CHAPTER 14

d and f - BLOCK ELEMENTS: TRANSITION ELEMENTS

After completing this lesson, you will be able to:

- Describe electronic structure of transition elements
- Explain why the electronic configuration for chromium and copper differ from those assigned using the Aufbauprinciple.
- Describe important reactions and uses of Vanadium, Chromium, Manganese, Iron and Copper
- Explain shapes, origin of colors and nomenclature of coordination compounds
- Relate the coordination number of jons to the crystal structure of the compounds of which they are a part.
- Define an alloy and describe some properties of an alloy that are different from the metals that compose it,
- Describe the reactions of potassium dichromate with oxalic acid and Mohr's salt
- Describe the reaction of Potassium manganate VII with ferrous sulphate, oxalic ac

Q1. Why d– Block elements are called Transition elements?

Answer

"The elements which have partially filled d or f-orbital either in their atomic states or in other common oxidation states are called transition elements." They are called d-block or f-block elements.

They are called transition elements because they show such properties which are transitional between highly reactive and strongly electropositive elements of s-block which form ionic bonds and p-block elements which form covalent compounds.

Series of Transition Elements:

The d=block elements consist of following three series of ten elements each:

1) From Scandium (Sc =21) to Zinc (Zn =30) – 3d-series
2) From Yttrium (Y =39) to Cadmium (Cd = 48) – 4d-series
3) From Lanthanum (La = 57) to Mercury (Hg = 80) – 5d-series

[Omitting Lanthanides (rare-earths)]

The f-block elements constitute two series which are:

1) From Cerium (Ce = 58) to Lutetium (Lu = 71) – 4f-series
2) From Actinium (Ac = 89) to Lawrentium (Lr = 103) which are called actinides. – 5f-series

General outermost configurations:

1) First series (d-block elements) = $(n-1)d^{1-10}ns^2$
2) Second series (f-block elements) = $(n-1)d^{1}(n-2)f^{1-14}ns^2$

Q2. Why is Zn-group included in Transition elements?

Answer

Zn, Cd and Hg are not regarded as transition elements because they have completely filled d-orbitals. It is appropriate to include these in transition elements because they form complexes with ammonia, halide ions and amines and their chemical behaviors is similar to transition elements.

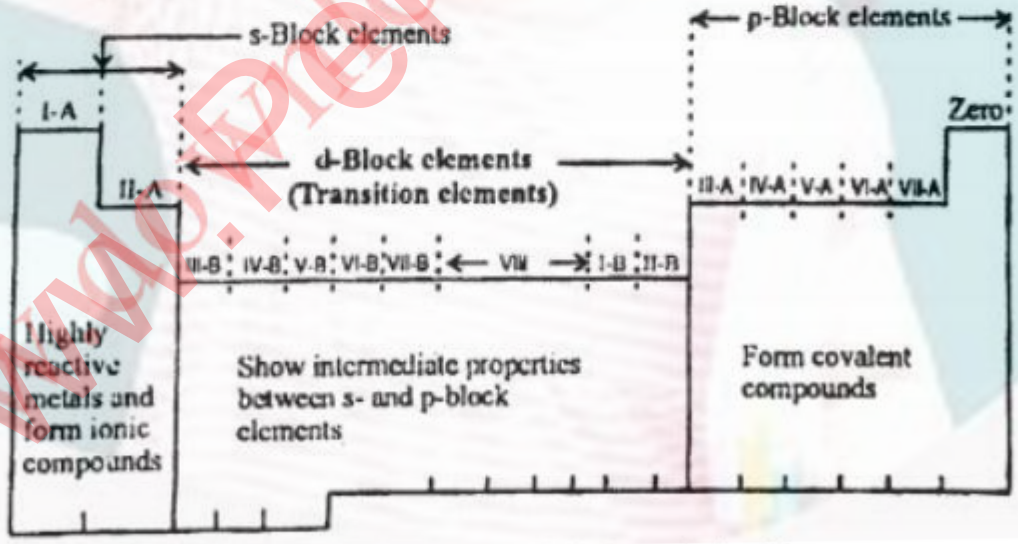
"Coinage metals are transition elements." Justify the statement.

Coinage metals are transition elements since Cu^{2+} has $3d^9$ configuration, Ag^{2+} has a $4d^9$ and Au^{3+} has $5d^8$ configuration, although all these metals have d^{10} configuration in atomic states.

Q3. Position of d-block elements in the periodic table:

Answer

Following diagram show the position of d-block elements in the periodic table.



Position of d-block elements in the periodic table

Q4. Typical and non-Typical Transition Elements.

Answer

The elements of the group II-B and III-B have the electronic distribution as follows:

II-B	III-B
Zn_{30} = ...$4s^2 3d^{10}$	Sc_{21} = ...$4s^2 3d^1$
Cd_{48} = ...$5s^2 4d^{10}$	Y_{39} = ...$5s^2 4d^1$
Hg_{80} = ...$6s^2 5d^{10}$	La_{57} = ...$6s^2 5d^1$

It is clear that the elements of II-B i.e. Zn, Cd and Hg do not have partially filled d-subshell in the elemental state or ionic state.

They do not show the typical properties of the transition elements to an appreciable extent.

The elements of the group III-B are Sc_{21}, Y_{31} and La_{57}. They do not show many of their properties typical of transition elements. In the compound state, they show tri-positive ion i.e. Sc^{+3}, Y^{+3} and La^{+3}. In this way they do not have any electron in d-orbital.

For the reason that the elements of group II-B and III-B are non-typical transition elements.

Non-Typical Transition Elements	Typical Transition Elements
II-B and III-B	IV-B, V-B, VI-B, VII-B, VIII-B and I-B

Q5. Give general features of Transition.

Answer

General Features of transition elements

1) They are all metallic in nature.
2) Some of the transition elements play an important role in the industry. These metals are Ti, Cr, Fe, Ni, Cu, Mo, W, Zr, Nb, Ta and Th etc.
3) They are all hard and strong metal with high melting and boiling points. They are good conductors of heat and electricity.
4) They form alloys with one another and other elements of periodic table as well.
5) With a few exceptions, they show variable oxidation states.
6) Their ions and compounds are colored in the solid state and the solution state.

Electronic Structure

Electronic distribution of d-block elements:

Table14.1

Sc_{21}	$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^{1}_{xy}\ 3d^{0}_{yz}\ 3d^{0}_{xz}\ 3d^{0}_{x^2-y^2}\ 3d^{0}_{z^2}$
Ti_{22}	$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^{1}_{xy}\ 3d^{1}_{yz}\ 3d^{0}_{xz}\ 3d^{0}_{x^2-y^2}\ 3d^{0}_{z^2}$
V_{23}	$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^{1}_{xy}\ 3d^{1}_{yz}\ 3d^{1}_{xz}\ 3d^{0}_{x^2-y^2}\ 3d^{0}_{z^2}$
Cr_{24}	$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{1}\ 3d^{1}_{xy}\ 3d^{1}_{yz}\ 3d^{1}_{xz}\ 3d^{1}_{x^2-y^2}\ 3d^{1}_{z^2}$
Mn_{25}	$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^{1}_{xy}\ 3d^{1}_{yz}\ 3d^{1}_{xz}\ 3d^{1}_{x^2-y^2}\ 3d^{1}_{z^2}$
Fe_{26}	$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^{\uparrow\downarrow}_{xy}\ 3d^{1}_{yz}\ 3d^{1}_{xz}\ 3d^{1}_{x^2-y^2}\ 3d^{1}_{z^2}$
Co_{27}	$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^{\uparrow\downarrow}_{xy}\ 3d^{\uparrow\downarrow}_{yz}\ 3d^{1}_{xz}\ 3d^{1}_{x^2-y^2}\ 3d^{1}_{z^2}$
Ni_{28}	$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^{\uparrow\downarrow}_{xy}\ 3d^{\uparrow\downarrow}_{yz}\ 3d^{\uparrow\downarrow}_{xz}\ 3d^{1}_{x^2-y^2}\ 3d^{1}_{z^2}$
Cu_{29}	$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{1}\ 3d^{\uparrow\downarrow}_{xy}\ 3d^{\uparrow\downarrow}_{yz}\ 3d^{\uparrow\downarrow}_{xz}\ 3d^{\uparrow\downarrow}_{x^2-y^2}\ 3d^{\uparrow\downarrow}_{z^2}$
Zn_{30}	$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^{\uparrow\downarrow}_{xy}\ 3d^{\uparrow\downarrow}_{yz}\ 3d^{\uparrow\downarrow}_{xz}\ 3d^{\uparrow\downarrow}_{x^2-y^2}\ 3d^{\uparrow\downarrow}_{z^2}$

Table14.2 – Detailed electronic configuration of the valence shell of first series of transition elements:

		$3d_{xy}$	$3d_{yz}$	$3d_{xz}$	$3d_{x^2-y^2}$	$3d_{z^2}$	4s
Sc_{21} =	(Ar)	1					1↓
Ti_{22} =	(Ar)	1	1				1↓
V_{23} =	(Ar)	1	1	1			1↓
Cr_{24} =	(Ar)	1	1	1	1	1	1
Mn_{25} =	(Ar)	1	1	1	1	1	1↓
Fe_{26} =	(Ar)	1↓	1	1	1	1	1↓
Co_{27} =	(Ar)	1↓	1↓	1	1	1	1↓
Ni_{28} =	(Ar)	1↓	1↓	1↓	1	1	1↓
Cu_{29} =	(Ar)	1↓	1↓	1↓	1↓	1↓	1
Zn_{30} =	(Ar)	1↓	1↓	1↓	1↓	1↓	1↓

Q6. Electronic distribution of 4d and 5d-series:

Answer

The following table shows the electronic distribution of 4d and 5d-block elements. The elements of the group number VI-B, i.e. Cr group shows the same abnormality except W_{74}.

Similarly, the elements of the group I-B that is Cu-family also show the abnormal distribution. Following table shows the electronic distribution of 3d, 4d, 5d series

Table 14.3: Electronic configurations of three series of d-block elements

3d-block elements		4d-block elements		5d-block elements	
Elements	**Electronic Configuration**	**Elements**	**Electronic Configuration**	**Elements**	**Electronic Configuration**
Sc (21)	$[Ar]3d^1 4s^2$	Y (39)	$[Kr]4d^1 5s^2$	La (57)	$[Xe]5d^1 6s^2$
Ti (22)	$[Ar]3d^2 4s^2$	Zr (40)	$[Kr]4d^2 5s^2$	Hf (72)	$[Xe]4f^{14} 5d^2 6s^2$
V (23)	$[Ar]3d^3 4s^2$	Nb (41)	$[Kr]4d^4 5s^1$	Ta (73)	$[Xe]4f^{14} 5d^3 6s^2$
Cr (24)	$[Ar]3d^5 4s^1$	Mo (42)	$[Kr]4d^5 5s^1$	W (74)	$[Xe]4f^{14} 5d^4 6s^2$
Mn (25)	$[Ar]3d^5 4s^2$	Te (43)	$[Kr]4d^6 5s^2$	Re (75)	$[Xe]4f^{14} 5d^5 6s^2$
Fe (26)	$[Ar]3d^6 4s^2$	Ru (44)	$[Kr]4d^7 5s^1$	Os (76)	$[Xe]4f^{14} 5d^6 6s^2$
Co (27)	$[Ar]3d^7 4s^2$	Rh (45)	$[Kr]4d^8 5s^1$	Ir (77)	$[Xe]4f^{14} 5d^7 6s^2$
Ni (28)	$[Ar]3d^8 4s^2$	Pd (46)	$[Kr]4d^{10}$	Pt (78)	$[Xe]4f^{14} 5d^9 6s^1$
Cu (29)	$[Ar]3d^{10} 4s^1$	Ag (47)	$[Kr]4d^{10} 5s^1$	Au (79)	$[Xe]4f^{14} 5d^{10} 6s^1$
Zn (30)	$[Ar]3d^{10} 4s^2$	Cd (48)	$[Kr]4d^{10} 5s^2$	Hg (80)	$[Xe]4f^{14} 5d^{10} 6s^2$

Q7. What is binding Energy? Discuss it in transition elements.

Answer

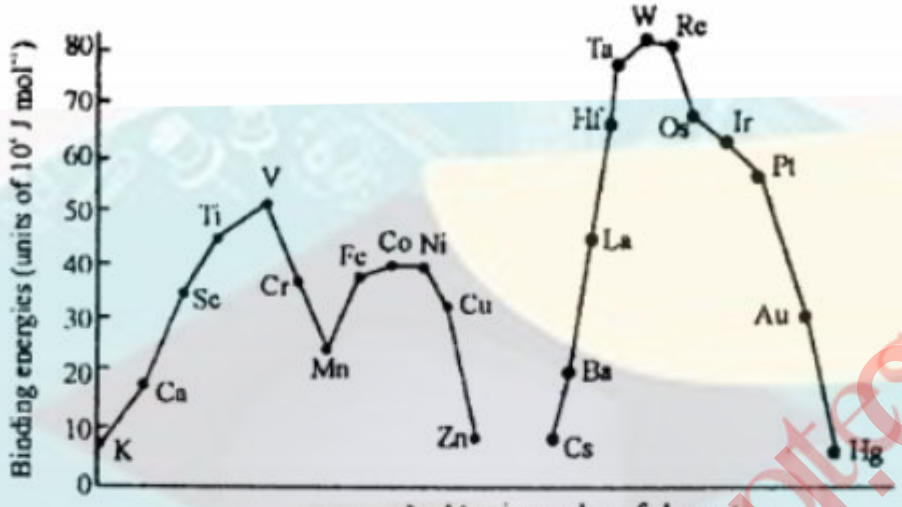
In order to understand the mechanical properties of transition elements, we should understand the binding energies. Transition elements are tough, malleable and ductile. The toughness of the metals is due to greater binding energies.

Reason

The s-electron of outermost shell takes part in chemical bonding. Anyhow, along with that the electrons of underlying half filled d-orbitals also participate in bonding.

Variation in binding energies

When we move from left to the right in any d-block series, the number of electrons increase up to group V-B; that is vanadium family and VI-B i.e. Cr family. After that the pairing of electron starts. The unpaired electrons become zero at group II-B. It means that binding forces go on increasing up to Cr and then decrease after that. This is shown for the elements of 3d and 5d series in the following graph.



Graphical picture of binding energy of 3d and 5d series of transition elements (qualitative view)

Q8. What is meant by variable oxidation states? Discuss with reference to transition metals.

Answer

Transition elements are electropositive, so they have positive oxidation states. All 3d series elements show an oxidation state of +2 in addition to higher oxidation states when the electrons of 4s-orbital take part in bonding.

They show variable oxidation states. The reason is that they have d-electrons in addition to s-electron for the purpose of bond formation. These elements have several (n-1) d and ns electrons. The energies of (n-1) d and ns orbitals are very close to each other. The (n-1) d electrons are as easily lost as ns electrons. In the highest oxidation states of first five elements, all s and d-electrons are used for bonding.

Among the 3d series, Mn has maximum oxidation states, and goes up to +7. The following table shows oxidation numbers +2 and +3 are more common. Positive oxidation states increase up to the middle of series and after that they decrease.

			3d	4s	Oxidation states
Sc	[Ar]	$3d^1 4s^2$	↑	↑↓	2 3
Ti	[Ar]	$3d^2 4s^2$	↑ ↑	↑↓	2 3 4
V	[Ar]	$3d^3 4s^2$	↑ ↑ ↑	↑↓	2 3 4 5
Cr	[Ar]	$3d^5 4s^1$	↑ ↑ ↑ ↑ ↑	↑	2 3 4 5 6
Mn	[Ar]	$3d^5 4s^2$	↑ ↑ ↑ ↑ ↑	↑↓	1 2 3 4 5 6 7
Fe	[Ar]	$3d^6 4s^2$	↑↓ ↑ ↑ ↑ ↑	↑↓	1 2 3 4 5 6
Co	[Ar]	$3d^7 4s^2$	↑↓ ↑↓ ↑ ↑ ↑	↑↓	2 3 4 5
Ni	[Ar]	$3d^8 4s^2$	↑↓ ↑↓ ↑↓ ↑ ↑	↑↓	2 3 4
Cu	[Ar]	$3d^{10} 4s^1$	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑	1 2 3
Zn	[Ar]	$3d^{10} 4s^2$	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	2

Table 14.4

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Q9. What is catalytic activity? Explain with examples.

Answer

Most of the transition elements are used as catalysts. The compounds of transition metals are also catalysts.

The reason is that the transition metals show variety of oxidation states. In this way, they can form intermediate products with various reactants.

They also form interstitial compounds which can absorb an activator to the reacting species. Some of the important examples of catalysts are as follows:

1) A mixture of ZnO and Cr_2O_3 is used for the manufacture of methyl alcohol.
2) Ni, Pt and Pd are catalysts for the hydrogenation of vegetable oil and saturation of alkenes and alkynes to alkanes.
3) MnO_2 can be used as a catalyst for the decomposition of H_2O_2.
4) $TiCl_4$ is used as catalyst for the manufacture of plastics.
5) V_2O_5 is used to oxidize SO_2 to SO_3 in the manufacture of H_2SO_4.
6) Fe is used as a catalyst for synthesis of NH_3 in Haber's process about 1% of Na_2O or K_2O and about 1% SiO_2 or Al_2O_3 are added as promotors. Mo is also sometimes used as a promotor.

Q10. What is magnetic behaviour? Explain Magnetic behaviour of transition metals.

Answer

Many transition elements and their compounds are paramagnetic. The compounds attracted into the magnetic field are called paramagnetic. Paramegnetism is due to the unpaired electrons present in the metals and their compounds. The substances which can be magnetized are called ferromagnetic. For example, Fe, Co and Ni are ferromagnetic. Some substances in which even number of electrons are present, and have paired spins are diamagnetic. They are slightly repelled by magnetic field. The magnetic moment (μ) is related to the number of unpaired electrons (n) by the equation:

$$\mu = \sqrt{n(n+2)}$$

It is measured in Bohr magneton, BM. By measuring magnetic moment, the nature of transition metal compound and oxidation state of transition metal can be calculated.

Q11. Where are alloys? How are they made? Give examples.

Answer

Alloy is mixture of two or more than two metals. Transition metals form alloys with each other.

Reason

Transition elements have almost similar sizes and atoms of the one metal can easily take up positions in crystal lattice of the other. They form substitutional alloys among themselves.

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Example

1) Alloy steels are the materials in which the iron atoms are substituted by Cr, Mn and Ni. Steel has more useful properties than iron.
2) Brass, bronze and coinage alloys are the best alloys.

Alloys of Metals	Composition	Properties and Uses
Brass	Cu = 60 – 80 % Zn = 20 – 40 %	It is a strong alloy of copper which is soft and flexible. It does not corrode. Due to low melting point, it is easy to use. It is used to make locks, keys, water taps, pipes, artificial jewellery, door handles and parts of machines
Bronze	Cu 90 - 95 % Sn 5 - 10 %	It is strong, brilliant and long lasting. It does not corrode. It is used to prepare medals, coins, badges and bullets etc. besides these; decorative articles are also made from this alloy.
Nichrome	Ni = 60 % Cr = 15 % Fe = 25 %	It is used in electric heaters and filaments of furnaces.

Properties

As alloys are prepared according to the requirements, their characteristics are different, yet few properties are common which are as follows:

1) Alloys are comparatively cheap.
2) They are strong and flexible but hard alloys can also be prepared.
3) They have long life because they do not corrode.
4) They are durable.
5) They have high melting points.
6) They are better conductor but non-conductor alloys are also prepared.

Q12. What are coordination compounds? Explain in detail.

Answer

Definition

Those compounds which contain complex molecules or complex ions capable of independent existence are called coordination compounds or complex compounds.

Such compounds are formed by the coordination of an electron pair donor to metal atom or an ion.

Explanation

In order to understand the complex compounds, let us mix two substances that is KCN and $Fe(CN)_2$. When this mixture is evaporated, a new compound is obtained. This compound when dissolved in water ionizes into K^+ and $[Fe(CN)_6]^{-4}$. On this basis the new compounds has been given the formula $K_4[Fe(CN)_6]$.

$$4KCN + Fe(CN)_2 \rightarrow K_4Fe(CN)_6$$

$$K_4Fe(CN)_6 \rightarrow 4K^+ + [Fe(CN)_6]^{-4}$$

$[Fe(CN)_6]^{-4}$ is called complex ion.

Parts of complex compound after dissociation in a solvent

A complex compound is mostly made up of two parts:

1) Positively charged ion or cation.
2) Negatively charged ion or anion.

For example in $K_4Fe(CN)_6$, K+ is a cation and $[Fe(CN)_6]^{-4}$ is the anion.

Complex ion as cation

In some of the complexes the positively charged ion is complex ion

$$[Cu(NH_3)_4]SO_4 \rightarrow [Cu(NH_3)_4]^{+2} + SO_4^{-2}$$

Complex cation

Complex ion as anion

In some of the complexes the negatively charged ion is the complex ion

$$K_4Fe(CN)_6 \rightarrow 4K^+ + [Fe(CN)_6]^{-4}$$

Components of complex compounds

Complex compound is consisted of three components:

1) A positively or negatively charged ion which is not complex.
2) A central metal atom or ion which is consisted of transition element.
3) Electron pair donor which is negatively charged, positively charged or neutral.

Let us discuss them one by one.

Central Metal atom or ion

A metal atom or ion is usually a transition element. It is surrounded by a number of ligands.

1) In $K_4[Fe(CN)_6]$, Fe^{+2} is the central metal ion. Six ligands (CN^- ions) are surrounding it.
2) In $K_3[Fe(CN)_6]$, Fe^{+3} is the central metal ion. Six ligands (CN^- ions) are surrounding it.
3) In $[Cu(NH_3)_4]SO_4$, Cu^{+2} is the central metal ion. Four ligands (NH_3 ions) are surrounding it.
4) In $[Ag(NH_3)_2]Cl$, Ag^{+2} is the central metal ion. Two ligands (NH_3) are surrounding it.

b) Ligand

The atom, ion (usually anions) or neutral molecule which surrounds the central metal atom or ion by donating the electron pair is called ligand.

Examples

1) In $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$, CN^- is the ligand.
2) In $[Cu(NH_3)_4]SO_4$ and $[Ag(NH_3)_2]Cl$, NH_3 is the ligand.

Types of Ligands

Depending upon number of donatable electron pairs, ligands are of many types:

1) Monodentate Ligands

Those ligands which have only one donatable electron pair. Such ligands may be negatively charged, or neutral.

Examples:

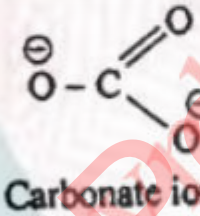
1) Negatively charged ligands F^-, Cl^-, Br^-, I^-, OH^-, CN^-
2) Neutral ligands H_2O, NH_3, CO

2) Bidentate ligands:

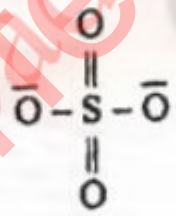
Those ligands which have two donatable electron pairs are called bidentate ligands.

Examples

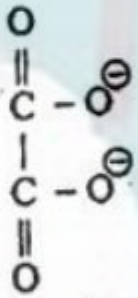
CO_3^{-2},	SO_4^{-2},	$(COO)_2^{-2}$,	NH_2-NH_2,	NH_2-CH_2-CH_2-NH_2
Carbonate ion,	Sulphate ion,	Oxalate ion,	Hydrazine,	Ethylene diamine



Carbonate ion



Sulphate ion



Oxalate ion

3) Tridentate ligands:

Those ligands which have three donatable electron pairs

Examples

$H_2NCH_2 - CH_2 - NH - CH_2 - CH_2 - NH_2$

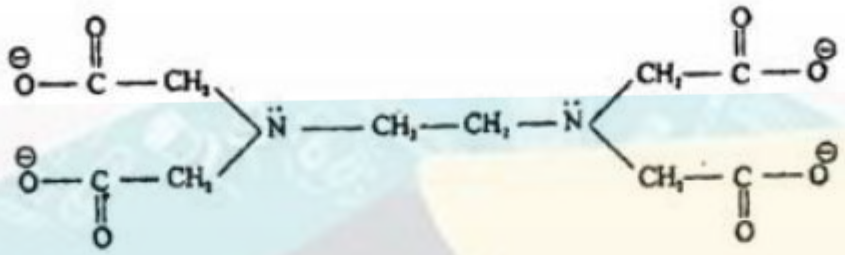
Diethylene triammine

4) Hexadentate ligands:

Those ligands which have six donatable electron pairs.

Example:

Ethylenediamenetetracetate (EDTA)



C) Coordination number or Ligancy:

It is the total number of the atoms of the ligands that can coordinate to the central metal ion. Numerically coordination number represents the total number of the chemical bonds formed between the central metal ion and the donor atoms of the ligands.

Example

1) In $K_4[Fe(CN)_6]$, the coordination number of Fe^{+2} is six.
2) In $[Cu(NH_3)_4]SO_4$, the coordination number of Cu^{+2} is four
3) In $[Ag(NH_3)_2]$, the coordination number of Ag^{+} is two
4) In $[Ni(CO)_4]$, the coordination number of Ni^{0} is four

D) Coordination Sphere

The central neutral atom or ion along with ligand is called coordination sphere. It is usually placed in the square brackets. It may be positively charged, negatively charged or neutral.

Examples

1) In $K_4[Fe(CN)_6]$, the ion $[Fe(CN)_6]^{-4}$ is the coordination sphere of this complex compound
2) In $[Cu(NH_3)_4]SO_4$, the ion $[Cu(NH_3)_4]^{+2}$ is the coordination sphere of this complex compound
1) In $K_3[Fe(CN)_6]$, the ion $[Fe(CN)_6]^{-3}$ is the coordination sphere of this complex compound
2) In $[Ag(NH_3)_2]Cl$, the ion $[Ag(NH_3)]^{+1}$ is the coordination sphere of this complex compound
3) In $[Ni(CO)_4]$, the ion $[Ni(CO)_4]$ is the coordination sphere of this complex compound

E) Charge on the coordination sphere

It is the algebraic sum of charges present on the central metal ion and total charge on the ligands.

Example

In $K_4[Fe(CN)_6]$ the charge on the coordination sphere can be calculated as follows.

$K_4[Fe(CN)_6] \rightarrow 4K^{+} + [Fe(CN)_6]^{-4}$

Since charge on each ligand is = -1

Charge on $6CN^-$ = -6

Charge on iron = +2

So the charge on the coordination sphere = -6+2 = – 4

Q13. Give method of nomenclature of complex compounds.

Answer

Complex compounds are named according to following rules give by IUPAC

1) Order of Ions

Cations are named first and then the anions. For example in $K_4[Fe(CN)_6]$, we will call K^+ first and then $[Fe(CN)_6]^{-4}$

In naming $[Cu(NH_3)_4]\ SO_4$, we will call $[Cu(NH_3)_4]^{+2}$ first and then SO_4^{-2}.

2) Naming of ligands:

a) The ligands which are negatively charged end in O. For example

F^-	= Fluoro
Cl^-	= Chloro
Br^-	= Bromo
I^-	= Iodo
CN^-	= Cyno
$CH_3\text{-}COO^-$	= Acetato
$C_2O_4^{-2}$	= Oxalato

a) Neutral ligands are called as such. For example

H_2O	Aquo or Aqua
NH_3	Ammine
CO	carbonyl

b) Positively charged ligands end in "ium". For example

$NH_2NH_3^+$	Hydrazinium
NO^+	Nitrosylium
NH_4^+	Ammonium

Order of ligands

All ligands are arranged alphabetically without any preference order. The numerical prefixes (di, tri, etc) are not considered.

1) More than one same type of ligands

In order to indicate more than one ligands, use prefixes as di for two, tri for three, tetra for four, penta for five and hexa for six.

2) Termination of name of metal

If the complex ion is negatively charged then the name of the metal ends in "ate". For example

In $K_4[Fe(CN)_6]$, the name is potassium hexacyanoferrate (II).

3) Oxidation number of metal ion

The oxidation number of the metal ion is represented by roman numeral in parenthesis following the name of the metal.

4) More than one polydentate ligands

If polydentate ligands are there, then in order to indicate their number, use bis for two, tris for three and tetrakis for four.

Examples

Keeping in view all the above rules the following names are proposed for the complex compounds according to IUPAC system:

a) In the following complexes, the complex ion has negative charge. So, the name of the metal ends in ate.

1) $K_4[Fe(CN)_6]$ Potassium hexacyanoferrate (II)
2) $K_3[Fe(CN)_6]$ Potassium hexacyanoferrate (III)
3) $Na[Mn(CO)_5]$ Sodium Pentacarbonylmanganate (-I)
4) $K_2[PtCl_6]$ Potassium hexachloroplatinate (IV)
5) $Na_2[Ni(CN)_4]$ Sodium tetracyanonickelate

b) In the following complexes the complex ion has positive charge. So the name of the metal is called as such:

1) $[Co(NH_3)_6]Cl_3$ Hexaamminecobalt (III) chloride
2) $[Co(F)_6]Cl_3$ Hexafluorocobalt (III) chloride
3) $[Cr(H_2O)_6]Cl_3$ Hexaaquochromium (III) chloride
4) $[Co(en)_2Cl_2]Cl$ Dichlorobisethylendiamminecoblat (III) chloride
5) $Ni(CO)_4$ Tetracarbonylnickel (O)
6) $[PtCl(NO_2)(NH_3)_4]SO_4$ Tetraammine chloronitro platinum (IV) sulphate
7) $[Co(NO_2)_3(NH_3)_3]$ Triamminetrinitrocoblat (III)

Shapes of Complex Ions with Coordination number 2, 4 and 6

The coordination number shown by metals in complexes are 2 to 9. The most common are 2, 3 and 6. Geometries corresponding to C.N's =2, 3, 4 and 5 are shown in Fig. 14.3

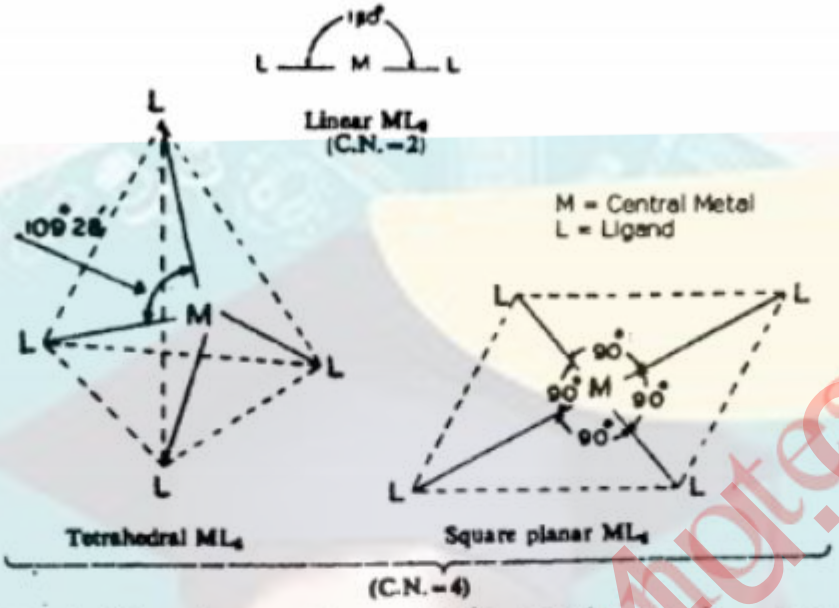
1) Coordination Number 2

The complexes having C.N=2 are linear, since this geometry provides minimum ligand-ligand repulsion. Cu^+, Ag^+ and in some cases Hg^{+2} form such complexes, e.g. $Cu(CN)_2$, $Cu(NH_3)_2^+$, $Ag(NH_3)_2^+$, $Ag(CN)_2^-$, $Au(CN)_2^-$, $Hg(NH_3)_2^{2+}$, $Hg(CN)_2$.

2) Coordination Number 4

Complexes with CN=4 may be tetrahedral or square planar in geometry. Complexes like

$ZnCl_4^{2-}$, $Cu(CN)_4^{2-}$, $Hg(CN)_4^{2-}$, $[Ni(CO)_4]^0$, $FeCl_4^-$,
$ZnBr_4^{2-}$, CuX_4^{2-}, ($X = Cl^-, Br^-, CNS^-$)
$Zn(CN)_4^{2-}$,
$Zn(NH_3)_4^{2-}$



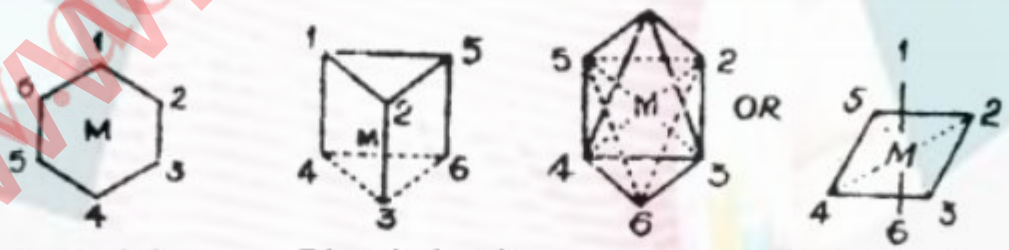
are tetrahedral. Oxyanions such as VO_4^{3-}, CrO_4^{2-}, FeO_4^{2-} and MnO_4^- are also tetrahedral.

Square planar geometry is found in complexes of Cu^{2+} Ni^{2+}, Pt^{2+}, Pd^{2+}, Au^{3+} etc ions e.g. $Ni(NH_3)_4^{2+}$, $Ni(CN)_4^{2-}$, $[Ni(dmg)_2]^0$, $Pt(NH_3)_4^{2+}$, $PdCl_4^{2-}$, $AuCl_4^-$, $[Cu(en)_2]^{2+}$,$Cu(NH_3)^{2+}$ etc.

1) Coordination Number 6

Complexes with C.N = 6 are the most common ones formed by transition metal ions.

Six ligands in a 6-coordination compound may be arranged round the central metal ion, M, either at the corners of hexagonal plane or at the apices of a trigonal prism or at the apices of a regular octahedron. These arrangements together with numbers designating substitution positions may be depicted as shown in fig. 14.4. An extensive study of the geometrical and optical isomers of complexes with C.N = 6 has however, shown that arrangement of six ligands in a 6- coordination compound is always octahedral and that the arguments concerning other possible geometries (i.e. hexagonal planar and trigonal prismatic geometries) are of historical interest only.



Hexagonal planar geometry | Trigonal prismatic geometry | Regular octahedral geometry

Q14. Why Transition metal complexes are coloured?

Answer

When white light is allowed to fall on a complex. The following things may occur:

i) The complex may absorb the whole of white light. In this case complex appears black.

ii) The complex may reflect or transmit the whole light. In this case it appears white.

iii) The complex may absorb some of it and may reflect or transmit the remaining light. In this case the complex has some color. i.e. it is colored. The absorption of light by the colored complexes takes place in the visible region of the spectrum which extends from 4000Å to 7000Å in wavelengths. The color of the absorbed light is different from that of the transmitted light. The relation between the colors of the absorbed and reflected light is shown in Fig. 14.5 the color of the transmitted light is called the complementary color of that of the absorbed light and is in fact the color of the complex.

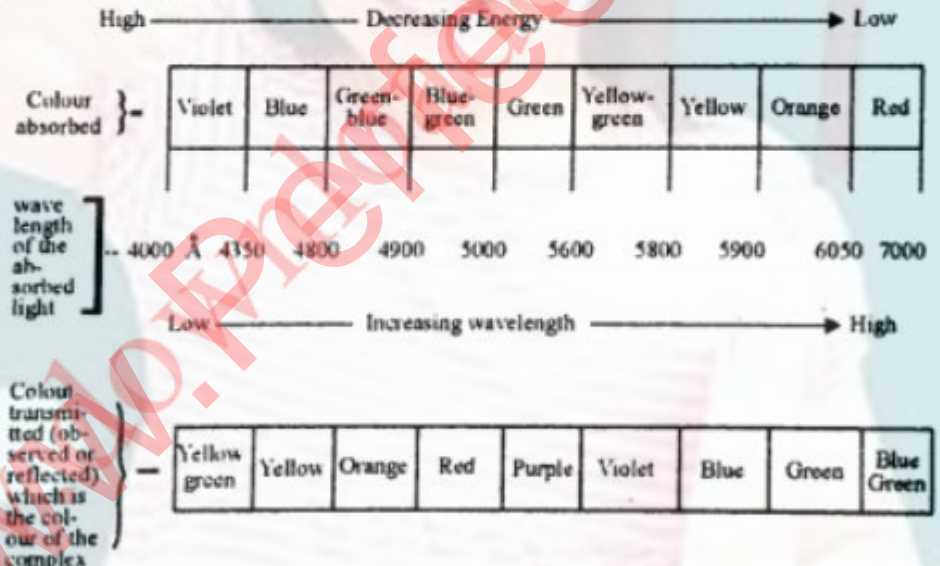
Thus

i) Hydrated cupric sulphate containing $[Cu(H_2O)_4]^{2+}$ ions is blue color of the transmitted light because it absorb yellow light.

ii) Cuprammonium sulphate containing $[Cu(NH_3)]^{2+}$ ions is violet because it absorbs yellow green light.

iii) $[Ti(H_2O)_6]^{3+}$ absorbs green light in the visible region and hence it is purple which is the color of the transmitted light.

The complex ions which absorb light in the infrared or ultraviolet regions of the spectrum are colorless, e.g. (i) anhydrous cupric sulphate is colorless since it absorbs light in the infrared region. (ii) $[Cu(CN)_4]^{4-}$ ion absorbs light in the ultraviolet region and hence is colorless.



With the help of visible absorption spectrum of a complex ion it is possible to predict the colour of the complex. For example, $[Ti(H_2O)_6]^{3+}$ ion shows absorption maxima at a wavelength of about 5000Å which corresponds to the wave number v = 20000 cm^{-1} as shown below:

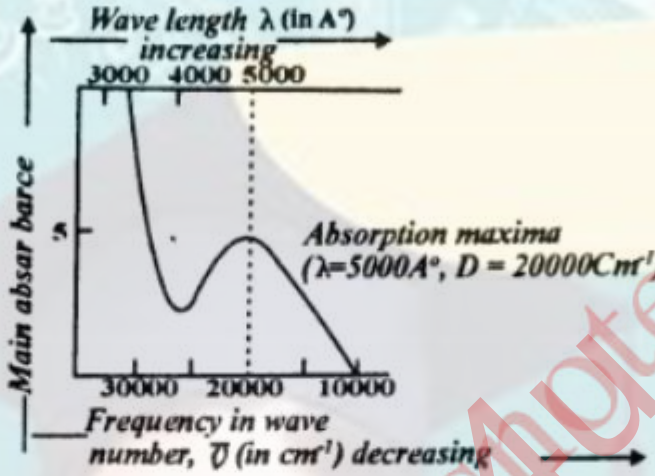
Since 1Å = 10^{-8}cm. wavelength, λ= 5000Å = 5000×10^{-8}cm

Consequently wave number,

$$v = 1/\lambda = 1/5000 \times 10^{-8}$$

$$= 1/5 \times 10^{-5}\ cm^{-1} = 0.2 \times 10^{5}\ cm^{-1} = 20000\ cm^{-1}$$

Light of this wavelength (5000Å) is green (Fig 14.5) and is absorbed by the complex ion. Thus the transmitted light is purple, which is in fact, the color of the ions.



Q15. Give chemistry of some important transition elements in detail.

Answer

1) Vanadium

In this topic we will discuss:

i) The conversion between various Vanadium Oxidation states and

ii) The use of Vanadium (V) oxide as a catalyst in the contact process.

Vanadium's oxidation states

Vanadium has oxidation states in its compounds of +5, +4, +3 and +2. This section looks at ways of changing between them. It starts with a bit of description, and then goes on to look at the reactions in terms of standard redox potentials (standard electrode potentials).

Observing the changes in the lab

Reducing vanadium (V) in stages to vanadium (II)

The usual source of vanadium in the +5 oxidation state is ammonium metavanadate, NH_4VO_3. This isn't very soluble in water and is usually first dissolved in sodium hydroxide solution.

The solution can be reduced using zinc and an acid - either hydrochloric acid or sulphuric acid, usually using moderately concentrated acid.

The exact vanadium ion present in the solution is very complicated, and varies with the pH of the solution. The reaction is done under acidic conditions when the main ion present is VO_2^+ - called the dioxovanadium (V) ion.

Note: The ion is usually written as VO_2^+, but is more accurately $[VO_2(H_2O)_4]^+$.

If you do the reaction in a small flask, it is normally stoppered with some cotton wool. This allows hydrogen (produced from a side reaction between the zinc and acid) to escape. At the same time it stops much air from entering. This prevents re-oxidation of the lower oxidation states of vanadium (particularly the +2 state) by oxygen in the air.

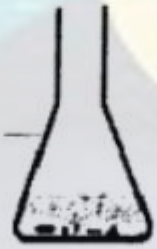
The reaction is usually warmed so that the changes happen in a reasonable time.

The reduction is shown in two stages. Some individual important colours are shown, but the process is one continuous change from start to finish.

The reduction from +5 to +4

Oxidation state = +5

VO_2^+



This isn't a new oxidation state. The green is a mixture of the original yellow and the blue that is being produced.

Oxidation state = +4

VO^{2+}

It is important to notice that the green colour you see isn't actually another oxidation state. it is just a mixture of the original yellow of the +5 state and the blue of the +4.

Do you know? Just like the VO_2^+ ion, the VO^{2+} ion will have water molecules attached to it as well - $[VO(H_2O)_5]^{2+}$. We usually use the simpler form.

The reduction from +4 to +2

The colour changes just continue.

Oxidation state = +4

VO^{2+}

Oxidation state = +3

"$V(H_2O)_6^{3+}$"

Oxidation state = +2

$V(H_2O)_6^{2+}$

The reason for the inverted commas around the vanadium (III) ion is that this is almost certainly a simplification. The exact nature of the complex ion will depend on which acid you use in the reduction process. The simplification is probably reasonable at this level.

Note: If you use hydrochloric acid, you get a ligand exchange reaction to give $[V(H_2O)_4Cl_2]^+$. This causes the green colour in the vanadium (III) solution.

If you use sulphuric acid, One source says that with sulphuric acid, you actually get the $[V(H_2O)_6]^{3+}$ ion which is a dull grey-blue colour. However, when checked this in the lab, you got *exactly* the same green colour with both acids.

One possibility is that you get another ligand exchange reaction with sulphate ions to

give $[V(H_2O)_5(SO_4)]^+$, but haven't been able to confirm this.

Re-oxidation of the vanadium (II)

The vanadium (II) ion is very easily oxidized. If you remove the cotton wool from the flask and pour some solution into a test tube, it turns green because of its contact with oxygen in the air. It is oxidized back to vanadium (III).

Note: It only changes this quickly if the solution is still warm. In the cold, the change is quite a lot slower.

If it is allowed to stand for a long time, the solution eventually turns blue as the air oxidizes it back to the vanadium (IV) state - VO^{2+} ions.

Adding nitric acid (a reasonably powerful oxidizing agent) to the original vanadium (II) solution also produces blue VO^{2+} ions. The vanadium (II) is again oxidized back to vanadium (IV).

Explaining the changes in terms of redox potentials (electrode potentials)

Using zinc as the reducing agent

The first stage of the series of reductions

Let's look at the first stage of the reduction - from VO_2^+ to VO^{2+}. The redox potential for the vanadium half-reaction is given by:

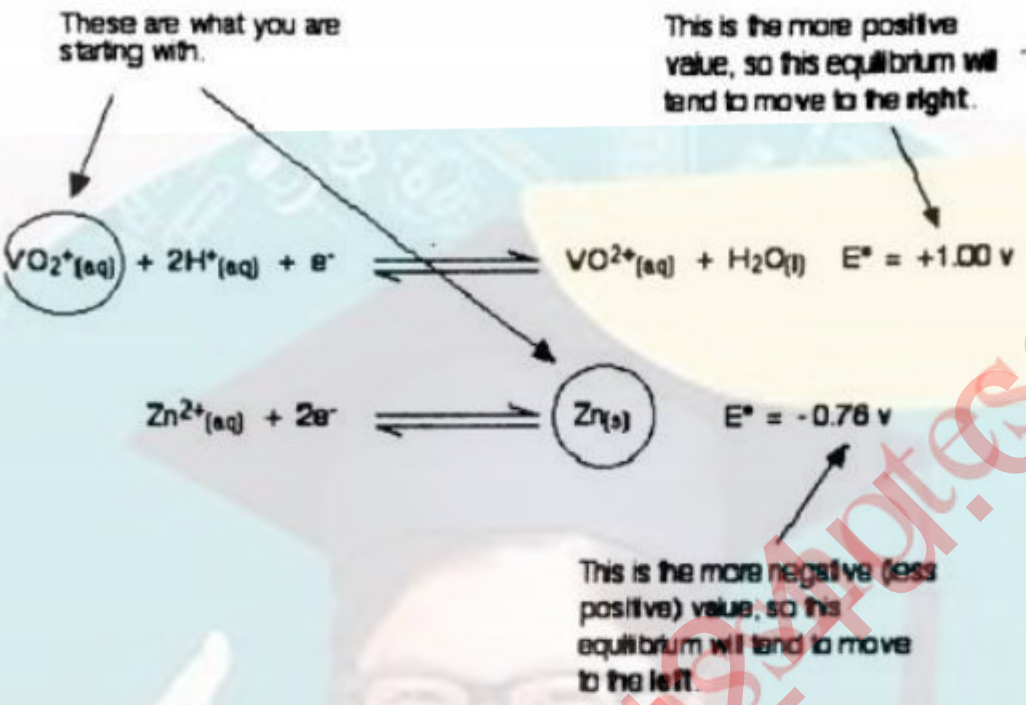
$$VO_2^+{}_{(aq)} + 2H^+{}_{(aq)} + e^- \rightleftharpoons VO^{2+}{}_{(aq)} + H_2O_{(l)} \quad E^\ominus = +1.00\ v$$

The corresponding equilibrium for the zinc is:

$$Zn^{2+}{}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)} \quad E^\ominus = -0.76\ v$$

The simple principle is that if you couple two of these half-reactions together, the one with the more positive $E^\ominus$ value will move to the right; the one with the more negative (or less positive) $E^\ominus$ moves to the left.

So, if you mix together zinc and VO_2^+ ions in the presence of acid to provide the H^+ ions:



That converts the two equilibria into two one-way reactions. You can write these down and combine them to give the ionic equation for the reaction if you want to.

$$2 \times (VO_2^+_{(aq)} + 2H^+_{(aq)} + e^- \longrightarrow VO^{2+}_{(aq)} + H_2O_{(l)})$$

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$$

$$2VO_2^+_{(aq)} + 4H^+_{(aq)} + Zn_{(s)} \longrightarrow 2VO^{2+}_{(aq)} + 2H_2O_{(l)} + Zn^{2+}_{(aq)}$$

The other stages of the reaction

Here are the E° values for all the steps of the reduction from vanadium (V) to vanadium (II):

$VO_2^+_{(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons VO^{2+}_{(aq)} + H_2O_{(l)}$ $E^\circ = +1.00$ v

$VO^{2+}_{(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons V^{3+}_{(aq)} + H_2O_{(l)}$ $E^\circ = +0.34$ v

$V^{3+}_{(aq)} + e^- \rightleftharpoons V^{2+}_{(aq)}$ $E^\circ = -0.26$ v

and here is the zinc value again:

$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$ $E^\circ = -0.76$ v

Remember that for the vanadium reactions to move to the right (which is what we want), their E° values must be more positive than whatever you are reacting them with.

In other words, for the reactions to work, zinc must always have the more negative value - and that's the case.

Zinc can reduce the vanadium through each of these steps to give the vanadium(II) ion.

Using other reducing agents

Suppose you replaced zinc as the reducing agent by tin. How far would the set of reductions go this time?

Here are the E° values again:

$$VO_2^+_{(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons VO^{2+}_{(aq)} + H_2O_{(l)} \quad E^\circ = +1.00\ v$$

$$VO^{2+}_{(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons V^{3+}_{(aq)} + H_2O_{(l)} \quad E^\circ = +0.34\ v$$

$$V^{3+}_{(aq)} + e^- \rightleftharpoons V^{2+}_{(aq)} \quad E^\circ = -0.26\ v$$

and here is the tin value:

$$Sn^{2+}_{(aq)} + 2e^- \rightleftharpoons Sn_{(s)} \quad E^\circ = -0.14\ v$$

In order for each reduction to happen, the vanadium reaction has to have the more positive E° value because we want it to go to the right. That means that the tin must have the more negative value.

In the first vanadium equation (from +5 to +4), the tin value is more negative. That works OK.

In the second vanadium equation (from +4 to +3), the tin value is again the more negative. That works as well.

But in the final vanadium reaction (from +3 to +2), tin no longer has the more negative E° value. Tin won't reduce vanadium (III) to vanadium (II).

Re-oxidation of the vanadium (II)

The vanadium(II) oxidation state is easily oxidized back to vanadium(III) - or even higher.

Oxidation by hydrogen ions

You will remember that the original reduction we talked about was carried out using zinc and an acid in a flask stoppered with a piece of cotton wool to keep the air out. Air will rapidly oxidize the vanadium (II) ions - but so also will the hydrogen ions present in the solution!

The vanadium (II) solution is only stable as long as you keep the air out, and in the presence of the zinc. The zinc is necessary to keep the vanadium reduced.

What happens if the zinc isn't there? Look at these E° values:

$$V^{3+}_{(aq)} + e^- \rightleftharpoons V^{2+}_{(aq)} \quad E^\circ = -0.26\ v$$

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \quad E^\circ = 0\ v$$

The reaction with the more negative E° value goes to the left; the reaction with the more positive (or less negative) one to the right.

That means that the vanadium (II) ions will be oxidized to vanadium (III) ions, and the hydrogen ions reduced to hydrogen.

Will the oxidation go any further - for example, to the vanadium (IV) state?

Have a look at the E° values and decide:

$$VO^{2+}_{(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons V^{3+}_{(aq)} + H_2O_{(l)} \qquad E^\circ = +0.34\ v$$

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \qquad E^\circ = 0\ v$$

In order for the vanadium equilibrium to move to the left, it would have to have the more negative E° value. It *hasn't* got the more negative E° value and so the reaction doesn't happen.

Oxidation by nitric acid

In a similar sort of way, you can work out how far nitric acid will oxidize the vanadium (II).

Here's the first step:

$$V^{3+}_{(aq)} + e^- \rightleftharpoons V^{2+}_{(aq)} \qquad E^\circ = -0.26\ v$$

$$NO_3^-{}_{(aq)} + 4H^+_{(aq)} + 3e^- \rightleftharpoons NO_{(g)} + 2H_2O_{(l)} \qquad E^\circ = +0.96\ v$$

The vanadium reaction has the more negative E° value and so will move to the left; the nitric acid reaction moves to the right.

Nitric acid will oxidize vanadium (II) to vanadium (III).

The second stage involves these E° values:

$$VO^{2+}_{(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons V^{3+}_{(aq)} + H_2O_{(l)} \qquad E^\circ = +0.34\ v$$

$$NO_3^-{}_{(aq)} + 4H^+_{(aq)} + 3e^- \rightleftharpoons NO_{(g)} + 2H_2O_{(l)} \qquad E^\circ = +0.96\ v$$

The nitric acid again has the more positive E° value and so moves to the right. The more negative (less positive) vanadium reaction moves to the left.

Nitric acid will certainly oxidize vanadium (III) to vanadium (IV).

Will it go all the way to vanadium (V)?

$$VO_2^+{}_{(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons VO^{2+}_{(aq)} + H_2O_{(l)} \qquad E^\circ = +1.00\ v$$

$$NO_3^-{}_{(aq)} + 4H^+_{(aq)} + 3e^- \rightleftharpoons NO_{(g)} + 2H_2O_{(l)} \qquad E^\circ = +0.96\ v$$

No, it won't! For the vanadium reaction to move to the left to form the dioxovanadium (V) ion, it would have to have the more negative (less positive) E° value. It hasn't got a less positive value, and so the reaction doesn't happen.

Note: There are several possible half-reactions involving the nitric acid with a variety of E° values. Two of these actually have E° values more positive than +1.00 and so, in principle, nitric acid could seem to be able to oxidize vanadium (IV) to vanadium (V) - but involving different products from the nitric acid.

In practice, if you do this reaction in the lab, the solution turns blue - producing the vanadium (IV) state. Just because the E° values tell you that a reaction is possible, you can't assume that it will actually happen. There may be very large activation energy barriers involved, causing the reaction to be infinitely slow!

You can work out the effect of any other oxidizing agent on the lower oxidation states

of vanadium in exactly the same way. But don't assume that because the E° values show that a reaction is *possible*, it will *necessarily* happen.

Vanadium (V) oxide as a catalyst in the Contact Process

The overall reaction

During the Contact Process for manufacturing sulphuric acid, Sulphur dioxide has to be converted into Sulphur trioxide. This is done by passing Sulphur dioxide and oxygen over a solid vanadium (V) oxide catalyst.

$$SO_2 + \tfrac{1}{2}O_2 \xrightarrow{V_2O_5} SO_3$$

How the reaction works

This is a good example of the ability of transition metals and their compounds to act as catalysts because of their ability to change their oxidation state (oxidation number).

The Sulphur dioxide is oxidized to Sulphur trioxide by the vanadium (V) oxide. In the process, the vanadium (V) oxide is reduced to vanadium (IV) oxide.

$$SO_2 + V_2O_5 \longrightarrow SO_3 + V_2O_4$$

The vanadium (IV) oxide is then re-oxidized by the oxygen.

$$V_2O_4 + \tfrac{1}{2}O_2 \longrightarrow V_2O_5$$

Although the catalyst has been temporarily changed during the reaction, at the end it is

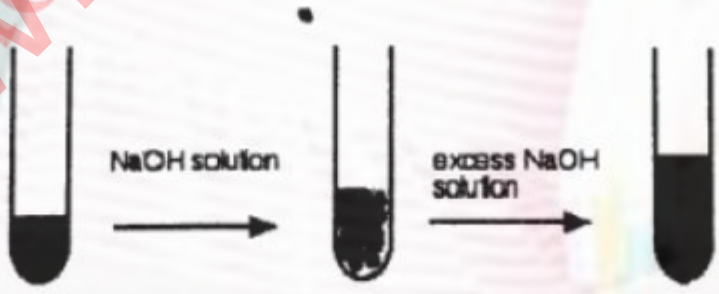
2) Chromium

In this topic we will discuss;

1) The interconversion of the various oxidation states of chromium.
2) The chromate (VI)-dichromate (VI) equilibrium;
3) The use of dichromate (VI) ions as an oxidizing agent (including titrations).

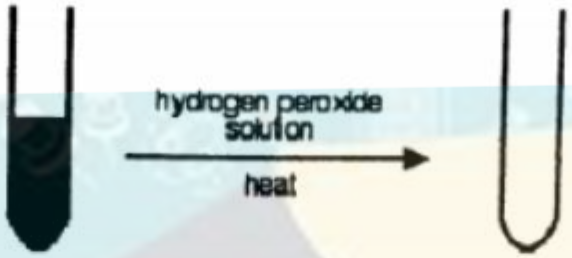
The oxidation of chromium(III) to chromium(VI)

An excess of sodium hydroxide solution is added to a solution of the hexaaquachromium(III) ions to produce a solution of green hexahydroxochromate(III) ions.



$[Cr(H_2O)_6]^{3+}$ $[Cr(H_2O)_3(OH)_3]$ $[Cr(OH)_6]^{3-}$

This is then oxidised by warming it with hydrogen peroxide solution. You eventually get a bright yellow solution containing chromate(VI) ions.



$[Cr(OH)_6]^{3-}$ CrO_4^{2-}

The equation for the oxidation stage is:

$$2[Cr(OH)_6]^{3-} + 3H_2O_2 \longrightarrow 2CrO_4^{2-} + 2OH^- + 8H_2O$$

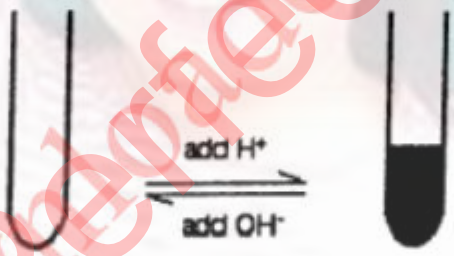
Some chromium(VI) chemistry

The chromate(VI)-dichromate(VI) equilibrium

You are probably more familiar with the orange dichromate(VI) ion, $Cr_2O_7^{2-}$, than the yellow chromate(VI) ion, CrO_4^{2-}.

Changing between them is easy

If you add dilute sulphuric acid to the yellow solution it turns orange. If you add sodium hydroxide solution to the orange solution it turns yellow.



CrO_4^{2-} $Cr_2O_7^{2-}$

The most important: If you had just produced the yellow chromate(VI) ions by oxidising chromium(III) ions using hydrogen peroxide, you can't convert them into dichromate(VI) ions without taking a precaution first.

In the presence of acid, dichromate(VI) ions react with any hydrogen peroxide which is left in the solution from the original reaction. To prevent this, you heat the solution for some time to decompose the hydrogen peroxide into water and oxygen before adding the acid.

The equilibrium reaction at the heart of the interconversion is:

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

If you add extra hydrogen ions to this, the equilibrium shifts to the right. This is consistent with Le Chatelier's Principle.

Adding hydrogen ions forces the position of equilibrium to the right

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

If you add hydroxide ions, these react with the hydrogen ions. The equilibrium tips to the left to replace them.

Adding hydroxide ions removes these hydrogen ions

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

... and the equilibrium moves to the left to replace them.

The reduction of dichromate(VI) ions with zinc and an acid

Dichromate(VI) ions (for example, in potassium dichromate(VI) solution) can be reduced to chromium(III) ions and then to chromium(II) ions using zinc and either dilute sulphuric acid or hydrochloric acid.

Hydrogen is produced from a side reaction between the zinc and acid. This must be allowed to escape, but you need to keep air out of the reaction. Oxygen in the air rapidly re-oxidises chromium(II) to chromium(III).

An easy way of doing this is to put a bit of cotton wool in the top of the flask (or test-tube) that you are using. This allows the hydrogen to escape, but stops most of the air getting in against the flow of the hydrogen.

Oxidation state = +6 | Oxidation state = +3 | Oxidation state = +2

$Cr_2O_7^{2-}$ | "$Cr(H_2O)_6^{3+}$" | $Cr(H_2O)_6^{2+}$

The reason for the inverted commas around the chromium(III) ion is that this is a simplification. The exact nature of the complex ion will depend on which acid you use in the reduction process. This has already been discussed towards the top of the page. The equations for the two stages of the reaction are:

EXERCISE

Q1: Select the right answer from the choices given with each question.

1) **Oxides and hydroxides of Group1 elements are:**
   a) Acidic
   b) Alhaline
   c) Neutral
   d) Amphoteric

2) **The flame colour of sodium metal or its compounds is:**
   a) A, Bright crimson
   b) Voilet
   c) Golden yellow
   d) Bright blue

3) **When sodium burn in air , it forms sodium:**
   a) Monixide
   b) Peroxide
   c) Oxide
   d) Superoxid

4) **The carbonates of alkali metal are not affected by heat except:**
   a) Li_2CO_3
   b) Na_2CO_3

c) K_2CO_3 d) Rb_2CO_3

5) **Green is characteristic flame colour of:**
a) Calcium b) Barium
c) Strontium d) Sodium

6) **All the carbonates, sulphates and phosphates of alkaline earth metals are _____ in water.**
a) Sprangly b) Soluble
c) Insoluble d) Less soluble

7) **The first ioniziatio energy is higher for the:**
a) Alkaline earth metals b) Alkali metals
c) Halogens d) Nobel gases

8) **Which one of the element has the maximum electron affinity?**
a) F b) Cl c) Br d) I

9) **Which pair has both members from same period of periodic table?**
a) Na – Ca b) Na – Cl c) Ca – Cl d) Cl – Br

10) **Melting points and boiling points of alkali metals:**
a) Decreases from top to bottom b) Increases from top to bottom
c) First increases then decreases d) Remains uncharged

11) **Which of the following oxides is amphoteric in nature?**
a) Rubidium oxide b) Barium oxide
c) Antimony d) Sulphur oxide

12) **Oxidizing power of halogen depends upon:**
a) Energy of dissociation b) Electron affinity
c) Heat of vaporization d) All of above

13) **Which of following oxides amphoteric is nature?**
a) Mgo b) BeO c) CO_2 d) SnO_2

14) **Select the correct increasing order of atomic radius?**
a) Ne > O > S > Al b) Ne < O > S > Al
c) Ne < O > S > Al d) Ne > O < S > Al

15) **Due to inert pair effect _____ oxidation state is more stable than _____ For Sn and Pb.**
a) 2+, 4+ b) 1+, 4+ c) 4+, 2+ d) 2+, 3+

16) **Highest electron affinity is shown by?**
a) F_2 b) I_2 c) Br_2 d) Cl_2

17) **Which is the strongest reducing agent?**
a) HF b) HCl c) Br_2 d) HBr

18) **Substance boiling at higher temperature among following is?**
a) HI b) HF c) HCl d) HBr

19) **Group VII-A elements are generally called:**

a) Halogens b) Nobel gases
c) Inert gases d) Metallods

20) **The radioactive element in halogen group is:**

a) Radon b) Radium c) Astatine d) Bromine

Answers

1)	b)	2)	c)	3)	b)	4)	a)	5)	b)
6)	c)	7)	d)	8)	b)	9)	b)	10)	a)
11)	c)	12)	b)	13)	b)	14)	c)	15)	a)
16)	d)	17)	d)	18)	b)	19)	a)	20)	c)

Q2: Give brief answers for the following questions.

Q1. Although Na and P are present in the same period their oxides are different in nature Na_2O is basic while P_2O_5 is acidic why?

Answer

Na and P are present in same period But Na_2O is basic and P_2O_5 is acidic:

Na is an alkali metal present in IA group and has one electron in its outermost shell, It gives a strong base (NaOH) on dissolving in water.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

Phosphorus is member of group – VA. It is non-metal and has five electrons on its outermost shell. P_2O_5 on dissolving in cold water produce meta phosphoric acid and on dissolving in hot water give orthophosphoric acid.

$$P_2O_5 + H_2O \xrightarrow[\text{(Cold)}]{} 2HPO_3 \quad \text{(metaphosphoric acid)}$$

$$P_2O_5 + 3H_2O \xrightarrow[\text{(Hot)}]{} 2H_3PO_4 \quad \text{(orthophosphoric acid)}$$

Q2. How acidic basic and amphoteric behaviour of oxides is explained?

Answer

Basic, Acidic and amphoteric behaviour of oxides:

Odides of alkali metals are basic in nature.

$$\underset{\text{(Base)}}{Na_2O} + \underset{\text{(Acid)}}{H_2SO_4} + H_2O \longrightarrow Na_2SO_4$$

Oxides of Be Saluminium are amphoteric in nature e.g $SO_3 + P_2O_5$

$$\underset{\text{(acid)}}{SO_3} + \underset{\text{(Base)}}{Na_2O} \longrightarrow \underset{\text{(Salt)}}{Na_2SO_4}$$

Oxides of Be saluminium are amphoteric

$$\underset{\text{(Acid)}}{BeO} + 2NaOH \longrightarrow \underset{\text{(Sodium beryllate)}}{Na_2BeO_2} + H_2O$$

$$\underset{\text{(Base)}}{BeO} + H_2SO_4 \longrightarrow BeSO_4 + H_2O$$

Q3. Why the elements of group 1 are called alkali metals?

Answer

Elements of group IA are metals and their oxides and hydroxides are alkaline in nature.

e.g $Na_2O + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O$

$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O$

Q4. Why all group of metals have low ionization energies?

Answer

All IA – group elements have one electron on their outermost shell. Except lithium all alkali metal have strong shielding or screening effect. As a result pull of nucleus on outermost electron decreases thats why outermost electron of alkali methods may be removed easily using low energy.

Q5. Why do the group 1 metals show strong electropositive character?

Answer

The metals which lose outermost electrons easily and give a stable cation are called (electropositive. And group IA metals lose their outermost single electron easily to complete their outermost stable octet Therefore they are electropositive metals.

Q6. Why do group 1 metals show strong reducing properties?

Answer

All alkali metals have one electron in their outermost shell and on losing one outermost electron their octet is completed which is a stable state. Therefore they try to lose their valence electron and all as good reducing agent.

Q7. Why different colours are imported by the atoms of the group 1 metals to the flame?

Answer

The outermost electron of group IA is ns^1. This electron is loosely hold with the nucleus.

When an element is brought to a flame of a burner the electron absorbs some energy and goes to higher energy orbital and is called excited. This excited electron absorbs energy during process of excitation Atoms of different elements absorb different energies therefore on dexitation they impart different colours to flame.

Q8. Why the elements of group 2 are called alkaline earth metals?

Answer

II – A group members are metals, their salts are found in earth and their oxides & hydroxides alkaline in nature. Therefore they are called alkaline earth metals.

e.g $CaO + H_2SO_4 \longrightarrow CaSO_4 + H_2O$

$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$

Q9. Why do the group 2 earth metals have high melting and boiling points than alkali metals?

Answer

The alkaline earth metals have two electrons in their outermost shell whereas group II – A have one electron in their outermost shell. Therefore there are strong metal–metal

bonds among group IIA. Therefore II – A members are harder and stranger than group I–A members. Therefore the melting and boiling point of group II–A members are higher than group I – A members.

Q10. How do group 1 metals resemble with group 2 metals?

Answer

Both group I–A and group II–A members

1) are metals.
2) are iso-electronic up to subshell.

e.g Li = 3 $Is^2, 2S^1$

Be = 4 $Is^2, 2S^2$

3) have alkaline oxides and hydroxides

e.g Na2O, MgO

NaOH, $CaCOH_2$

4) are good conductors for heat and electricity can react with halogens to form salts. e.g NaCl, $CaCl_2$

Q11. How do group 1 metals differs from group 2 metals?

Answer

Group IA Metals	Group IIA Metals
1) Their have one electron in their outermost shell. 2) They are monovalent i.e M^{+1}.	Their atoms have two electons in their outermost shell. They are divalent i.e M^{+2}
3) They are soft metals.	They are hard metals
4) Their melting and boiling points are lone.	Their melting and boiling points are high.
5) Their carbonates are solube in water.	Their carbonates are insoluble in water.
6) Their carbonates are stable towards heat $Na_2CO_3 \xrightarrow{\Delta} X$	Their carbonates decompose on heating. $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$
7) Their hydroxides are stable towards heat $NaOH \xrightarrow{\Delta} X$	Their hydroxides decompose on heating. $Ca(OH)_2 \xrightarrow{\Delta} CaO + H_2O$

Q12. Discuss the metallic and non-metallic character of group 4 elements.

Answer

Metallic and Non Metallic charcter of Group IV A Elements.

Metallic character of Group iv – A elements increase from top to bottom.

iv – A.

C, Si — Non – metals

Ge – semi metals

Sn, Pb – Metals

Q13. Discuss the general trends of group 7 elements.

Answer

General Group Trends of Group VII – A Elements

i) Trends in physical states:

As attractive forces among their molecules increase from F_2 to I_2, therefore.

F_2, Cl_2 — gases

Br_2 – Liq

I_2 – solid

Trends in Electronegativity

Electronegativity decrease from top to bottom in halogen group. i.e. Decreases from F to I.

iii) Trends in Electron Affinity

Due to high electron density, the E.A value of E is low. And E.A value of remaining halogens decrease from Cl to I.

iv) Bond Enthalpy in halogens

Due to very small size and high electron density F atoms repell each other in F_2. As a result the bond dissociation. Energy of F_2 is lower than the remaining halogens B D E of remaining halogens decrease from Cl_2 to I_2

v) Trends as oxidising agents

Oxidising ability of halogens decrease from F2 to I_2.

$$F_2 > Cl_2 > Br_2 > I_2$$

vi) Trends of Activity of Halogen halides

Due to strong H – bonds, the HF ionizes slightly, therefore is a weak acid. Other halo acids ionize completely and are strong acids.

Their acidic strength increases from HF to HI

$$HF < HCl < HBr < HI$$

(weakest acid) (Strong acid)

Q14. Why the term halogen is used for group 7 elements.

Answer

Halogen means salt forming. The elements of Group VII–A on reaction with alkali and

alkaline earth metals form salts. e.g.

$$2Na + Cl_2 \longrightarrow 2NaCl \text{ (Salt)}$$
$$2K + Br_2 \longrightarrow 2K\,Br \text{ (Salt)}$$
$$Ca + Cl_2 \longrightarrow CaCl_2 \text{ (Salt)}$$

Q15. Why does fluorine differ from other members of its group?

Answer

Flourine differs from its Group members in following respects.

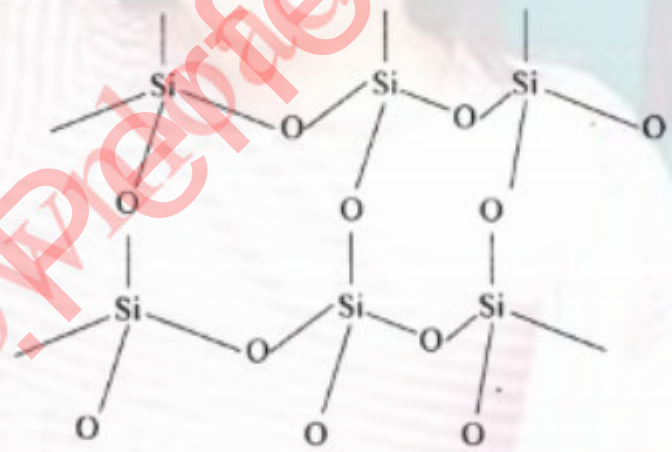
1) Very small size of F atom and $\overset{\ominus}{F}$ ion.
2) Very high 1st Ionization Energy and Elecronegativity.
3) Low BDE of F_2 as compared to Cl_2 to Br_2.
4) Restriction of valence shell to an octet.
5) CaF2 & Mg F_2 are insoluble in water whereas $CaCl_2$ f $CABr_2$ are soluble.

Q16. What is the structure of CO_2 and SiO_2 and why they differ?

Answer

Structure of CO_2 & SiO_2 & their Difference

CO_2 is a Linear shaped molecule (O = C = O) having zero dipole moment. Therefore exists as gas. Si isa big sized atom as compared to C. That is why SiO_2 molecule is tetra hederal in shape. Therfore it has a strong network. And that is why it exists i solid crystalline form.



(Network of SiO_2 molecules)

Q17. CO_2 is a gas while SiO_2 is a solid although C and Si belong to the same group.

Answer

Please see answer of Q16.

Q18. Explain why nitrates and carbonates of Li are not stable?

Answer

Li^+ is very small in size and has high charge density. It takes O^2 from nitrate as well in carbonate and forms Li_2O on heating i.e. $4Li\,NO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$

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b) Explain the order F>Cl> Br>I with respect to oxidizing agent or power.

Answer

a) Why is the bond enthalpy of F–F less as compared to Cl – Cl and Br– Br?

Due to very high electronegeitivity of F attract the electrons towards their nuclei with greater force which hardly allows the electrons to be shared to form a covalent bond. Small amount of supply of energy increases the Kinetic energy of atom and break the bond between atoms.

In case of Cl_2 and Br_2 the electronegativityof Cl and Br atoms are moderate and easily allow atoms to share the electrons to form stable covalent bond therefore Cl_2 and Br_2 exist stable gaseous molecules.

The order F>Cl> Br>I with respect to oxidizing agent

The electronegativityorder of halogen is:

i) Element F> Cl> Br> I

Electronegetivity 4.0>, 3.2>, 3.0>, 2.5

Due to highest value of electronegativityF may attract and lake the electron from a substance and oxidize with more force as the order of electronegativitydecreases towards I therefore oxidizing power towards I also decreases.

Q13. a) Why is flourine much stronger oxidizing agent than chlorine?
b) HCl is strong acid as compared to HF. Why?

Answer

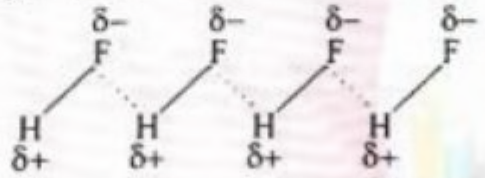
a) Why is flourine much stronger oxidizing agent than chlorine?

The electronegativityof F is 4.0 which is maximum in periodic table due to its high electonegitivity it may take an electrons from a sub stance to complete its octate whereas Cl has somewhat lower electronegativityand has low oxidizing power.

b) HCl is strong acid as compared to HF. Why?

Due to very high electronegativity F, the molecule HF is highly polar.

There are strong hydrogen bonds between HF molecules.



As a result the power of HF to release proton is decreases. As a result HF behaves as weaker acid than HCl which is completely ionized on dissolving in water.

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Short Answers and Questions

Q1: Why are they called transition elements?

Answer

The elements which have partially filled d or f-orbital either in their atomic states or in other common oxidation states are called transition elements.

They are called d-block or f-block elements. They are also called transition elements because they show such properties which are transitional between highly reactive and strongly electropositive elements of s-block which form ionic bonds and p-block elements which from covalent compounds.

Q2: Write down the f general f feature of transition elements.

Answer

1) They are ,ll metallic nature.
2) Some of the transition elements play an important role in the industry. These metals are Ti, Cx, Fe, Ni, Cu, Mo, W and Th etc.
3) They are all heard and strong metal with high melting and boding points. They are good conductors of heat and electricjty.
4) They form alloys with one another and other elements of periodic table as well.
5) With a few exceptions, they show variable oxidation states.
6) Their ions and compounds are colored in the solid state and the solution state.

Q3: Why is Zn group included in transition elements?

Answer

Zn, Cd and Hg are not regarded as transition elements because they have completely filled d orbitals. It is appropriate to include these in transition elements because they

form complexes with ammonia halide ions and amines and their chemical behaviours is similar to transition elements.

Q4: What are oxidation state of transition elements?

Answer

Transition elements are electropositive, so they have positive oxidation states. All 3d series elements show an oxidation state of +2 in addition to higher oxidation states when the electrons of 4s orbital take part in bonding.

They show variable oxidation states. The reason is that they have d electrons in addition to s-electron for the purpose of bond formation. These elements have several (n-1) d and ns electrons. The energies of (n-1) d and ns orbitals are way close to each other. The (n-1) d electrons are easily lost as ns electrons. In the higher oxidation states of first five elements, all s and d-electrons are sued for bonding. Among the 3d series Mn has maximum oxidation states, and goes up to +7.

Q5: Why transition elements are used as catalyst?

Answer

Most of the transition elements are used as catalyst. The compounds of transition metals are also catalyst. The reason is that the transition metals show variety of oxidation states. In this way, they can form intermediate products with various reactants.

They also from interstitial compounds which can absorbs an activator to the reacting species. Some of the important catalyst.

1) A mixture of Zno and Cr_2O_3 is used for the manufacture of methyl alcohol.
2) Ni, Pt and Pd are catalyst for the hydrogenation of vegetable oil and saturation of alkenes and alkynes to alkanes.
3) MnO_2 can be used as catalyst for the decomposition of H_2O_2.
4) Tid4 is used as catalyst for the manufacture of plastics.
5) N_2O_5 is used to oxidize SO_2 to SO_3 in the manufacture of H_2SO_4.

Q6: Why transition metals from alloy with each other and write down the properties of alloy?

Answer

Alloy is mixture of two or more than two metals. Transition metals form alloy with each other.

Transition elements have almost similar sizes and atoms of the one metal can easily take up positions in crystal lattice of the each other. They form substitution alloy among themselves. E.g. Brass, bronze and coinage alloys are the base alloys.

Properties:

As alloys are prepared according to the requirements, their characteristics are different yet few properties are common which are as follows

1) Alloys are comparatively cheap.
2) They are strong and flexible but hard alloys can also be prepared.
3) They have long life because they do not corrode.

4) They are durable.
5) They have high melting points.

Q7: Define coordination compounds, and explain them.

Answer

Those compounds which contain complex molecules or complex ions capable of independent existence are called coordination compounds or complex compounds.

Such compound are formed by the coordination of an electron pair donor to metal atom or ion.

In order to understand let us mixture substances that is KCN and $Fe(CN)_2$. When this evaporated a new compound is obtained. This compound when dissolved in H_2O ionizes into K^+ and $[Fe(CN)_6]^{-4}$. On this basis the new compounds has been given the formula $K_4[Fe(CN)_6]$.

$$4KCN + Fe(CN)_2 \longrightarrow K_4Fe(CN)_6$$

Complex compound is consisted of these compounds

1) A positively or negatively charged ion which is not complex.
2) A central metal atom or ion which is consisted of transition elements.
3) Electron pair donor which is negatively charged, positively charged or neutral.

Q8: Define ligand? and write down its types?

Answer

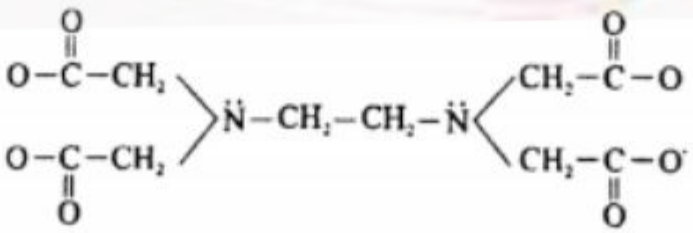
The atom ion or neutral molecule which surrounds the central metal atom or ion by donating the electron pair is called ligand.

Examples

In $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ CN^- is the ligand.

Types

1) Monodentate ligands. Those ligands which have only one donatable electron pair. Such ligand may be negatively charged or neutral. E.g. Negatively charged ligands F^-, Cl^-, Br^-, I^-
Neutral ligand H_2O, NH_3, CO.
2) Bidentate ligands. Those ligands which have two donatable electron pairs are called bidentate ligands. E.g. CO_3^{-2}, SO_4^{-2}, $NH_2 - CH_2 - CH_2 - NH_2$.
3) Tridentate ligands. Those ligands which have 3 donatable electron pairs.
E.g. $H_2NCH_2 - CH_2 - NH - CH_2 - CH_2 - NH_2$.
4) Hexadentate ligands. Those ligands which have six donatable electron pairs e.g. ethylenediaminetetracetate (EDTA).



Q9: Define charge on coordination sphere or ligancy with examples?

Answer

It is the algebraic sum of charges present on the central metal ion and total charge on the ligands.

Examples

In K_4 [Fe $(CN)_6$] the charge present on the central metal ion and total charge on the ligands.

Example: In K_4 [Fe $(CN)_6$] the charge on the coordination sphere can be calculates as follow

$$K_4 [Fe (CN)_6] \longrightarrow 4K^+ + [Fe (CN)_6]^{-4}$$

Since charge on each ligand is = –1

Charge on $6CN^-$ = -6

Charge on iron = +2

So the charge on the coordination sphere = –6 + 2

= –4

Q10: Define coordination member 6 with example?

Answer

Complexes with C.N = 6 on the most common ones formed by transition metal ions.

Sin ligands in a 6-coordination compound may be arranged round the central metal ion M either at the corners of hexagonal plane or at the apices of a trigonal prism or at the apices of a regular octahedron. These arrangements together with members of designating substitution positions may be depicted C.N= 6 has the arrangement of six ligands in a 6-coordination are tetrahedral oxyanions such as VO_4^{3-}, CrO_4^{2-}, FeO_4^{2-} and MnO^- are also tetrahedral. Sugar planner geometry is found in complexes of Cu^{2+}, Ni^{2+}, Pt^{2+} and Au^{2+} etc ions.

Q11: Write down the Re-oxidation of the vanadium (III)?

Answer

The vanadium (III) ion is very cosily oxidized if you remove the cotton wool from the flask and pour some solution into a test tube, it turns green because of its contact with oxygen in the air. It is oxidized back to vanadium (III).

If it is allowed to stand for a long time the solution eventually turns blue as the air oxidized it back to the vanadium (IV) state –VO^{2+} ions.

The first stage of this series of equations

$$VO^{2+} + 2H^+ + e^- \longleftrightarrow VO^{2+} + H_2O + E = +1.00\ V$$

The corresponding equilibrium for the zinc is

$$Zn^{2+} + 2e^- \longleftrightarrow ZnE^\circ = -0.76V$$

So if you mix together zinc and VO_2^+ ions the presence of acid to provide the H^+ ions.

$$VO_2^+ + 2H^+ + e^- \longleftrightarrow VO^{2+} + H_2O + E^\circ = +1.00V$$

$$Zn^{2+} + 2e^- \longleftrightarrow 2n + E^- = -0.76V$$

You can write these down and combine them to give the ionic equations for the

reaction if you want to.

$$2 \times (VO_2^+ + 2H^+ + e^- \longrightarrow VO^{2+} + H_2O)$$
$$Zn \longrightarrow Zn^{2+} + 2e^-$$
$$2VO_2^+ + 4H^+ + Zn \longrightarrow 2VO^{2+} + 2H_2O + Zn^{2+}$$

The other stage of the reaction

E° values for all the steps of the reduction from vanadium (V) to Vanadium (II).

$$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O_{(l)} \quad E^\circ = +1.00V.$$
$$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O_{(l)} \quad E^\circ = +0.34V.$$
$$V^{3+} + e^- \rightleftharpoons V^{2+} \quad E^\circ = -0.26V.$$

And here is the zinc value again.

$$Zn^{2+} + 2e^- \rightleftharpoons Zn. \quad E^\circ = -0.76V$$

Q12: Write down the oxidation of vanadium (II) by nitric acid?

Answer

First step:

$$V^{3+} + e^- \rightleftharpoons V^{2+} \quad E^\circ = -0.26V.$$
$$NO_3^- + 4H^+ + 3e^- \rightleftharpoons NO + 2H_2O \quad E^\circ = +0.96V.$$

The vanadium reaction has the more negative E° value and so while move to the left the nitric acid reaction moves to the right.

Nitric acid will oxidize vanadium (II) to vanadium (III).

The second stage is

$$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O \quad E^\circ = +0.34V$$
$$NO_3^- + 4H^+ + 3e^- \rightleftharpoons NO + 2H_2O \quad E^\circ = +0.96V.$$

The nitric acid again has the move position E° value and so moves to the light. The move negative (less positive) vanadium reaction moves to the left.

Nitric acid will certainly oxidize vanadium (III) to vanadium (IV)

$$VO_3^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O \quad E^\circ = +1.00V$$
$$NO_3^- + 4H^+ + 3e^- \rightleftharpoons NO + 2H_2O \quad E^\circ = +0.96V.$$

Q13: Write down the uses of potassium dichromate (VI) as an oxidizing agent in organic chemistry?

Answer

Potassium dichromate (VI) solution acidified with dilute sulphuric acid is commonly used as an oxidising agent in organic chemistry. It is a reasonably strong oxidising agent without being so powerful that it takes the whole of the organic molecule. It is used to

Oxidise secondary alcohols to ketones.

Oxidise primary alcohols to aldehydes.

Oxidise primary alcohols to carboxylic acid.

If the alcohol is in excess and you distill of the aldehyde as soon as it is formed you get

ethanol as the main product.

$$Cr_2O_7^{2-} + 8H^+ + 3CH_3CH_2OH \longrightarrow 2Cr^{3+} + 7H_2O + 3CH_3CHO$$

If the oxidising agent is in excess and you don't allow the product to escape for examples by heating the mixture under reflux

$$2Cr_2O_7^{2-} + 16H^+ 3CH_3CH_2OH \longrightarrow 4Cr^{3+} + 11\ H_2O + 3CH_3COOH$$

In organic chemistry these equations are often simplified to concentrate on what is happening to the organic molecules. For example the last two could be written.

$$CH_3CH_2OH + [O] \longrightarrow CH_3CHO + H_2O$$

$$CH_3CH_2OH + 2\ [O] \longrightarrow CH_3COOH + H_2O$$

The oxygen written is square bracket means oxygen from an oxidising agent.

Q14: Write down the reaction of manganese (II) ions in solutions oxidation states.

Answer

Hydroxide ions remove hydrogen ions from the H_2O ligands attached to the manganese ion.

Once a hydrogen ion has been removed from two of the H_2O molecules, you are left will a complex with no charge a neutral complex.

This is insoluble in H_2O and a precipitate is formed.

$$[Mn(H_2O)_6]^{2+} + 2OH^- \longrightarrow [Mn(H_2O)_4(OH)_2] + 2H_2O$$

The reaction of hexaaquamanganese (II) ions with ammonia solution.

Ammonia can act as both as base and a legand. In this case at usual lab concentrations it simply act as base removing hydrogen ions from the aqua complex.

$$[Mn(H_2O)_6]^{2+} + 2NH_3 \longrightarrow [Mn(H_2O)_4(OH)_2] + 2NH_4^+$$

Q15: Write down the using potassium manganate (VII) as an oxidising agent in organic chemistry?

Answer

Potassium manganate (VII) is usually used in neutral or alkaline solution in organic chemistry. Acidified potassium manganate (VII) tends to be a rather destructively strong oxidising agent, breaking carbon-bends. The potassium manganate (VII) solution is usually made mildly alkaline with sodium carbonate solution, and the typically colour changes are.

In testing for a C=C double bond.

Potassium manganate (VII) oxidises carbon, carbon double bound, and so goes through the colour change.

Ethane for example is oxidised to ethane 1-2 diols.

$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + H_2O + [O] \xrightarrow{KMnO_4} \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$$

The oxygen in square brackets is taken to mean oxygen from an oxidising agents.

Oxidation of aromatic side chains.

iron (II) hydroxide precipitate to iron (III) hydroxide especially around top of the tube. The darkening of the precipitate comes from the some effect.

In the iron (III) case.

$$[Fe(H_2O)_6]^{3+} \xrightarrow[\text{solution}]{NaOH} [Fe(H_2O)_3(OH)_3]$$

Q19: Write down the reaction of the iron ions with ammonia solution.

Answer

Ammonia can act as both a base and a ligand. In these cases it simply act as a base removing ions from the aqua complex.

In the iron (II) case.

$$[Fe(H_2O)_6]^{2+} + 2NH_3 \longrightarrow [Fe(HO_2)_4(OH)_2] + 2NH_4^+$$

$$[Fe(H_2O)_6]^{2+} \xrightarrow[\text{solution}]{\text{ammonia}} [Fe(H_2O)_4(OH)_2]$$

On standing precipitate darkens and turns orange around the top.

The appearance is just the same as in when you add sodium hydroxide solution. The precipitate again changes colour as the iron (K) hydroxide complex is oxidised by the air to iron (III) hydroxide.

In the iron (III) case.

$$[Fe(H_2O)_6]^{3+} + 2NH_3 \longrightarrow [Fe(HO_2)_3(OH)_3] + 3NH_4^+$$

Q20: Write down the oxidation state and reaction, of hexaaqua copper (II) ions with carbonate ions?

Answer

Oxidation state

The colour changes are

$$[Cu(H_2O)_6]^{2+} \xrightarrow[\text{ammonia}]{\text{small amount}} [Cu(H_2O)_4(OH)_2] \xrightarrow[\text{of ammonia}]{\text{on excess}} [Cu(NH_3)_4(H_2O)_2]^{2+}$$

The reaction of hexaaqua copper (II) ions with carbonate ions.

You simply get a precipitate of copper (II) carbonate.

$$Cu^{2+} + CO_3^{2-} \longrightarrow CuCO_3$$

$$[Cu(H_2O)_6]^{2+} \xrightarrow{CO_3^{2-}} CuCO_3$$