THE OPEN UNIVERSITY OF SRI LANKA
B.Sc/ B.Ed Degree Programme/ Stand Alone Courses in Science- Level 3
Final Examination- 2007/2008
CHU 1221/ CHE 4221 Basic Principles in Chemistry – Paper I1
Duration – 2 hours

Date – 12.06.2008 Time – 2.00 p.m- 4.00 p.m

Instructions to candidates:

*Answer any four (4) questions **out of six (6).**

* **If more than four questions are answered** only the first four answers in the order written will be marked.

* Write down **clearly the number of the question as given on the question paper on the left hand column of the answer book.**

* **Before handing over the answer script make sure that you have entered your index number, title of the question paper and the numbers of the questions you have answered on the cover page of the answer book.**

Gas constant *(R)*	$= 8.314\ J\ K^{-1}\ mol^{-1}$
Avogadro constant*(L)*	$= 6.023 \times 10^{23}\ mol^{-1}$
Faraday constant*(F)*	$= 96\ 500\ C\ mol^{-1}$
Plank constant*(h)*	$= 6.63 \times 10^{-34}\ J\ s$
Velocity of light*(c)*	$= 3.00 \times 10^{8}\ m\ s^{-1}$
Protonic charge*(e)*	$= 1.602 \times 10^{-19}\ C$
Rydburg constant*(R_H)*	$= 1.097 \times 10^{7}\ m^{-1}$
Permitivity of free space,ε_0	$= 8.854 \times 10^{-12}\ C^2 N^{-1} m^{-2}$
1 eV	$= 1.602 \times 10^{-19}\ J$
bar	$= 10^5\ Pa\ (N\ m^{-2})$
1 a.m.u	$= 1.665 \times 10^{-27}\ kg$
$\log_e (X)$	$= 2.303 \log_{10} (X)$

1.(a) The atomic spectrum of sodium contains two bright yellow lines, one at 589.0 nm and the other at 599.6 nm.
(i)Which one of the two lines gives greater energy per photon?
(ii) If a sodium arc light is to produce 1.000 kilowatt ($1000\ J\ s^{-1}$) of radiant energy using the line with high energy, how many moles of sodium atoms must emit photons per second?

(20 marks)

(b) Bohr's formula for the energy levels of the hydrogen atom can be modified to apply for one electron species such as He^+ as follows:

$$E_n = -k\frac{z^2}{n_i^2}$$

(i) Identify z and n

(ii) Using $k = 2.179 \times 10^{-18}$ J, calculate the energy needed to remove an electron from a He^+ ion in the ground state.

(iii) Write down the relevant equation for the process mentioned in (ii).

(iv) How does a Bohr orbit differ from an orbital?

(30 marks)

(c) Write down the electronic configurations of the following atoms/ions.

(i) Cr^{3+} (ii) Fe (iii) N^{3-}

(Relative atomic mass Cr = 24; Fe = 26; N = 7)

(15 marks)

(d)(i) The percentage of chloride ions in a sample of sea water was determined by titrating 25.00 cm^3 sample with silver nitrate causing precipitation of silver chloride. It required 42.58 cm^3 of 0.299 mol dm^{-3} silver nitrate solution to reach the equivalence point. Calculate the mass percentage of chloride ions in the sea water if its density is 1.025 g cm^{-3}.(Relative atomic mass of Cl = 35.5)

(ii) Hard water contains Ca^{2+}, Mg^{2+} and Fe^{2+}, which interferes with the action of soap and leave an insoluble coating on the sides of the containers when heated. Water softeners replace these ions with Na^+. If 1.0×10^3 dm^3 of hard water contains 0.010 mol dm^{-3} Ca^{2+} and 0.0050 mol dm^{-3} Mg^{2+}, how many moles of Na^+ are needed to replace these ions?

(35 marks)

2.(a) Define the terms, " ionization potential" and " electron affinity"

(b) Draw the Born- Haber cycle for LiBr(s). Hence calculate its lattice energy, using the data (**kJ mol^{-1}**) given below:

Ionization potential of lithium	= 520
Enthalpy of sublimation of lithium	= 134.7
Enthalpy of vaporization $Br_2(l)$	= 15.46
Bond dissociation energy of $Br_2(g)$	= 111.7
Electron affinity of Br	= – 324
Standard enthalpy of formation of LiBr(*s*)	= –351.2

(26 marks)

(c) Draw the Lewis structures for the following:

(i) H_2S (ii) SF_4 (iii) SF_6 (S= 16)

Predict their geometries.

(24 marks)

(d) Draw the shapes of the molecular orbital formed when the following atomic orbitals combine.

(i) *s* and *s* (ii) *p* and *p* (Consider *x*- axis as the internuclear axis)

Label them as σ or π. Indicate the anti bonding orbitals with an asterik (*)

(30 marks)

(e) Sketch the molecular orbital energy level diagram for O_2 and O_2^+.
For each species, calculate the bond order and comment on the magnetic properties.

(20 marks)

3. Attempt all the parts (a) –(f). However, full marks for this question will be given to those who score about 100 out of the allotted 120 marks. Pro-rata marks will be awarded to other candidates.

(a) Using Boyle's law, Charles' law and Avogadro's law show that the value of the gas constant (R) is independent of the nature of the gas.

(20 marks)

(b) The compressibility factor (Z) of a mole of gas can be given by an expression of the form

$$Z = (\text{constant})\left(\frac{\pi\phi}{\theta}\right)$$

(i) Define the quantity represented by the symbol θ in the above equation.
(ii) What is the quantity represented by the symbol ϕ.
(iii) Deduce the Law of corresponding states using the above expression.

(18 marks)

(c)Under what conditions and/or to what type of systems will the following thermodynamically deducible expressions apply?

(i) $\left(\frac{p_1}{p_2}\right)^{1-\gamma} = \left(\frac{T_2}{T_1}\right)^{\gamma}$ (ii) U = H- PV

(iii) $\Delta U = n C_{v,m} \Delta T$

(16 marks)

(d) Define "Thermal Capacity" (C) of a substance using a mathematical expression. Indicate to what type of system the concept of thermal capacity will apply.

(14 marks)

(e) Calculate the mean square speed of oxygen gas $\left(C_{p,m} = \frac{7R}{2}\right)$ at 100 K.

(Relative atomic mass of O =16)

(24 marks)

05. (a)

(f) 100 moles of ice melt under standard atmospheric pressure at its melting point of 0 ^{0}C with a standard enthalpy of fusion, ΔH_f^0, of 6.0 kJ mol^{-1}. Molar volume of ice and water at 0 ^{0}C are 20.0 and 18.0 cm^3 mol^{-1} respectively.
Calculate

(i) the work done, w
(ii) the change in internal energy, ΔU
(iii) the change in Gibbs free energy, ΔG
(iv) the change in entropy, ΔS

(b)

accompanying the melting process. (28 marks)

4.(A)(a) What is the **operational definition** of acids and bases ? Classify LiH, SO_3, HCN and P_4O_{10} as acids or bases according to the operational definition.

(b) Write the **self-ionization** reaction of formic acid (HCO_2H). Write an equation for the dissociation of formic acid in water.

(c) Write the balanced equation for the oxidation of sulfur dioxide to sulfate ions by dichromate ions in acidic solutions.

(d) Given that, $E^0_{(Cd2+/Cd)} = -0.43$ V and $E^0_{(Pb2+/Pb)} = -0.126$ V.
Calculate the E^0 and ΔG^0 for the cell reaction, $Cd(s) + Pb^{2+}(aq) \rightarrow Cd^{2+}(aq) + Pb(s)$

(50 marks)

(B)(a) In an experiment carried out to study the kinetics of the reaction between two substances, A and B, the overall order of the reaction was found to be 2.
Write three (3) possible rate equations for the reaction between A and B.

(b) At a certain temperature the rate of reaction between nitrogen monoxide, NO, and hydrogen, H_2 was investigated. The following data was obtained.

$[NO]$/mol dm^{-3}	$[H_2]$/mol dm^{-3}	Rate/ mol dm^{-3}s^{-1}
1.0	1.0	0.02
1.0	3.0	0.06
3.0	1.0	0.18

(i) Use the above data to deduce the rate equation for the reaction.
(ii) Use your answer in b(i) to calculate the value of the rate constant.

(c) Explain why an increase in temperature increases the rate of a reaction. State the effect of an increase in temperature on the value of the rate constant.

(50 marks)

5.(a) Write down the mathematical expression that defines the following:

(i) Electric Field Strength – **E**

(ii) Ionic Mobility – **U**

(iii) Charge Density – **J**

and hence write down the corresponding **SI** units.

(18 marks)

(b) Mass (**m**) of an ion discharged on an electrode during electrolysis can be calculated using the expression, $m = \frac{QM}{ZF}$.

(i) Identify, clearly, the rest of the symbols in the above expression.

(ii) During an experiment involving electrolysis, it was found that 10 mg of a metal was deposited when an average current of 100 mA was passed through a solution of its ions for a period of 5.0 minutes. Calculate the charge number of the metal ion. (Assume the relative atomic mass of the metal to be 96.5).

(20 marks)

(c) The molar conductivity of an electrolyte in water is 2.5×10^{-2} S m^2 mol^{-1}. A student prepares 500.00 cm^3 of an aqueous solution of this electrolyte containing 5.00×10^{-2} moles of it.

(i) Calculate the concentration of this solution in **mol m^{-3}**

(ii) Calculate the conductivity of this solution in **S cm^{-1}**
(neglect conductivity due to water)

(20 marks)

(d) The following equation refers to the Onsager limiting law applicable to 1:1 electrolytes at very low concentrations

$$\Lambda = m\sqrt{C} + \Lambda_o$$

(i) Give an example of a 1:1 electrolyte.

(ii) Identify, clearly, the symbols in the above expression.

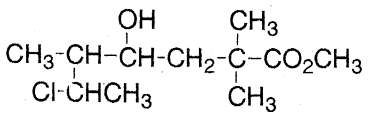
(iii) A student wishes to determine Λ_o of a certain 1:1 electrolyte using the above law.
Briefly outline the steps involved (experimental details not necessary).
Sketch the shape of the graph expected in this experiment.

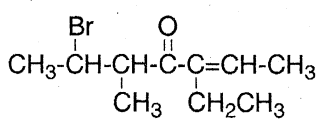
(iv) Suppose Λ equals **p** when C = 0.0036 mol dm^{-3} and Λ equals **q** when C = 0.0025 mol dm^{-3}, calculate the expected value of Λ_o in terms of **p** and **q** (**p, q** are in arbitrary units)

(42 marks)

6.Answer all parts.

(a) Give the IUPAC names of the following compounds.

i. 

ii. 

(20 Marks)

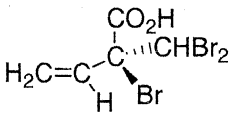
(b) i. Give the structure of 4-chloro-2-hydroxyhex-4-enal

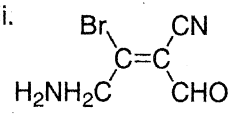
ii. How many stereoisomers are possible for the above compound?

iii. Draw the structure of (2*S*,4*Z*) 4-chloro-2-hydroxyhex-4-enal

(20 Marks)

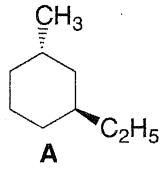
(c) Determine the stereochemistry of chiral centres (as *R* or *S*) and double bonds as (*E* or *Z*) of the following compounds.

i. 

ii. 

(10 Marks)

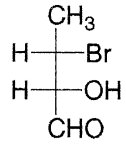
(d) Draw conformations for the following compound **A**. Giving reasons state which is the more stable conformation.

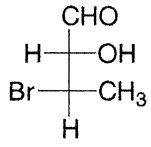


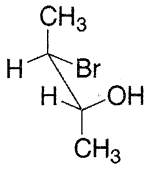
A

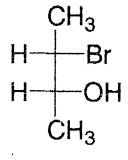
(20 Marks)

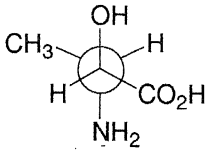
(e) State the stereochemical relationship (enantiomers or diastereoisomers or same) between compounds in each of the following pairs.

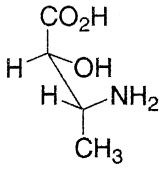
i. 



ii. 



iii. 



(30 Marks)