

Biyani's Think Tank

Concept based notes

Inorganic Chemistry

(B.Sc. Part-II)

Anupam Singh

Deptt. of Science

Biyani Girls College, Jaipur



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Ph : 0141-2338371, 2338591-95 • Fax : 0141-2338007

E-mail : acad@biyanicolleges.org

Website :www.gurukpo.com; www.biyanicolleges.org

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Preface

I am glad to present this book, especially designed to serve the needs of the students. The book has been written keeping in mind the general weakness in understanding the fundamental concepts of the topics. The book is self-explanatory and adopts the “Teach Yourself” style. It is based on question-answer pattern. The language of book is quite easy and understandable based on scientific approach.

Any further improvement in the contents of the book by making corrections, omission and inclusion is keen to be achieved based on suggestions from the readers for which the author shall be obliged.

I acknowledge special thanks to Mr. Rajeev Biyani, *Chairman* & Dr. Sanjay Biyani, *Director (Acad.)* Biyani Group of Colleges, who are the backbones and main concept provider and also have been constant source of motivation throughout this Endeavour. They played an active role in coordinating the various stages of this Endeavour and spearheaded the publishing work.

I look forward to receiving valuable suggestions from professors of various educational institutions, other faculty members and students for improvement of the quality of the book. The reader may feel free to send in their comments and suggestions to the under mentioned address.

Author

Syllabus

Section-A

Uni-I Transition elements : Electronic configuration and comparative study of elements of first transition series with respect to atomic and ionic radii ionisation potentials, redox magnetic catalytic activity. colour and behaviour of transition metal ions.

Uni-II Lanthanides and Actinides : General study, electronic configuration. oxidation states. magnetic properties. complexation behavior of transition metal ions.

Unit-II Lanthanides and Actinides : General study, electronic configuration. oxidation states. magnetic properties, complexation behaviour. Lanthanide contraction. separation of Lanthanides, comparison of lanthanides and Actinides. super heavy elements.

Section-B

Unit-III Coordination Chemistry: Werner's theory Nomenclature chelates: Stereochemistry of different coordination numbers: Isomerism in coordination complexes: Elementary idea of valence bond & crystal field theories to explain bonding in transition metal complexes: Explanation of magnetism, geometry and colour of coordination complexes: on the basis of the above theories Defects of CFT adjusted CFT Jahn-Teller effect.

Unit-IV Study of Rare Metals : Chemistry of the following metals with respect to their separation and isolation, oxidation, states and coordination behavior-Zr, Hf, V, Mo, W, Th and Platinum metals.

Section-C

Unit-V : (i) Complex Ligands. stabilisation of lower oxidation states in complexes, Metal Carbonyl. Synthesis, Structure and bonding mononuclear complexes). Metal nitrosyl.

Unit-VI: (a) Crystalfield stabilisation energy- Application of Crystal field stabilisation energy in explaining ionic radii of divalent ions of first transition series Heat of hydration of divalent ions of first transition series.

(b)Catalysis- Homogeneous and heterogeneous catalysis theories of catalysis- Applications in Industry.

Note : Each Paper will contain nine questions having three questions in each section. Candidates are required to attempt five questions in all selecting one question from each section.

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Chapter 1

Actinides

Q.1 What are actinides?

Ans. These are the fourteen elements from thorium to lawrencium which follow actinium in the periodic table. These are also called as actinons or actinoids.

Q.2 Discuss the similarities and dissimilarities between lanthanides and actinides.

Ans. Similarities between actinides and lanthanides

- (1) Both of them have +3 oxidation state.
- (2) In both the cases 'f' orbitals are progressively filled.
- (3) Actinide and lanthanide contraction takes place.
- (4) Absorption spectra have sharp lines like bands which appear due to "f - f" transition.
- (5) Both of them have low electro-ivity and are very reactive.
- (6) Nitrates, perchlorates and sulphate of trivalent actinides and lanthanides are soluble while hydroxides, fluorides and carbonates are insoluble.
- (7) Both of them show ion exchange behaviour.

Difference between lanthanides and actinides

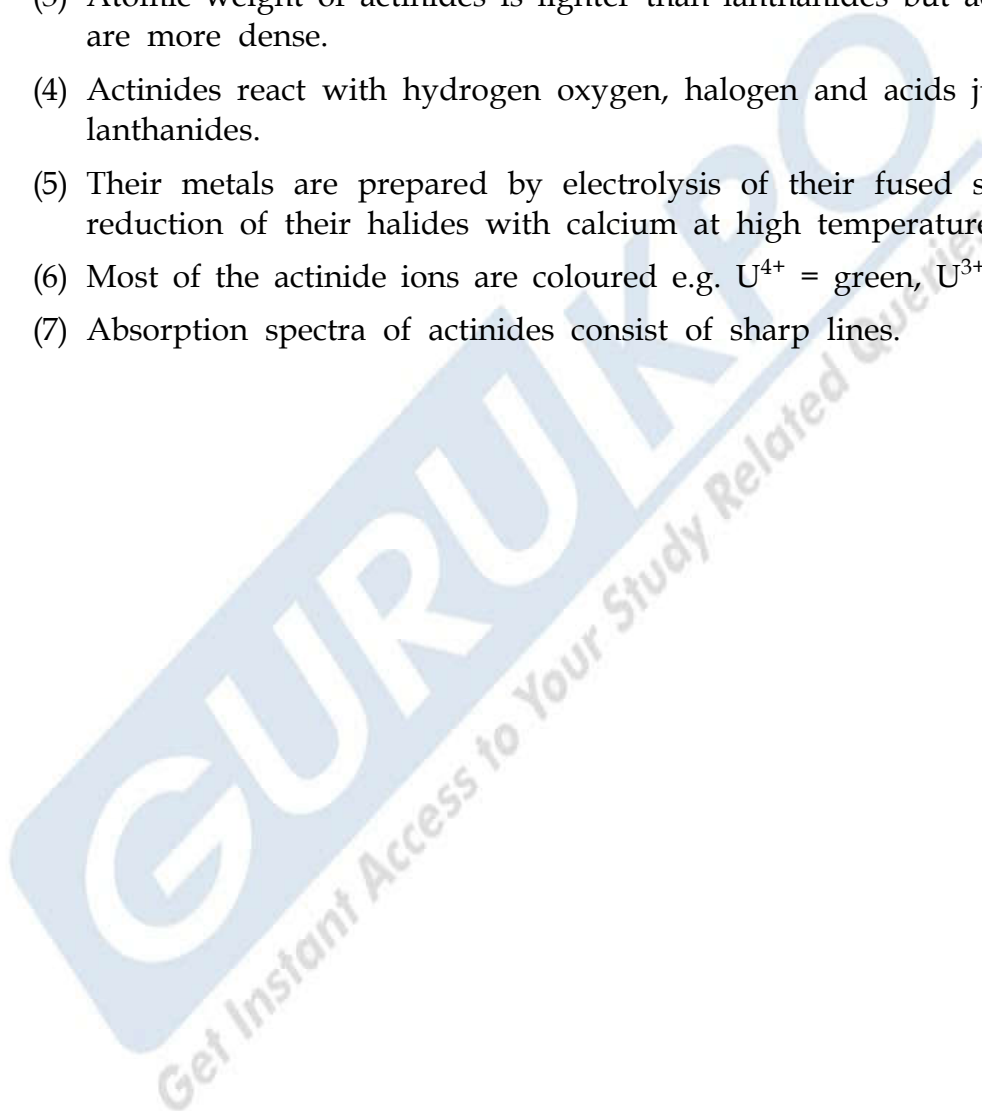
Lanthanides	Actinides
(1) In μ_f and 5d sub-shell, there is a large energy gap ? B'Coz of this they are having same chemistry.	(1) There is a small gap between 5f and 6 d levels so there is a difference in the chemistry of these elements.
(2) + 4 is the maximum oxidation state experienced by lanthanides e.g. + 4 ? in Ce	(2) They are having variable oxidation et ate and it is because of low binding energy of 5f.
(3) 4 f experience high binding energy.	(3) 5 f experience low binding energy.
(4) In lanthanides mostly ions are not coloured.	(4) Here most of the ions are coloured e.g. U^{4+} (Green), UO^{2+} (Yellow), U^{3+} (red)
(5) 4 f electrons experiences greater shielding effect.	(5) 5 f eldctrons experiences less shielding effect.
(6) They do not form complexes easily.	(6) They can form complexes easily.
(7) Except promethium, generally they are non-radioactive.	(7) All of them are radioactive in nature.
(8) Compounds are less basic in nature.	(8) Compounds are more basic in nature.
(9) They can't form oxocations.	(9) They can form oxocation needes. E.g UO_2^{2+} , UO^+

Q.3 Why actinides have greater tendency of forming complexes than lanthanides?

Ans. Actinides have greater tendency of forming complex than lanthanides because of lower binding energies and less effective shielding by the electrons of the 5f as compared to 4f electron.

Q.4 Explain the general properties of Actinides.

- Ans.**
- (1) In this series all the metals are with fairly high melting point e.g. Th = 1320 K (lower m.pt than transition elements).
 - (2) Ionic radius decreases along the series which is called as actinide contraction.
 - (3) Atomic weight of actinides is lighter than lanthanides but actinides are more dense.
 - (4) Actinides react with hydrogen oxygen, halogen and acids just like lanthanides.
 - (5) Their metals are prepared by electrolysis of their fused salts by reduction of their halides with calcium at high temperature.
 - (6) Most of the actinide ions are coloured e.g. U^{4+} = green, U^{3+} = Red
 - (7) Absorption spectra of actinides consist of sharp lines.



Chapter 2

Oxidation and Reduction

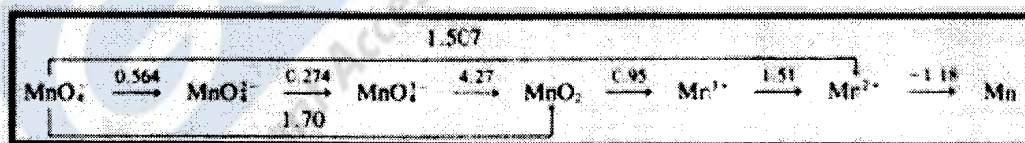
Q.1 What is Latimer diagram?

Ans. A Latimer diagram is a diagram in which the chemical species in the highest oxidation state is placed at the left end and a series of the reduced chemical species of the same atom are arranged to the right-hand side in the order of the oxidation states, and the standard reduction potentials (/V) are written above the line which connects each state.

This diagram is convenient for discussing a redox reaction.

Since electric potential differs between an acidic and a basic solution, different diagrams are required depending on the pH of the solution.

The Latimer diagram for a series of manganese species in acidic solution is shown below.

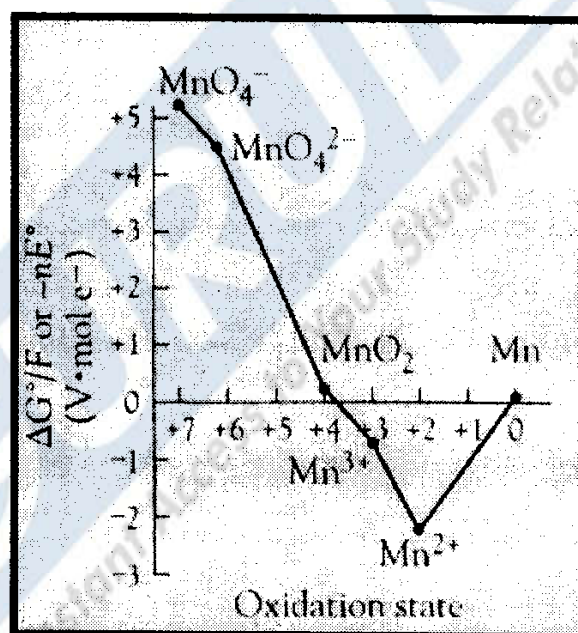


The Standard reduction potential for the reduction half-reaction involving the two species joined by the arrow is shown above the arrow. Latimer diagrams show the redox information about a series of species in a very condensed form. From these diagrams you can predict the redox behavior of a given species. The more positive the standard reduction potential,

the more readily the species on the left is reduced to the species on the right side of the arrow. Thus, highly positive standard reduction potentials indicate that the species at the left is a good oxidizing agent. Negative standard reduction potentials indicate that the species to the right behaves as a reducing agent.

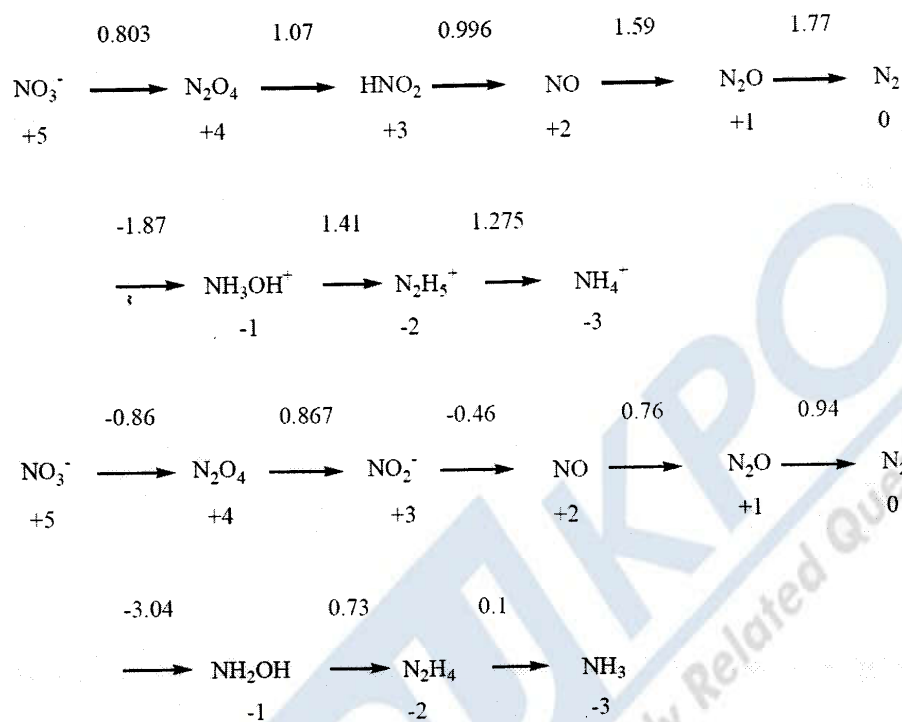
Q.2 What is Frost diagram? Explain it with reference to manganese?

Ans. Frost or oxidation state diagrams plot the relative free energy of a species versus oxidation state. These diagrams visually show quite a bit about the properties of the different oxidation states of a species. Frost diagrams can be constructed from Latimer diagrams. The values to be plotted on the y-axis are obtained by multiplying the number of electrons transferred during an oxidation state change by the standard reduction potential for that change.



Q.3 How to construct a Latimer diagram taking the series of the oxides and hydrides of nitrogen in acidic solution as an example?

Ans. For oxides and hydrides in a acidic solution



The additivity of the state function ΔG^0 is used in order to calculate the standard reduction.

Potential between oxidation states.

$$\begin{aligned}
 \Delta G^0 &= \Delta G_1^0 + \Delta G_2^0 \\
 - (n_1 + n_2)FE^0 &= -n_1FE_1^0 - n_2FE_2^0
 \end{aligned}$$

Where the free energy change and electric potential between adjacent states are ΔG_1^0 , E_1^0 , ΔG_2^0 , E_2^0 , respectively, and the number of transferred electrons n_1, n_2 . Namely

$$E^0 = \frac{n_1E_1^0 + n_2E_2^0}{n_1 + n_2}$$

For example, in the reduction of NO_3^- to HNO_2 , two electrons are transferred to form HNO_2 via N_2O_4 and the potential becomes

$$E^0 = \frac{0.803V + 1.07V}{2}$$

Example 3.2 Calculate the reduction potential of the reduction of NO_3^- to NO_2^- in a basic solution.

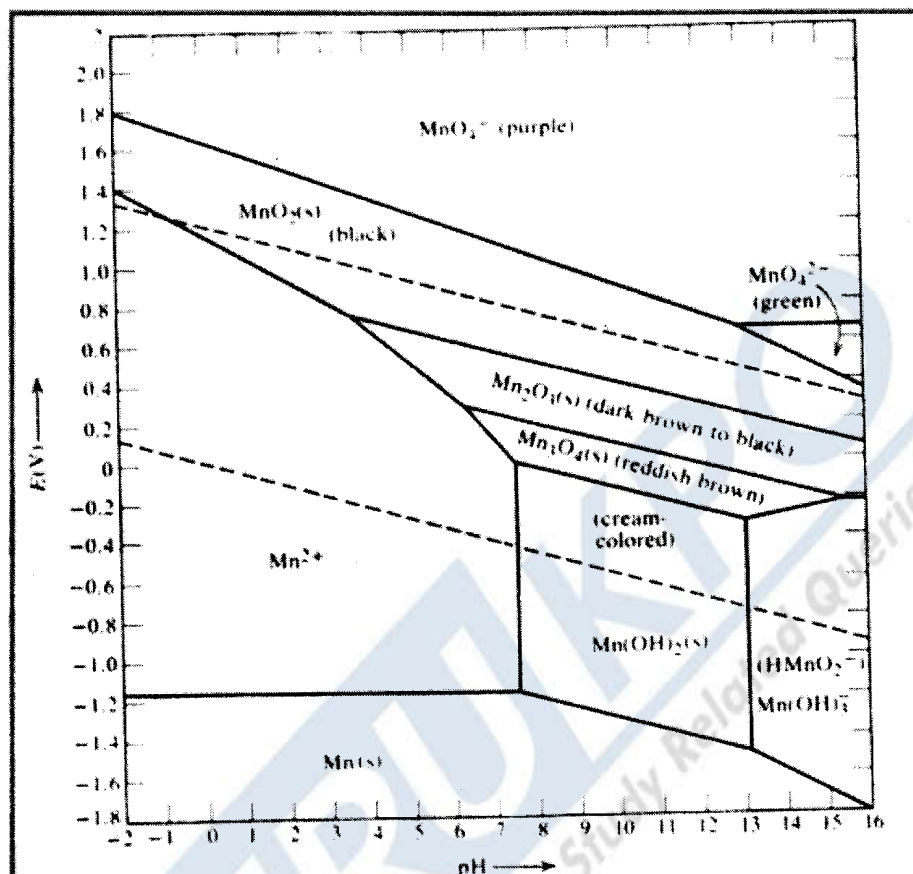
Ans. $E^0 = \frac{-0.86V + 1.867V}{2} = 0.004V$

Q.4 What is Pourbaix Diagrams or EH-PH diagram? How to read Pourbaix Diagrams?

Ans. Pourbaix or eh-pH diagrams depict the thermodynamically form of an element as a function of potential and pH. The Pourbaix diagram is a type of predominance diagram- it shows that predominate form in an element will exist under a given set of environmental conditions. These diagrams give a visual representation of the oxidizing and reducing abilities of the major stable compounds of an element and are used frequently in geochemical, environmental and corrosion applications.

Reading a Pourbaix Diagram

- Vertical lines separate species that are in acid-base equilibrium.
- Non vertical lines separate species related by redox equilibria.
 - Horizontal lines separate species in redox equilibria not involving hydrogen or hydroxide ions.
 - Diagonal boundaries separate species in redox equilibria in which hydroxide or hydrogen ions are involved.
- Dashed lines enclose the practical region of stability of the water solvent to oxidation or reduction.



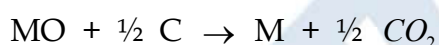
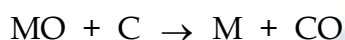
Uses of Pourbaix Diagram

- Any point on the diagram will give the thermodynamically most stable (and theoretically most abundant) form of that element at a given potential and pH condition.
- Strong oxidizing agents and oxidizing conditions are found only at the top of Pourbaix diagrams.
- Strong oxidizing agents have lower boundaries that are also high on the diagram. Permanganate is an oxidizing agent over all pH ranges. It is very strongly oxidizing at low pH.
- Reducing agents and reducing conditions are found at the bottom of a diagram and not elsewhere.

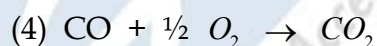
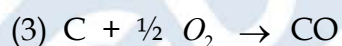
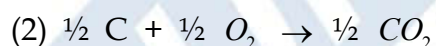
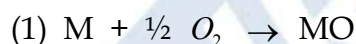
- Strong reducing agents have low upper boundaries on the diagram. Manganese metal is a reducing agent over all pH ranges and is strongest in basic conditions.
- When the predominance area for a given oxidation state disappears completely above or below a given pH and the element is in an intermediate oxidation state, the element will undergo disproportionation MnO_4^{2-} tends to disproportionate.
- A species that ranges from the top to the bottom of the diagram at a given pH will have no oxidizing or reducing properties at that pH.

Q.4 Explain Ellingham diagram with examples?

Ans. When metal oxides get reduced by carbon, one of the following process occur



These equilibria can be discussed in terms of the thermodynamic function of the reactions

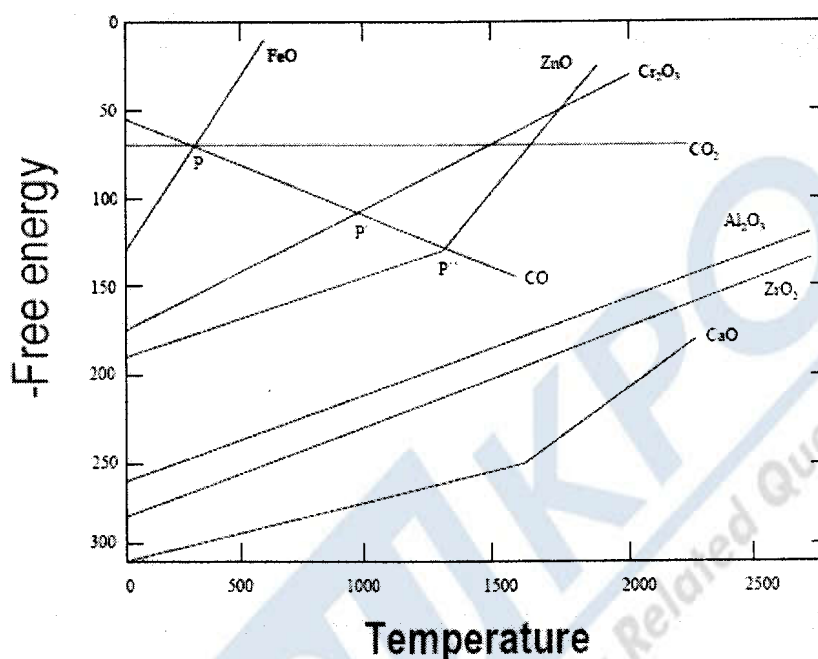


Temperature dependence of these reactions depend on the entropy change.

$(d\Delta G/dT)_P = -\Delta S$ ΔS° of reaction 3 is higher than that of 2, since there is an increase in number of moles.

In entropy units, the former is only 0.1 and the later is 8.5.

Thus, ΔG decreases sharply with temperature for 3.

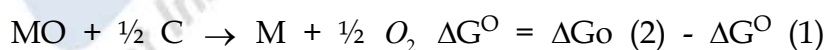


The Gibbs function for reaction 1 represents the metal's affinity for oxygen. At room temperature ΔH^0 dominates ΔG^0 . The entropy of rxn is about the same for different metals because of similar volume change. Thus ΔG has similar temperature dependence for different metals.

Look at the graph. The kinds correspond to evaporation of the metals.

Reduction of oxide by carbon depends on the affinity of metal to oxygen in comparison to carbon. Gibbs function for the relevant processes can be expressed in terms of the Gibbs functions for the oxidation reaction.

Inverting 1 and adding to 3



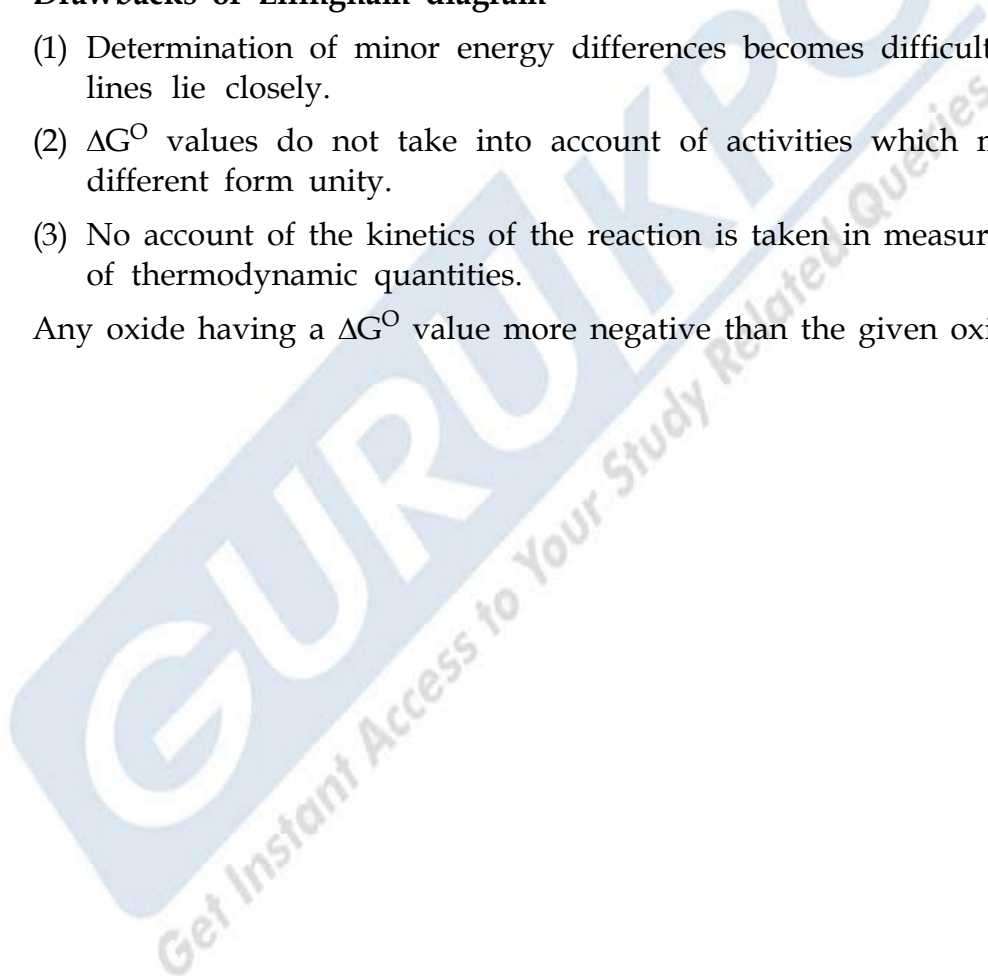
Equilibrium lies to the right if $\Delta G^0 < 0$.

This will happen if ΔG° (1) lies below the carbon reaction 2- 4. At any temperature the feasibility of the reaction can be predicted examining the diagram. CuO can be reduced to copper any temperature above room temperature. Ag_2O can be decomposed above 200°C simply by heating. Above 200°C the decomposition is spontaneous. Al_2O_3 can be decomposed only above 2000°C . It cannot be reduced to metal by CO even up to 3000°C . Position of equilibrium at any temperature can be obtained by measuring the vertical separation between the lines. Similar curves can be drawn for sulphides, nitrides, phosphates, halides, etc.

Drawbacks of Ellingham diagram

- (1) Determination of minor energy differences becomes difficult if the lines lie closely.
- (2) ΔG° values do not take into account of activities which may be different from unity.
- (3) No account of the kinetics of the reaction is taken in measurements of thermodynamic quantities.

Any oxide having a ΔG° value more negative than the given oxide can



Chapter 3

Lanthanides

be used to reduce the oxide.

Q.1 What are lanthanides?

Ans. They are also called as inner-transition elements. These elements (atomic number 58-71) follow lanthanum (at. No - 57) and are called as lanthanides or lanthanones and this series is called as lanthanide series.

Q.2 What is lanthanide contraction?

Ans. In the case of lanthanide atoms (or ions) the nuclear charge increases with atomic number while the differentiating electron is being added in an inner orbital (4f). The shielding of one 4 f electron by another from the increasing nuclear charge is not perfect and this is because of difference in the shapes of orbitals. As the atomic number increases, the effective nuclear charge experienced by each 4 f electron also increases. This causes a slight reduction in the entire 4fⁿ shell. The successive contraction accumulates and the total effect for all the lanthanones is the lanthanide contraction.

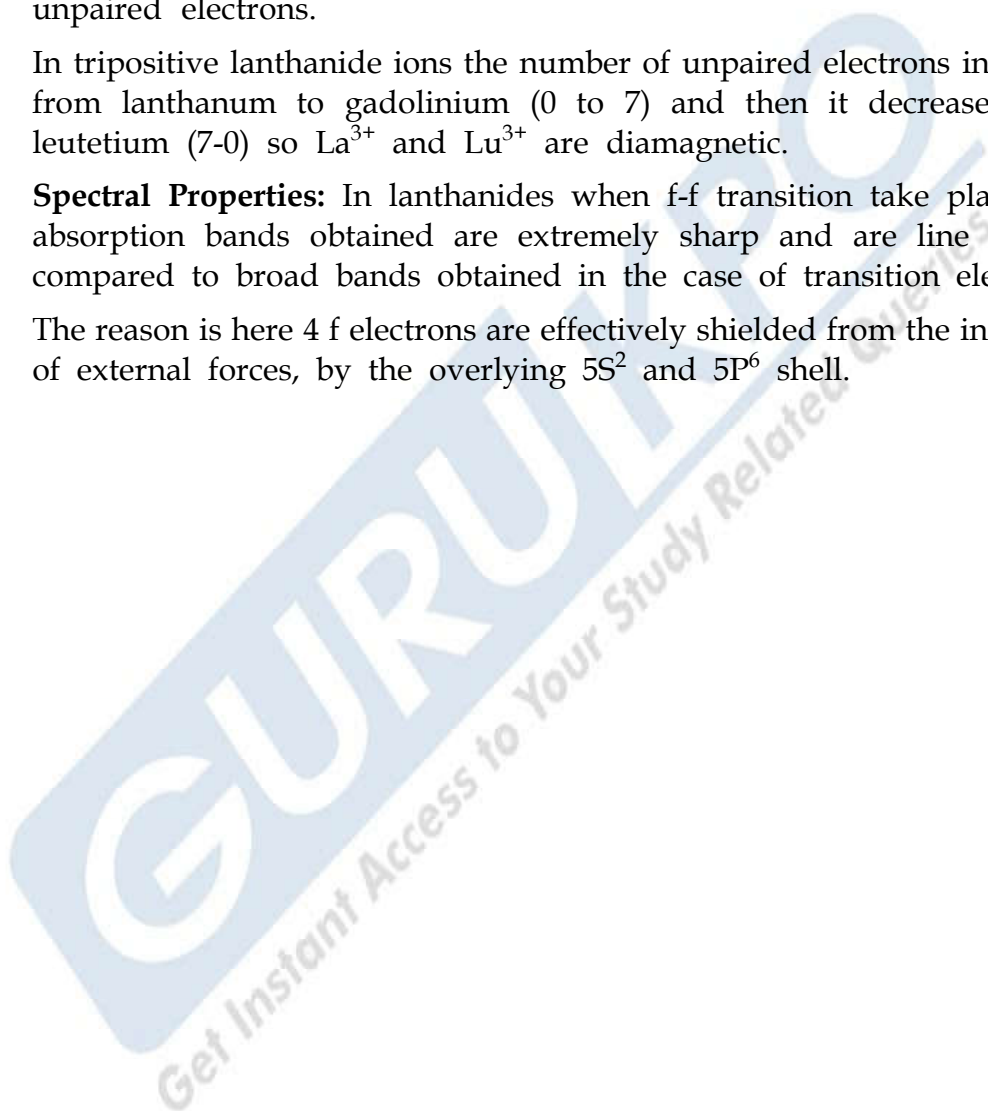
Q.3 Explain spectral and Magnetic properties of lanthanides?

Ans. Magnetic Properties: All the tripositive ions of lanthanones are paramagnetic in nature except La^{3+} and Lu^{3+} (they don't contain any unpaired electron). This paramagnetism is contributed by spin of the electron as well as by its orbital motion. Here observed paramagnetism is due to electron spin only and it depends mostly on the number of unpaired electrons.

In tripositive lanthanide ions the number of unpaired electrons increases from lanthanum to gadolinium (0 to 7) and then it decreases upto leutetium (7-0) so La^{3+} and Lu^{3+} are diamagnetic.

Spectral Properties: In lanthanides when f-f transition take place, the absorption bands obtained are extremely sharp and are line like as compared to broad bands obtained in the case of transition elements.

The reason is here 4 f electrons are effectively shielded from the influence of external forces, by the overlying $5s^2$ and $5p^6$ shell.



Chapter 4

Non-Aqueous Solvents

Except water all the liquids used to dissolve solutes are called as non-aqueous solvents.

Q.1 Give classification of solvents.

Ans. Classification of solvents depends upon some particular physical or chemical properties. There are various classifications given which is like this-

- (i) Classification based on proton donor and proton acceptor behaviour.
- (ii) Classification based on ionising and non-ionising solvents.
- (iii) Aqueous and non-Aqueous solvents.

Q.2 What are protonic or protic solvents? Explain them with example.

Ans. Protonic Solvents: Protonic solvents are divided into three series-

(a) Protogenic solvents: These are acidic in nature. They have tendency to donate protons.

e.g. HF, CH₃COOH, HCN

(b) Protophilic solvents: These are basic in nature and have the tendency to accept protons.

e.g. amine, ammonia and pyridine.

(c) Amphiprotic solvents: These are amphoteric in nature. They donate or accept protons depending upon the nature of reacting substances.

e.g. CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, H_2O

NON-PROTONIC OR NON-PROTIC SOLVENTS-

They neither donate nor accept protons e.g. CCl_4 , BrF_3 , C_6H_6

(II) IONISING AND NON-IONIZING SOLVENTS:

They undergo auto-dissociation and polar in nature.

e.g. $2\text{SO}_2 \rightleftharpoons \text{SO}^{2+} + \text{SO}_3^{2-}$

$2\text{HF} \rightleftharpoons \text{H}_2\text{F}^+ + \text{F}^-$

Non-ionising solvents: These are non-ionising in nature and are non-polar and have low dielectric constant.

e.g. CCl_4 , C_6H_6

Aqueous and non-aqueous solvents:-

Non aq. Solvent - except water all other solvents are called as non-aq solvents.

Aq. Solvents - H_2O

Q.3 Write down the physical properties of ionising solvents.

Ans. Physical properties of ionising solvents:-

- (1) Melting and boiling points
- (2) Dipole moment
- (3) Dielectric constant
- (4) Viscosity
- (5) Electrical conductivity
- (6) Association

Q.4 Explain the following chemical properties of ionising solvents:-

(a) Auto-dissociation

(b) Levelling effect

(c) Solvolysis

Ans. Auto-dissociation: - All ionising solvents undergo self-ionisation which is called as auto-dissociation. These are weak conductors of electricity.



These solvents get dissociated into 2 parts. One part is acidic in nature and another one is basic in nature.

Levelling effect: Acidic and basic strength depends upon the nature of solvents. If there is large difference in the proton donor tendency of the acid and the solvents then acid is fully ionised in such solvents and act as a strong acid but if the difference is less, than acid is not fully ionised.

e.g. HBr, HCl, HI

All these acids are strong acid in water and water is called as leveling solvents and this effect is called as leveling effect.

Strength of these acids in acetic acid is different so acetic acid is called as differentiating solvents for these acids.

Order of proton-donor tendency of acids:-



The Strength of bases in liquid ammonia solution is different so the order will be in this way -



Solvolysis:- The process by which a solute enters into solution by reacting with solvent is called as solvolysis.

During this process, the solvent molecular is split into 2 parts which become attached to a solute molecule or an ion.

e.g. hydrolysis

Q.5 Explain the physical properties of ammonia (used as a solvent).

Ans. (1) Liquid temperature range:- M.pt and B.pt of liquid ammonia is less than that of H₂O.

(2) Viscosity: Viscosity of ammonia is less than H₂O.

Vis of Liq ammonia = 0.241

Viscosity of H₂O = 1.0

So in ammonia, ionic reactions take place faster than H₂O.

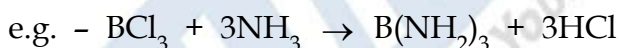
(3) Proton affinity:- Proton affinity of liq. NH₃ is more than H₂O so it acts as a leveling solvent for strong acids and weak acids. It is a differentiating solvent for strong bases.

(4) Dipole moment and dielectric constant:- The value of dipole moment and dielectric constant of liquid ammonia is less than of H₂O. So ionic compounds are less soluble in liquid NH₃ than H₂O. But the solubility of organic compounds is more in liq NH₃ in comparison to H₂O.

(5) Hygroscopicity: NH₃ is highly hygroscopic so it is having limitation as a solvent. So reactions of ammonia are possible in air-tight containers only.

Q.6 What is ammonolysis or ammonolytic reactions?

Ans. These reactions are double decomposition reactions. Here ammonia acts as a reactant. These reactions are also called as solvolysis reactions.



Q.7 Give at least two advantages of using liquid ammonia as a solvent.

Ans. (1) It dissolves alkali metals without reacting with them.
(2) For strong reducing agents liquid NH₃ is used as a solvent instead of H₂O because H₂O can react with them to liberate H₂.

Q.8 Explain the following reactions in liquid SO₂ solvent.

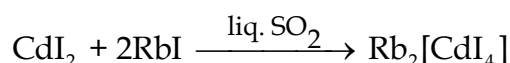
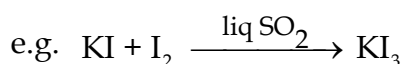
(1) Complex formation reactions.

(2) Reactions with organic compounds.

Ans. (1) Complex formation reactions:-

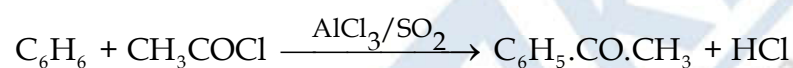
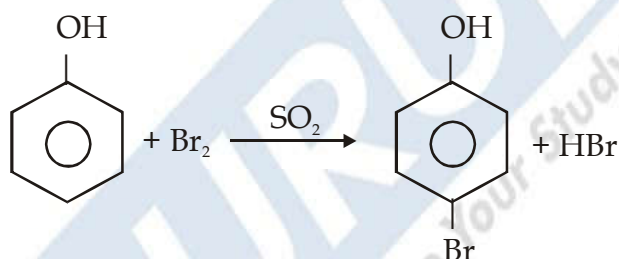
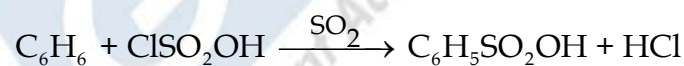
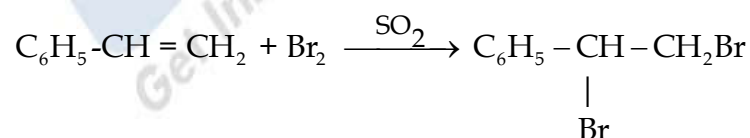
Complex formation reactions occurs in two ways:-

- (i) Solubility of precipitate in excess of its own anion.
- (ii) Complex formation not involving any precipitation.

**(2) Reactions with organic compounds:**

Liq NH_3 is a good solvent in organic synthetic reactions. And the reason is its inertness towards organic compounds and non-inflammability.

e.g. [I] Substitution Reactions:-

(a) Friedal Craft acetylation and Friedal Craft alkylation:-**(b) Bromination:-****Diagram****(c) Sulphonation:-****[II] Addition reaction:-**

Chapter 5

Coordination Compounds

Q.1 How can you classify inorganic compounds on the basis of complex formation.

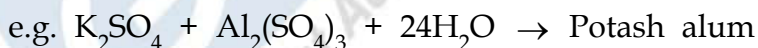
Ans. We can classify them into three parts:-

- (1) Simple salts
- (2) Double salts
- (3) Complex compounds

Simple salts:- When an acid reacts with an alkali then after neutralisation salt formation takes place.

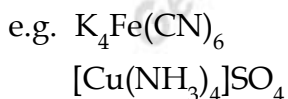


Double Salts: When a solution containing two or more salts is allowed to evaporate, then we get crystals of double salts.



Formula of Potash alum - $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

Complex Compounds: Complex Compounds are also called as coordinate compounds.



A Complex compound contains cations and anions. They can either be simple or complex.

Q.2 Explain the following -

(a) Coordination Compounds

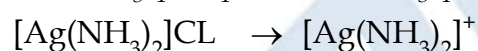
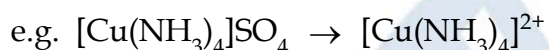
(b) Complex ion

(c) Ligand

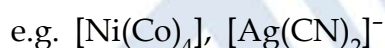
Ans. Coordination Compounds:- A Coordination Compound contains a central metal atom or cation. It is surrounded by a suitable number of anions or neutral molecules. It generally retains its identity in both solution and solid state.

A Coordination compound contains one or more complex ions.

Complex ion



Complex ion:- A Complex ion is an electrically charged species. It carries positive and - ve charges. Here the central atom or ions is surrounded by a suitable number of neutral molecules or - ve ion which are called as ligands.



Ligand: The neutral molecules or ions that surround the metal ion in a complex are called as ligands.

Ligands are generally polar molecules which have atleast one unshared pair of valence electrons.

The atom in the ligand which is involved in the formation of coordinate bond with central metal atom is called as donor atom. A ligand contains one or more donor sites. Depending upon the number of donor sites ligands can be classified as-

Unidentate \rightarrow with one donor site.

Bidentate \rightarrow with 2 donor site.

Tridentate → with 3 donor site

Tetradentate → with 4 donor site.

Hexadentate → with 6 donor site.

Q.3 What is Werner's Theory? Give its main points.

Ans. Alfred Werner in 1893 gave a theory for giving name to complex compounds. This theory not only explains the properties of coordinate compounds but also explains its structure.

Main Points of Werner theory are -

(1) Metals has $\left\{ \begin{array}{l} \text{Primary linkage} \\ \text{Secondary linkage} \end{array} \right.$

Pm. Linkage → satisfied by - ve ions

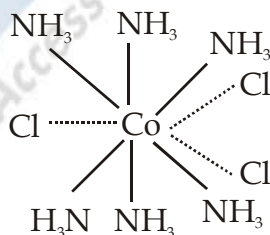
Sec. linkage → satisfied by either - ve ions or neutral ions

Pm. Valencies → are ionisable-also indicates oxidation no. of metal ion.

Sec. Valencies → non-ionisable valencies-refers to coordination number.

(2) Each metal atom have a characteristics number of secondary valencies about the central atom. These valencies are projected in the space about the central atom and it is in such a way that it assigns of definite geometry to the coordination compound.

e.g. - $\text{CoCl}_3 \cdot 6\text{NH}_3$



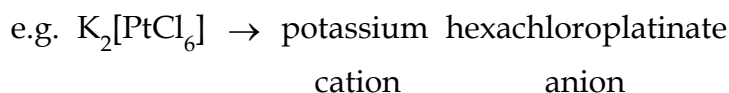
Dotted line represent pm. Valency

Bold line → sec. valency

Q.4 Explain the main points of a complex compound. IUPAC nomenclature).

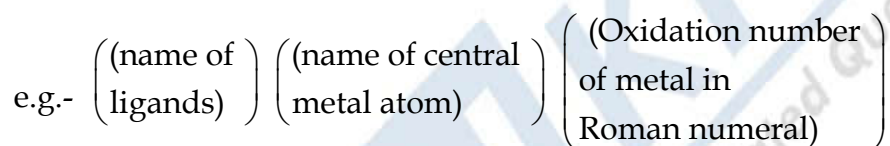
Ans. (1) Order of naming ions:-

Positive ion is named first followed by the name of negative ion. Preference is given to cation then to an anion.



For non-ionic complexes, the name of complex is written in one word.

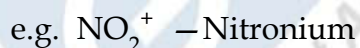
(2) Naming of Co-ordination sphere:- In naming the complex, the name of the ligands is written first followed by the name of the central ion. The oxidation number of the central metal atom is expressed by Roman numeral in parenthesis just after the name of the central metal atom.



(3) Naming of ligands - The central metal ion in a complex is surrounded by positive or negative or neutral ligands. If ligand carries a negative charge then, the name ends with the word 'O'



(4) If the legands carries a positive charge, then name of the ligand has an ending of 'ium'.



(5) The metals and ligands so arranged are enclosed in square brackets. The charge on the complex ion is calculated on the basis of the oxidation state of the metal and charges of ligands.

(6) The cations and anion are multiplied by the whole numbers that the total of positive and negative charges become zero. And the oxidation state of metal is generally not mentioned.

- (6) The number of each kind of ligands are specified by the prefixes di, tri, tetra etc.
- (7) Geometrical isomers are named by the use of the term cis or trans designating the position of ligands.
- (8) Complicated ligands are generally represented by abbreviations.
e.g. Pyridine → py
ethylenediamine → en

Q.5 What are isomers? How many types of isomers are possible in coordination compounds? Explain.

Ans. The two or more chemical compounds with identical chemical formula but different structures are called as isomers and this phenomenon is called as isomerism.

Depending upon the position and arrangement of ligands around the metal ion, we can classify them into 2 parts -

- (A) Structural Isomers
- (B) Stereo Isomers

These are the isomers which have different arrangement of ligands around the central metal atom.

Structural isomers are further classified like this -

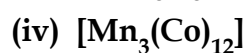
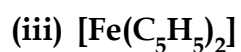
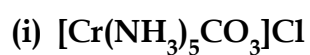
- (1) Ionisation isomers
- (2) Coordination isomers
- (3) Linkage isomers
- (4) Coordination - position isomers
- (5) Hydrate isomers
- (6) Polymerisation isomerism.

STEREOISOMERS:- When two coordination compounds have same structural formula but differ in the spatial arrangement of ligands around central metal atom, are called as stereoisomers.

These are of two types -

- (1) Geometrical isomers.
- (2) Optical isomers

Q.6 Write down the IUPAC names of the following complexes.

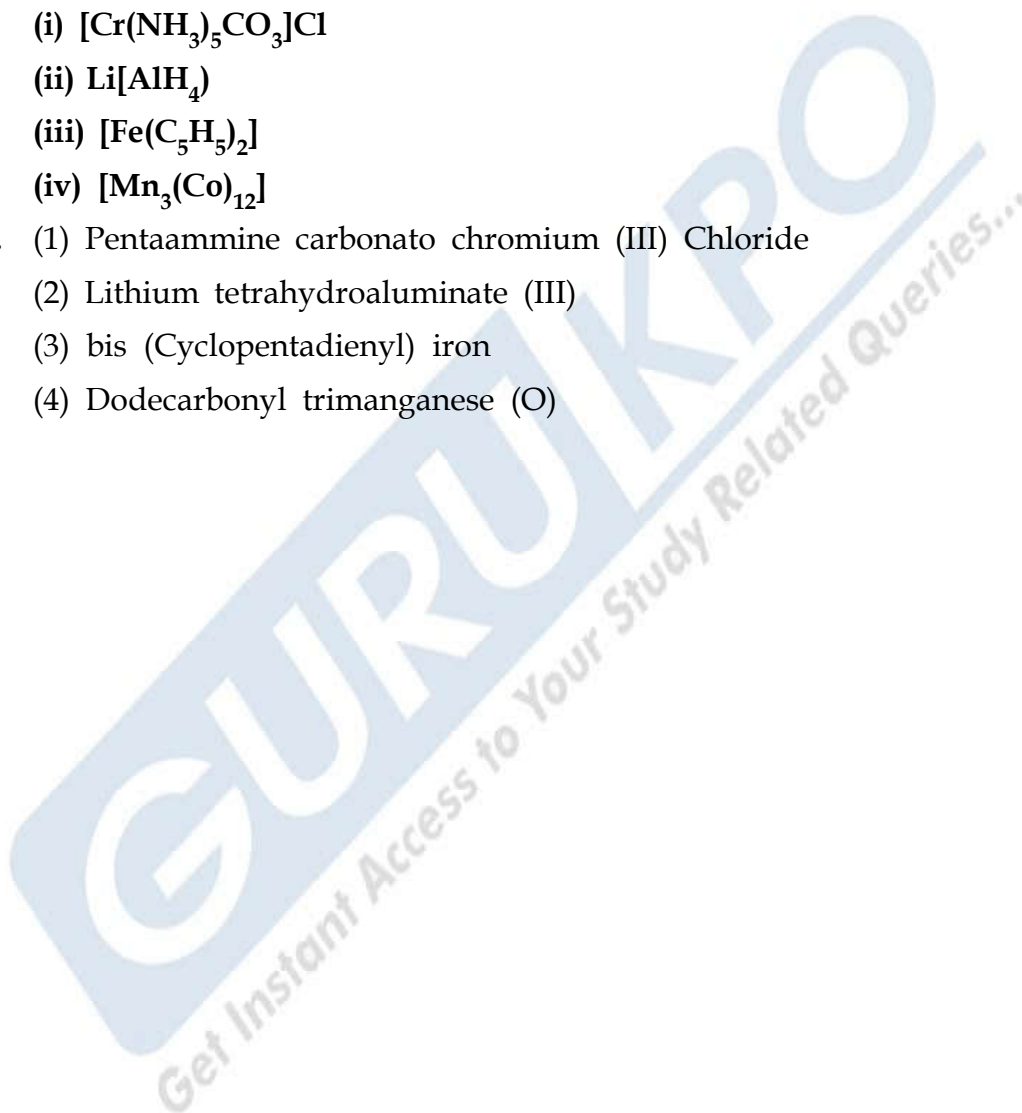


Ans. (1) Pentaammine carbonato chromium (III) Chloride

(2) Lithium tetrahydroaluminate (III)

(3) bis (Cyclopentadienyl) iron

(4) Dodecarbonyl trimanganese (0)

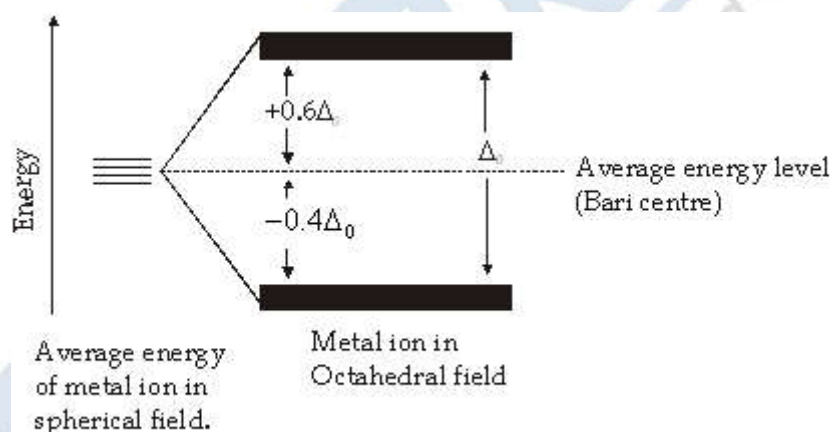


Chapter 6

Chemistry of Elements of Second and Third T.S.

Q.1 Explain Crystal field splitting of energy levels in an octahedral field.

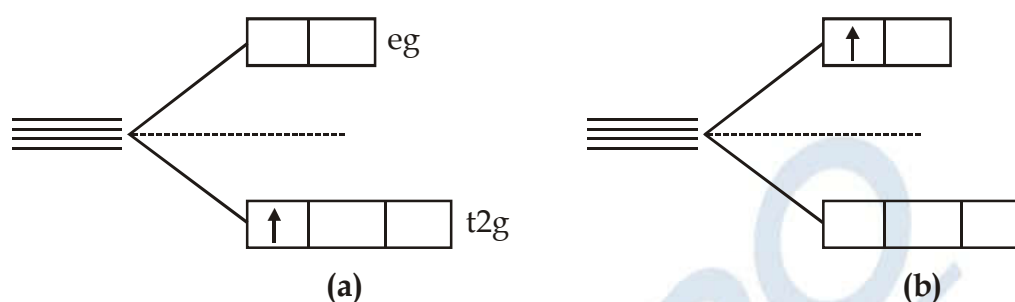
Ans.



The energy gap Δ_0 between the t_{2g} and e_g levels can be measured easily by recording UV visible spectrum of the complex.

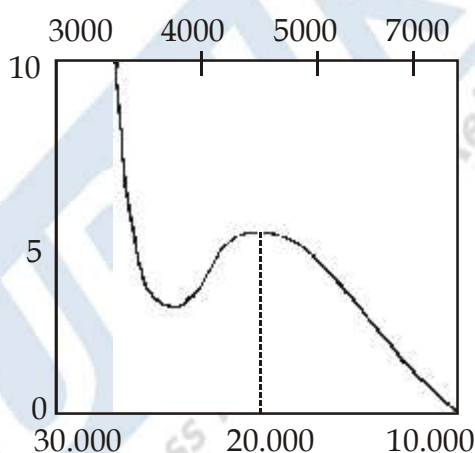
The average of two sets of orbitals t_{2g} and e_g is taken as the zero; this is known the Bari centre. The difference in energy between the two d levels is given either of the symbols Δ_0 or $10 Dq$. It follows that the e_g orbitals are $+0.6\Delta_0$ above the average level, and the t_{2g} orbitals are $-0.4\Delta_0$ below the average.

In a complex like $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ The Ti^{3+} ion has one d electron. In the complex this will occupy the orbital with the lowest energy i.e. t_{2g} orbitals.



d^1 Configuration: (a) ground state, (b) excited state

The complex absorbs light of the appropriate wavelength (energy) to promote the electron from t_{2g} level to the e_g level.



The electronic spectrum for $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is given in above figure.

The steep part of the curve is from 27,000 to 30,000 cm^{-1} (in the UV region) is due to charge transfer. The d-d transition is the single broad peak with a maximum frequency at 20,300 cm^{-1} .

The above method is the most convenient method of measuring Δ_0 values. However, Δ_0 values can also be obtained from values of observed lattice energies and those calculated using the Born-Landé equation.

Because the crystal field splitting of d orbitals, the single d electron in $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ occupies an energy level $2/5\Delta_0$ below the average energy

of the d orbitals. As a result the complex is more stable. The crystal field stabilization energy (CFSE) is in the case $2/5 \times 2/3 = 97 \text{ KJ Mol}^{-1}$.

The substitution of nitrogen containing ligands for the water molecules in aqua complex $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ intensifies the blue colours.

$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ Blue

$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ - Dark Blue

$[\text{Cu}(\text{Cn})_2(\text{H}_2\text{O})_2]^{2+}$ - Intense dark blue

The variation in colours is due to the change in Δ_o in the following and this shifts the absorption band from far-red to middle red.

$\text{H}_2\text{O} < \text{NH}_3 < \text{en}$

Q.2 What are the factors which influence the magnitude of crystal field splitting energy (Δ)

- Ans.**
- (1) Charge on metal ion.
 - (2) No. of d-electrons.
 - (3) Principal quantum number of d-orbitals of metal ion.
 - (4) Strong field and weak field ligands.
 - (5) Size of ligand.
 - (6) Geometry of the complex.

Q.3 Why the magnitude of the crystal field splitting Δ_t in tetrahedral complex is less than octahedral field?

- Ans.** There are two reasons for it-
- (1) There exist four ligands instead of six so ligand field is only $2/3$ in size. So ligand field splitting also get reduced to two third of the size.
 - (2) The direction of orbitals does not coincide with the direction of ligand. Hence crystal field splitting again get reduced.

Q.4 What are noble metals? Discuss their properties.

- Ans.** Ruthenium, Osmium, Rhodium, Iridium, Palladium and Platinum are

generally called as Noble metals.

Generally these occur with the sulphide ores of copper and nickel. These metals when heated yield their compounds. Osmium get easily oxidised by air into volatile tetroxide and ruthenium to the non-volatile dioxide.

These metals are generally hard in nature so they are used for making electrical contacts, pen nib tips and for making special crucibles.



Chapter 7

Acids and Base

Q.1 Explain Arrhenius concept of acids and bases with examples.

Ans. Arrhenius concept (water ion concept) -

Svante Arrhenius (Swedish in 1887).

Acc to Arrhenius theory an acid is defined as a hydrogen compound which in aqueous solution gives hydroxyl ion a base is hydroxide compound which in aqueous solution gives hydroxyl ions or a hydrogen ion and the process of neutralization occurs by the union of H and Hydroxyl ion to form water.

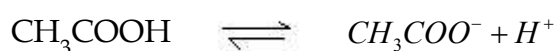
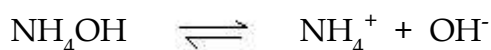
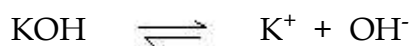
H.A. - aq. Soln $\rightarrow H^+ + A^-$

H.A. aq Sol $\rightarrow H^+ + A^-$

Examples:- Acid:- HCl, HNO₃, CH₃COOH, H₂SO₄

Base:- NaOH, KOH, NH₄OH

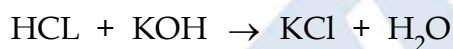




HCl and HNO₃ are completely ionised in water and are called as strong acids and acids like CH₃COOH are weakly ionised are called as Weak Acid.

In Bases NaOH and KOH are strong whereas NH₄OH and CaOH₂ are weak bases.

Acids and Bases react to give salt and water and this process is called as Nutralisation.



Utility of Arrhenius Concept:-

Arrhenius theory is able to explain about the heat of nutralisation of all strong acids and strong Bases (always constant) (-57.1 KJ)

Q.2 What are the limitations of water-ion system.

Ans. Limitations of water ion system:-

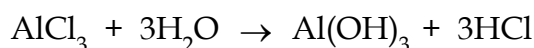
- (1) The Arrhenius concept of acids and Bases was only in terms of water and not for other solvent so when these acids like HCL, H₂SO₄ are dissolved in water are considered as acid but not in other solvents e.g. - Benzene
- (2) It was not able to explain the properties of salts like Ammonium nitrate (NH₄NO₃) in liq. Ammonia system, where H ions are not present.

This was unable to explain the basicity of an aqueous soln of NH₃ and

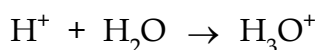
he gave no prove for the existence for ammonium hydroxide compound.



He was not able to give a proper explanation for the acidity of the salt like AlCl_3 . He said that these salts hydrolised but it was totally untrue.



The hydration energy of the Hydrogen ion is about 256 Kcals/mole and it was expected that this ion exist only in hydrated form so it put emphasis on hydrogen ion in aqueous solution.



This theory unable to explain about acid base Rx it occurs in gaseous state or in non aqueous solvent.

It was unable to explain about the basic nature of some metal oxide like Na_2O , CaO .

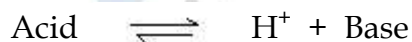
Q.3 Explain in detail the Concept of Bronsted and Lowry for acids and base.

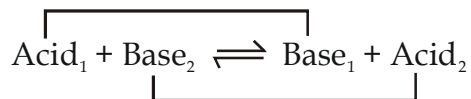
Ans. Bronsted and Lowry Concept (Proton donor acceptor system)

An acid is a substance which has tendency to loose 1 or more protons and a base is a substance that has a tendency to gain proton. It can be divided into 3 types -

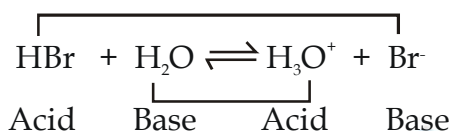
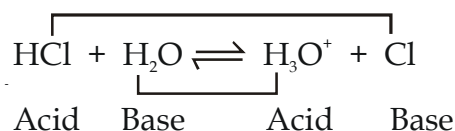
- (1) Molecular (HCl)
- (2) Cationic⁺ (Fe)
- (3) Anionic (HSO_4^-)

The Reaction of an acid with a base produces another acid and a base so we can say that relationship involves 2 acids and 2 bases and both of them are called as conjugate pair.



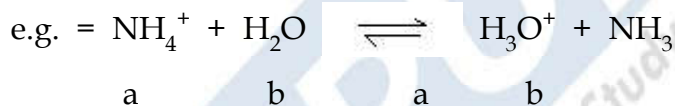


NOTE: HCl and HBr in liq state are poor conductor of electricity because they are covalent compounds but in water soln these compounds are strong electrolytes.

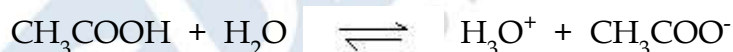


Certain covalent compounds they may become strong electrolytes by solvations.

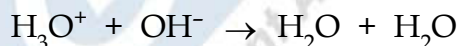
In aqueous soln ammonium ion (NH_4^+) may act as an acid.



Acetic acid is a weak acid and it gives only few hydronium ion in solution and it is covalent compound and here water act as a base.



Acc to Bronsted theory all those compound having - ve ion are called as base because they combine to a proton.



The strength of an acid depends on the strength of a solvent as a base i.e. on its ability to accept a proton from an acid. We can classify solvents into 4 parts.

(1) Protophilic:-

e.g. \rightarrow liq NH_3 (Proton acceptor)

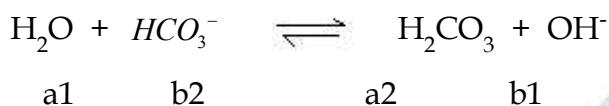
(2) Protogenic:-

H_2SO_4 and HF (Proton donors)

(3) Amphiprotic:- H_2O (act both as proton donors as well as proton acceptors)

(4) Aprotic:- liq SO_2 (neither proton donor nor proton acceptor)

Conclusion:- Protophilic solvent are basic, protogenic solvents are acids, water can act as an acid or base.



The stronger the acid the weaker must be its conjugate base and strength of a base is measured by its capacity to give proton. The acid or basic nature of the compound depends on the nature of the solvent used.

Bronsted Lowry defined acid and bases in the terms of the substance themselves not in term of aq. Soln.

Q.4 What are levelling and differentiating Solvents.**Ans. Levelling solvent and differentiating solvent**

The strength of protonic solvent depends upon the nature of solvent in which acid is dissolved. The solvents in which complete transfer of proton takes place are called as levelling solvents.

e.g. \rightarrow HCl, H_2SO_4 , HCl_4 , HNO_3 are completely ionised in water so water is a levelling solvent for these acids but, these are partially ionised in CH_3COOH so CH_3COOH is a differentiating solvent for these acids.

e.g. \rightarrow HF and HCl get completely ionised in liq Ammonia to give 100% of NH_4^+ ions so NH_3 is a levelling solvent for HF and HCl, but in water, only HCl is completely ionised not HF.

Bases: - Bases like NaOH, NaO C_2H_5 , NaNH_2 , NaH they show equal base strength that's why behaves as strong bases as water so water is a levelling solvent for these bases but in liq NH_3 their basic strength varies so NH_3 is differentiating solvent.

Q.5 What is the utility of Bronsted-Lowry Concept?**Ans. Utility of Bronsted-Lowry Concept:-**

- It defines acids and bases in terms of their substances and not in terms of their aqueous solution.
- This concept is able to explain the basic nature of many substance like HSO_4^- , $\text{C}_2\text{H}_5\text{O}^-$
- It is able to explain the reason why aq soln of Na_2CO_3 is basic in nature (due to proton acceptor capacity of CO_3 ions)
- This concept is able to explain the hydrolysis of certain salt e.g. aq. Soln of FeCl_3 is acidic in nature.

Reason: Because the proton donor ability of hydrated ferric ion is more than this proton acceptor property of Cl^- ion this makes FeCl_3 soln acidic.

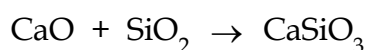
Q.6 Explain the strength of oxyacids and their conjugate bases with example.**Ans. Strength of oxyacids and their conjugate base:-**

- Oxyacids are derivative of H_2O and the H molecule of water is replaced by some other groups or atom.
- The increase in the oxidation no. of the atom replacing H atom of H_2O increases the acid strength.
- Those oxyacids will have the similar composition and the same oxidation no. for central atom. In that case the acidic strength decreases as the electronegativity decreases.

Q.7 Explain Lux-flood concept of acids and bases.

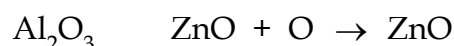
Ans. The Lux-flood concept (oxide ion concept). This concept was proposed by H-Z Luse (1939) and further given by Flood. They described acid base on the bases of oxide ion and it was a non protonic theory.

Acid:- An acid is a substance that accept oxide ion and base is a substance that donates oxide ion so, here acid is an acceptor of oxide ion & base is a donor of oxide ions.



base acid

Some substances are amphoteric in nature (When they show both the tendency to loose and gain an oxide ion).



This concept of lux and flood is used in metallurgy and ceramic industry becomes there we deal anhydrous system at high temperature.

Q.8 What is Solvent-System Concept? Also explain its limitations.

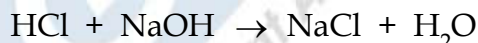
Ans. Solvent-System Concept:-

In S-S concept an acid is a solute that increases the conc of the cation of the solvent and base is a solute that increases the conc of the anion of the solvent.



here, in H_2O the solute which increases the conc of hydronium ions are acids (HCl , HNO_3 , H_2S) and the substances which the conc of OH^- ions are bases so in the e.g. of NH_3 solute it give NH_4^+ ion, they act a an acid.

NOTE:- When acid and bases react together they produce salts. Even in solvent system when they are mixed together they produce salts.

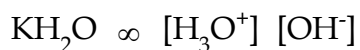
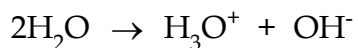


Solvent system and solvolysis:-

Solvent system concept is generally used to classify a solvolysis Reaction For e.g. - We can compare hydrolyses with solvolysis by non aq. solvent.

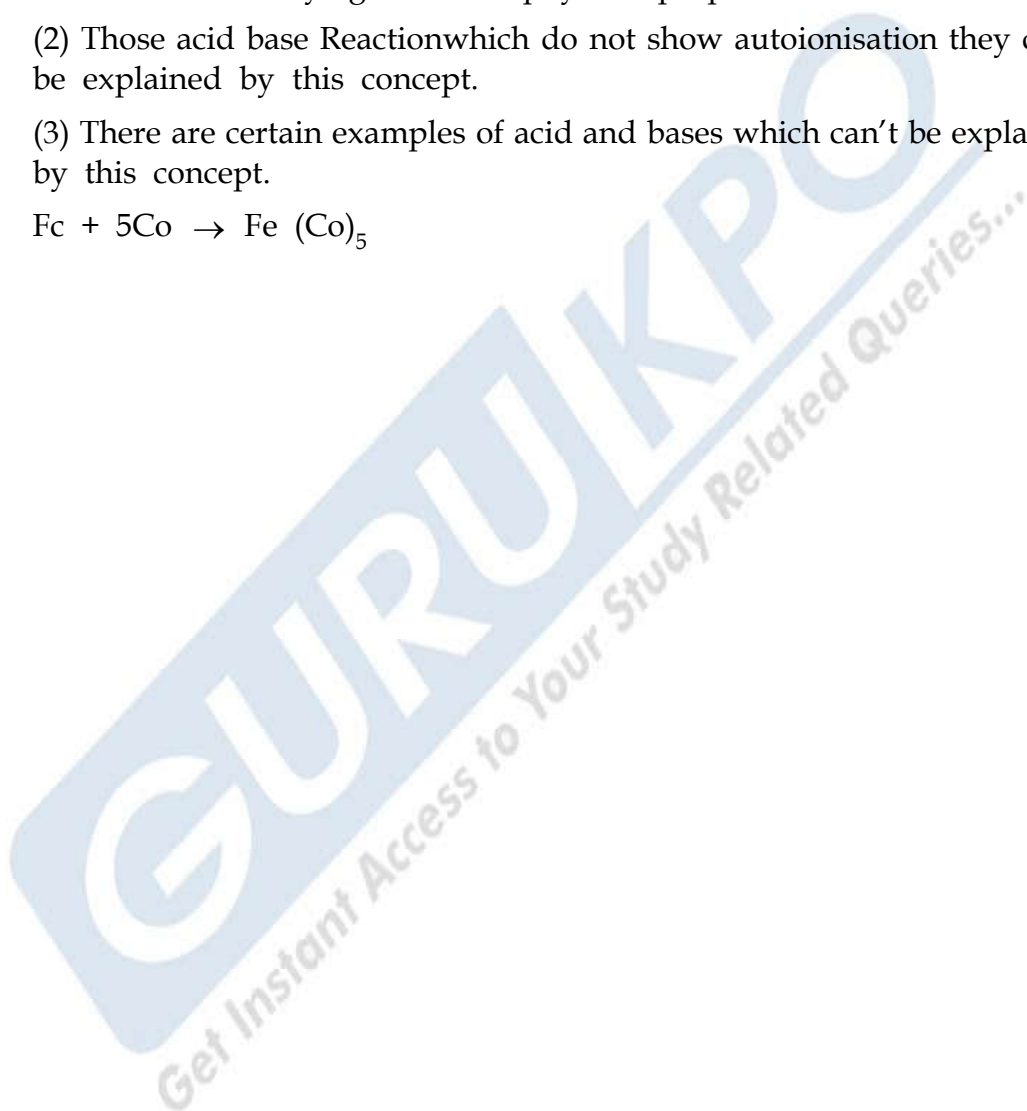
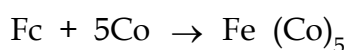


$$K_{\text{AB}} \propto [\text{A}^+] [\text{B}^-]$$



Limitations of Solvent-System Concept:-

- (1) It lays too much stress on ionic reaction and chemical property of solvents but totally ignores the physical properties of solvent
- (2) Those acid base Reaction which do not show autoionisation they can't be explained by this concept.
- (3) There are certain examples of acid and bases which can't be explained by this concept.



Chapter 8

Chemistry of Elements of First Transition Series

Q.1 Define Transition elements.

Electronic configuration: $ns^2 (n-1)d^{1-10}$

Ans. Definition - The d-block elements may thus be defined as elements having partly filled d sub-shell in their elementary form or chemical significant oxidation states.

Q.2 Why are the d-block elements are also called transition elements.

Ans. These are so called because their properties are intermediate between S block elements and P block elements and they are transitory in nature.

Q.3 Why Zn, Cd, Hg are not included in the d-Block element?

Ans. Acc to definition: Elements having partly filled d-sub shell in their elementary form are called as 'd-block elements'.

But these Zn ? $3d^{10}4s^2$

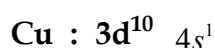
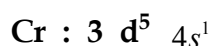
Cd ? $4d^{10}5s^2$

Hg ? $5d^{10}6s^2$

Elements having completely filled (n-1)d sub shell.

They do not show much resemblance with other d-block elements except for their ability to form complex with ligands like NH_3 , amines and halide ions.

Q.4 Why the electronic configuration of



→ is irregular.

Ans. In their case an e⁻ is "borrowed out of turn" from an orbital of similar energy. This is due to the fact that ?

(i) half-filled and fully filled sub shells have extra stability.

(ii) The 3d and 4s sub shells are very close in energy.

- Thus Cr gains extra stability by shifting one e⁻ from the 4s to the 3d level to give a half-filled 3d sub shell and a half-filled 4s sub shell.
- In Cu the shifting of one 4s electron to 3d sub shell gives a filled 3d sub shell and a half filled sub shell.

Q.5 What are the general characteristic and trends in variation of size of Transition elements?

Ans. (1) Atomic and Ionic Size

In a period –

Left to right decrease in Atomic radius

Left to right increase in Atomic no.

Q.6 Why in a transition series the size of (left to right) elements remain same (constant) ?

Ans. In a transition state from going left to right size of elements remain same because two opposite forces work there:

(i) Because of nuclear attraction decrease in size takes place.

– B'coz of shielding effect increase in size takes place.

These both force balance each other so the size of element remain constant.

Q.7 The Covalent radii of vanadium First Transition series and niobium second transition series are 1.22 \AA and 1.34 \AA respectively but the covalent radii of Tantalum (III T.S.) is 1.34 \AA .

Ans. When we go to I.T.S. to II T.S.

(i) 1 Shell is increased which increases the size

(ii) Nuclear charge is also increased which decreases the size.

(+ 18) Nuclear charge is less effective than the increase in 1 shell. So the radii of vanadium (I.T.S.) is 1.22 \AA but Niobium (II. T.S.) is 1.34 \AA

If shell is increased in size > Nuclear charge is effected.

When we go to II T.S. to III T.S. there are two effects which work together.

(i) One shell is increased which increases the size.

(ii) Increase in nuclear charge (+32) decreases the size.

Q.8 Name the elements having lowest and highest density.

Ans. Lowest density - Sc

Highest density - Os

Q.9 Density of the elements of the III T.S. become very high. Why?

Ans. Atomic weight of III T.S. \gg II T.S. It is –

– due to Lanthanide contractions

In going from II T.S. to III T.S. following force work.

(i) If 1 Shell is increased increase in volume take place.

(ii) If nuclear charge inc., dec. in volume takes place.

So they balance each other and the volume remain same.

$$D = \frac{M}{V}$$

So the density of element of the III T.S. become very high.

Q.10 In a transition series when we go from left to right the I.P. remains same. Why?

Ans. There are two opposite force which work:

(i) **Nuclear attraction** : Nuclear attraction increase size decreases.

(ii) **Shielding effect** : Increase in shielding effect results in dec. of size.

- These both balance their effect, so the size remains same.
- because the size remains same so the ionization potential also remains same.

Q.11 Some elements like Mo & W, Ru & Os and Pd & Pt. have higher ionization potentials then their congeners in the preceding period.

Ans. When we go to 4d to 5d series or II to III T.S. these two opposite forces do effect:

(i) If 1 Shell is increased it increases the size.

(ii) Nuclear charge (+32) increases, it decreases the size.

But in these elements Nuclear charge (+32) increases due to lanthanide contraction so the I.P. of these element have higher then their congeners in the preceding period.

Which results from the relatively large increase in nuclear charge without expansion to higher electron shells.

Q.12 The II I.P. value for Cr ($3d^54s'$) and Cu ($3d^{10}4s'$) are, however, markedly higher then those of their neighbours. Why.

Ans. This is because after the removal of one electron from Cr and Cu atoms they are left with extra stable sub-shell $3d^5$ and $3d^{10}$ respectively.

Q.13 Transitional elements have high heats of sublimation. Why?

Ans. Due to the existence of covalent bonding and due to d-d overlapping?

The metal ions decreases the tendency to react. This is why, the transition elements have rather a tendency to remain unreactive or noble. This tendency is quite pronounced in gold and platinum.

Reactivity of T. element decreases from I to II T.S.

i.e. reactivity of I.T.S. > the reactivity of (greater II T.S.)

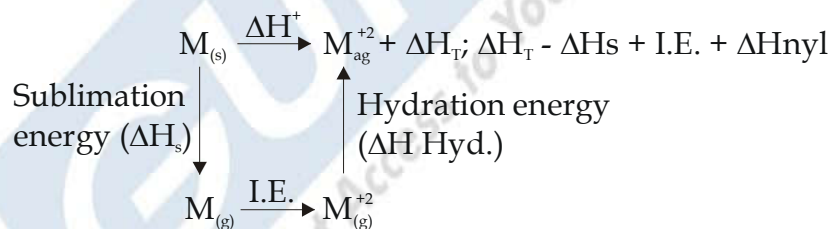
Q.14 Why the elements of third T.S. are least reactive among the Transition elements?

Ans. Because of their

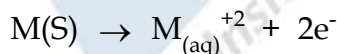
- Small size
- high I.P. (ionization potential)
- very high heats of sublimation
- Low heats of hydration of their metal ions.

Q.15 The transition elements possess this tendency and should be good reducing agents. But they are not a good reducing agent as the metals of groups I, II, III. Why?

Ans. The reducing capacity of a metal depends on it's tendency to be oxidized easily into ions. This is explained as



The total energy (enthalpy) change, ΔH_T for the process



is equal to the sum of the enthalpy of sublimation of metal, total ionization energy (Sum of I.E. & I.E.₂) of metal enthalpy of hydration of metal ion, M^{2+} . The electrode potentials are measured of the value of ΔH_T . The transition elements possess this tendency and should be good

reducing agents. But they are not a good reducing agent as the metal of group I, II & III. This is due to their high heats of vaporization, high ionization energy and low heats of hydration of their ions.

- Copper has a positive electrode potential and is not able to displace H^+ ions from acid solutions. The tendency of copper to change into cupric ion is extremely small. Hence copper is poor reducing agent.
- (T. metals are weaker reducing agents than alkali metals and alkaline earth metals).

Q.16 Explain Metallic Character of Transition elements.

Ans. All transition elements have only one or two electrons in their outermost valency shell and consequently are metallic in nature. They have

- Metallic lustre
- Possess high densities
- Good conductors of heat and electricity.
- Copper, Silver and Gold possess high thermal and electrical conductivities.

These metals show an increasing tendency to remain unchanged or noble in nature.

This is favoured by:

- Heats of sublimation
- High ionization energy.
- Low heat of Solution.
- They differ from non-transition metals in being hard and brittle.
- Mercury is an exception. It is a liquid (Hardness and brittleness are the properties which are associated with covalent bonding.)

Q.17 Transition metals are good conductors of heat and electricity.

Ans. It appear that in addition to metallic bonding (pr. of free metal ions embedded in a 'sea' of free mobile electrons), there must be some

covalent bonding of unfilled d-orbitals due to d-d overlapping.

The no. of such bonds are responsible for the hardness of these metals depending upon their strength.

Q.18 Why metals are hard up to VI group while Zn, Hg ? Cd are soft?

Ans. The no. of unpaired d-e⁻ increases up to group 6 and decrease often because of pairing. Therefore metals are hard up to VI group while Zn, Hg and Cd are soft.

- In Most cases of Transitional elements the packing is the closest (hep or ccp) with coordination no. 12.

- Coordination no. 8 ? bcc

Q.19 Metals in group 9 and 11 are more ductile than other metals. Why?

Ans. This is due to the fact that they crystallize with fcc (Cubic close packing) structure, and therefore, have more no. of planes where deformation can take place.

* Other metals generally crystallize either in hep or bcc structure. Cu (3d¹⁰, 4s'), Pd (4d¹⁰) and Au (d¹⁰6s') are called typical Transition metals as the d-e⁻ in these elements are still available for chemical bonding.

Q.20 Explain the magnetic properties of the elements of 1st T.S.

Ans. Magnetic Properties

- It is well known that the movement of an electric charge produces a magnetic effect.
- An e⁻ in atom spins about it's own axis. Because the e⁻ is electrically charged, the spin about it's axis gives it the properties of a small magnet with north and south pole.
- The 2e⁻ of a pair spin in opposite direction. This means that their e⁻ of a pair spin in opposite direction.

This means that their magnetic movements will cancel each other because their north and south poles are opposite.

- In a bar magnet the magnetic movement is given by the pole strength multiplied to the length.