(27)   Your Roll No. 2024

Sr. No. of Question Paper : 1526   G

Unique Paper Code   : 2172012301

Name of the Paper   : DSC: Chemistry of d- and f- Block Elements & Quantitative, Inorganic Analysis

Name of the Course   : **B.Sc. (Hons) Chemistry**

Semester   : III

Duration : 2 Hours   Maximum Marks : 60

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.

2. Attempt *four* questions in all.

3. All Questions carry equal marks.

1. Explain the following giving reasons:

    (a) Transition elements generally show variable oxidation states.

P.T.O.

(b) CrO_3 is strongly oxidising while WO_3 is stable.

(c) Titanium(III) ions are attracted by the magnetic field, while titanium(IV) ions are repelled.

(d) Clay minerals cleave easily into thin sheets.

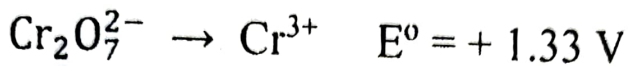(e) Lanthanides show sharp bands in the absorption spectra while transition elements show broad bands.   (5x3)

2.   (a) Give reason:

     (i) Mn(II) ion shows the maximum magnetic character amongst the bivalent metal ions of the 3d series.

     (ii) Cu(II) salts are blue while Zn(II) salts are colourless.

  (b) Write the electronic configuration and give the number of unpaired electron(s) present in 4f orbitals of the following:

     (i) Gadolinium (Atomic number 64)

     (ii) Terbium (Atomic number 65)

  (c) Actinides have a greater tendency to form complexes than lanthanides. Explain.   (3x5)
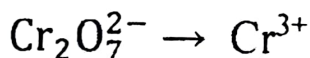
3. (a) Explain the catalytic properties of transition elements with the help of suitable examples.

(b) Construct the Latimer diagram for Cr in acidic medium:

$$Cr_2O_7^{2-} \rightarrow Cr^{3+} \quad E^o = +1.33 \text{ V}$$
$$Cr^{3+} \rightarrow Cr^{2+} \quad E^o = -0.41 \text{ V}$$
$$Cr^{2+} \rightarrow Cr \quad E^o = -0.91 \text{ V}$$

(i) Write half cell reaction for the conversion of:

$$Cr_2O_7^{2-} \rightarrow Cr^{3+}$$

(ii) Is there any tendency of Cr^{2+} to reduce to Cr? Give reason.

(iii) Calculate skip step emf for $Cr^{3+} \rightarrow$ Cr change.

(c) Define Digestion. What is the importance of digestion in gravimetric analysis? (3x5)

4. (a) Explain the separation of lanthanides by ion exchange method.

(b) What are silicates? Briefly describe various types of silicates with suitable example.

P.T.O.

(c) What are the conditions of good wash liquid in gravimetric analysis? How will it be ensured that the washing of the precipitate is complete by means of qualitative method? (3x5)

5. (a) What is Lanthanide contraction? What are the major consequences of lanthanide contraction?

(b) Write a short note on Silicones.

(c) Compare the magnetic properties of transition elements and lanthanides. (3x5)

6. (a) Draw the structures of the following:

(i) Borax

(ii) cyclic-$[NPCl_2]_3$

(b) What is supersaturation? How it can be kept in low value?

(c) Choose the correct option and give reason for the same.

Greater number of oxidation states: Fe or Mn

Good reducing agent: Ce(II) or Sm(II) (3×5)

(1000)

Sr. No. of Question Paper : 4342   G

Unique Paper Code   : 32171301

Name of the Paper   : Inorganic Chemistry-II: s- and p- Block Elements

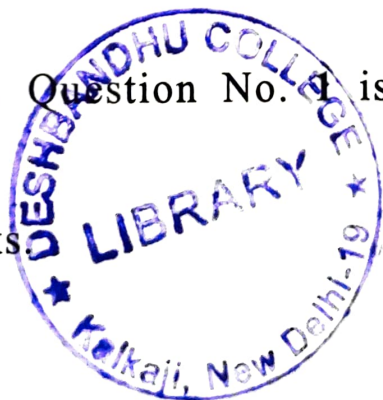Name of the Course   : **B.Sc. (Hons) Chemistry (LOCF)**

Semester   : III

Duration : 3 Hours   Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.

2. Attempt **five** questions in all. Question No. 1 is compulsory.

3. **All** Questions carry equal marks.

1. Explain the following giving reasons : **(any five)**

    (a) CCl_4 does not act as a Lewis acid while $SiCl_4$ does.

(b) Borazine is more reactive than Benzene.

(c) Amongst the alkali metals Lithium has got the highest ionisation enthalpy, despite this it is as good a reducing agent as cesium in aqueous solution.

(d) Carbon is a versatile reducing agent used in the extraction of metals, but it is unsuitable sometimes as a reducing agent.

(e) Phosphorus, arsenic and antimony form pentahalides, but nitrogen and bismuth do not.

(f) B^{3+} ion doesn't exist in solid or solution state.

(g) Zeolites are used as water softeners. (3×5)

2.   (a) Select the correct answer in each category given below and justify your answer. **(any four)**

(i) A halogen which does not exhibit positive oxidation state: Flourine or chlorine

(ii) Better lewis base: Trimethylamine or trisilylamine

(iii) Stronger reducing agent: CH_4 or SiH_4

(iv) Hydride having higher thermal stability: NH_3 or PH_3

(v) Stronger oxidising agent: $HOCl$ or $HClO_4$

(b) Explain with the help of Ellingham diagram, the reducing nature of carbon and carbon monoxide.

(c) Graphite is soft, has low density and is a good conductor of electricity but diamond is extremely hard, has high density and is a non-conductor of electricity. Explain why?   (6,4,5)

4

3. Justify the following statements, giving reason :

(a) Methane, ammonia and water have same hybridisation but different structures.

(b) Nitrogen is an inert gas while phosphorous is a highly reactive solid.

(c) CO_2 is a gas while SiO_2 is a high melting solid.

(d) Rubidium as compared to sodium has greater electrical conductivity in aqueous solution.

(e) Dilute solution of sodium in liquid ammonia is blue coloured, paramagnetic in nature and behaves as a true solution. (3×5)

4. (a) What is Inert pair effect? How does it vary down the group 14 elements? Explain.

(b) Draw the structure of S_8 molecule and explain the effect of heating on Sulphur.

(c) Discuss the structures of **any two** of the following :

   (i) Phosphorous pentoxide

   (ii) Basic beryllium acetate

   (iii) Xenon hexaflouride

(d) Silicon analogues of alkene and alkyne are not known. Give reason. (4,4,4,3)

5. (a) Which has greater bond angle and why? NH_3 or NF_3.

(b) Which will have greater ionic radius and why? Gallium or Aluminium.

(c) A group 2 metal (M) occurs naturally in great abundance as carbonate. Metal (M) reacts with cold water forming compound (A), which is a strong base. Aqueous solution of (A) is used in the qualitative test for carbonate ion. Metal (M) combines with H_2 to give a saline hydride (B), which behaves as a drying agent. Identify (M), (A) and (B) giving balanced chemical reactions.

(d) Write short notes on **any two** of the following :

    (i) van Arkel de Boer Method

    (ii) Clathrate compounds

    (iii) Phosphonitrilic halides   (3,3,3,6)

6.   (a) Potassium permanganate which is insoluble in benzene, dissolves readily in it in the presence of 18-crown-6-ether. Explain giving reason.

(b) Which is oxidising in nature and why? PbO or PbO$_2$

(c) Discuss the structure of XeF$_2$ using Molecular orbital theory.

(d) Justify the statement: Unlike ethane, diborane is an electron deficient compound. How do you explain the structure of diborane then?

(e) Write balanced chemical reactions for **any three** of the following :

   (i) Diborane reacts with ammonia in the ratio 1:2 at 200°C.

   (ii) Borazine reacts with methanol.

   (iii) Sulpur dioxide reacts with acidified solution of potassium dichromate.

(iv) Lithium nitrate is heated. (3×5)

[This question paper contains 8 printed pages.] *9073*

(29)   Your Roll No. 2024

Sr. No. of Question Paper : 4510   **G**

Unique Paper Code   :   32171303

Name of the Paper   :   Chemistry C – VII Physical Chemistry III : Phase Equilibria and Electrochemical Cells

Name of the Course   :   **B.Sc. (H) Chemistry**

Semester   :   III

Duration : 3 Hours   Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.

2. Attempt **six** questions in all, selecting at least **two** questions from each section.

3. Question number **1** is compulsory.

4. Use of scientific calculator, log tables and graph paper is permitted.

P.T.O.

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \text{ and } 1 \text{ F} = 96500 \text{ C mol}^{-1}$$
$$E^\circ_{Cu^{2+}|Cu} = 0.337 \text{ V}; \quad E^\circ_{Cr^{3+}|Cr} = -0.774 \text{ V}$$
$$E^\circ_{Fe^{3+},Fe^{2+}|Pt} = 0.771 \text{ V}; \quad E^\circ_{MnO_4^-|Mn^{2+}|H^+} = 1.51 \text{ V};$$
$$E^\circ_{Cd|[Cd(NH3)4]^{2+}} = -0.61 \text{V}; \quad E^\circ_{Cd^{2+}|Cd} = -0.40 \text{ V}.$$

Section A

1. Answer any **five** questions given below :

   (i) In water system, fusion curve of ice is inclined towards pressure axis. Explain. (3)

   (ii) Ice and common salt mixtures can be used for producing temperatures as low as −21.1°C. Explain. (3)

   (iii) Is it possible to separate an azeotropic mixture into two pure components by isobaric fractional distillation? Explain. (3)

   (iv) What are reversible cells? Explain with an example. (3)

   (v) The effect of temperature and pressure on adsorption process is in accordance with Le Chatelier's principle. Explain. (3)

(vi) Polarities of cathode and anode in a galvanic cell are opposite to those in an electrolytic cell. Explain giving reasons.   (3)

(vii) The e.m.f. of the hydrogen electrode is linearly dependent only on the pH of the solution. Explain.   (3)

2.   (i) The absence of a few components in some phases does not alter the phase rule relation, $F = C - P + 2$. Derive the above conclusion by taking the following system of *three* components distributed over *four* phases :   (4)

B+C	A+C+B	A+B+C	A+B+C
Phase I	Phase II	Phase III	Phase IV

(ii) The steam distillation of a liquid X with molar mass 120 g mol^{-1} is observed to occur at a temperature of 89.0°C when the total pressure is 0.911 bar. Assuming complete immiscibility of this liquid with water, calculate the mass of X in 200 g of distillate. The vapour pressure of water at 89.0°C is 0.6747 bar.   (4)

(iii) Derive the Langmuir adsorption isotherm for a gas on a solid and discuss the limiting cases.   (4)

3.   (i)   Starting with the Duhem-Margules equation, derive a relation to show that the vapour phase is richer in the more volatile component for a binary system A-B.   (4)

     (ii)   With the help of a suitable diagram, discuss the fractional distillation process of a two-component system which exhibits negative deviation from ideal behaviour.   (4)

    (iii)   On heating a mixture of m-toluidine and glycerol, turbidity appears at t_1 and on further heating turbidity is lost at t_2. Plot the phase diagram on the basis of the data and report the upper and lower consolute temperatures. Label the various regions with the number of phases and degrees of freedom.   (4)

Mass % of m- toluidine	18	20	40	60	80	85
t_1(°C)	48	18	8	10	19	25
t_2(°C)	53	90	120	118	83	53

4.   (i)   State and derive Lever rule.   (4)

     (ii)   Solute (X) shows normal molecular mass in water and is associated in benzene. Find the order of association from the following data

on the distribution of (X) between water and benzene :   (4)

Concentration in H_2O, g L^{-1}	Concentration in Benzene, g L^{-1}
0.020	0.1025
0.042	0.452
0.064	1.049
0.122	3.811

(iii) Derive the integrated form of Clausius-Clapeyron equation for liquid-vapour equilibrium.   (4)

5.   (i) Explain, giving reasons :   (4)

(a) A eutectic mixture has a definite composition and a sharp melting point yet it is not a compound.
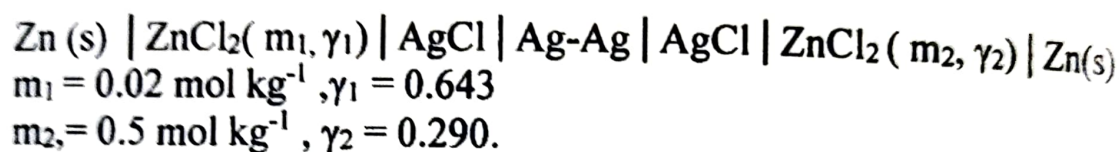
(b) Succinic acid alters the C.S.T of phenol-water system when added as impurity at constant pressure.

(ii) Au and Sb melt at 1060°C and 630°C respectively and form a compound $AuSb_2$, which melts congruently at 850°C. Two eutectic points are observed – one at 10 mol % Au at temperature 530°C and the other at 50 mol % Au at 700°C. Sketch the simplest phase diagram consistent with the information and label all the phase regions. Draw a cooling curve for a melt containing 60 mol % of Sb.   (6)

(iii) Explain the statement "physisorption does not occur at temperatures that are much above critical temperature of adsorbate".

(2)

Section B

6.   (i) Find the cell reaction and calculate the potential of the following cell at 298 K.

(4)

Zn (s) | ZnCl$_2$(m$_1$, γ_1) | AgCl | Ag-Ag | AgCl | ZnCl$_2$ (m$_2$, γ_2) | Zn$_{(s)}$
m$_1$ = 0.02 mol kg^{-1} ,γ_1 = 0.643
m$_2$,= 0.5 mol kg^{-1} , γ_2 = 0.290.

(ii) Derive an expression for calculating liquid junction potential for a cell in which electrodes are reversible with respect to cation.   (4)

(iii) Predict whether following data of adsorption of acetic acid over 1 g of charcoal at 25°C follows Freundlich adsorption isotherms. Also determine its constants k and n.   (4)

[acid]/mol L^{-1}	0.05	0.1	0.5	1.0
Mass adsorbed/g	0.04	0.06	0.12	0.16

7.   (i) Using Gibbs-Helmholtz equation derive the expressions for ΔG and ΔH.   (4)

(ii) The emf of the cell　　　　　　　　　　　　(4)

Ag | AgCl(s) | KCl (aq) | Hg_2Cl_2(s) | Hg
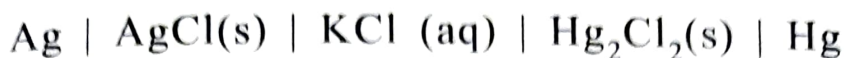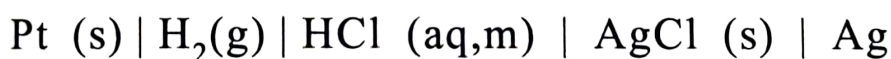
is 0.0421V at 298 K and the temperature coefficient is 3.4×10^{-4}V K^{-1}. What is the reaction taking place in the cell and what are the free energy, enthalpy and entropy changes at 298 K.

(iii) Describe a glass electrode. What are its limitations? Explain, how the pH of a solution is determined using a glass electrode.　　　(4)

8.　(i) The potential of Hamed cell　　　　　(4)

Pt (s) | H_2(g) | HCl (aq,m) | AgCl (s) | Ag

at 25°C has the following values. Determine the standard electrode potential of silver-silver chloride electrode.

$m/10^{-3}$	3.215	5.619	9.138
E_{cell}/V	0.520	0.49257	0.46860

(ii) Discuss the criteria of spontaneity of a cell reaction in terms of cell potential. In which direction will the following reactions be spontaneous when all concentrations are unity? Give reason.　　　(4)

(a) $2Cr + 3Cu^{2+} \rightleftharpoons 2Cr^{3+} + 3Cu$

(b) $Mn^{2+} + 4H_2O + 5Fe^{3+} \rightleftharpoons MnO_4^- + 8H^+ + 5Fe^{2+}$
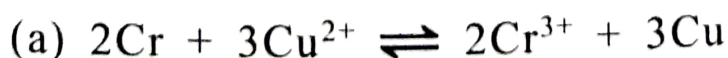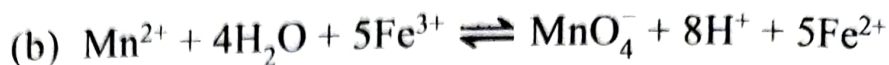
(iii) Derive the following relation between the pressure required to produce a fixed amount of adsorption and the enthalpy of adsorption. Explain how it can be used to determine the enthalpy of adsorption of a gas on solid.

$$\ln\left(\frac{p}{p^0}\right) = \frac{\Delta_{ads}H}{R}\frac{1}{T} + constant \qquad (4)$$

9. (i) Determine the standard equilibrium constant for the following reaction at 298 K.

$Cd^{2+} + 4\ NH_3 \leftrightarrow [Cd(NH_3)]_4^{2+}$ \qquad (4)
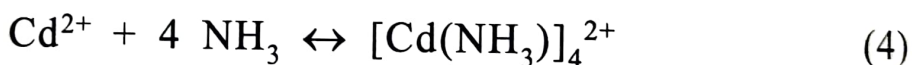
(ii) What is a reference electrode? Give one example; write its cell representation and Nernst equation. \qquad (4)

(iii) Justify the following statements : \qquad (4)

(a) If the standard potential of $E^0_{M^{n+}|M}$ is positive, then M^{n+} ions can be reduced to M by hydrogen gas under standard conditions.

(b) Instead of pieces of charcoal, activated charcoal is used in adsorption studies.