

Introduction: ①

Transition elements are those elements which have partially filled d or f orbitals either in their atomic or in any common oxidation states. They are located between s and p block elements in the periodic table. The transition elements, for the sake of convenience, may be divided into two main categories.

- a. The main transition elements or the 'd' block elements.
- b. The 'f' block elements (Inner transition elements)

We will discuss the main transition elements only.

The main transition elements

These elements have partially filled (n-1) d orbitals in the ground state of their free atom or at least in one of their common ions. They are commonly known as d block elements and are further subdivided into four transition series.

- i The first transition series: This includes the elements from scandium (^{21}Sc) to copper (^{29}Cu). These elements have partially filled 3d orbitals.
- ii The second transition series: This includes nine elements starting from Yttrium (^{39}Y) to silver (^{47}Ag). These elements have partially filled 4d orbitals.
- iii The third transition series: This series includes the elements Lanthanum (^{57}La) and elements from Hafnium (^{72}Hf) to Gold (^{79}Au), all of which have partially filled 5d orbitals.
- iv The fourth transition series: This is incomplete transition series. It includes elements Actinium (^{89}Ac) and Rutherfordium

(^{104}Rf) to Meitnerium (^{109}Mt). These elements have partially filled 6d Orbitals.

Table 14.1 Transition elements series

I	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
II	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
III	La	Hf	Ta	W	Re	Os	Ir	Pt	Au
IV	Ac								

14.1

General Features

14.1.1

General Features of Transition Elements

- 1 They are all hard metals and have high melting and boiling points. This is due to high nuclear charge and small atomic radius.
- 2 They are good conductors of heat and electricity.
- 3 Most of these elements show variable valencies or oxidation states. This is due to fact that in addition to the outermost "s" electrons, transition elements can use (n-1) d electron, ((n-1)d and 'ns' electrons of comparable energy) in bond formation. So varying number of electrons can take part in bond formation leading to variable valencies.
- 4 Their compounds are mostly coloured in solid state and in solution. Colour is due to the incomplete "d" orbitals in which electronic transition is possible.
- 5 Some of these elements form paramagnetic compounds because of the presence of unpaired electrons.
- 6 They have the ability to form complexes because of the involvement of vacant d- orbitals.

- 7 They form alloys with the d and f- block elements and also with the elements of other blocks.

14.1.2

Electronic structure

When we build up the electronic configurations of the atoms, we find that each transition metal series results from the belated filling of an inner subshell of electrons. Thus the first series (fourth period) corresponds to the filling of 3d subshell as shown in table 14.2. The “pre-transition” element calcium ($Z=20$) has an $[\text{Ar}] 4s^2$ configuration. Scandium ($Z=21$), the first transition metal in this series, has the configuration $[\text{Ar}] 3d^1 4s^2$. Addition of electrons to the 3d subshell continues until, at Zinc ($Z=30$), the 3d subshell is filled, with the 4s subshell still containing two electrons, as it did with calcium: $[\text{Ar}] 3d^{10} 4s^2$. This transition from an empty 3d subshell to a filled one occurs with only two irregularities, one at Chromium ($Z=24$) and the other at Copper ($Z=29$).

The second, third and fourth transition metal series correspond to the filling of the 4d, 5d and 6d subshells respectively. The general valence shell electronic configuration of atoms of d-block elements may be written as

$$(n-1)d^{1-10} ns^{0,1,2}$$

In the lanthanides (^{58}Ce to ^{70}Yb) and Actinides (^{89}Ac to ^{103}Lw) series valence shell electron goes to “4f” and “5f” orbitals respectively.

The atomic and ionic radii of the first transition series (3-d block elements) decrease slightly from left to right in a period. This gradual decrease is due to the increase in nuclear charge, which results in greater attractive force between the nucleus and the outer electrons. Copper the

last member of the transition series, shows a slight increase in atomic radius, which is the result of repulsion between the outer electrons. The atomic and ionic radii are given in table 14.2. The transition metals have high density because they possess greater mass to volume ratio.

Table 14.2 Electronic configuration and physical properties of transition metals

Elements	Atomic number	Electronic configuration	Atomic radius/nm	Ionic radius/nm	Density at 298K gm/cm ³	E.N	Melting point °C	I.P kJ/mol
Sc	213s ² 3p ⁶ 3d ¹ 4s ²	144	.81	2.99	1.2	1530	630
Ti	223s ² 3p ⁶ 3d ² 4s ²	132	.76	4.54	1.3	1680	680
V	233s ² 3p ⁶ 3d ³ 4s ²	122	.74	6.11	1.45	1917	650
Cr	243s ² 3p ⁶ 3d ⁵ 4s ¹	117	.69	7.19	1.55	1890	650
Mn	253s ² 3p ⁶ 3d ⁵ 4s ²	117	.66	7.42	1.6	1247	720
Fe	263s ² 3p ⁶ 3d ⁶ 4s ²	116	.64	7.87	1.65	1535	760
Co	273s ² 3p ⁶ 3d ⁷ 4s ²	116	.63	8.90	1.7	1490	760
Ni	283s ² 3p ⁶ 3d ⁸ 4s ²	115	.62	8.90	1.75	1452	740
Cu	293s ² 3p ⁶ 3d ¹⁰ 4s ¹	115	.66	8.94	1.75	1083	750

14.1.3

Binding Energy

Transition metals are generally tough having great mechanical strength due to strong metallic bonding. This is because, apart from s-electrons of the outermost shell, the unpaired electrons of underlying d-orbitals also participate in bonding.

In moving from left to right in any transition series, the number of unpaired electrons increases up to group VB and VIB, after that pairing takes place and the number of unpaired electrons goes on decreasing until it becomes zero at group IIB. Therefore, binding energy increases up to group VIB and then progressively decreases up to group IIB. For example in 3d series binding energy increases up to Vanadium and then decreases up to Zinc.

14.1.4 Variable Oxidation states

Most of the transition metals show several oxidation states in their compounds. The cause of showing different oxidation states is that in addition to using electrons in the outermost sub-shell namely "ns", a variable number of inner (n-1)d electrons can also be used in bond formation.

The common oxidation states of each element include +2 or +3 or both. However +3 state is more common at the beginning of series and +2 state is more common at the end of series as shown in table 14.3.

Element Name and Symbol	Atomic Number	Common Oxidation States	Electron Configuration	
Scandium (Sc)	21	+3	Sc: [Ar] 4s ² 3d ¹	Sc: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1\downarrow}{3d}$ — — —
Titanium (Ti)	22	+4	Ti: [Ar] 4s ² 3d ²	Ti: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ — —
Vanadium (V)	23	+2, +3, +4, +5	V: [Ar] 4s ² 3d ³	V: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ —
Chromium (Cr)	24	+2, +3, +6	Cr: [Ar] 4s ¹ 3d ⁵	Cr: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$
Manganese (Mn)	25	+2, +3, +4, +6, +7	Mn: [Ar] 4s ² 3d ⁵	Mn: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$
Iron (Fe)	26	+2, +3	Fe: [Ar] 4s ² 3d ⁶	Fe: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$
Cobalt (Co)	27	+2, +3	Co: [Ar] 4s ² 3d ⁶	Co: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$
Nickel (Ni)	28	+2	Ni: [Ar] 4s ² 3d ⁷	Ni: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$
Copper (Cu)	29	+2	Cu: [Ar] 4s ¹ 3d ¹⁰	Cu: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$
Zinc (Zn)	30	+2	Zn: [Ar] 4s ² 3d ¹⁰	Zn: [Ar] $\frac{1\downarrow}{4s}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$ $\frac{1\downarrow}{3d}$

Table 14.3

The highest oxidation state from Sc^{+3} to Mn^{+7} corresponds to the involvement of all the electrons outside the Argon core. After this the increasing nuclear charge binds the d-electrons more tightly, so onward from Fe to Zn only the weakly held electrons of "4s" subshell are involved in oxidation state.

14.1.5 Catalytic properties

Most of the transition metals and their compounds are used as catalyst. Some common examples are Pt, Ni, Fe, Cr, V_2O_5 etc. Catalytic property of these elements is due either to the use of their d-orbital or the formation of interstitial compounds which absorb and activate the reacting substances.

Transition metals have variable oxidation states and hence are capable of forming intermediate compounds which help in the formation of desired product e.g. finely divided Iron is used as a catalyst in Haber Bosch process for the synthesis of ammonia. The application of V_2O_5 , in the conversion of SO_2 to SO_3 for the manufacture of H_2SO_4 by contact process, the use of TiCl_4 in the polymerization of ethene to polythene polymer, the application of Ni, Pd or Pt in the catalytic hydrogenation of unsaturated hydrocarbons and the use of Cu in the oxidation of ethanol to acetaldehyde are examples of catalytic properties of transition elements.

14.1.6 Magnetic behaviour

Substances show two different types of behaviours when subjected to an external magnetic field. If a substance is weakly attracted by a strong magnetic field, it is called paramagnetic substance whereas a substance

weakly repelled by magnetic field is called diamagnetic substance.

Paramagnetic behaviour is due to the presence of one or more unpaired electrons in an atom, ion or molecule of the substance. The attraction is a result of interaction of magnetic field produced by spinning electron with the external field. In diamagnetic substances the electrons are paired up due to which magnetic field of oppositely spinning electrons cancel each other.

An extreme case of paramagnetism is called ferromagnetism as shown by Fe^{+3} and Mn^{+2} ions which have five unpaired electrons each.

14.1.7

Alloy Formation

Transition metals have another great characteristics that they easily mix with each other. This is because all the d-block metals have about the same atomic size. This allows them to replace one another easily in crystal lattice. When two or more metals mix or replace one another, we call the mixture an alloy.

Brass is a good example of alloy which is a mixture of copper and zinc. These elements and alloys are essential for the existence of life and also for of its progression through time. (Bronze age, Iron age etc.) Some of the important alloys and their uses are shown in table 14.4.

Alloy	Composition	Uses
Brass	Cu = 60 – 80 % Zn = 20 – 40 %	Domestic utensils, cartridges, casting, condensers
Bronze	Cu = 75 – 90 % Sn = 10 – 25 %	Statues, coins, bells, blades, machine parts
Steel	Fe = 90 – 95 % C = 0.1 – 2 %	Cutlery, car bodies Bridge, utensils
Gold (18 carat)	Au = 70 – 75 % Cu = 20 – 25 %	Jewellery, Electrical devices. Tooth filling, statues.

Table 14.4

14.2

COORDINATION COMPOUNDS

14.2.1

Complex Ion

Most transition elements can form complex ions, in which the metal ion is surrounded by groups of negative ions, or molecules for example if you add ammonia to a solution containing Cu(II) ions, a pale blue precipitate of Cu (II) hydroxide forms. It dissolves again if you add more ammonia, giving a deep blue solution, because a soluble complex ion forms.

In this complex, four ammonia molecules and two water molecules surround Cu^{+2} ion. Its formula is $[\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{+2}$

$\text{Na}_3 [\text{Co} (\text{NO}_2)_6]$ sodium hexanitrocobaltate (III)

$\text{Na}_3 [\text{Fe} (\text{CN})_6]$ sodium hexacyanoferrate (III)

In cationic and neutral complexes the name of the metal remains the same. Whereas in anionic complexes the name of the metal is followed by ate e.g. Cr becomes Chromate, Fe, ferrate, Co Cobaltate, Cu Cuprate and Ag Argentate. Other examples are:

$\text{K}_3 [\text{Fe}(\text{CN})_6]$ Potassium hexacyanoferrate (III)

$\text{Na}_2 [\text{Fe} (\text{NO}) (\text{CN})_5]$ Sodium pentacyanonitrosylferrate (III)

$[\text{Co} (\text{en})_2 \text{Cl}_2]$ Dichloro-Bis-ethylenediamine cobalt (II)

14.2.3 Shapes of complex ions

Coordination compounds have definite geometrical shapes because the bond formed between central metal atom and the ligands are directional in nature.

Hence, the ligands are arranged around central metal atom in a clear spatial geometry. This geometry depends on the number of ligands (coordination number) and type of hybridization taking place in central metal atom.

Complexes with coordination number four and six are very common. The former exists in two geometrical shapes, tetrahedral and square planar while those having coordination number six exist in octahedral shape.

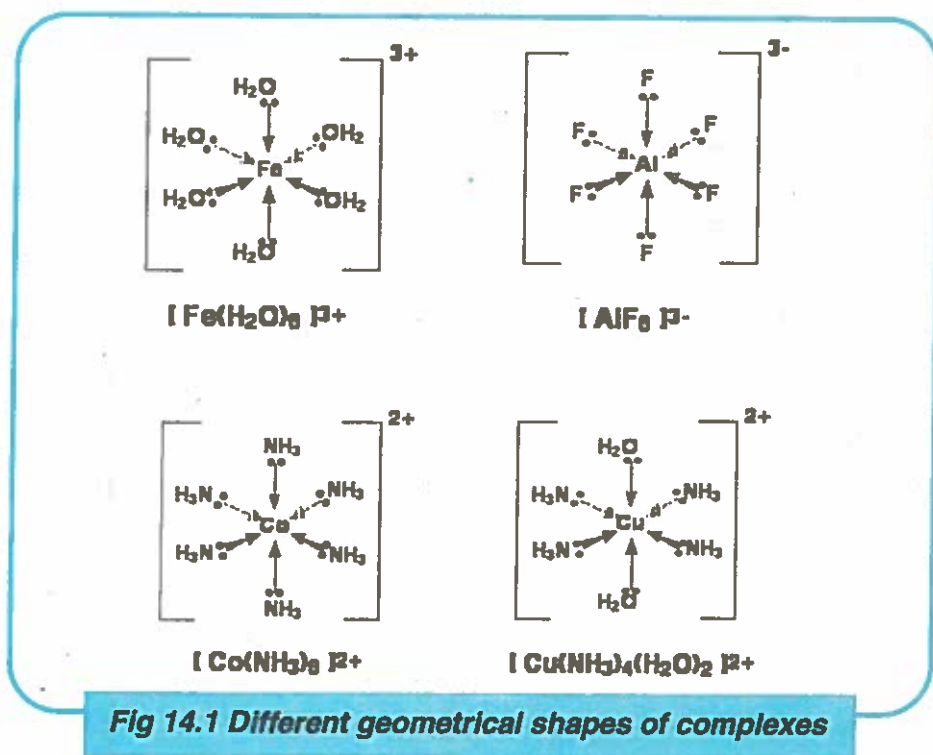
Complexes having coordination number five are less common. These complexes exist in two main possible geometries i.e. trigonal bipyramidal and square pyramidal shapes.

6-coordinated complex ions

These are complex ions in which the central metal ion is forming six coordinate covalent bonds or in simple words the central metal ion is attached to six ligands.

These ions have an **octahedral** shape. Four of the ligands are in one plane, while the fifth one lying above and the sixth one below the plane.

The diagram shows four fairly random examples of octahedral ions.

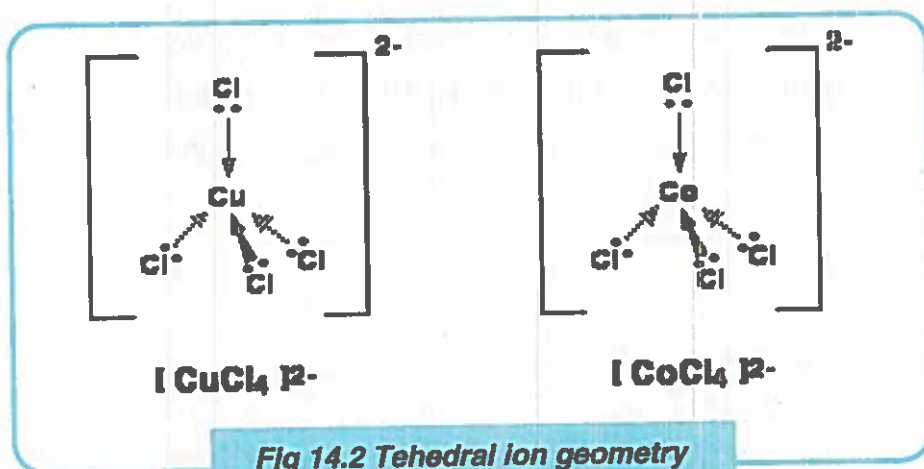


4-co-ordinated complex ions

These are far less common, and they can take up one of two different shapes.

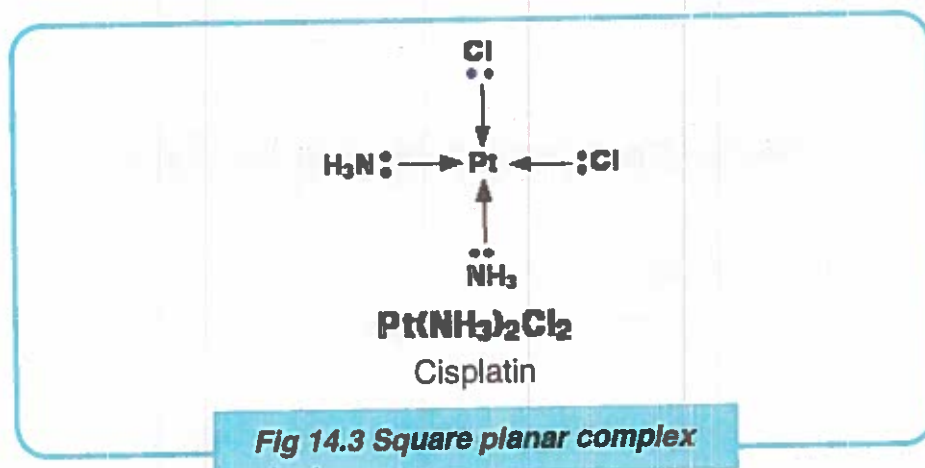
Tetrahedral ions

The copper(II) and cobalt(II) ions have *four* chloride ions bonded to them rather than six, because the chloride ions are too big to fit any more around the central metal ion.



A square planar complex

Occasionally a 4-co-ordinated complex turns out to be square planar. There's no easy way of predicting that this is going to happen. The only one you might possibly come across at this level is **cisplatin** which is used as an anti-cancer drug.



14.2.4 Colours of complexes (8)

Most of the compounds of the transition metals are coloured in solid or solution state. The colour of the transition metal ions is due the presence of unpaired electrons or incomplete d-orbitals. When light is allowed to fall on a substance, it absorbs from it the light of a particular colour whose wavelength is in the visible region ($4000 - 7000 \text{ \AA}$) and reflects the remaining light which has the colour complementary to that of the absorbed light. This complementary colour which is actually the colour of reflected light becomes the colour of the substance.

The ions which have completely filled or empty d-orbitals are colourless e.g. Cu^+ ($3d^{10}$), Zn^{+2} ($3d^{10}$) and Sc^{+3} ($3d^0$), Ti^{+4} ($3d^0$) are colourless.

Colours of hydrated cations of the elements of first transition series is given in following table 14.5.

Ion	Outer configuration	No. of unpaired electrons	Colour
Sc^{3+}	$3d^0$	0	Colourless
Ti^{3+}	$3d^1$	1	Purple
Ti^{4+}	$3d^0$	0	Colourless
Cr^{3+}	$3d^3$	3	Blue
Mn^{2+}	$3d^5$	5	Green
Fe^{3+}	$3d^5$	5	Yellow
Co^{2+}	$3d^7$	4	Blue
Ni^{2+}	$3d^8$	2	Green
Cu^{2+}	$3d^9$	1	Blue
Zn^{2+}	$3d^{10}$	0	Colourless

Table 14.5

14.3**Chemistry of some important Transition Elements** (9)**14.3.1****VANADIUM****I. INTRODUCTION**

Vanadium, symbol V, silvery-white metallic element with an atomic number of 23. It was discovered in 1801 in Mexico by Andrés Manuel del Rio, but it was mistaken for a form of chromium. Vanadium was rediscovered in about 1830 by the Swedish chemist Nils Gabriel Sefström. The element was named after Vanadis, goddess of beauty and love in Scandinavian mythology.

14.3.1.1**Oxidation States**

The oxidation state of an element is related to the number of electrons that an atom loses or gains or appears to use when joining with another atom in compounds. It also determines the ability of an atom to oxidize or to reduce other atoms or species. Almost all the transition metals have multiple potential oxidation states. Oxidation states of atoms depend upon unpaired electrons in d-orbitals.

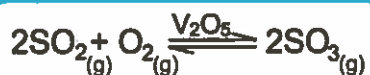
Compounds of vanadium in +5, +4, +3 and +2 oxidation states are important. The compounds in the lower oxidation states are good reducing agents. They are also ionic in character and on account of incomplete electron shell they are also coloured. The compounds in the higher oxidation states are generally colourless due to the empty electron shell. When a colourless compound of V^{+5} ($3d^0 4s^0$) is reduced by suitable reducing agent, it first turns blue VO^{+2} ($3d^1 4s^0$), then green V^{+3} ($3d^2 4s^0$) and finally violet V^{+2} ($3d^3 4s^0$). Vanadium also shows +1, 0, -1 oxidation

states in the compounds $[V(dipy)_3]^{+1}$, $V(CO)_6$ and $[V(CO)_6]^{-1}$ respectively.

14.3.1.2 As Catalyst In Contact process

The contact process is the common method of producing sulfuric acid in high concentrations needed for industrial processes. Platinum was formerly employed as a catalyst for the reaction, but as it is susceptible to poisoning by arsenic impurities in the sulfur feedstock, vanadium oxide (V_2O_5) is now preferred.

(V_2O_5) is used as catalyst in various oxidation reactions involving the use of O_2 as the oxidizing agent e.g. conversion of SO_2 to SO_3 in the manufacture of H_2SO_4 .



V_2O_5 is also used in the oxidation of alcohols and hydrogenation of olefins.

14.3.2

Chromium

Introduction to Chromium

Chromium, symbol Cr, atomic number 24 is a shiny metallic element. Being brilliant, hard, and corrosion-resistant, chromium makes a durable and attractive coating for other metals and is an important component of stainless steel.

The element was discovered in 1797 by the French chemist Louis Nicolas Vauquelin, who named it chromium (Greek *chroma*, "color") because it forms a large number of coloured compounds.

Chromium is a common element; overall it ranks about 21st in natural abundance among the elements in earth crust. Chromium has an atomic weight of 51.996; the element melts at 1907°C (3465°F), boils at 2672°C (4842°F), and has a specific gravity of 7.2.

Chromium is not found native. Its most common minerals are chromite or chrome iron stone ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$). It is also found as chrome ochre (Cr_2O_3) and crocite (PbCrO_4). Large quantities of chrome iron stone are found in Rhodesia, Transvaal, Turkey, Russia, India and Pakistan.

14.3.2.1 Oxidation States

The important and stable compounds of chromium are those in which chromium has +6, +3 and +2 oxidation states. The element in +3 oxidation state is most stable and hence $\text{Cr}(+2)$ compounds are strong reducing agents while those of $\text{Cr}(+6)$ are strong oxidizing agents.

With the increase in oxidation state of the element,

- (a) The acidic character of oxides increases with increasing oxidation state.

Oxides	CrO	Cr_2O_3	CrO_3
Oxidation state of Cr	+2	+3	+6
Nature	Basic	Amphoteric	Acidic

- (b) Similarly the covalent character of the compounds also increases. Thus $\text{Cr}(+2)$ compounds are ionic, $\text{Cr}(+3)$ compounds ionize to some extent while those of $\text{Cr}(+6)$ are covalent.

The compounds in which chromium shows +6 oxidation state are chromium trioxide (CrO_3), potassium chromate (K_2CrO_4) and Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$).

$\text{Cr}(+3)$ compounds are also called chromic compounds. These may be considered derived from chromic oxide, Cr_2O_3 . These are formed either by oxidation of $\text{Cr}(+2)$ or by reduction $\text{Cr}(+6)$ compounds such as chromate or dichromate. Examples of chromic compounds are chromic chloride (CrCl_3), chromic sulphate ($\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$).

$\text{Cr}(+2)$ compounds are called chromous salts. These salts are unstable and tend to oxidize on exposure to air into corresponding $\text{Cr}(+3)$ compound. Some of chromous salts are, CrCl_2 , CrS , $\text{CrSO}_4 \cdot 7\text{H}_2\text{O}$, CrCO_3 etc.

14.3.2.2 The Chromate - Dichromate Equilibrium

When solid potassium chromate, K_2CrO_4 is dissolved in water it forms a yellow solution. When solid potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$ is dissolved in water the resulting solution is orange. The colors come from the negative ions: $\text{CrO}_4^{2-}(\text{aq})$ and $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$. However, in solution these ions are actually in equilibrium as indicated by the equation:



Figure 14.4



This is dynamic equilibrium and sensitive to the acidity and basicity of solution. According to Le-Chatelier's principle, the addition of acid to the

reactant shifts the equilibrium towards right and yields more dichromate (orange). On the other hand, the addition of base promotes the conversion of dichromate to chromate.



14.3.2.3 Reduction of Chromate (VI) ions with Zn and an Acid :-

Dichromate VI ions (for example, in Potassium dichromate (VI) solution) can be reduced to Chromium (III) ions Chromium (II) ions using Zinc and either dilute Sulphuric acid or Hydrochloric acid. The equations for the two stages of the reaction are:

For the reduction from +6 to +3



For reduction from +3 to +2

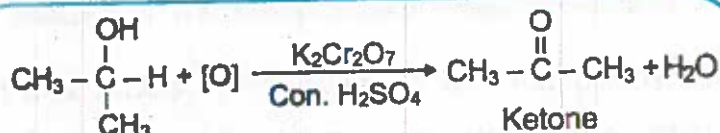


14.3.2.4 Potassium Dichromate(VI) as an oxidizing agent in organic chemistry:

Potassium dichromate (VI) solution acidified with dilute sulphuric acid is commonly used as an oxidising agent in organic chemistry.

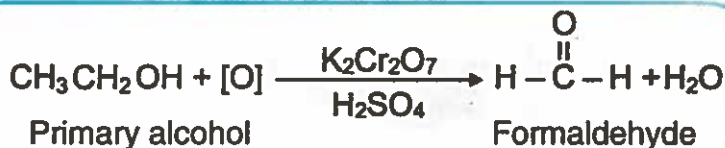
For example

It oxidise secondary alcohols to ketones

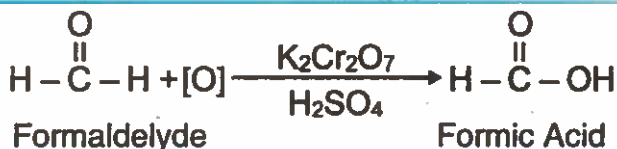


Secondary alcohol

In case of primary alcohol



Formaldehyde is further oxidized to formic acid, under the above condition.



Tertiary alcohols are not oxidized by potassium dichromate.

14.3.2.5 Potassium Dichromate as an oxidizing agent in titrations:

In redox titration a standard solution of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) is used to determine the unknown concentration of a solution of Fe^{+2} .

Dichromate ion reduces to chromium(III) ions.

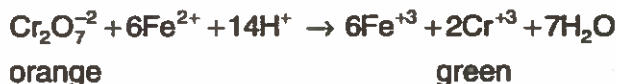


Fe(II) is oxidized to Fe(III)



Therefore, 1 mole of $\text{Cr}_2\text{O}_7^{2-}$ (the oxidizing agent) reacts with 6 moles of Fe^{2+} (the reducing agent) to form 6 moles of Fe^{3+} and 2 moles of Cr^{3+} .

Thus, in net ionic form:



The molecular form of the equation can be written as:



The 1:6 mole ratio with respect to the amounts of $\text{Cr}_2\text{O}_7^{2-}$ and Fe^{2+} is consumed.

14.3.3

Manganese: 13)

Manganese, symbol Mn, is silvery white, brittle metallic element used principally in making alloys. Manganese is one of the transition elements of the periodic table. The atomic number of manganese is 25.

Manganese was first isolated in 1774 by the Swedish chemist Johan Gottlieb Gahn. Manganese metal corrodes in moist air and dissolves in acid. The element melts at 1245°C (2271°F), boils at 2061°C (3742°F), and has a specific gravity of 7.4. Its atomic weight is 54.938.

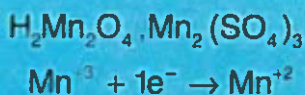
Manganese does not occur in the free state, except in meteors, but is widely distributed over the world in the form of ores, such as pyrolusite, rhodochrosite, franklinite, psilomelane, and manganite. The principal ore is pyrolusite. The element's name comes from the Latin word *magnes*, "magnet" and was chosen because pyrolusite is magnetic. Manganese ranks about 12th in abundance among elements in Earth's crust. Ukraine, Georgia, and South Africa are important producers of manganese.

14.3.3.1 Oxidation State of Manganese:

In accordance with electronic configuration of manganese ($3d^5 4s^2$). It shows a maximum oxidation state of +7. In addition to this state it also shows lower oxidation state such as +6, +4, +3 and +2.

Manganese compounds where 'Mn' is in oxidation state +7, which are restricted to the unstable oxide Mn_2O_7 and compounds of intensely purple permanganate ion (MnO_4^{-1}) are powerful oxidizing agents.

Mn^{+6} is present in MnO_3 in the salt of Manganic acid (H_2MnO_4). The free acid is unknown. Its salts are called manganates e.g. K_2MnO_4 . The compounds having Mn^{+4} are very limited in number. The most familiar compound of Mn^{+4} is MnO_2 . The compound of Mn^{+3} is called manganic compound. In aqueous solution Mn^{+3} ion is quite unstable since it is easily reduced to Mn^{+2} ions e.g.



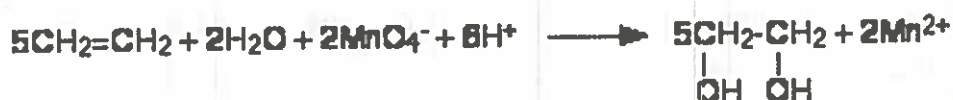
Mn^{+2} is the most stable oxidation state of Mn in neutral or acidic solution. Mn^{+2} ion exist as pale pink hexaaqua $[Mn(H_2O)_6]^{+2}$ which is quite stable to oxidation. The stability of Mn^{+2} is due to half filled 3d-orbital. The compounds of Mn^{+2} are called manganous compounds such as MnO , $MnCO_3$, $MnSO_4$, $MnCl_2$.

14.3.3.2 Potassium permanganate (VII) as an oxidizing agent in organic chemistry:

Alkenes react with potassium permanganate(VII) solution in the cold. The colour change depends on whether potassium manganate(VII) is used under acidic or alkaline conditions.

Manganate(VII) ion is strong oxidising agent, and in the first instance oxidise ethene to ethane-1,2-diol (old name: ethylene glycol).

Under acidic conditions, the permanganate(VII) ions are reduced to manganese(II) ions.



Under alkaline conditions, the permanganate(VII) ions are first reduced to green manganate(VI) ions . . .



. . . and then further to dark brown solid manganese(IV) oxide (manganese dioxide).

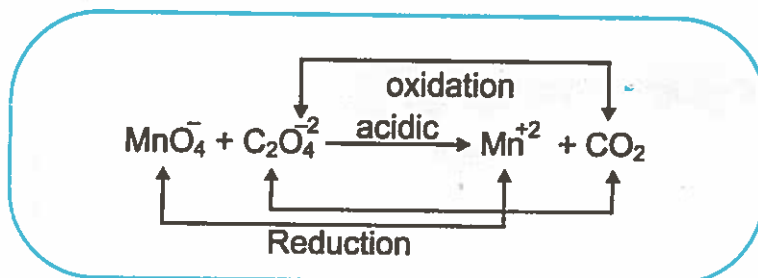


14.3.3.3

Potassium permanganate (VII) as an oxidizing agent in titrations:

KMnO_4 is a strong oxidizing agent with intense dark purple colour. During reduction the purple permanganate ion changes into colourless Mn^{+2} ion.

The solution turns from dark purple to faint pink colour at equivalence point. The reduction of permanganate requires strong acidic conditions. For example oxalate ion reduces permanganate ion in acidic conditions.



No additional indicator is used in this titration because KMnO_4 acts itself as an indicator.

KMnO_4 solution is also used to find the concentration of Fe(II) ions in a solution. The redox reaction is given as under.



14.3.4

Iron:

Iron is a transition metal with a symbol (Fe) and Atomic number 26. It has two relatively stable oxidation states in its compounds (+2 and +3). It also forms a variety of complex ions such as $[\text{Fe}(\text{H}_2\text{O})_6]^{+2}$, $[\text{Fe}((\text{H}_2\text{O})_6)]^{+3}$. It has characteristically coloured compounds e.g. Iron (II) salts (pale green), Iron (III) salts (yellow or brown). Iron is used to catalyse the synthesis of ammonia through Haber's process.

Iron rarely occurs in free state since it is highly reactive. Its important ores are red haematite (Fe_2O_3), Brown haematite or limonite ($2\text{FeO}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), magnetite Fe_3O_4 etc. Iron ore is processed for the

following three varieties of Iron which differ from each other mainly in their carbon content i.e. cast iron or pig iron (2–3%), wrought or malleable Iron (0.1–0.25%) steel (0.25–2%).

14.3.4.1 Oxidation States of Iron

Most common oxidation states of iron are +2 and +3 but it can also exist in the form of Fe^{4+} , Fe^{5+} and Fe^{6+} . Fe^{6+} is very rare oxidation state of iron.

Iron in the +2 oxidation state is known as the Ferrous ion. This ion is pale green in colour and is very easily oxidized to ferric ion. Even traces of dissolved oxygen in solution will accomplish this oxidation. Solution of Ferrous ion is sometimes used as reducing agent. Complexes of the ferrous ions usually have octahedral geometry, such as;

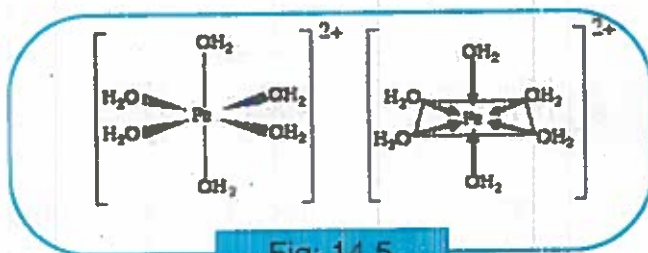


Fig: 14.5

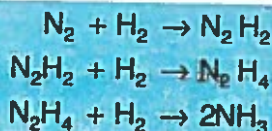
When ferrocyanide added to solution containing Ferric ions, a precipitate known as prussian blue $\text{Fe}_4 [\text{Fe}(\text{CN})_6]_3$ is formed. This compound is used in making blueprint and as a bluing agent in laundry.

Iron in +3 oxidation state is known as Ferric ion. Most solutions containing ferric ions are usually yellow or yellow-brown due to formation of $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$.

14.3.4.2 Iron as catalyst in Haber's Process (6)

In the Haber process hydrogen reacts with nitrogen to produce ammonia. Without catalyst the process would proceed too slowly to be economically viable.

The reaction takes place according to the following steps:



However breaking open the nitrogen triple bond to form N_2H_2 is very difficult and resulting compound is highly unstable and is likely to dissociate almost as soon as it forms. The formation of N_2H_2 is highly endothermic. So the above reactions do not proceed easily without the use of catalyst.

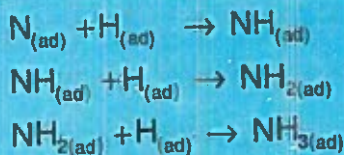
The hydrogen and Nitrogen are adsorbed on metallic iron surface. The hydrogen almost immediately splits into its component atoms by sharing or exchange of electrons with the catalyst surface



The nitrogen molecules split into their component atoms and they lock into the surface of the iron catalyst. This is the slowest step and so limits the rate of the entire process.



The hydrogen atoms migrate across the surface of the catalyst and react with nitrogen and produce ammonia molecules that are still bound to the surface.



The assembled ammonia molecules are desorbed from surface in the form of gas

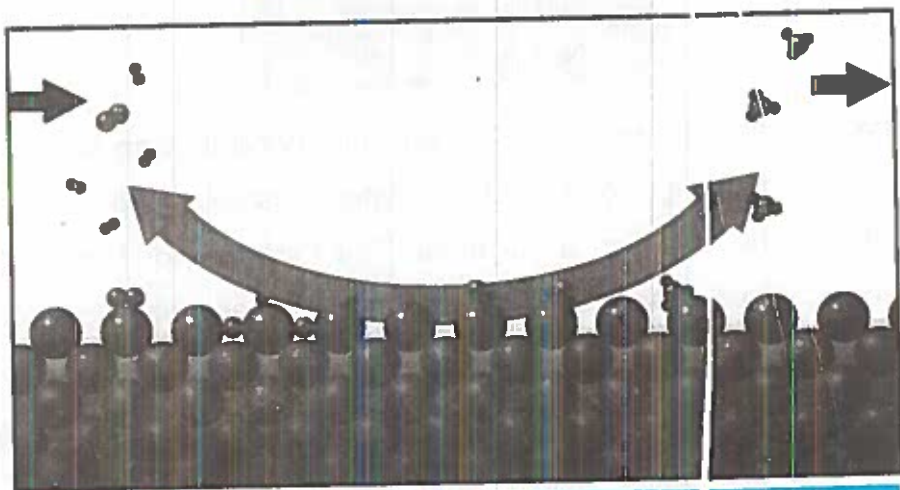


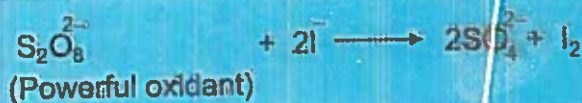
Fig: 14.6 Catalytic action of iron surface in Haber Process

14.3.4.3

Iron ions in the reaction between persulphate ions and iodide ions

The reaction between persulphate ions (peroxodisulphate ions), $\text{S}_2\text{O}_8^{2-}$, and iodide ions in solution can be catalysed using either iron(II) or iron(III) ions.

The overall equation for the reaction is:



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



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

14.3.4.4 Reaction of Hexaaqua iron (II), Hexaaqua Iron (III) with water and Ammonia

Many hexaaqua complex ions can undergo acid base reaction with water to produce a solution of pH less than seven. These are not redox reaction because during the reaction no change in the oxidation state of central metal occurs e.g.

In Iron (II) case



In Iron (III) case



Fe^{+3} (Ferric) give a more acidic solution than Fe^{+2} (ferrous) ions.

In case of Alkaline solution OH^- ions remove H_3O^+ ions and equilibrium shifts more towards forward direction and more H^+ are lost from the complex in stages until a precipitate is formed.



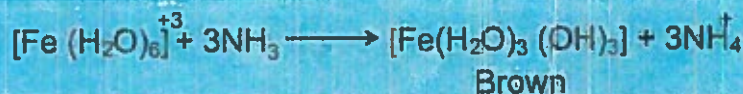
In case of Fe (II) complex the reaction in alkaline medium does not proceed because it is energetically unfavourable.

Ammonia can act both as a base and a ligand. Here it simply acts as a base, removing H^+ from the aqua complex.

In Iron (II) case



In Fe (III) case

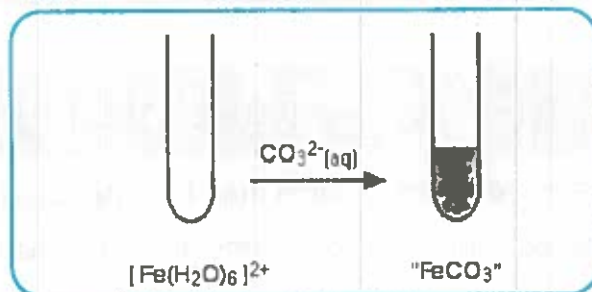


14.3.4.5 Reactions of the iron ions with carbonate ions

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

Iron(II) ions and carbonate ions

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



Iron(III) ions and carbonate ions

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

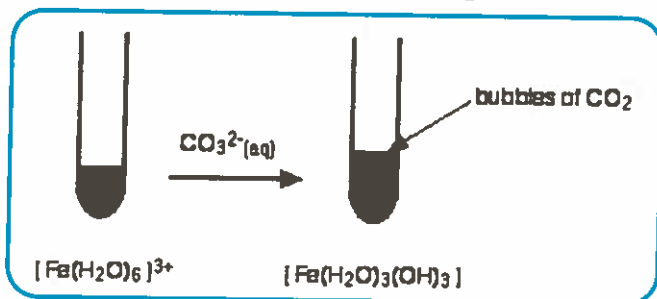
If you add sodium carbonate solution to a solution of hexa aqua iron(III) ions, you get exactly the same precipitate as if you added sodium hydroxide solution or ammonia solution.

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

Depending on the proportions of carbonate ions to hexa aqua 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.

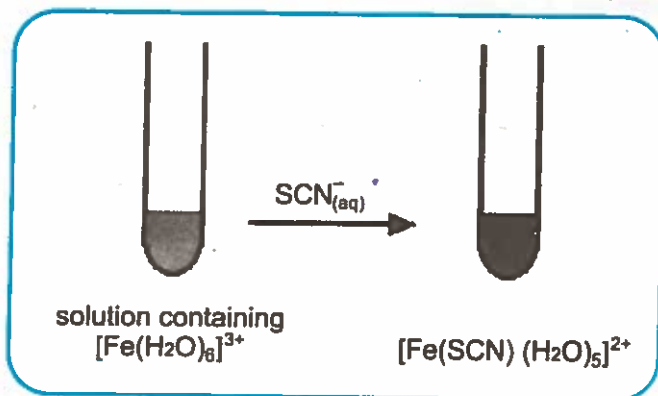


Apart from the carbon dioxide, there is nothing new in this reaction:



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 $[\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}$.



14.3.5 Copper: (18)

INTRODUCTION

Copper, symbol Cu, is brownish-red metallic element that is one of the most widely used metals. Copper is one of the transition elements of the periodic table. The atomic number of copper is 29.

Copper was known to prehistoric people and was probably the first metal from which useful articles were made. Copper objects have been found among the remains of many ancient civilizations, including those of Egypt, Asia Minor, China, southeastern Europe, Cyprus (from which the word *copper* is derived), and Crete (Kriti). It was known to Native Americans, however these ores were found by the European explorers. It is also found in the pure state.

The principle ores of copper are

- | | |
|--------------------|--|
| (i) Malachite | $\text{CuCO}_3\text{Cu}(\text{OH})_2$ |
| (ii) Azurite | $2\text{CuCO}_3\text{Cu}(\text{OH})_2$ |
| (iii) Chalcocite | Cu_2S |
| (iv) Copper pyrite | CuFeS_2 |

14.3.5.1 Oxidation States:

Copper exhibits a variety of oxidation states in its compounds which are mostly coloured. The two principal oxidation states of copper are +1 and +2. Copper (I) compounds are expected to be diamagnetic in nature and are usually colourless. Examples of these compounds are Cu_2O , CuCl , CuBr etc. In solid compounds copper (I) is often the more stable state at moderate temperatures. The copper (II) ion is usually more stable in aqueous solutions. Compounds of this ion are called cupric compounds

and are usually coloured. Examples are CuO , CuF_2 , CuCl_2 , CuCO_3 , CuSO_4 etc.

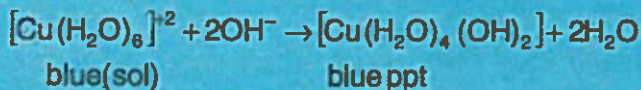
Copper(III) is most characteristically found in oxides. A simple example is potassium cuprate, KCuO_2 , a blue-black solid. The best studied copper(III) compounds are the cuprate superconductors. Yttrium barium copper oxide ($\text{YBa}_2\text{Cu}_3\text{O}_7$) consists of both Cu(II) and Cu(III) centres. Like oxide, fluoride is a highly basic anion and is known to stabilize metal ions in high oxidation states. Indeed, both copper(III) and even copper(IV) fluorides are known, K_3CuF_6 and Cs_2CuF_6 , respectively.

14.3.5.2 Reactions of Hexaaqua copper (II) ions with Hydroxide ions, ammonia and carbonate ions ⁽¹⁹⁾

The simplest ion formed by copper in a solution is the typical blue Hexaaqua copper (II) ion. This complex ion performs the following reactions.

(a) Reaction with Hydroxide Ions:

Hydroxide ions (from NaOH solution) remove H^+ ions from water ligands attached to the copper ion. It results in neutral complex which is insoluble in water and precipitation occurs. The chemical reaction is

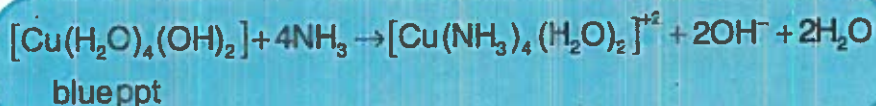


(b) Reaction with Ammonia:

When a small amount of ammonia is added to solution of hexaaqua copper (II) ions, it pulls out the H^+ ions from the complex ion exactly like above.

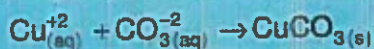


The precipitate dissolves in the presence of excess ammonia.



(c) Reaction with carbonates:

The Hexaaqua copper (II) ions are not strongly acidic enough to release CO_2 from carbonates. In these cases precipitation of metal carbonate takes place which is represented by the following reaction.



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Transition metals and their compounds when dissolved mostly form coloured solutions. Different metals are known for their specific colour used as paints such as cobalt (II) nitrate (red), $\text{K}_2\text{Cr}_2\text{O}_7$ (orange), KCrO_4 (yellow), Nickel (II) Chloride (green) KMnO_4 (purple), while titanium oxide is an important ingredient in white paint.

Key Points:

- Transition elements are those elements which have partially filled d or f orbitals either in their atomic state or in any common oxidation state.
- The oxidation state of an element is related to the number of electrons that an atom loses, gains, or appears to use when joining with another atom in compounds.
- Those substances which are attracted in magnetic field are called paramagnetic substances and the phenomenon is known as paramagnetism.
- Transition metal atoms have similarity in their structure hence they are able to replace one another in the metallic lattice and form alloys.
- Coordination compounds have definite geometrical shapes because the bond formed between central metal atom and the ligands are directional in nature.
- Ionic and covalent compounds of transition metals are mostly coloured.
- All forms of Cr(VI) are powerful oxidizing agents, and oxidize any CH bonds on a carbon with an oxygen as far as possible without breaking any carbon-carbon bonds
- Fe (II) compounds are octahedral in geometry.
- Per manganate (VII) ions are strong oxidizing agents which oxidize ethane to ethyl alcohol.

EXERCISE

80

Exercise

1. Select the most appropriate choice given at the end of each question?
1. The Transition metals Copper and.....are best electrical conductors.
(a) Iron (b) Vanadium (c) Chromium (d) Manganese
2. Transition elements usually exhibit.....valencies.
(a) variable (b) Normal (c) permanent (d) unchangeable
3. The coordination compound $[(\text{Cu}(\text{Cl}_4))]^{2-}$ exists inshape.
(a) tetrahedral (b) octahedral (c) square planner (d) rhombic
4. The oxidation state of Chromium in $\text{CrO}_2 \text{Cl}_2$ is.....
(a) 2 (b) 3 (c) 4 (d) 6
5. A compound Potassium dichromate is used in dying and.....industry.
(a) Tanning (b) Cement (c) Paper (d) Glass
6. Acidified Potassium permanganate acts as an..... agent.
(a) Oxidizing (b) reducing (c) bleaching (d) colouring
7. The paramagnetic nature of a substance depends on:
(a) The number of electron in the outermost orbit.
(b) The number of electron that are easily ejected.
(c) The number of unpaired electrons.
(d) The number of lone pair of electrons.
8. V_2O_5 is used as catalyst in the:
(a) Manufacture of Ammonia.

- (b) oxidation of Ammonia to Nitric Acid.
(c) polymerization of ethane to polythene.
(d) Manufacture of Sulphuric Acid
9. Select element which is not ferromagnetic.
(a) Fe (b) Co (c) Sb (d) Ni
10. The coordination number of iron in $[(\text{Fe}(\text{CN})_6)]^{4-}$ is :
(a) 2 (b) 3 (c) 4 (d) 6
11. Select ligand which is bidentate:
(a) H_2O (b) NH_3 (c) CO (d) $\text{C}_2\text{O}_4^{2-}$
12. Cu^{+2} salt solution is blue in colour due to transition of electron from:
(a) s to p orbital (b) d to d orbital
(c) p to d orbital (d) p to p orbital
13. Potassium dichromate acts as a strong:
(a) Oxidizing agent (b) Reducing agent
(c) Bleaching agent (d) Dehydrating agent.
14. When solid potassium chromate, K_2CrO_4 is dissolved in water it forms asolution.
(a) yellow (b) pink (c) red (d) violet
15. Which ions are used as catalyst in the reaction between persulphate ions and iodide ions?
(a) Lead (b) Iron (c) copper (d) chromium.

Short questions

1. Answer the following questions:

- (I) What is meant by the term "transition elements"?
(II) Write down the electronic configuration of first transition series?

- (III) Comment on the electronic configuration of chromium and copper?
- (IV) Explain the catalytic behavior of transition elements?
- (V) How coordination compounds are formed by transition elements?
- (VI) Write a short note on the variable oxidation state.
- (VII) What is the oxidation state of Fe in FeCl_3 ?
- (VIII) What is the oxidation state of chromium in $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$?

Long questions

1. What are the general characteristics of transition elements?
2. Explain the nomenclature of coordination compounds?
3. Explain the role of iron and Vanadium as catalysts?
4. Discuss Chromium and Manganese compounds as oxidizing agents.
5. What are complex ions? Explain their shape and colours?
6. Give Reasons.
 - i) Fe is a catalyst in Haber process while not in the preparation of sulphuric acid.
 - ii) Why Iron has variable valencies.
 - iii) The oxidation state of neutral compound is zero?
 - iv) Existence of paramagnetism and ferromagnetism.