Total No. of Printed Pages-4

Roll No. _____

1(CCE-M)6

CHEMISTRY-I

[05]

Time Allowed : 3 Hours

Maximum Marks : 300

INSTRUCTIONS

i) Answers must be written in English.

ii) The number of marks carried by each question is indicated at the end of the question.

iii) The answer to each question or part there of should begin on a fresh page.

iv) Your answer should be precise and coherent.

v) The part/parts of the same question must be answered together and should not be interposed between answers to other questions.

*vi) candidate should attempt any **FIVE** questions.*

vii) If you encounter any typographical error, please read it as it appears in the text book.

viii) Candidates are in their own interest are advised to go through the General Instructions on the back side of the title page of the Answer Script for strict adherence.

ix) No Continuation sheets shall be provided to any candidate under any circumstances.

x) Candidates shall put a cross (X) on blank pages of answer Script.

xi) No blank page be left in between answer to various questions.

xii) No programmable Calculator is allowed.

xiii) No stencil (with different markings) is allowed.

xiv) In no circumstances help of scribe will be allowed.

Note: Attempt any **FIVE** questions.

1. a) Consider atoms with the following electron configurations : **(3×20=60)**

$1s^2 2s^s 2p^6$

$1s^2 2s^2 2p^6 3s^1$

$1s^2 2s^2 2p^6 3s^2$

Which atom has the largest first ionization energy, and which one has the smallest second ionization energy? Explain your choices. **(12)**

b) The first ionization energy for phosphorus is 1012 kJ/mol,and that for sulfur is 1000 KJ/mol. Why? **(12)**

c) Order the following bonds according to polarity: H-H,O-H,Cl-H,S-H, and F-H. **(12)**

d) Consider the reaction between pyridine and heptyl bromide, to make 1- heptylpyridinium bromide. It is an equilibrium reaction with an equilibrium constant K=40. What is the rate constant of back reaction K-1. If the value of the forward rate constant $K_1=2.4 \times 10^3\ dm^3\ mol^{-1}S^{-1}$? **(12)**

e) Define **(12)**

i) Bathochromic shift

ii) Hypsochromic shift

iii) Hyperchromic shift and

iv) Hypochromic shift

2. a) What is meant when two or more orbitals are said to be disintegrate? **(15)**

b) How many quantum numbers are needed to identify an electron in at atom? **(15)**

c) How does the concept of an orbit in the Bohr model of the hydrogen atom differ from the concept of an orbital in quantum theory? **(15)**

d) The first cyclotron was built in 1930 at the university of California, Berkeley, and was used to accelerate molecular ions of Hydrogen, H_2^+, to a velocity of 4×10^6 m/s. If the relative uncertainty in the velocity of the H_2^+ ion was 3 %, What was the uncertainty of its position? **(15)**

3. a) Which of the following bonds are polar? **(15)**

C-Se,C-O,Cl-Cl,O=O,N-H,C-H.

In the bond or bonds that you selected which atom has the greater electronegativity?

b) Can molecule of carbon monoxide in the atmosphere absorb photons of IR radiations? Explain why or why not? **(15)**

c) Give examples of neutral homonuclear and heteronuclear diatomic molecules that are isoelectronic with C_2^{2-}. **(15)**

d) Predict the bond dissociation enthalpy of HI using the following information.

$\chi^p(H) = 2.20$ D(H-H)=+ 435.8KJ mol^{-1}.

$\chi^p(I) = 2.66$ D(I-I)=+ 152.3KJ mol^{-1}. **(15)**

4. a) How is the entropy change that accompanies a reaction related to the entropy change that happens when the reaction runs in reverse? **(15)**

b) An apparatus consists of two bulb of the same volume connected by a tap. Initially, the tap is closed with one bulb containing nitrogen gas and the other oxygen gas. Both bulbs are at the same temperature and pressure. **(15)**

i) What happens when the tap is opened? What will be the equilibrium state of the system?

ii) What are the signs of $\Delta H, \Delta S$ and ΔG for the process in (i)

iii) Is this consistent with the second law of Thermodynamics?

c) Calculate the entropy change when 3.0 mol of nitrogen gas are heated from 25^0 to 50^0 C at constant pressure. (C_p for $N_2(g)$ is 29.13 JK^{-1} mol^{-1}) **(15)**

d) Show that $\Delta S = q_{rev}/T$. **(15)**

5. a) The decomposition of A is second order in A. What effect does doubling the concentration of A have on the rate constant? **(10)**

b) For the reaction of NO and H_2

$2NO\ (g) + 2H_2\ (g) \rightarrow N_2(g) + 2H_2O\ (g)$

The rate equation is given by, rate of reaction = K $[NO]^2\ [H_2]$

(1) What are the orders of the reaction with respect to NO and H_2?

(2) What is the overall order of the reaction

(3) What happen to the rate of reaction if :

(A) $[H_2]$ were doubled:

(B) $[H_2]$ were halved:

(C) [NO] were doubled:

(D) [NO] were increased by a factor of three? **(30)**

c) Why do average rates of most of the reactions change with time? **(10)**

d) Discuss the collision theory of bimolecular reactions. **(10)**

6. a) The standard reaction potentials of the half- reactions in single-use alkaline batteries are

$Zn(O)(l) + H_2O(l) + 2e^- \rightarrow Zn(s) + 2OH^-(aq)$ E0= -1.25V

$2MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)$ E0=0.15V

What is the net ionic equation for the cell reaction and the value of E^0cell? **(24)**

b) Write a half reaction for the oxidation of magnetite (Fe_3O_4) to hematite (Fe_2O_3) in acidic ground water. **(12)**

c) Suppose the current from a battery is used to electroplate an object with silver. Calculate the mass of silver that would be deposited by a battery that delivers 1.7 A-h of charge. **(12)**

d) How is the value of the equilibrium constant affected by scaling up or down the coefficients of the reactants and products in the chemical equation describing the reaction? **(12)**

7. a) Explain the difference between cubic closest-packed and hexagonal closest-packed arrangements of identical spheres. **(15)**

b) Calculate the density of iron (ferrite) in grams per cubic centimeter, given that its bcc unit cell has an edge length of 287 pm. (Molar mass of Fe is 55.845 g/mol) **(15)**

c) In a Beer law cell, the aqueous solution of a substance of known concentra tion absorbs 10 percent of the incident light. What fraction of the incident light will be absorbed by the same solution in a cell five times as long?**(15)**

d) Discuss (i) The Grotthus-Draper and (ii) The Stark-Einstein laws of photo chemistry. **(15)**

8. a) Does the complex ion $[Co(NH_3)Br(en)_2]^{2+}$ exhibit geometrical isomerism? Does it exhibit optical isomerism too? **(15)**

b) Draw structures of the following. **(15)**

i) $[Co(C_2O_4)_2(H_2O)_2]$-

ii) $[Ir(NH_3)_3Cl_3]$

iii) $[Pt(NH_3)_4I_2]^{2+}$

iv) $[Cr(en)(NH_3)_2l_2]^+$

c) The carbonate ion (CO_3^{2-}) can act as either a monodentate or a bidentate ligand Draw a picture of CO_3^{2-} coordinating to a metal ion as a monodentate and as a bidentate ligand. The carbonate ion can also act as a bridge between two metal ions. Draw a picture of a CO_3^{2-} ion bridging between two metal ions. **(15)**

d) Sketch and explain the most likely pattern for the crystal field diagram for the complex ion trans-diamminetetracyanonickelate (II), where CN^- produces a much stronger crystal field than NH_3.

Explain completely and label the d orbitals in your diagram. Assume the NH_3 ligands lie on the z axis. **(15)**