CHAPTE R 14

d and f - BLOCK ELEMENTS:

TRANSITION ELEMENTS

After completing this lesson, you will be able to:

- Explain why the electronic configuration from chromium and copper differ from those assigned using the Aufbau principle.
- Describe important reaction and use of Vanadium, Chromium, Manganese, Iron and Copper
- Explain shapes, origin of colors and nomenclature of coordination compounds.
- Relate the coordination number of ions to the crystal structure of the compounds which they are a part
- Define an alloy and describe some propertied of an alloy that are different from metals that compose it

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 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:

I) 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:

I) 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 configurators:

I) First series (d-block elements) = $(n\text{-}1)d^{1\text{-}10}\ ns^2$.

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

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.

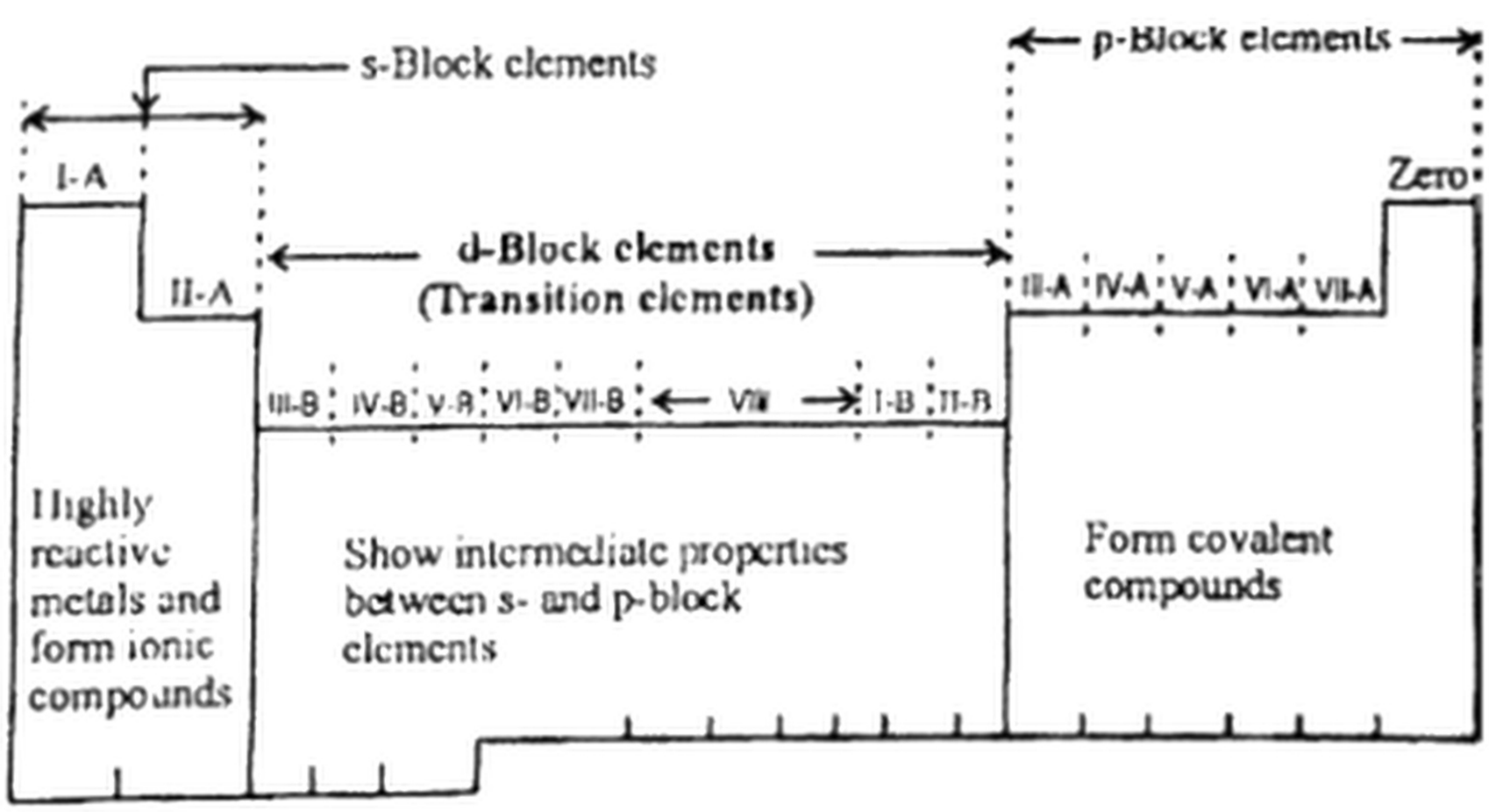
"Coinage metals are transition elements." Justify the statement.

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 distribution as follows:

II-B	III-B
Zn_{30} = ... $4s_2 3d^{10}$	Sc_{21} = ...$4s_2 3d^1$
Cd_{48} =....$5s^2 4d_{IO}$	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-E	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

I) 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

$Sc_{21} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1_{xy}\ 3d^0_{yz}\ 3d^0_{xz}\ 3d^0_{x^2-y^2}\ 3d^0_{z^2}$

$Ti_{22} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1_{xy}\ 3d^1_{yz}\ 3d^0_{xz}\ 3d^0_{x^2-y^2}\ 3d^0_{z^2}$

$V_{23} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1_{xy}\ 3d^1_{yz}\ 3d^1_{xz}\ 3d^0_{x^2-y^2}\ 3d^0_{z^2}$

$Cr_{24} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^1_{xy}\ 3d^1_{yz}\ 3d^1_{xz}\ 3d^1_{x^2-y^2}\ 3d^1_{z^2}$

$Mn_{25} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1_{xy}\ 3d^1_{yz}\ 3d^1_{xz}\ 3d^1_{x^2-y^2}\ 3d^1_{z^2}$

$Fe_{26} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2_{xy}\ 3d^1_{yz}\ 3d^1_{xz}\ 3d^1_{x^2-y^2}\ 3d^1_{z^2}$

$Co_{27} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2_{xy}\ 3d^2_{yz}\ 3d^1_{xz}\ 3d^1_{x^2-y^2}\ 3d^1_{z^2}$

$Ni_{28} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2_{xy}\ 3d^2_{yz}\ 3d^2_{xz}\ 3d^1_{x^2-y^2}\ 3d^1_{z^2}$

$Cu_{29} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^2_{xy}\ 3d^2_{yz}\ 3d^2_{xz}\ 3d^2_{x^2-y^2}\ 3d^2_{z^2}$

$Zn_{30} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2_{xy}\ 3d^2_{yz}\ 3d^2_{xz}\ 3d^2_{x^2-y^2}\ 3d^2_{z^2}$

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 "-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

Similarly, the elements of the group I-B that is Cu-family also show the abnormal distributi0A. Following table shows the electronic distribution of3d, 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)	$[Kr]4d^5 5s^2$	W(74)	$[Xe]4f^{14} 5d^4 6s^2$
Mn(25)	$[Ar]3d^5 4s^2$	Te(43)	$[Kr]4d^7 5s^1$	Re(75)	$[Xe]4f^{14} 5d^5 6s^2$
Fe(26)	$[Ar]3d^6 4s^2$	Ru(44)	$[Kr]4d^8 5s^1$	Os(76)	$[Xe]4f^{14} 5d^6 6s^2$
Co(27)	$[Ar]3d^8 4s^2$	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)	$[Xe]4f^{14} 5d^9 6s^2$
Cu(29)	$[Ar]3d^{10} 4s^1$	Ag(47)	$[Kr]4d^{10} 5s^2$	Au(79)	$[Xe]4f^{14} 5d^{10} 6s^2$
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

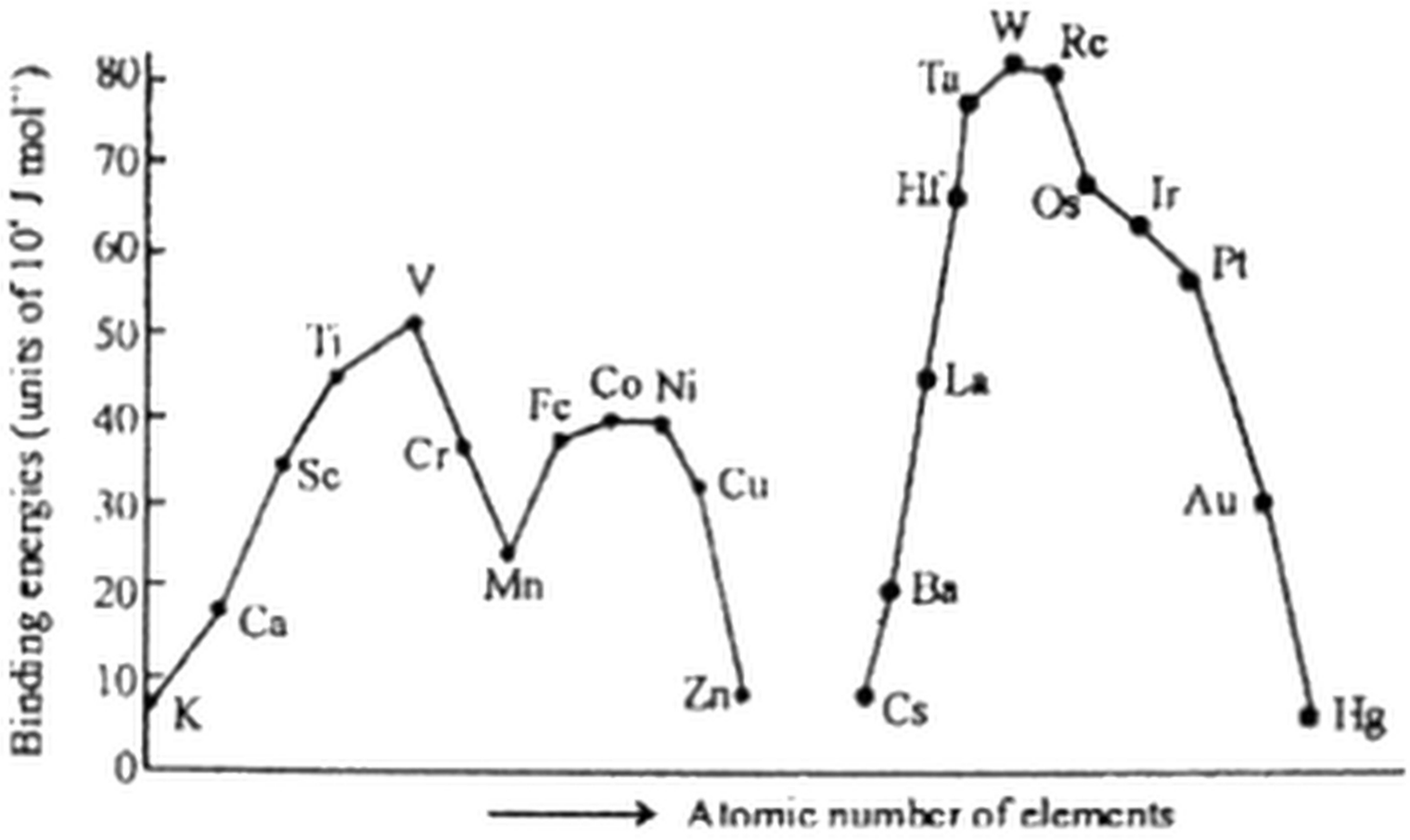
In order to understand the mechanical properties of transition elements, we should understand the binding energies. Transition elements are tough, malleable and ductile. The toughness of the metals is due to greater binding energies.

Reason

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

Variation In blinding 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

Sd series of transition elements (quality 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-l) d and ns electrons. The energies of (n-l) d and ns orbitals are very close to each other. The (n-l) 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

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:

I) A mixture of ZnO and Cr-z03 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) MnO2 can be used as a catalyst for the decomposition of H2O.

4) TiC14 is used as catalyst for the manufacture of plastics.

5) V2O5 is used to oxidize SO2 to S(Y3 in the manufacture of H2SO4.

6) Fe is used as a catalyst for synthesis ofNH3 in Haber's process about 1% of Na2O or K2O and about 1% SiO2 or A12O3 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 Paramagnetism 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 (p) 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.

Example

I) 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 %	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.

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
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 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:

I) 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:

I) 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.

I) 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 pair. Such ligands may be negatively charged, or neutral.

Examples:

1) Negatively charged ligands F^-, Cl^-, Br^-, I^-, OH^-, CN^-

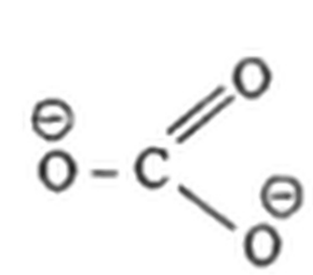
2) Neutral ligands H_2O, NH_3, CO

2) Bidentate ligands:

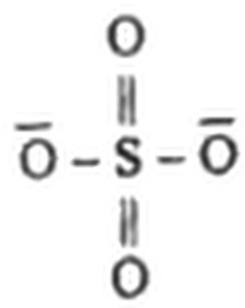
Those ligands which have two donatable electrons pairs are called bidentate ligands.

Examples

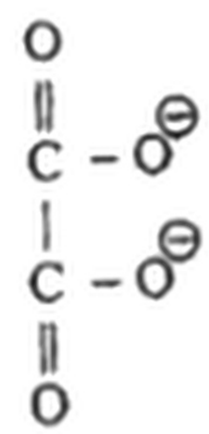
CO_3^{-2},	SO_4^{-2},	$(COO)_2^{-2}$,	NH_2-NH_2,	NH_2-CH_2-CH_2-NH_2
Carbonate ion,	Sulphate ion,	Oxalate ion,	Hydrazine,	Ethylene diamine



Carbonate ion



Sulphate ion



Oxalate ion

3) Tridentate ligands:

Those ligands which have three donatable pairs Examples

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

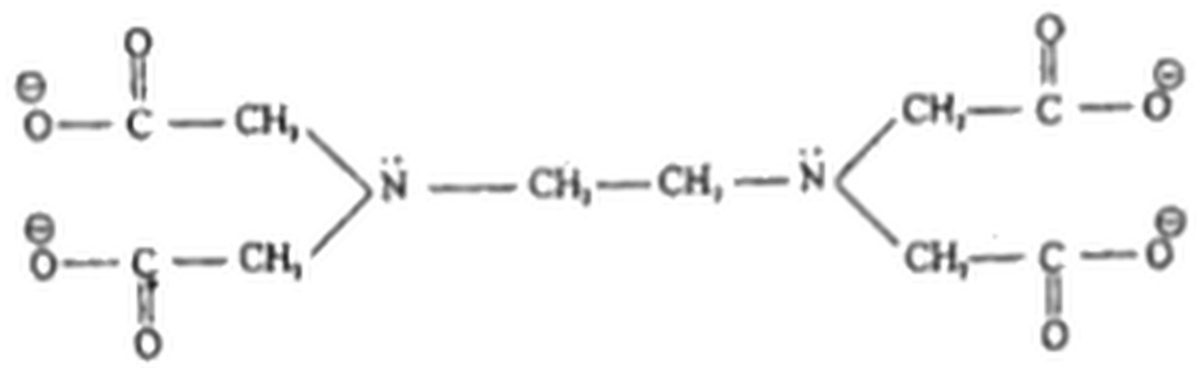
Diethylene triammine

4) Hexadentate ligands:

Those ligands which have six donatable electron pairs.

Example:

Ethylenediaminetetracetate (EDTA)



C) Coordination number or Ligancy:

It is the total number of the atoms of the ligands that can coordinate to the central meta) 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

I) 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 ofNi^0 is four

D) Coordination Sphere

The central 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

I) In $K_4[Fe(CN)_6]$, the ion $[Fe(CN)_6]^{-4}$ is the coordination sphere of this complex compound.

2) In $[Cu(NH_3)_4]SO_4$, is the coordination sphere of this complex compound.

3) In $[Ag(NH_3)_2]$, is the coordination sphere of this complex compound.

4) In $[Ni(CO)_4]$, 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.

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 given 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 $K_4[Fe(CN)_6]^{-4}$

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 legends which are negatively charged end in O. for Example

F^- = Fluro

Cl- = Chloro

Br = Bromo

I- = Iodo

CN- = Cyno

CH_3-COO = acetate

$C_2O_4^{-2}$ = Oxalato

a) Natural ligands are called as such. For example

H_2O Aquo or Aqua

NH_3 Ammime

CO carbonyl

b) Positively charged ligandsend in "ium". For Example

$NH_2NH_3^+$	hydrazinium
NO^+	Nitrosulium
$NH4^+$	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 ligand, 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 ligand

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

I)Potassium hexacyanoferrate (II)

2)Potassium hexacyanoferrate (III)

3)Sodium Pentacarbonyl manganate (-1)

4) K2[PtC16] Potassium hex chloroplatinate (IV)

5) Sodium tetracyano nickelate

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

I) Hexaamminecobalt (III) chloride

2) Hexafluorocobalt (III) chloride

3)Hexaaquochromium (III) chloride

4)Dichlorobisethylendiamminecoblat (III) chloride

5) Ni(CO)4 Tetracarbonylnickel (O)

6) Tetraammine chloronitro platinum (IV) sulphate

7)Triamminetrinitrocoblat (III)

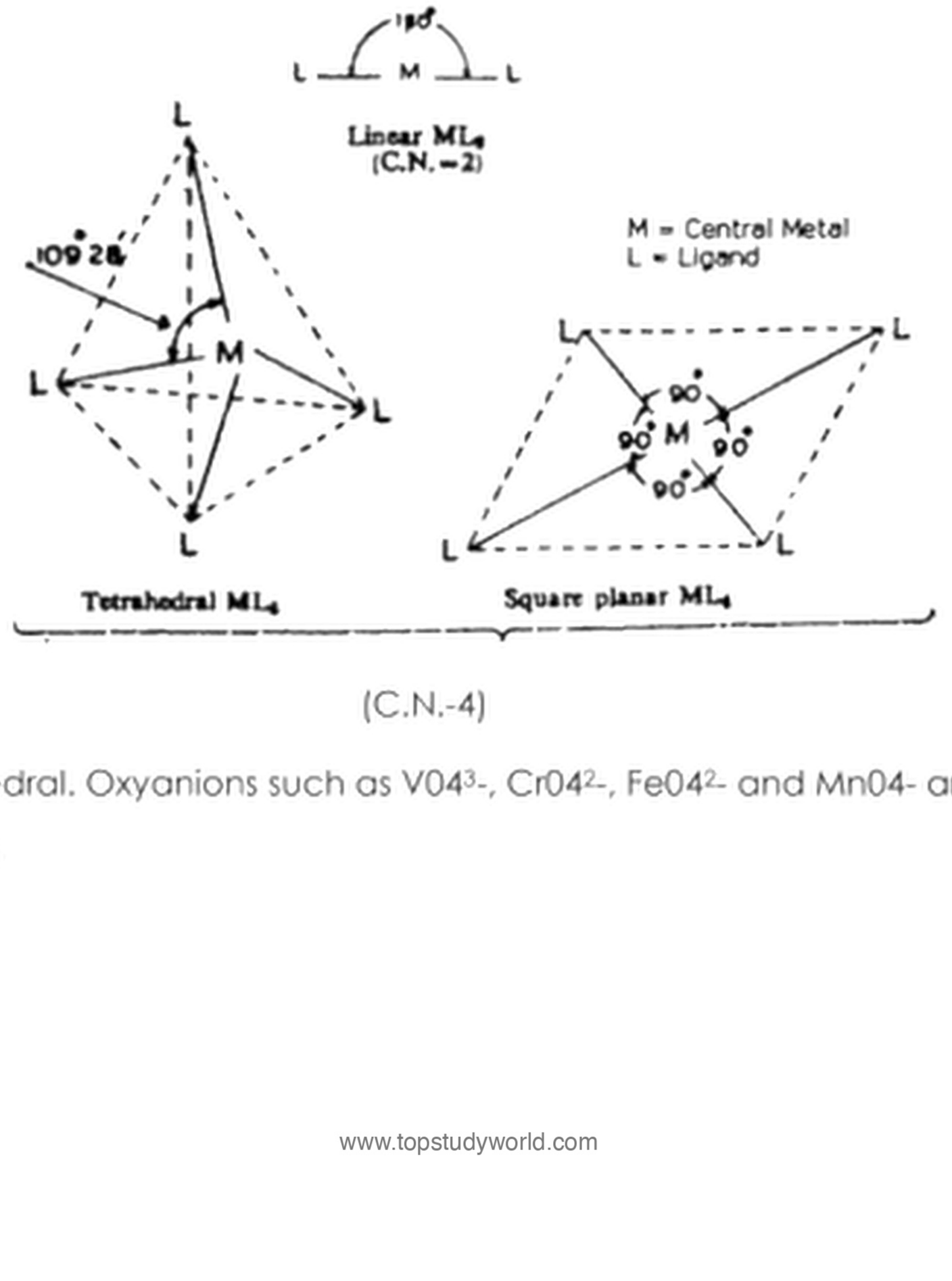
Shapes of Complex Ions with Coordination number 2, 4 and 6

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-

2) Coordination Number 4

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



(C.N.-4)

are tetrahedral. Oxyanions such as $V04^{3-}$, $Cr04^{2-}$, $Fe04^{2-}$ and Mn04- are also tetrahedral.

Square planar geometry is found in complexes of Cu^{2+} Ni^{2+} Pt^{2+}, Pd^{2+}, Au^{3} etc ions

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 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 metrical 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.

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 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.

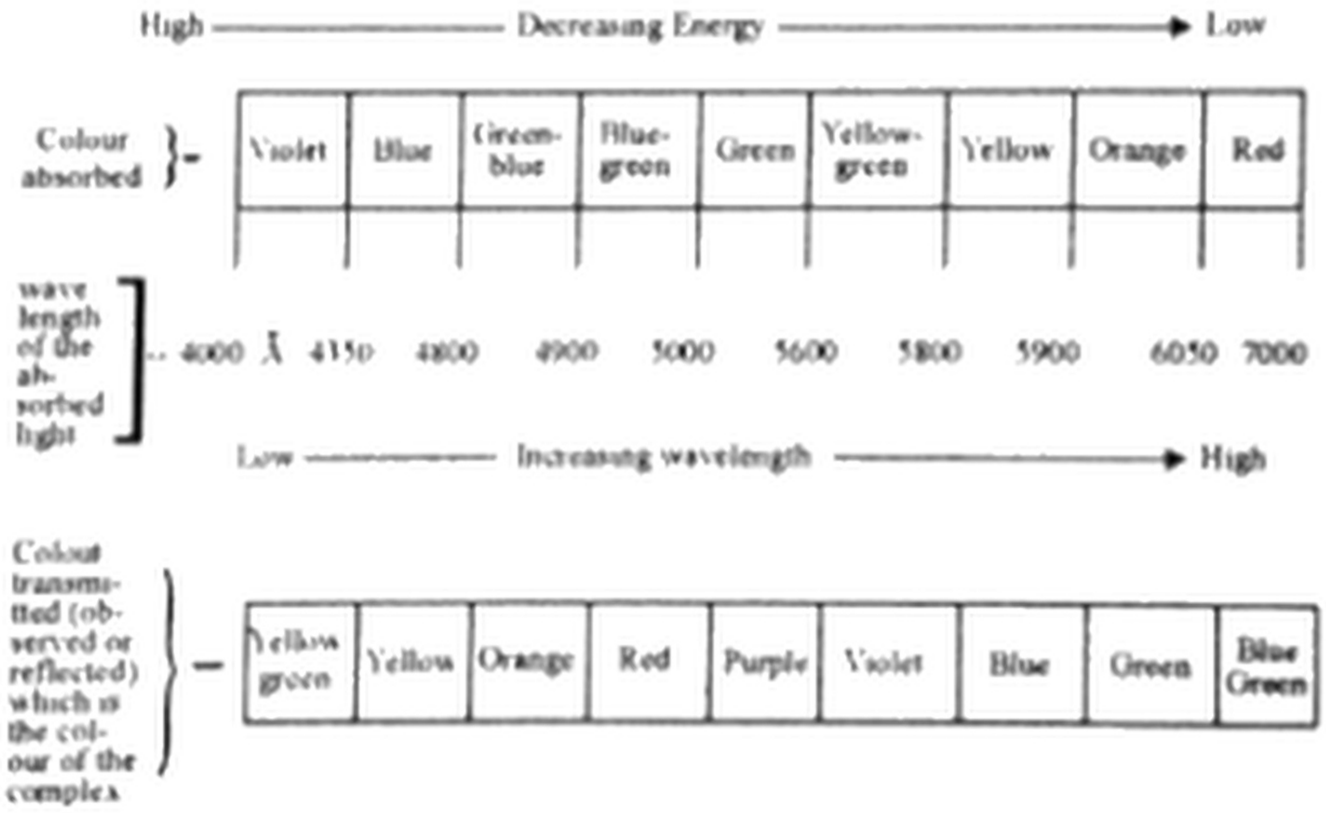
Thus

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-I as shown below:

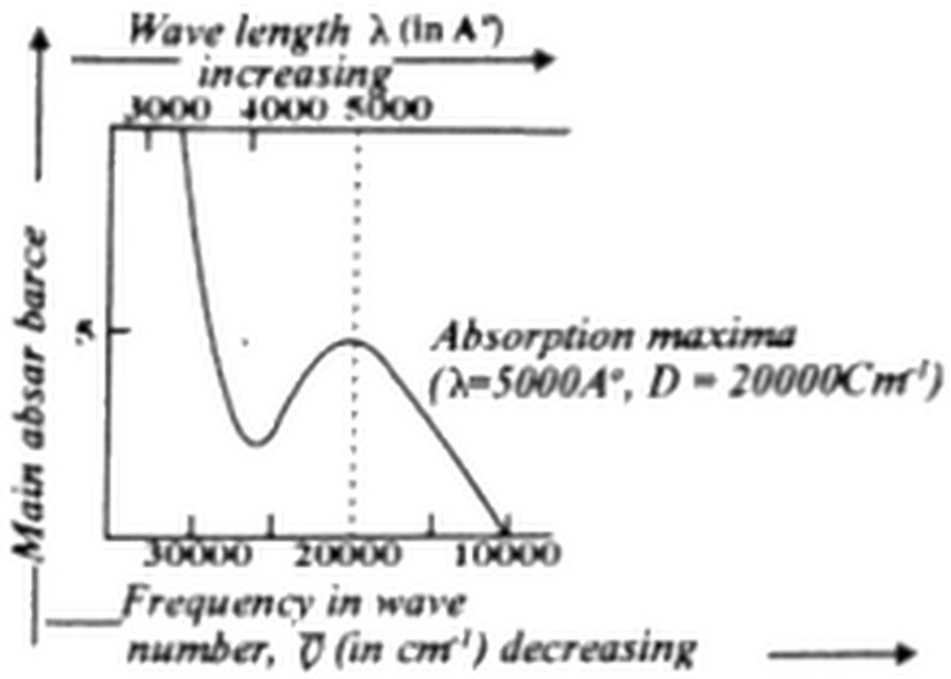
Since $1A^{\circ} = 10^{-8}$cm, wavelength, $\lambda = 5000\ A^{\circ} = 5000 \times 10^{-8}$cm

Consequently wave number,

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

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

Light of this wavelength (5000A) 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 bf the solution. The reaction is done under acidic conditions when the main ion present is V02+ - called the dioxovanadium (V) ion.

Note: The ion is usually written as VO2 , but is more accurately [VO2 (HO) d˚.

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 V02+ ion, the $V0^{2+}$ 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 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 the reducing agent

The first stage of the series of reductions

Let's look at the first stage of the reduction - from V02+ to VO^{2+}. The redox potential for the vanadium half-reaction is given by:

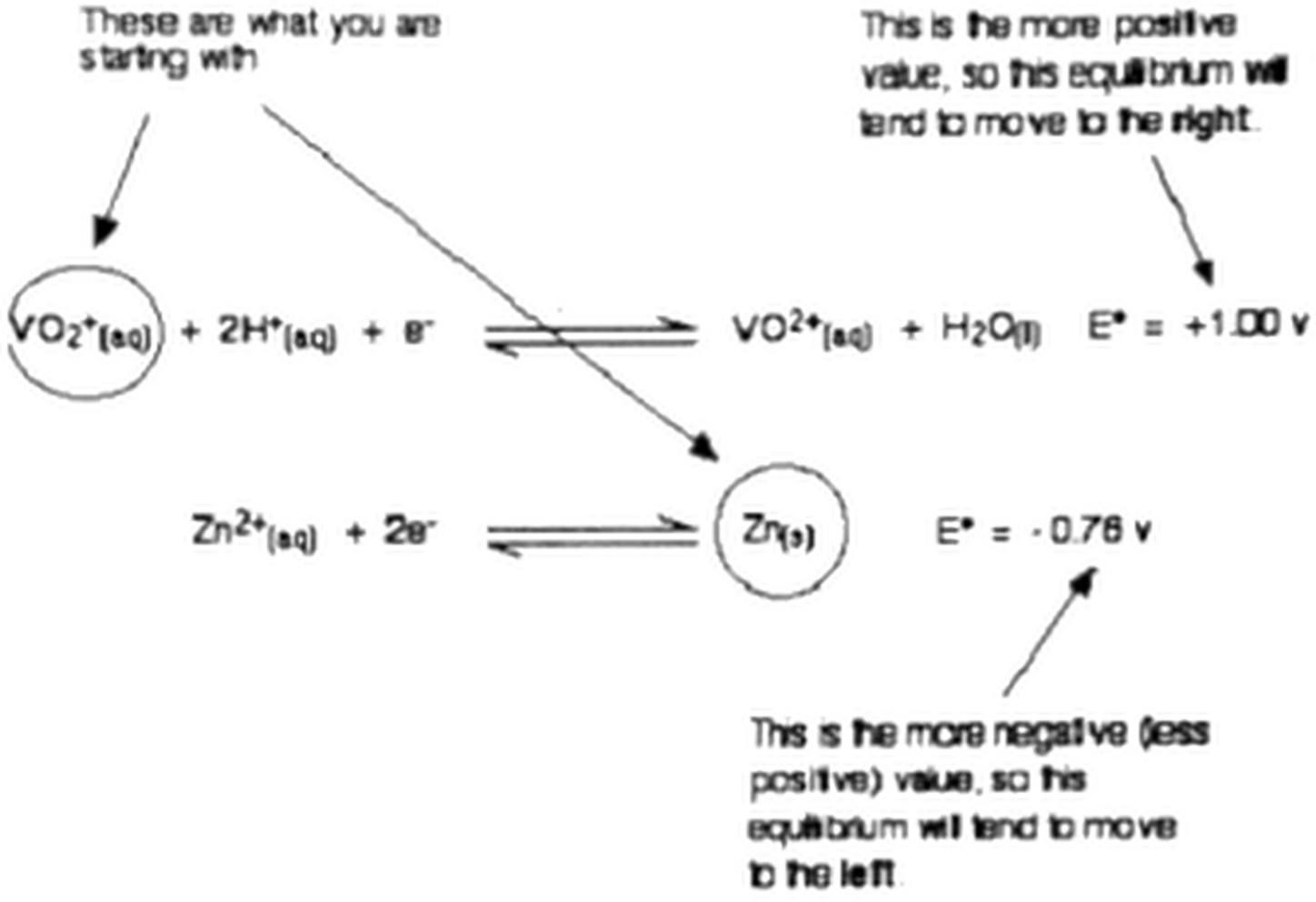
$$VO^{2+}_{(aq)} + 2H^{+}_{(aq)} + e^{-} \rightleftharpoons VO^{2+}_{(aq)} + H_2O_{(l)} \quad E^{0} = +1.00\ V$$

The corresponding equilibrium for the zinc is:

$$Zn^{2+}_{(aq)} + 2e^{-} \rightleftharpoons Zn_{(s)} \quad E^{0} = -076\ v$$

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 $V0^{2+}$ 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 $E^{\ominus}$ values for all the steps of the reduction from vanadium (V) to vanadium (II):

$$VO^{2+}_{(aq)} + 2H^{+}_{[aq]} + e^{-} \rightleftharpoons Vo^{2+}(aq) + H2O(1)) \quad E' = +100v$$

$$VO^{2+}_{(aq)} + 2H^{+}_{[q]} + e^{-} \rightleftharpoons V^{3+}_{(aq)} + H_2O \quad E^0 = +0.34\ v$$

$$V^{3+}(aq) + e^{-} \rightleftharpoons V^{2+}(aq) \quad E^0 = -026v$$

and here is the zinc value again:

$$Zn2+(aq) + 2e- \rightleftharpoons Zn_{[s]} \quad E^0 = -0.76v$$

Remember that for the vanadium reactions to move to the right (which is whnt we want), their E^{O} 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 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^{O} values again:

$$VO2^{+}_{(aq)} + 2H^{+}_{[aq]} + e- \rightleftharpoons V02+(aq) + H20(l) \quad E' = +1.00\ v$$

$$VO2+(aq) + 2H+(aq) + e- \rightleftharpoons v3+(aq) + H2ql) \quad E' = +0.34\ V$$

$$v\ 3+(aq) + e- \rightleftharpoons v2+(aq) \quad E' -0.26\ v$$

and here is the tin value:

$$Sn2+(aq) + 2e- \rightleftharpoons Sn(s) \quad E' = -0.14\ v$$

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(H) 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 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:

$$V^{3+}_{(aq)} + e^{-} \rightleftharpoons V^{2+}_{(aq)} \quad E^{0} = -0.26\ v$$

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

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:

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

$$2H^{+}_{(aq)} + 2e^{-} \rightleftharpoons H_{2(g)} \qquad E^{\circ} = +0.96\ v$$

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

(11).

Here's the first step:

$$v3+(aq) + e- \rightleftharpoons V2+(aq) \qquad E' = -026\text{V}$$

$$NOy(aq) + 4H+(aq) + 3e- \rightleftharpoons NOt9) + 2H20(l) \qquad E^{0} = +0.96\ v$$

The vanadium reaction has the more negative E° value and so will inove 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:

$$v02t(aq) + \qquad + g- \rightleftharpoons v3+(aq) + H20(l)$$

$E' = +0.34\ V$

$E' = +0.96\ v$

$$NO\ddot{y}(aq) + 4H+(aq) + ae- \rightleftharpoons NOG) + 2H2qI)$$

The nitric acid again has the more positive E^{O} 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)?

$$V02+(aq) + 2H+(aq) + e- \rightleftharpoons v02+(aq) + \qquad E' = +1.00\ v$$

$$NO\ddot{y}(aq) + \qquad + ae- \rightleftharpoons ßqg) + 2H20(I) \qquad = +096\ v$$

No, it won't! For the vanadium reaction to move to the left to form the dioxo vanadium (V) ion, it would have to have the more negative (less positive) EO 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 EO values. Two of these actually have EO 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^{O} values tell you that a reaction is possible, you can't assume that it will actually happen. There may be very large activation energv 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^{O} 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 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.

$$V_2O_4 + \tfrac{1}{2}\, 0_2 \longrightarrow V_2O_5$$

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

2) Chromium

In this topic we will discuss;

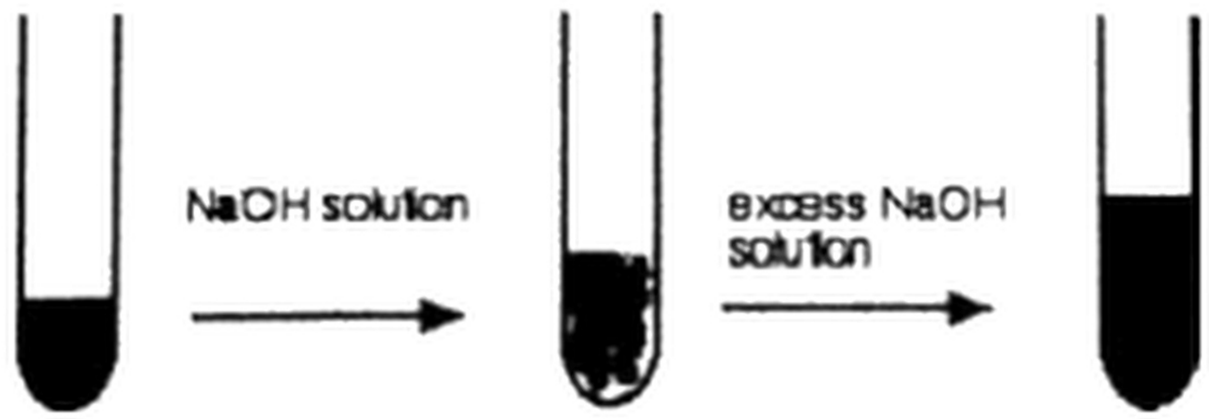
I) The interconversion of the various oxidation states of chromium.

2) The chromate (VI)-dichromate (VI) equilibrium;

3) The use of dichromate (VI) ions as an oxidizing agent (including titrations).

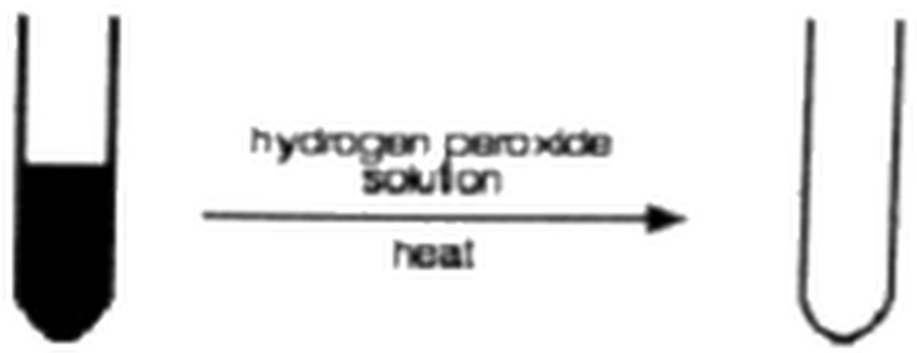
The oxidation of chromium(III) to chromium (VI)

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:

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

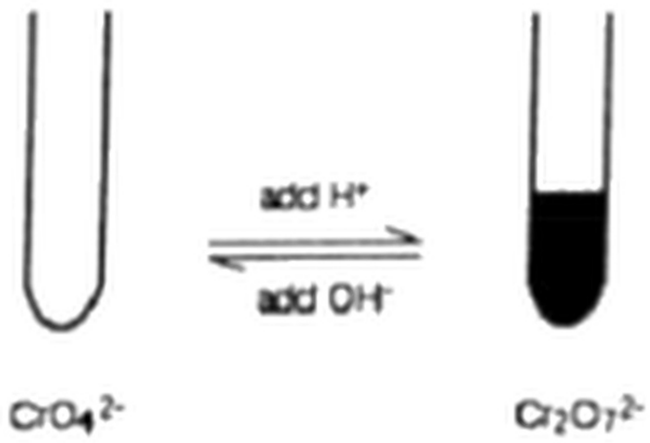
Some chromium (VI) chemistry

The chromate (VI)-dichromate (VI) equilibrium

You are probably more familiar with the orange dichromate (VI) ion, $Cr2O7^{2-}$, 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.



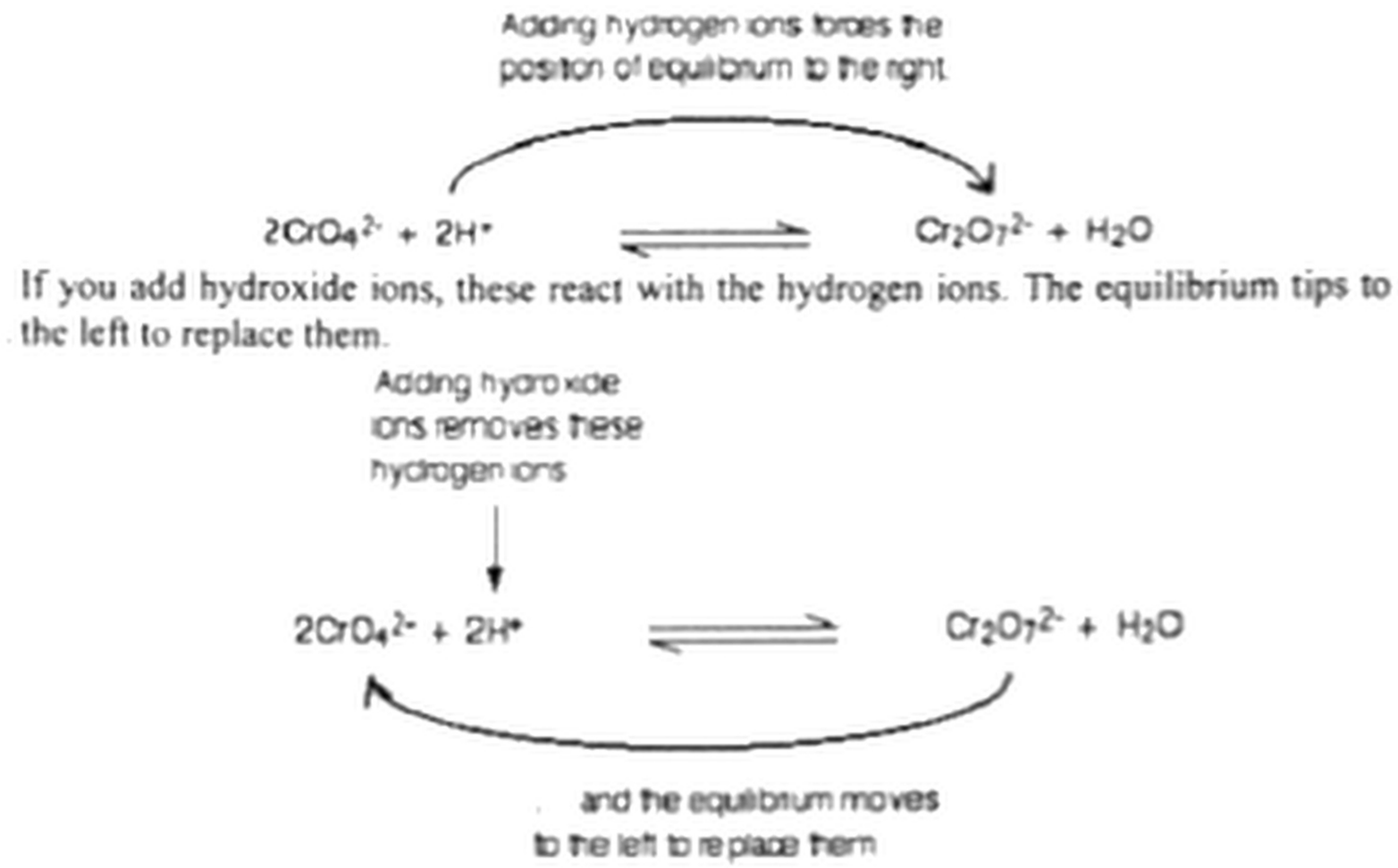
The most important: If you had just produced the yellow chromate (VI) ions by oxidising chromium(III) ions using hydrogen peroxide, you can't convert them into dichromate (VI) ions without taking a precaution first.

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 Chatellier's Principle.



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

Dichromate (VI) ions (for example, in potassium dichromate(V1) 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-oxidizes 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.

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:

For the reduction from +6 to +3

$$Cr_2O_7^{2+} + 14H^+ + azn \longrightarrow 2Cr3^+ + 7H_2O^+ + 3Zn^{2+}$$

For the reduction from +3 to +2

$$2Cr^{3+} + Zn \longrightarrow 2Cr^{2+} + Zn^{2+}$$

Using potassium dichromate (VI) as an oxidizing agent in organic chemistry

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 to pieces! (Potassium manganate (VII) solution has some tendency to do that.) It is used to:

I) oxidise secondary alcohols to ketones;

2) oxidise primary alcohols to aldehydes;

3) oxidise primary alcohols to carboxylic acids.

For example, with ethanol (a primary alcohol), you can get either ethanal (an aldehyde) or ethanoic acid (a carboxylic acid) depending on the conditions.

4) If the alcohol is in excess, and you distil off the aldehyde as soon as it is formed, you get ethanal as the main product.

$$Cr_2O_7^{2-} + BH^+ + 3CH_3CH_2OH \longrightarrow 2Cr^{3+} + 7H_2O + 3CH_3COOH$$

5) If the oxidising agent is in excess, and you don't allow the product to escape - for example, by heating the mixture under reflux (heating the flask with a condenser placed vertically in the neck) - you get ethanoic acid.

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

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 in square brackets just means "oxygen from an oxidising agent".

Using potassium dichromate (VI) as an oxidising agent in titrations

Potassium dichromate (VI) is often used to estimate the concentration of iron(II) ions in solution. It serves as an alternative to using potassium manganate (VII) solution.

In practice

There are advantages and disadvantages in using potassium dichromate (VI).

Advantages

I) Potassium dichromate(VI) can be used as a primary standard. That means that it can be made up to give a stable solution of accurately known concentration. That isn't true of potassium manganate(VII).

2) Potassium dichromate(VI) can be used in the presence of chloride ions (as long as the chloride ions aren't present in very high concentration).

3) Potassium manganate(VII) oxidizes chloride ions to chlorine; potassium dichromate(VI) quite a strong enough oxidising agent to do this. That means that you don't get unwanted side reactions with the potassium dichromate(VI) solution.

Disadvantages

I) The main disadvantage lies in the colour change. Potassium manganate(VII) titrations are self-indicating. As you run the potassium manganate(VII) solution into the reaction, the solution becomes colourless. As soon as you add as much as one drop too much, the solution becomes pink - and you know you have reached the end point.

2) Unfortunately potassium dichromate(VI) solution turns green as you run it into the reaction, and there is no way you could possibly detect the colour change when you have one drop of excess orange solution in a strongly coloured green solution.

3) With potassium dichromate(VI) solution you have to use a separate indicator, known as a redox indicator. change colour in the presence of an oxidising agent.

4) There are several such indicators - such as diphenylamine sulphonate. This gives a violet-blue colour in the presence of excess potassium dichromate(VI) solution. However, the colour is made difficult by the strong green also present.

The end point of a potassium dichromate(VI) titration isn't as easy to see as the end point of a potassium manganate(VII) one.

The calculation

The half-equation for the dichromate(VI) ion is:

$$CC_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr_3+ + 7H_2O$$

. . and for the iron(II) ions is:

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

Combining these gives:

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$$

You can see that the reacting proportions are I mole of dichromate(VI) ions to 6 moles of iron(II) ions.

Once you have established that, the titration calculation is going to be just like any other one.

Testing for chromate(VI) ions in solution

Typically, you would be looking at solutions containing sodium, potassium or ammonium chromate(VI). Most chromates are at best only slightly soluble; many we would count as insoluble.

The bright yellow colour of a solution Suggests that it would be worth testing for chromate(VI) ions.

Testing by adding an acid

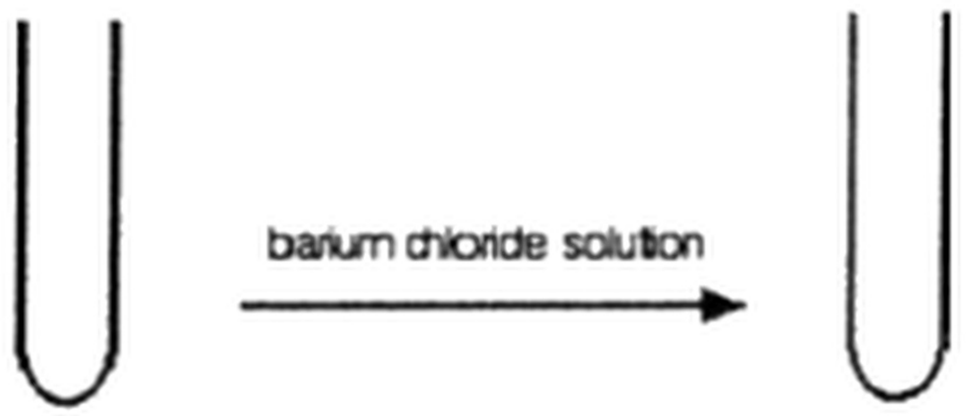
If you add some dilute sulphuric acid to a solution containing chromate(VI) ions, the colour changes to the familiar orange of dichromate(VI) ions.

You can't rely on this as a test for chromate(VI) ions, however. It might be that you have a solution containing an acid-base indicator which happens to have the same colour change!

Testing by adding barium chloride (or nitrate) solution

Chromate(VI) ions will give a yellow precipitate of barium chromate(VI).

$$Ba^{2+}_{(aq)} + CrO_4^{2-}{}_{(aq)} \longrightarrow BaCrO_{4(s)}$$

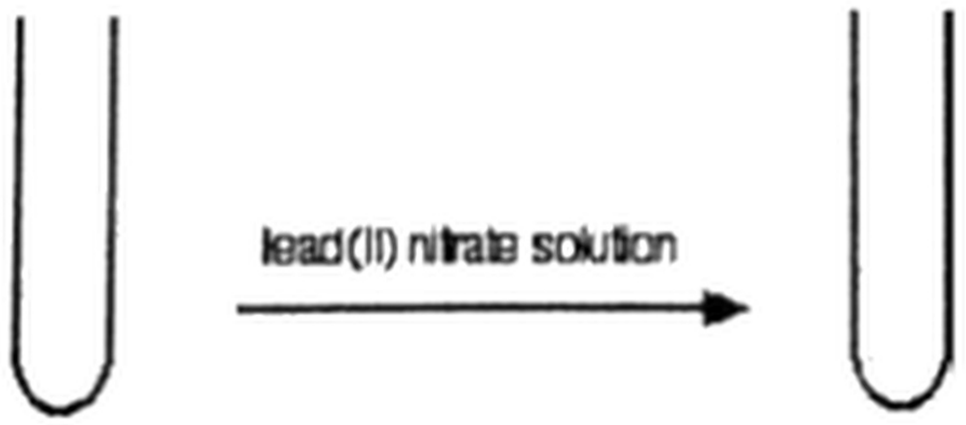


yellow precipitate

Testing by adding lead(II) nitrate solution

Chromate(VI) ions will give a bright yellow precipitate of lead(II) chromate(VI). This is the original "chrome yellow" paint pigment.

$$Pb^{2+}_{(aq)} + CrO_4^{2-}{}_{(aq)} \longrightarrow PbCrO_{4(s)}$$



bright yellow precipitate
"chrome yellow"

3) Manganese

In this topic we will discuss:

i) The Oxidation States

ii) Two simple reactions of manganese (II) ions in solution).

iii) The use of potassium manganate(VII) (potassium permanganate) as an oxidizing agent including its use in titrations.

The Oxidation States

Manganese can exist in a number of oxidation states, but is most stable in an oxidation state of +2, +4 or +7

In the +7 oxidation state it exists as the intense purple ion $Mn0^4$. This can be reduced to the pale pink Mn^{2+} by Fe^{2*} in acidic solution:

$Mn0^4(aq) + 8H+(aq) + 5e- \text{-¥ } Mn^{2+}(aq) + 4H20(l)$ $Fe^{2+}(aq) \text{ -¥ } Fe^{3+}(aq) + e-$

Overall

$$Mn0^4(aq) + 8H+(aq) + 5Fe^{24}(aq)\ Mn^{2+}(aq) + 4H20(l) + 5Fe^{3+}(aq)$$

Reactions of manganese (II) ions in solution/ Oxidation States

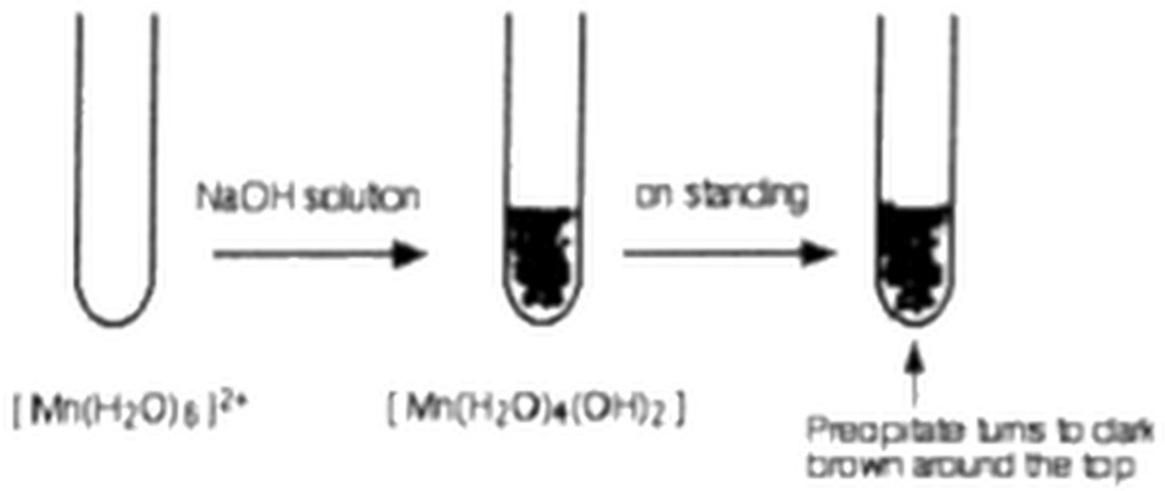
i) The reaction of hexaaquamanganese(II) ions with hydroxide ions

Hydroxide ions (from, say, sodium hydroxide solution) remove hydrogen ions from the water ligands attached to the manganese ion.

Once a hydrogen ion has been removed from two of the water molecules, you are left with a complex with no charge - a neutral complex. This is insoluble in water and a precipitate is formed.

$$[Mn(H_2O)_6^{2+}] + 2OH \longrightarrow [Mn(H_2O)_4(OH_2)] + 2H_20$$

In the test-tube, the colour changes are:

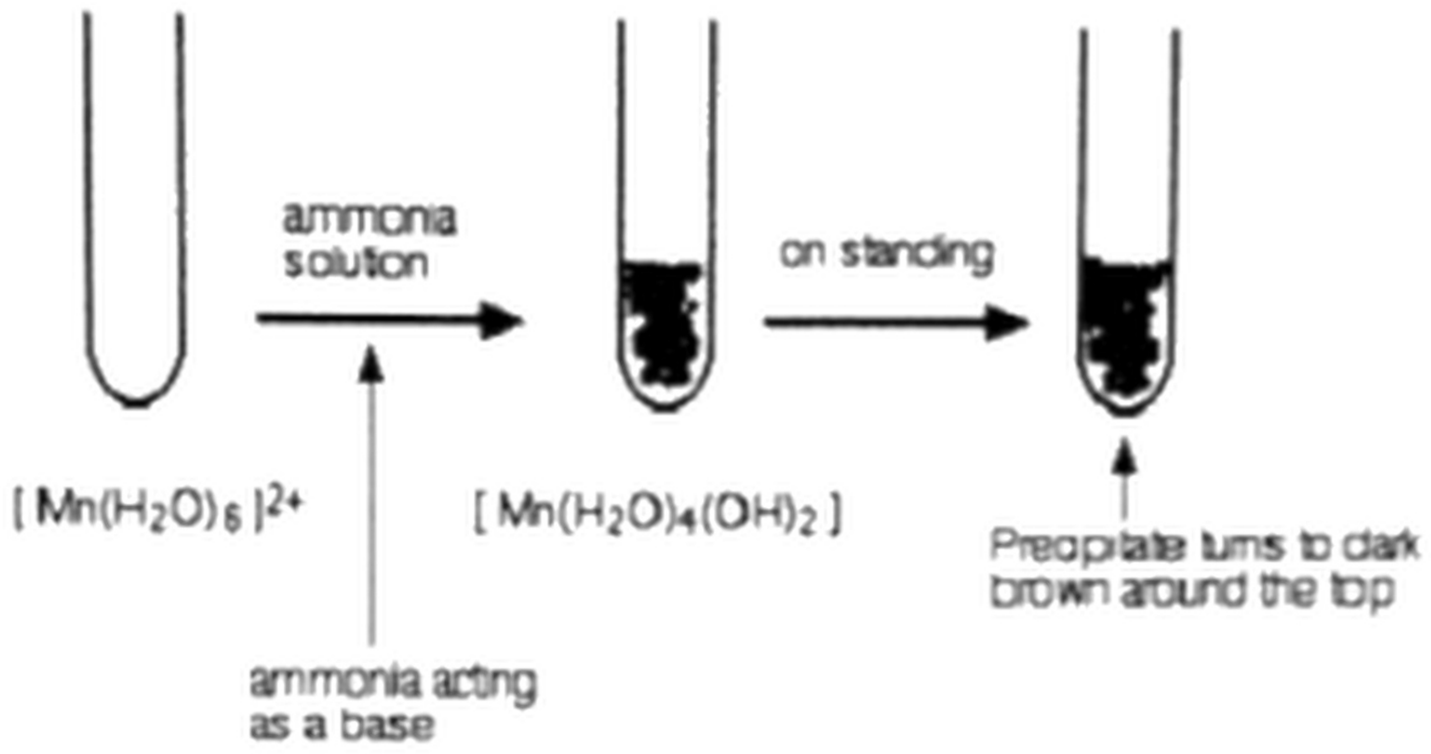


It has been shown the original solution as very pale pink, but in fact it is virtually colourless. The pale brown precipitate is oxidised to darker brown manganese(III) oxide in contact with oxygen from the air.

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

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

$$[Mn(H_2O)_6^{2}] + 2NH_3 \longrightarrow [Mn(H_2O)_4(OH_2)] + 2NH^{4+}$$



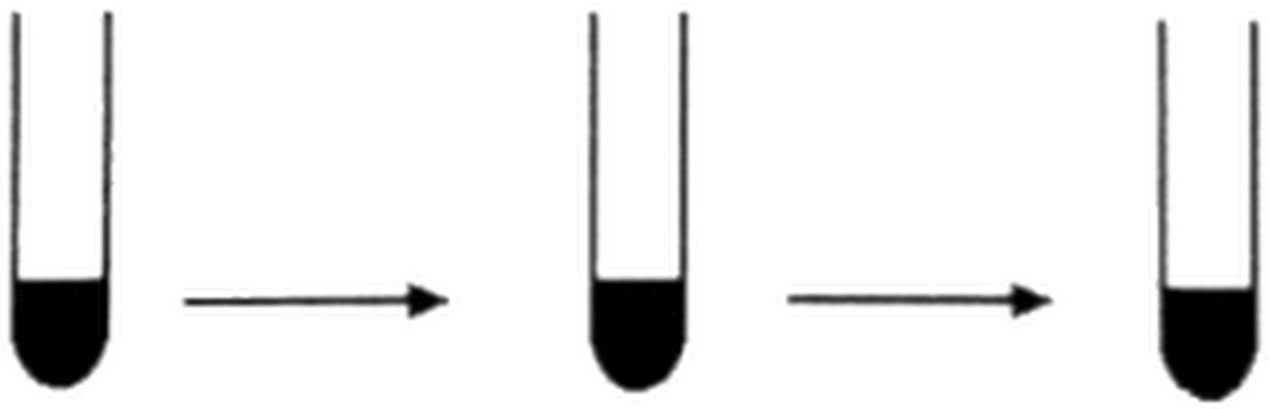
Again, it has been shown the original solution as the palest pink I can produce, but in fact it is virtually colourless. The pale brown precipitate is oxidised to darker brown manganese(III) oxide in contact with oxygen from the air.

There is no observable difference in appearance between this reaction and the last one.

Some potassium manganate(VII) chemistry

Potassium manganate(VII) (potassium permanganate) is a powerful oxidising agent.

Using potassium manganate(VII) as an oxidising agent in organic chemistry 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-carbon bonds. The potassium manganate(VII) solution is usually made mildly alkaline with sodium carbonate solution, and the typical colour changes are:



Original dark purple manganate(VII) ion MnO_4^-	Reduced to dark green manganate(VI) ion MnO_4^{2-}	Further reduced to black precipitate of MnO_2

In testing for a C=C double bond

Potassium manganate(VII) oxidizes carbon-carbon double bonds, and so goes through the colour changes above.

Ethene, for example, is oxidised to ethane-I ,2-diol.

$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + H_2O + [O] \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$$

CH_2 CH_2OH

The oxygen in square brackets is taken to mean "oxygen from an oxidising agent". This abbreviated form of the equation is most commonly used in organic chemistry. You are very unlikely to have to write the complete ionic equation for this reaction at this level. To be honest, this isn't a good test for a carbon-carbon double bond, because anything which is even mildly reducing would have the same effect on the potassium manganate(VII) solution.

You could, however, use this reaction simply as a means of making the diol.

In the oxidation of aromatic side chains

Alkaline potassium manganate(VII) solution oxidizes any hydrocarbon side chain attached to a benzene ring back to a single -COOH group. Prolonged heating is necessary.

For example

In the case of the ethyl side chain, you will also get carbon dioxide. With longer side chains, you will get all sorts of mixtures of other products - but in each case, the main product will be benzoic acid.

Using potassium manganate(VII) as an oxidising agent in titrations

Background

Potassium manganate(VII) solution is used to find the concentration of all sorts of reducing agents. It is always used in acidic solution.

For example, it oxidizes

iron(II) ions to iron(III) ions

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

hydrogen peroxide solution to oxygen

$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$$

ethanedioic acid to carbon dioxide (This reaction has to be done hot.)

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \longrightarrow 2CO_2 + 2H + 2e^-$$

sulphite ions (sulphate(IV) ions) to sulphate ions (sulphate(VI) ions)

$$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-$$

In each case, the half-equation for the manganate(VII) ions in acidic solution is:

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

These equations can be combined to give you an overall ionic equation for each possible reaction. That, of course, also gives you the reacting proportions.

For example, when the equations are combined, you find that I mole of Mn04- ions react with 5 moles of Fe^{2+} ions. Having got that information, the titration calculations are just like any other ones.

Doing the titration

The potassium manganate(VII) solution always goes into the burette, and the other solution in the flask is acidified with dilute sulphuric acid.

As the potassium manganate(VII) solution is run into the flask it becomes colourless. The end point is the first faint trace of permanent pink in the solution showing that there is a tiny excess of manganate(VII) ions present.

Problems with the use of potassium manganate(VII) solution

There are two things you need to be aware of:

I) Potassium manganate(VII) can't be used in in the presence of ions like chloride or bromide which it oxidizes. An unknown amount of the potassium manganate(VII) would be used in side reactions, and so the result would be inaccurate.

This is why you don't acidic the solution with hydrochloric acid.

Potassium manganate(VII) isn't a primary standard. That means that it can't be

2) made up to give a stable solution of accurately known concentration.

3) It is so strongly coloured that it is impossible to see when all the crystals you have used have dissolved, and over a period of time it oxidizes the water it is dissolved in to oxygen.

4) Bottles of potassium manganate(VII) solution usually have a brown precipitate around the top. This is manganese(IV) oxide - and is produced when the manganate(VII) ions react with the water.

You have to make up a solution which is approximately what you want, and then standardize it by doing a titration. This is often done with ethane dioic acid solution, because this is a primary standard.

4) IRON

In this topic we will discuss:

I) Oxidation state

2) Iron as catalyst in Haber's Process and in reaction between per sulphate and iodide ions.
3) Reaction of Hex aqua Iron (II) and (111) with water, ammonia, Carbonate and Thiocyanate ions.

Oxidation State

Iron exists in two common oxidation states, +2 (Fe^{2+}) and +3 (Fe^{3+}). In aqueous solution, the Fe is readily oxidized from Fe^{2+} to Fe3+:

$$Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + e^-$$

The Fe^{2+} ion is thus a reducing agent. Concentrations of Fe^{3+} in solution can be determined by titration with oxidizing agents.

Iron as catalyst in the Haber Process

The Haber Process combines nitrogen and hydrogen into ammonia. The nitrogen comes from the air and the hydrogen is obtained mainly from natural gas (methane). Iron is used as a catalyst.

$$N2(g) + 3H2(g) \overset{Fe}{\rightleftharpoons} 2NH3(g)$$

Iron ions as a catalyst in the reaction between persulphate ions and iodide ions

The reaction between persulphate ions (peroxodisulphate ions), $S208^{2}$, and iodide ions in solution can be catalyzed using either iron(II) or iron(III) ions.

The overall equation for the reaction is:

$$S2082- + 21- \longrightarrow 2S042- + 12$$

For the sake of argument, we'll take the catalyst to be iron(II) ions. The reaction happens in two stages.

$$S208^{2-} + 2Fe^{2+} \longrightarrow 2S04^{2-} + 2Fe^{3+}$$

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

If you use iron(III) ions, the second of these reactions happens first.

This is a good example of the use of transition metal compounds as catalysts because of their ability to change oxidation state.

Reactions of iron ions in solution

The simplest ions in solution are:

- the hexaaquairon(II) ion $[Fe(H_2O)_6]^{2+}$
- the hexaaquairon(III) ion $[Fe(H_2O)_6]^{3+}$

a) T Reactions of the iron ions with hydroxide ions

Hydroxide ions (from, say, sodium hydroxide solution) remove hydrogen ions from the water ligands attached to the iron ions.

When enough hydrogen ions have been removed, you are left with a complex with no charge - a neutral complex. This is insoluble in water and a precipitate is formed.

In the iron(II) case

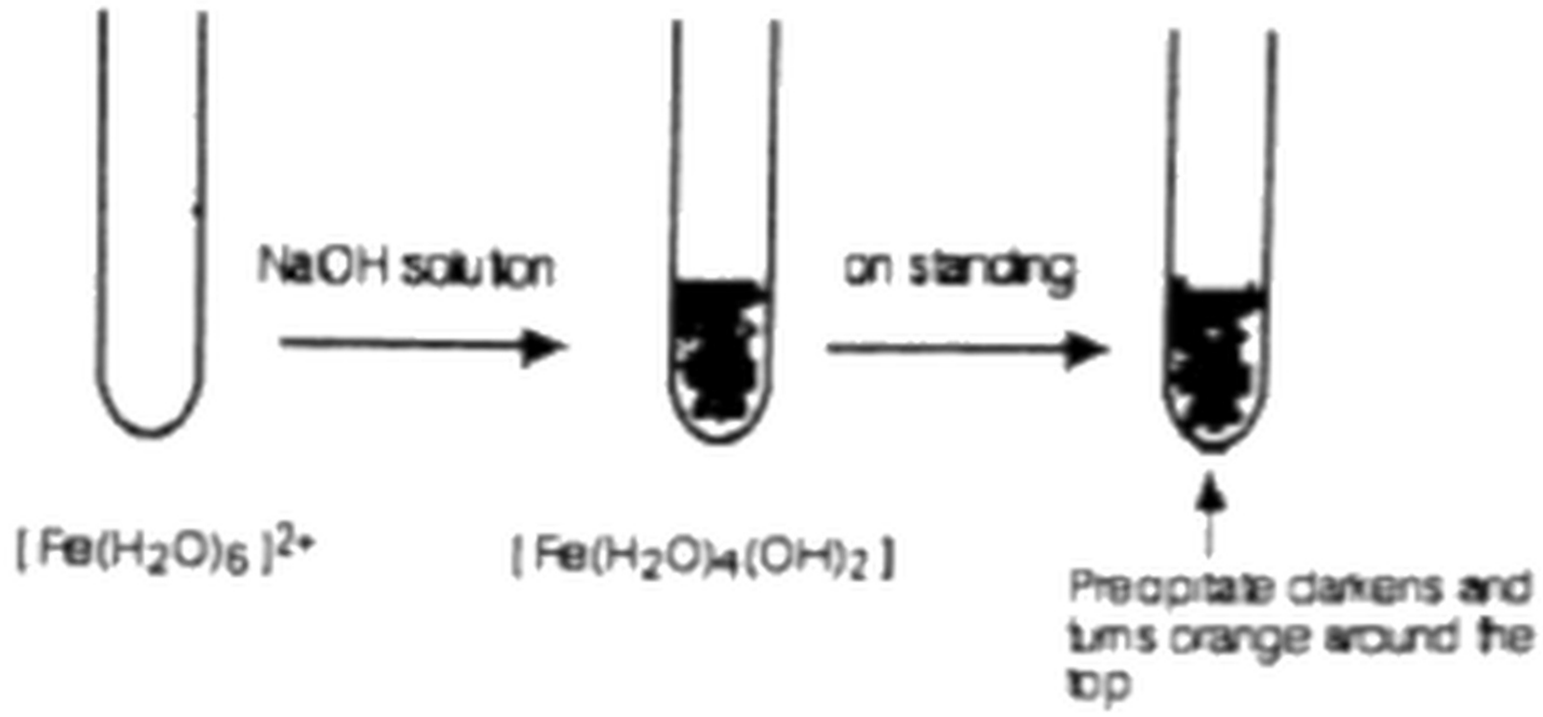
$$[Fe(H_2O)_6]^{2+} + 2OH^- \longrightarrow [Fe(H_2O)_4(OH)_2] + 2H_2O$$

In the iron (III) case

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

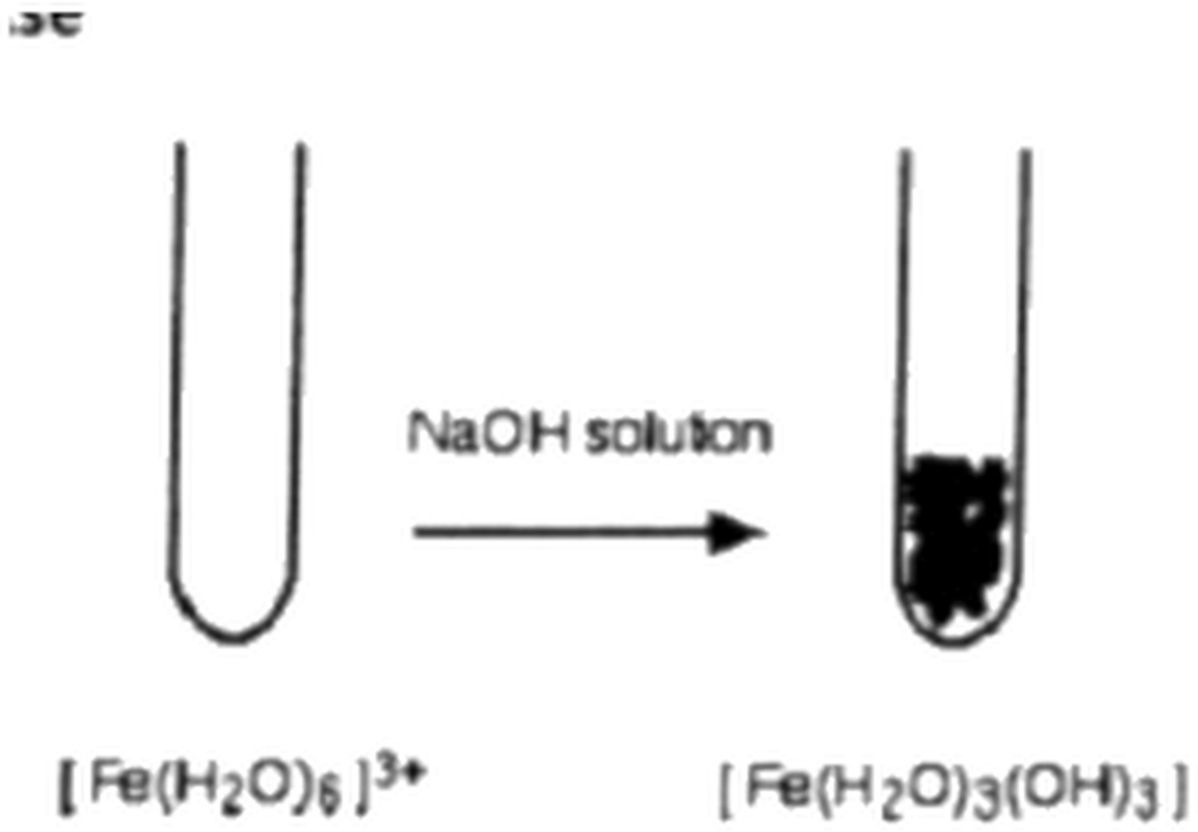
the test-tube, the colour changes are

In the iron(II) case



Iron is very easily oxidised under alkaline conditions. Oxygen in the air oxidises the iron(II) hydroxide precipitate to iron(III) hydroxide especially around the top of the tube. The darkening of the precipitate comes from the same effect.

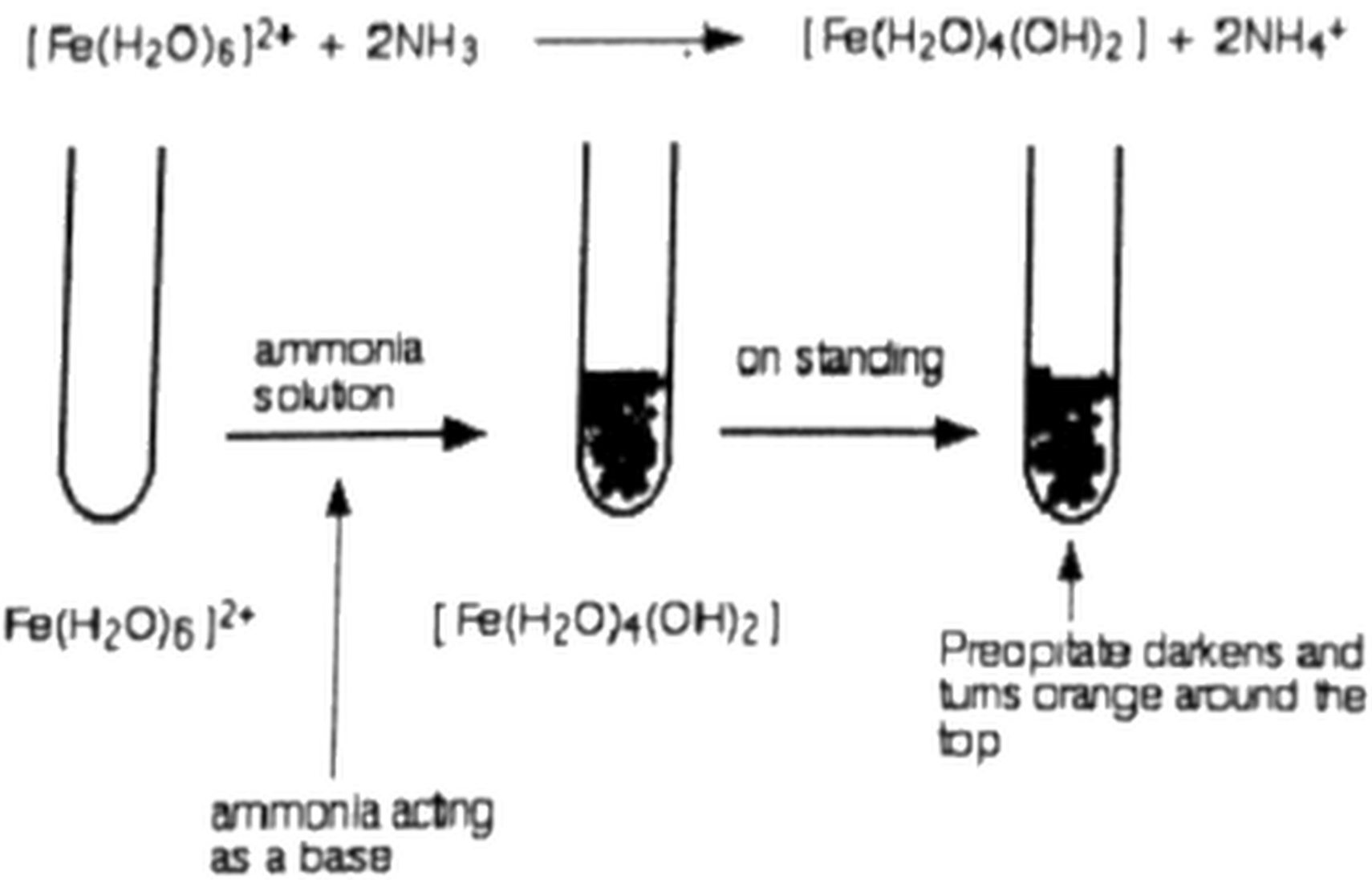
In the iron(III) case



b) Reactions of the iron ions with ammonia solution

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

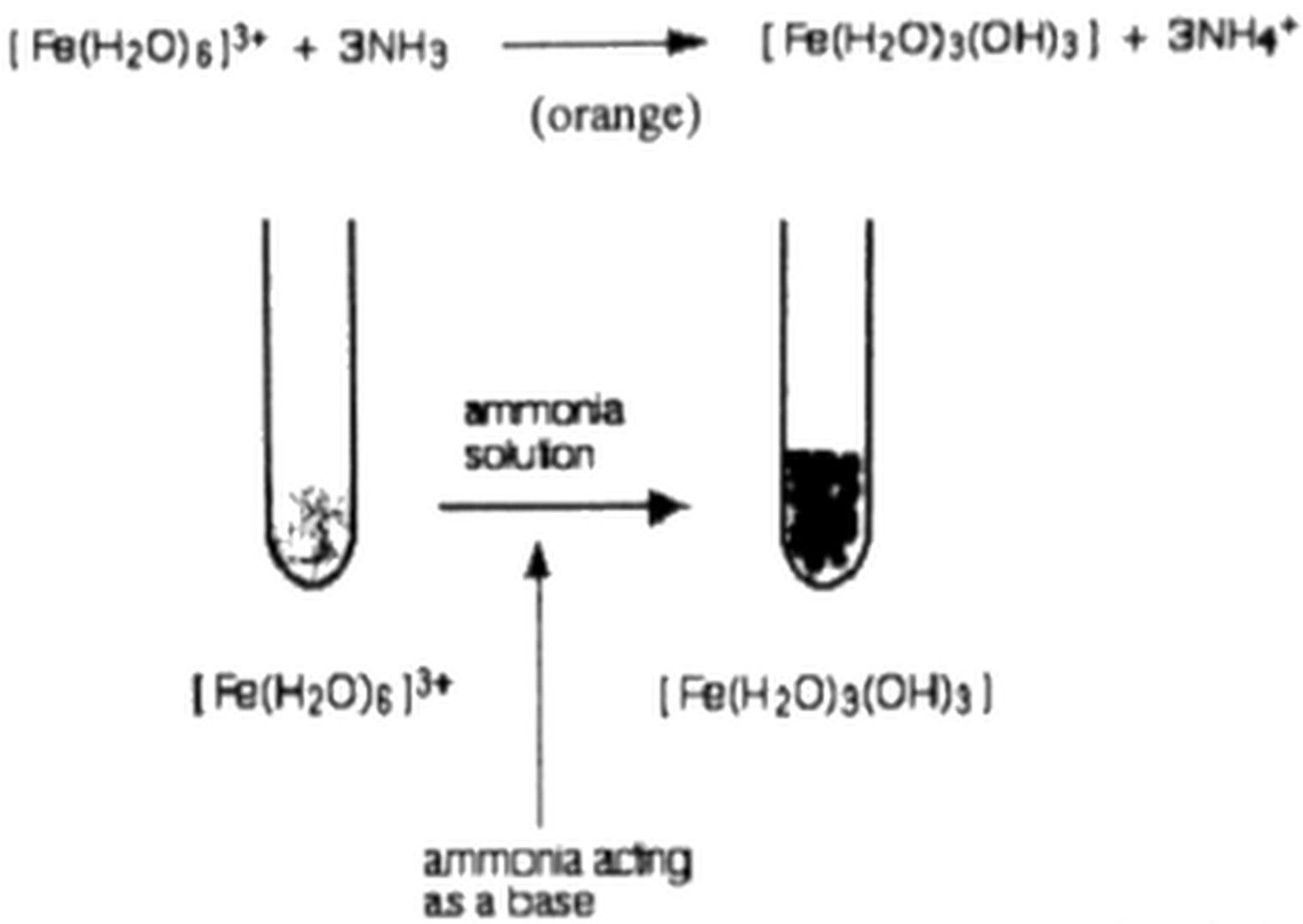
In the iron(II) case



The appearance is just the same as in when you add sodium hydroxide solution.

The precipitate again changes colour as the iron(II) hydroxide complex is oxidized by the air to iron(III) hydroxide.

In the iron(III) case



The reaction looks just the same as when you add sodium hydroxide solution.

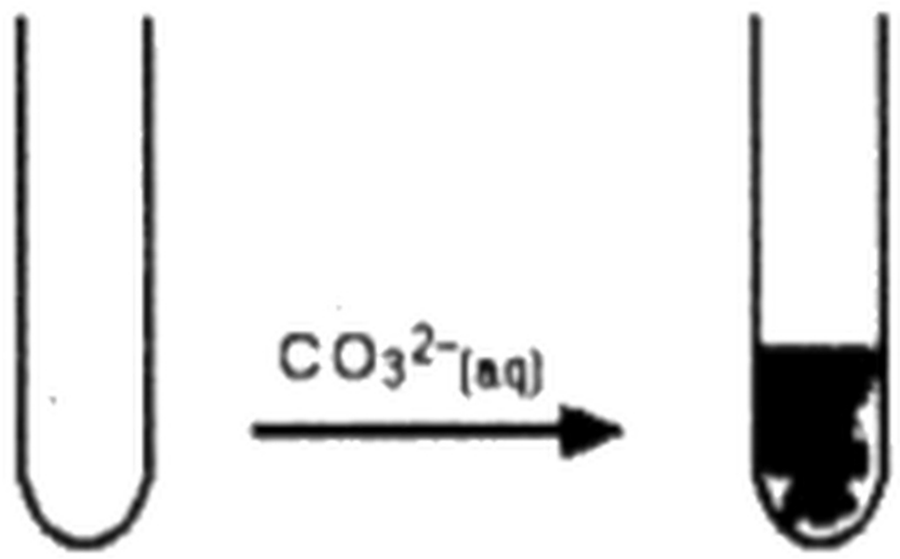
Reactions of the iron ions with carbonate ions

There is an important difference here between the behaviour of iron(II) and iron(III) ions.

a) Iron(II) ions and carbonate ions

You simply get a precipitate of what you can think of as iron(II) carbonate.

$$Fe^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \longrightarrow FeCO_{3(s)}$$



Iron(III) ions and carbonate ions

The hexaaquairon(III) ion is sufficiently acidic to react with the weakly basic carbonate ion.

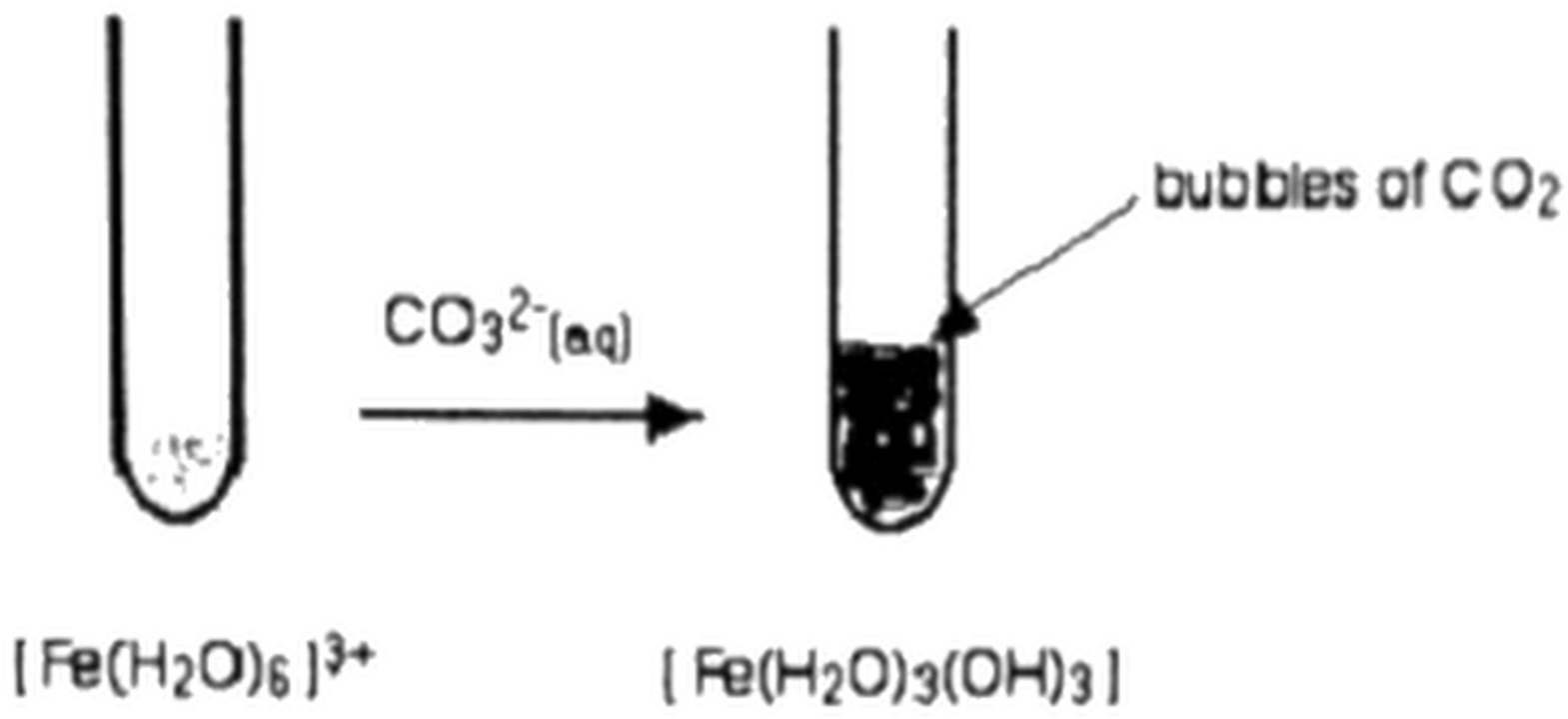
If you add sodium carbonate solution to a solution of hexaaquairon(III) ions, you get exactly the same precipitate as if you added sodium hydroxide solution or ammonia solution.

This time, it is the carbonate ions which remove hydrogen ions from the hexaaqua ion and produce the neutral complex.

Depending on the proportions of carbonate ions to hexaaqua ions, you will get either hydrogen carbonate ions formed or carbon dioxide gas from the reaction between the hydrogen ions and carbonate ions. The more usually quoted equation shows the formation of carbon dioxide.

$$2[Fe(H_2O)_6]^{3+} + 3CO_3^{2-} \longrightarrow 2[Fe(H_2O)_3](OH_3) + 3CO_2 + 3H_2O$$

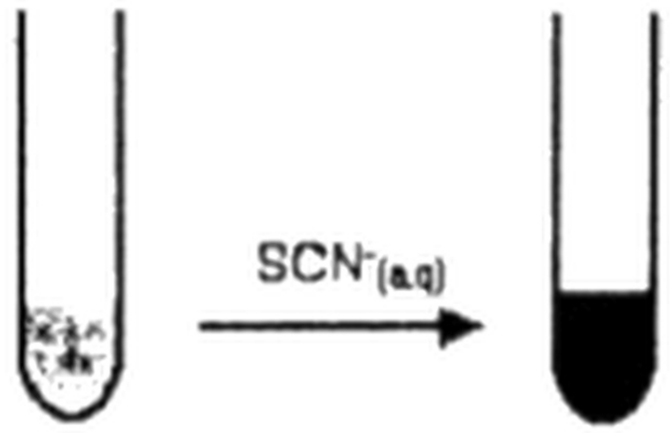
Apart from the carbon dioxide, there is nothing new in this reaction:



b) Testing for iron(III) ions with thiocyanate ions

This provides an extremely sensitive test for iron(III) ions in solution.

If you add thiocyanate ions, SCN-, (from, say, sodium or potassium or ammonium thiocyanate solution) to a solution containing iron(III) ions, you get an intense blood red solution containing the ion



solution containing $[Fe(H_2O)_6]^{3+}$ $[Fe(SCN)(H_2O)_5]^{2+}$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

These combine to give the ionic equation for the reaction:

$$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

5) Copper

i) The Oxidation States

ii) The reaction of hexaaquacopper

(II) ions with hydroxide ions, Ammonia and

Carbonate ion

The Oxidation States of Copper

Copper exists in two common oxidation states, +1 (Cu^{+}) and +2 (Cu^{2+})..In aqueous solution, the Cu is readily oxidized from Cu^{+} to Cu^{2+}

$$Cu^{+}(aq)\ Cu^{2+}(aq) + e-$$

The Cu^{+} ion is thus a reducing agent. Concentrations of Cu^{2+} in solution can be determined by titration with oxidizing agents.

The reaction of hexaaquacopper(II) ions with hydroxide ions

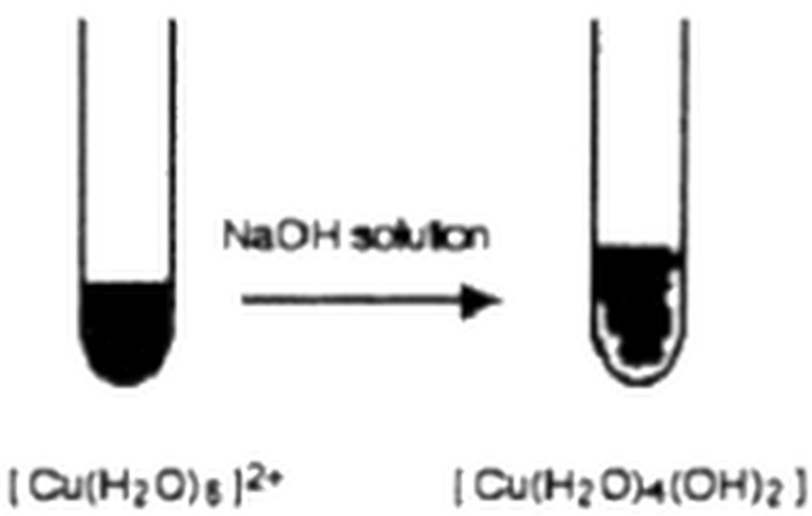
Hydroxide ions (from, say, sodium hydroxide solution) remove hydrogen ions from the water ligands attached to the copper ion.

Once a hydrogen ion has been removed from two of the water molecules, you are left with a complex with no charge - a neutral complex. This is insoluble in water and a precipitate is formed.

$$[Cu(H_2O)_6]^{2+} + 2OH^- \longrightarrow [Cu(H_2O)_4(OH)_2] + 2H2O$$

(blue)

In the test-tube, the colour change is



Reactions of hexaaquacopper(II) ions with ammonia solution

The ammonia acts as both a base and a ligand. With a small amount of ammonia, hydrogen ions are pulled off the hexaaqua ion exactly as in the hydroxide ion case to give the same neutral complex.

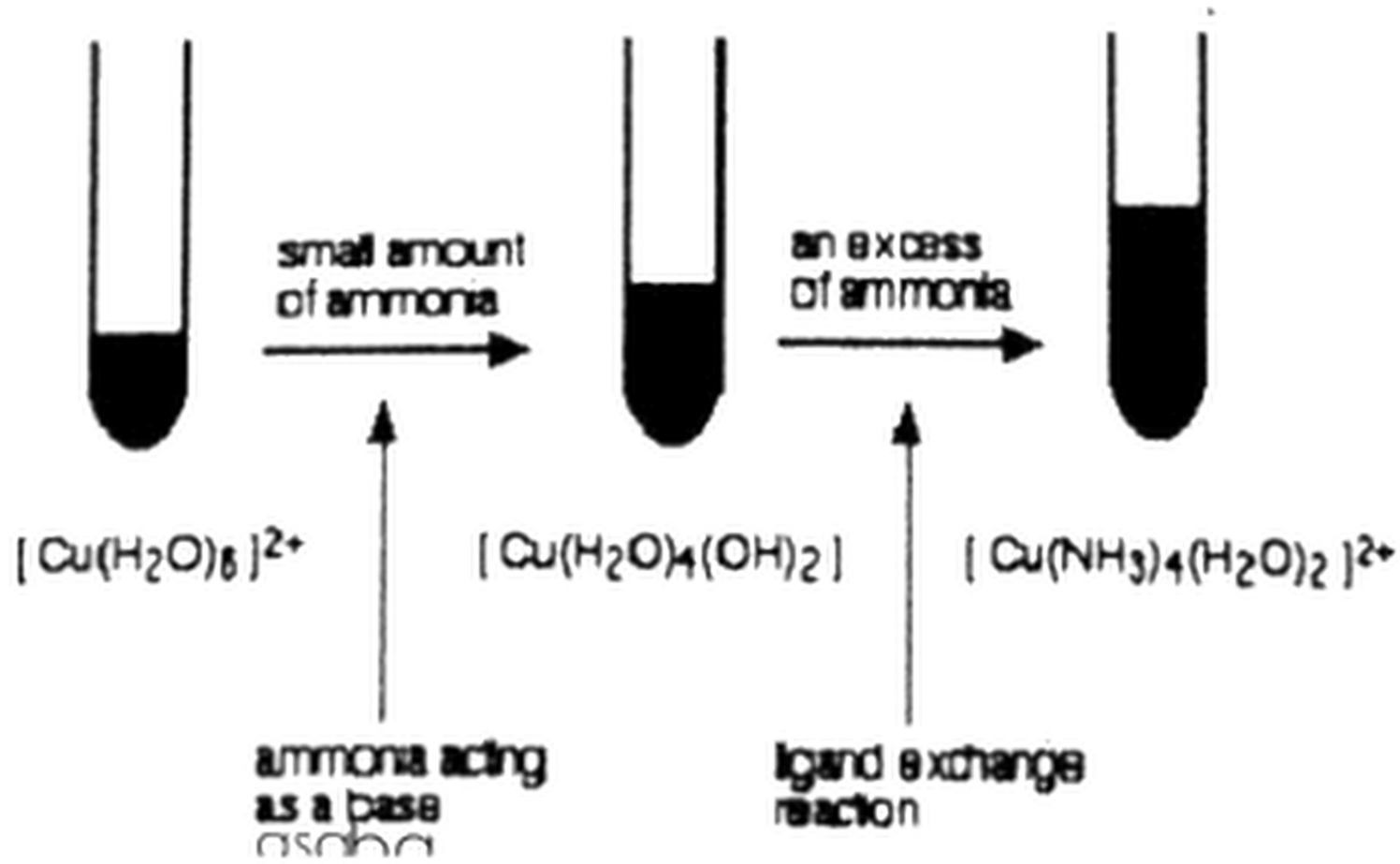
$$[Cu(H_2O)_6]^{2+} + 2NH_3 \longrightarrow [Cu(H_2O)_4(OH)_2] + 2NH4+$$

That precipitate dissolves if you add an excess of ammonia.

The ammonia replaces water as a ligand to give tetraamminediaquacopper(II) ions. Notice that only 4 of the 6 water molecules are replaced.

$$[Cu(H_2O)_6]^{2+} + 4NH3 \longrightarrow [Cu(H_2O)_4(OH)_2] + H2^+ + 4H_2O$$

The colour changes are:

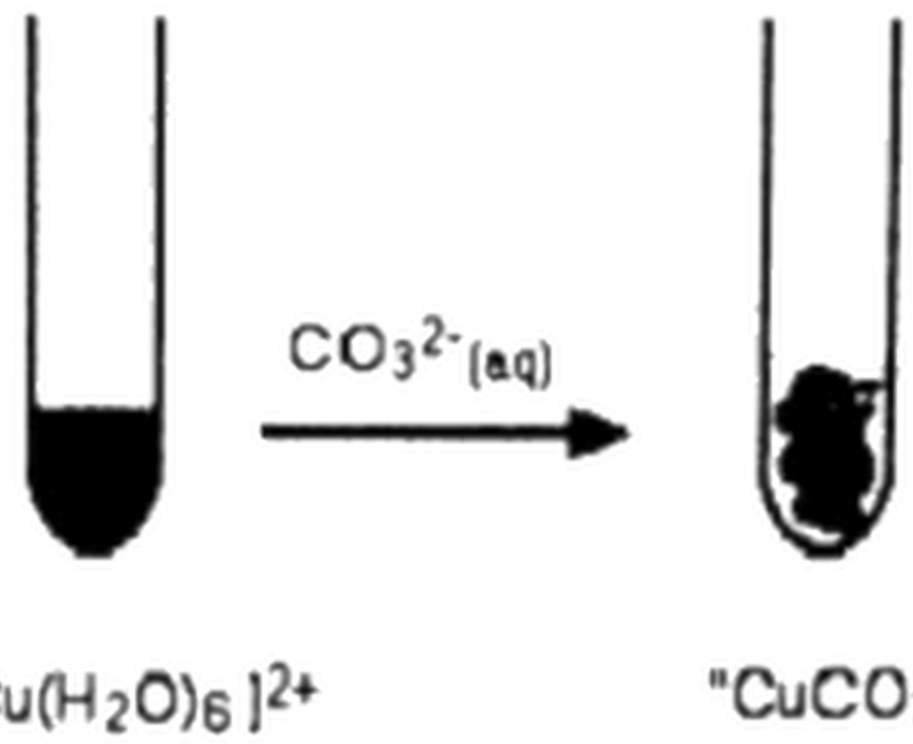


The reaction of hexaaquacopper(II) ions with carbonate ions

You simply get a precipitate of what you can think of as copper(II) carbonate.

$$Cu^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \longrightarrow CuCO_{3(s)}$$

(blue)



Transition and Elements

Certain transition elements such as Cu, Cr, etc are used in Paints. Mostly copper and its different compounds are used in paints.

Name of compound	Uses
Lead Monoxide	It is used in paints, vulcanizations of rubber and for the preparation of red lead. It is used in the manufacture of varnished, glazes, plasters and enamels. It is used in the manufacture of flint glass.
Lead Suboxide	It is black in color and found in powder form It is used as pigment in paints It is used in lead storage.
Lead Dioxide	Lead dioxide is a reddish brown powder and used as pigment in paints.
Triplumbic Tetra oxide Red Lead	It is used as red paint when mixed with linseed oil It is used in glass for making glazes It is used in match industry
Basic Lead Carbonate	It is used as white paint for wood because of its good covering power and protection It is used in making pottery glazes.