks)

(c) (i) Write down the mathematical form of the second law of thermodynamics based on the entropy change that takes place in an experimental system.

(ii) Deduce the second law based on the entropy change that concurrently takes place in the universe.

(25 marks)

Part B

(a) Write down (no proof required) the equations representing the variation of vapour pressure with temperature for

(i) any univariant system involving two phases.

(ii) Any univariant system involving two phases, where one phase is an ideal gas.

(20 marks)

(b) The equilibrium vapour pressures of sulphur dioxide in the solid and liquid states are given by the equations;

$$\ln\left(P_{solid}\right)/Pa = 29.28 - 4308\,K/T$$

$$\ln\left(P_{liquid}\right)/Pa = 24.05 - 3284\,K/T$$

where T is the thermodynamic temperature. Calculate

(i) the temperature and pressure of the triple point of sulphur dioxide.

(ii) The enthalpy and the entropy of fusion of sulphur dioxide at the triple point.

(45 minutes)

(c) Define partial molar volume and write down its mathematical expression.

(20 marks)

(d) The variation of the thermodynamic equilibrium constant K of a reaction at the thermodynamic temperature T is given by the equation, $\ln(K) = 20.00 - \left[\frac{750}{T/K}\right]$.

Calculate ΔG^0 for this reaction at $57^\circ C$.

(15 marks)

The End