



**G. C. E. (Advanced Level)**

**CHEMISTRY**

**Grade 12**

**Unit 6: Chemistry of *s*, *p* and *d* Block Elements**

**Department of Science  
Faculty of Science and Technology  
National Institute of Education  
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**Chemistry**

Resource Book

Grade 12

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## **Message from the Director General**

The National Institute of Education takes opportune steps from time to time for the development of quality in education. Preparation of supplementary resource books for respective subjects is one such initiative.

Supplementary resource books have been composed by a team of curriculum developers of the National Institute of Education, subject experts from the national universities and experienced teachers from the school system. Because these resource books have been written so that they are in line with the G. C. E. (A/L) new syllabus implemented in 2017, students can broaden their understanding of the subject matter by referring these books while teachers can refer them in order to plan more effective learning teaching activities.

I wish to express my sincere gratitude to the staff members of the National Institute of Education and external subject experts who made their academic contribution to make this material available to you.

**Dr. (Mrs.) T. A. R. J. Gunasekara**

Director General

National Institute of Education

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## **Message from the Director**

Since 2017, a rationalized curriculum, which is an updated version of the previous curriculum is in effect for the G.C.E (A/L) in the general education system of Sri Lanka. In this new curriculum cycle, revisions were made in the subject content, mode of delivery and curricular materials of the G.C.E. (A/L) Physics, Chemistry and Biology. Several alterations in the learning teaching sequence were also made. A new Teachers' Guide was introduced in place of the previous Teacher's Instruction Manual. In concurrence to that, certain changes in the learning teaching methodology, evaluation and assessment are expected. The newly introduced Teachers' Guide provides learning outcomes, a guideline for teachers to mould the learning events, assessment and evaluation.

When implementing the previous curricula, the use of internationally recognized standard textbooks published in English was imperative for the Advanced Level science subjects. Due to the contradictions of facts related to the subject matter between different textbooks and inclusion of the content beyond the limits of the local curriculum, the usage of those books was not convenient for both teachers and students. This book comes to you as an attempt to overcome that issue.

As this book is available in Sinhala, Tamil, and English, the book offers students an opportunity to refer the relevant subject content in their mother tongue as well as in English within the limits of the local curriculum. It also provides both students and teachers a source of reliable information expected by the curriculum instead of various information gathered from the other sources.

This book authored by subject experts from the universities and experienced subject teachers is presented to you followed by the approval of the Academic Affairs Board and the Council of the National Institute of Education. Thus, it can be recommended as a material of high standard.

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Director

Department of Science

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Director General

National Institute of Education

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Director, Department of Science

National Institute of Education

**Mr. R. S. J. P. Uduporuwa**

Former Director, Department of Science

National Institute of Education

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#### **Cover Page**

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#### **Supporting Staff**

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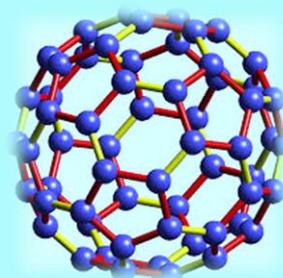
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# 4. Chemistry of s, p and d Block Elements



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## Introduction

This section describes the physical and chemical properties of elements in *s*, *p* and *d* blocks. This section will help to identify trends and patterns among elements in the periodic table.

### *s* Block Elements

#### 4.1 Group 1 elements

All Group 1 elements are metals except hydrogen which is a nonmetal. Unlike most other metals, they have low densities. All Group 1 elements have the valence shell electron configuration of  $ns^1$  therefore, they are highly reactive.

Sodium can be found naturally as various salts such as NaCl (rock salt) and  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  (borax). Some examples of naturally occurring potassium salts are KCl (sylvite) and  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (carnallite).

##### 4.1.1 Group trends

All alkali metals are lustrous. They are high electrical and thermal conductors. These metals are soft and become even softer when progress down the group. The melting point of Group 1 metals decreases down the group. The values given in Table 4.1 below can be used to understand the trends among these elements. Group 1 metals always show oxidation number of +1 when they form compounds. Most compounds are stable ionic solids.

**Table 4.1** Properties of Group 1 elements

	Li	Na	K	Rb	Cs
Ground state electronic configuration	$[\text{He}]2s^1$	$[\text{Ne}]3s^1$	$[\text{Ar}]4s^1$	$[\text{Kr}]5s^1$	$[\text{Xe}]6s^1$
Metallic radius/ pm	152	186	231	244	262
Melting point/ °C	180	98	64	39	29
Radius of $\text{M}^+$ / pm	60	95	133	148	169
1 <sup>st</sup> ionization energy/ $\text{kJ mol}^{-1}$	520	495	418	403	375
2 <sup>nd</sup> ionization energy/ $\text{kJ mol}^{-1}$	7298	4562	3052	2633	2234

Increase in the atomic radius from Li to Cs makes the ionization energy of these elements to decrease down the group, and this can be used to explain the chemical properties of Group 1 elements. Reactivity of the Group 1 elements increases down the group.

\*\* When writing equations in inorganic chemistry, it is not always essential to indicate the physical state of reactants or products. However, always balance equations must be written to consider as a complete answer.

**4.1.2 Reactions of Group 1 elements**

With oxygen (O <sub>2</sub> )	$4M + O_2 \longrightarrow 2M_2O$
With excess oxygen (O <sub>2</sub> ) Na form peroxides	$2Na + O_2 \longrightarrow Na_2O_2$
With excess oxygen (O <sub>2</sub> ) K, Rb and Cs form superoxides	$M + O_2 \longrightarrow MO_2$
With nitrogen (N <sub>2</sub> ) only Li forms stable nitride	$6Li + N_2 \longrightarrow 2Li_3N$
With hydrogen (H <sub>2</sub> )	$2M + H_2 \longrightarrow 2MH$
With water (H <sub>2</sub> O)	$2M + 2H_2O \longrightarrow 2MOH + H_2$
With acids (H <sup>+</sup> )	$2M + 2H^+ \longrightarrow 2M^+ + H_2$

**Reaction with water**

Group 1 metals show an increase in reactivity with water down the group. The reactivity trend with water is as follows.

Li	Na	K	Rb	Cs
Gently	Vigorously	Vigourously with ignition	Explosively	Explosively

Lithium reacts non-vigorously with water or with water vapour available in the air to produce lithium hydroxide and hydrogen gas. However, both sodium and potassium react vigorously with water to produce metal hydroxide and hydrogen gas. These reactions are highly exothermic except with Li.

**Reactions with oxygen/ air**

Lithium can react both with oxygen and nitrogen. When heated, lithium burns to produce lithium oxide (Li<sub>2</sub>O), a white powder. With nitrogen gas, lithium gives lithium nitride (Li<sub>3</sub>N). However, both sodium and potassium do not react with nitrogen gas. When sodium is burnt in air, sodium peroxide is mainly produced with some sodium oxide. In contrast, when potassium is burnt in air, potassium superoxide is formed as the main product with some potassium oxide and peroxide. Oxidation numbers of oxygen in sodium or potassium peroxide are -1 and in potassium superoxide, oxidation numbers are -1 and 0.

Group 1 metal oxides react with water to produce metal hydroxides as shown below.



When heated, lithium forms lithium nitride with nitrogen. Only lithium forms a stable alkali-metal nitride. With water, lithium nitride produces ammonia and lithium hydroxide.



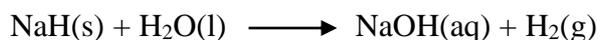
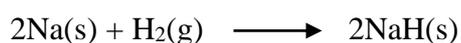
Group 1 hydroxides react with carbon dioxide to produce relevant carbonates. These carbonates can further react with carbon dioxide to produce metal hydrogen carbonates.



Sodium hydrogen carbonate is less soluble than sodium carbonates in water.

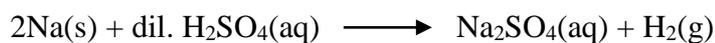
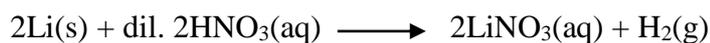
### Reactions with hydrogen gas

Group 1 elements react with hydrogen to produce solid, ionic metal hydrides. In these hydrides, hydrogen has the oxidation number of  $-1$ . These metal hydrides react vigorously with water to produce hydrogen gas.



### Reactions with acids

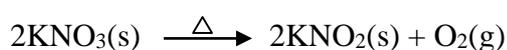
Lithium, sodium and potassium react vigorously with dilute acids to produce hydrogen gas and relevant metal salts. These reactions are highly exothermic and explosive. A few selected reactions are shown below.



#### 4.1.3 Thermal stability of salts

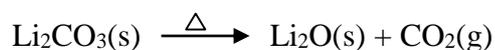
##### Decomposition of nitrates

Group 1 nitrates are used as fertilizers and explosives. These nitrates decompose upon heating.  $\text{LiNO}_3$  decomposes to produce lithium oxide, nitrogen dioxide and oxygen. However, the other Group 1 nitrates on heating produce relevant metal nitrite and oxygen.



**Decomposition of carbonates**

Carbonates are stable and they will melt before they decompose into oxides. However,  $\text{Li}_2\text{CO}_3$  is less stable and decomposes readily.

**Decomposition of bicarbonates**

Decomposition of bicarbonates of Group 1 is shown below.



Thermal stability increases down the group.

**4.1.4 Solubility of Group 1 salts**

All Group 1 salts are soluble in water except some lithium salts such as  $\text{LiF}$ ,  $\text{Li}_2\text{CO}_3$  and  $\text{Li}_3\text{PO}_4$ . All these salts are white solids unless the salt anion is a coloured ion.

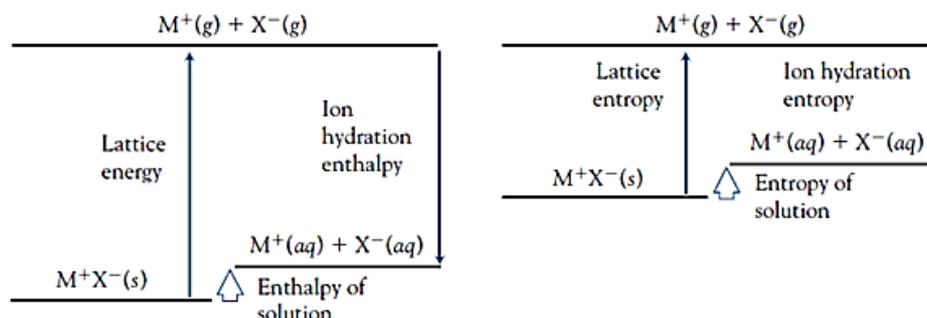
Solubility of Group 1 halides increase down the group is shown in Table 4.2.

**Table 4.2** The solubility of halides of sodium

Salt	Solubility/ mol L <sup>-1</sup>
NaF	0.99
NaCl	6.2
NaBr	9.2
NaI	12.3

Variation in the solubility can be understood using the energy cycle for the solvation of ionic solids. The solubility can be explained using Gibbs free energy. For almost all ionic solids of Group 1, are soluble in water due to the negative Gibbs free energy in the solvation process.

Enthalpy and entropy cycles for the solvation process are shown below.



**Figure 4.1** Enthalpy and entropy cycles for the solvation process

Using these two energy cycles, enthalpy and entropy change of solvation can be calculated and these calculated values are given in Table 4.3. Free energy is calculated using the equation,

$$\Delta G^{\theta} = \Delta H^{\theta} - T \Delta S^{\theta}$$

**Table 4.3** Free energy change of salts during solvation

Salt	Enthalpy change/ kJ mol <sup>-1</sup>	Entropy change × T (K × kJ mol <sup>-1</sup> K <sup>-1</sup> )	Free energy change/ kJ mol <sup>-1</sup>
NaF	+ 1	-2	+3
NaCl	+ 4	+13	-9
NaBr	-1	+18	-19
NaI	-9	+23	-32

Calculated Gibbs free energies match with the solubility trend for the sodium halides. The free energy change gets more negative from sodium fluoride to sodium iodide.

#### 4.1.5 Flame test

The flame test can be used to identify alkali metals and their compounds. Flame colours of Group 1 metals and compounds are given below.

Lithium – Crimson red

Sodium – Yellow

Rubidium – Red-violet

Caesium – Blue - violet

Potassium – Lilac

#### 4.2 Group 2 elements

Group 2 elements are known as alkaline earth metals. They are less reactive than Group 1 metals due to its valence shell  $ns^2$  electron configuration.

Both calcium and magnesium can be found naturally in dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ). Magnesite ( $\text{MgCO}_3$ ), kieserite ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ) and carnallite ( $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ ) are

examples of minerals with magnesium. Fluoroapatite  $[3(\text{Ca}_3(\text{PO}_4)_2) \cdot \text{CaF}_2]$  and gypsum  $(\text{CaSO}_4 \cdot 2\text{H}_2\text{O})$  are commercially important calcium containing minerals.

#### 4.2.1 Group trends

Beryllium and magnesium are greyish metals and other Group 2 metals are soft and silvery in colour. Group 2 metal oxides produce basic oxides except for BeO which shows amphoteric properties. Beryllium behaves similar to Al and this can be understood using the diagonal relationship between Al and Be in the periodic table.

Elements of Group 2 have higher densities and stronger metallic bonds compared to the Group 1 metals. This is due to the availability of a greater number of electrons to form a stronger metallic bond and their smaller size in atomic radii.

The first ionization energies of Group 2 elements are higher than that of Group 1 elements due to their electron configuration of  $ns^2$ . Elements become more reactive and produce +2 oxidation state easily down the group. The properties of Group 2 elements are given in Table 4.4.

**Table 4.4** Properties of Group 2 elements

	Be	Mg	Ca	Sr	Ba
Ground state electronic configuration	$[\text{He}]2s^2$	$[\text{Ne}]3s^2$	$[\text{Ar}]4s^2$	$[\text{Kr}]5s^2$	$[\text{Xe}]6s^2$
Metallic radius/ pm	112	160	197	215	224
Melting point/ °C	1560	923	1115	1040	973
Radius of $\text{M}^{2+}$ / pm	30	65	99	113	135
1 <sup>st</sup> ionization energy/ kJ mol <sup>-1</sup>	899	736	589	594	502
2 <sup>nd</sup> ionization energy/ kJ mol <sup>-1</sup>	1757	1451	1145	1064	965
3 <sup>rd</sup> ionization energy/ kJ mol <sup>-1</sup>	14850	7733	4912	4138	3619

**4.2.2 Reactions of alkaline earth Group 2 elements**

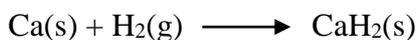
With oxygen (O <sub>2</sub> )	$2M + O_2 \longrightarrow 2MO$
With excess oxygen (O <sub>2</sub> ) Ba forms its peroxide	$Ba + O_2 \longrightarrow BaO_2$
With nitrogen (N <sub>2</sub> ), at high temperatures	$3M + N_2 \longrightarrow M_3N_2$
With water (H <sub>2</sub> O(l)), at room temperature (e.g.: Ca, Sr and Ba)	$M + 2H_2O \longrightarrow M(OH)_2 + H_2$
With hot water (H <sub>2</sub> O(l)) (e.g.: Mg reacts slow)	$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$
With steam (H <sub>2</sub> O(g))	$Mg + H_2O \longrightarrow MgO + H_2$
With acids (H <sup>+</sup> )	$M + 2H^+ \longrightarrow M^{2+} + H_2$
With hydrogen (H <sub>2</sub> ), at high temperatures with Ca, Sr, Ba at high pressure with Mg	$M + H_2 \longrightarrow MH_2$
With concentrated acids	$Mg + 2H_2SO_4 \longrightarrow MgSO_4 + SO_2 + 2H_2O$ $Mg + 4HNO_3 \longrightarrow Mg(NO_3)_2 + 2NO_2 + 2H_2O$

**Reaction with water**

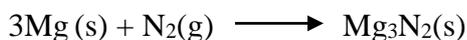
Beryllium does not react with water, but it reacts with steam. The reaction of magnesium with water at room temperature is negligible. However, magnesium reacts slowly with hot water. Calcium, strontium and barium react readily with cold water. Reaction with water produces metal hydroxide and hydrogen gas.

**Reactions with hydrogen**

All Group 2 elements, except Be, react with hydrogen to produce metal hydrides which are ionic solids. In these hydrides, hydrogen has an oxidation number of – 1. These metal hydrides (not violent as Group 1) react vigorously with water to produce hydrogen gas.

**Reaction with nitrogen**

All Group 2 elements burns in nitrogen to form M<sub>3</sub>N<sub>2</sub>, nitrides. These nitrides react with water to produce ammonia in the same way as lithium does.



### 4.2.3 Thermal stability of salts

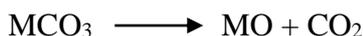
#### Decomposition of nitrates

Upon heating, Group 2 nitrates behave much similar to lithium nitrate. Group 2 nitrates decompose to produce metal oxide, nitrogen dioxide and oxygen. All Group 2 nitrates are soluble in water.



#### Decomposition of carbonates

Thermal stability of these carbonates increases down the group. Thermal stability of these carbonates increases with the size of the cation. The polarizing power of the cation decreases down the group due to the decrease of charge density of the cation. Carbonate anion attached to  $\text{Mg}^{2+}$  cation is highly polarized than that of carbonate attached to  $\text{Ba}^{2+}$ . Highly polarized carbonate anion can undergo decomposition easily and this explains the lower decomposition temperature of  $\text{MgCO}_3$  than that of  $\text{BaCO}_3$ . The general decomposition of metal carbonates is shown below.



Decomposition temperature increases from 540 °C for  $\text{MgCO}_3$  to 1360 °C for  $\text{BaCO}_3$ .

#### Decomposition of bicarbonates

Group 2 hydrogen carbonates are only stable in aqueous solutions and solid Group 2 hydrogen carbonates are not stable at room temperature.



### 4.2.4 Solubility of Group 2 salts

Solubility of Group 2 changes depending on the compound. Some compounds such as nitrate, nitrite, halides, hydroxides, sulphides, bicarbonates all are soluble in water.

The solubility varies down the group for certain compounds such as hydroxides, sulphate, sulphite, carbonate, phosphate and oxalate showing the patterns given in Table 4.5.

Salts of Group 2 metals with uninegative anions, such as chloride and nitrates are generally soluble. However, salts formed with anions containing more than one negative charge, such as carbonates and phosphates, are insoluble. All carbonates are insoluble except  $\text{BeCO}_3$ . Hydrogen carbonates are more soluble than carbonates. The solubility of Group 2 sulphates changes from soluble to insoluble when comparing solubility from  $\text{MgSO}_4$  to  $\text{BaSO}_4$ . On the other hand, hydroxides change solubility from insoluble to soluble when moving down the group. For example,  $\text{Mg}(\text{OH})_2$  is sparingly soluble whereas  $\text{Ba}(\text{OH})_2$  is soluble and produces a strongly basic solution.

**Table 4.5** Solubility of Group 1 and 2 compounds

	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>
Cl <sup>-</sup>	aq	aq	aq	aq	aq	aq
Br <sup>-</sup>	aq	aq	aq	aq	aq	aq
I <sup>-</sup>	aq	aq	aq	aq	aq	aq
OH <sup>-</sup>	aq	aq	IS	SS	SS	aq
CO <sub>3</sub> <sup>2-</sup>	aq	aq	IS	IS	IS	IS
HCO <sub>3</sub> <sup>-</sup>	aq	aq	aq	aq	aq	aq
NO <sub>2</sub> <sup>-</sup>	aq	aq	aq	aq	aq	aq
NO <sub>3</sub> <sup>-</sup>	aq	aq	aq	aq	aq	aq
S <sup>2-</sup>	aq	aq	aq	aq	aq	aq
SO <sub>3</sub> <sup>2-</sup>	aq	aq	SS	IS	IS	IS
SO <sub>4</sub> <sup>2-</sup>	aq	aq	aq	SS	IS	IS
PO <sub>4</sub> <sup>3-</sup>	aq	aq	IS	IS	IS	IS
CrO <sub>4</sub> <sup>2-</sup>	aq	aq	aq	aq	IS	IS
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	aq	aq	SS	IS	IS	SS

*aq – soluble, IS – insoluble, SS – sparingly soluble*

**4.2.5 Flame test**

Alkaline earth metals and compounds produce characteristic colours with the flame, and the flame test can be used to identify these elements using the flame colors shown below.

Calcium – Orange-red

Strontium – Crimson red

Barium – Yellowish-green

**p Block Elements****4.3 Group 13 elements****4.3.1 Group trends**

Boron is a metalloid, and most of the boron compounds are covalent. However, aluminium is a metal with amphoteric properties. Gallium, indium and thallium are metals. The first member, B, of Group 13 is different from the other members due to its smaller atomic radius. Boron shows a strong diagonal relationship with Si in Group 14. All elements in Group 13 produce +3 oxidation state. The properties of Group 13 elements are given in Table 4.6.

**Table 4.6** Properties of Group 13 elements

	<b>**B</b>	<b>Al</b>	<b>**Ga</b>	<b>**In</b>	<b>**Tl</b>
Ground state electronic configuration	[He]2s <sup>2</sup> 2p <sup>1</sup>	[Ne]3s <sup>2</sup> 3p <sup>1</sup>	[Ar]3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>1</sup>	[Kr]4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>1</sup>	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>1</sup>
Metallic radius/ pm	-	143	153	167	171
Covalent radius/ pm	88	130	122	150	155
Melting point/ °C	2300	660	30	157	304
Radius of M <sup>3+</sup> / pm	27	53	62	80	89
1 <sup>st</sup> ionization energy/ kJ mol <sup>-1</sup>	799	577	577	556	590
2 <sup>nd</sup> ionization energy/ kJ mol <sup>-1</sup>	2427	1817	1979	1821	1971
3 <sup>rd</sup> ionization energy/ kJ mol <sup>-1</sup>	3660	2745	2963	2704	2878

*\*\*Not a part of current G. C. E. (A/L) syllabus*

**4.3.2 Aluminium**

Aluminium is the third most abundant element in the earth crust. The exposed surface of aluminium produces a layer of Al<sub>2</sub>O<sub>3</sub>. This layer makes aluminium resistant to further reactions with oxygen. Due to this impermeable layer, Al can be considered as a non-reactive element with air.

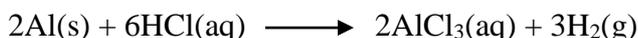
**Reactions of aluminium**

Aluminium reacts readily with O<sub>2</sub> and halogens. Also, it reacts with N<sub>2</sub>.

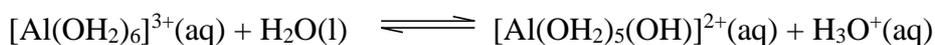




Aluminum is less reactive than Groups 1 and 2 elements. Similar to beryllium, aluminium reacts with both acids and bases. The equations for the reactions of Al with acids and bases are given below.



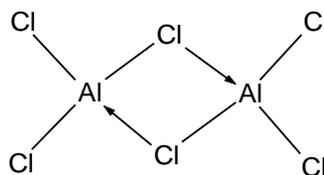
Aluminium ion in aqueous solution is expected to be present as hexaaquaaluminium ion. However, hydrolysis of Al<sup>3+</sup> produces [Al(OH<sub>2</sub>)<sub>5</sub>(OH)]<sup>2+</sup> (pentaquaahydroxidoaluminium ion) and then produces [Al(OH<sub>2</sub>)<sub>4</sub>(OH)<sub>2</sub>]<sup>+</sup> (tetraquadihydroxidoaluminium ion) as shown below.



Addition of OH<sup>-</sup> ions to aluminum ions first produces a gelatinous precipitate of aluminum hydroxide. With excess OH<sup>-</sup> ions, the precipitated aluminum hydroxide is converted to tetrahydroxidoaluminate complex ion.



Group 13 elements can have six electrons in their valence shell by forming three covalent bonds due to their ns<sup>2</sup>np<sup>1</sup> electron configuration. As a result, many of the Group 13 covalent compounds have an incomplete octet, so can act as Lewis acids to accept a pair of electrons from a donor. These compounds with incomplete octet are called **electron deficient compounds**. Both B and Al compounds with incomplete octet form dimers in the gaseous phase to satisfy the octet rule (Figure 4.2).



**Figure 4.2** Structure of gaseous Al<sub>2</sub>Cl<sub>6</sub>

## 4.4 Group 14 elements

### 4.4.1 Group trends

Due to the formation of covalent bond network structure, the first three elements of group 14 have high melting points. Carbon is a nonmetal, whereas silicon and germanium are metalloids. Last two elements in the group, tin and lead are metals.

Carbon can be found in nature mainly in coal, crude oil, calcite ( $\text{CaCO}_3$ ),  $\text{CO}_2$  in air, magnesite ( $\text{MgCO}_3$ ) and dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ). Graphite, diamond and fullerenes are the allotropic forms of carbon. Fullerenes are recently found, and most well-known fullerene is  $\text{C}_{60}$ , buckminsterfullerene (or bucky-ball). Carbon is the basis of life and the most important element in organic chemistry. Silicon and germanium are mainly used in the semiconductor industries. In addition, silicon is heavily used in inorganic polymer industry.

The properties of Group 14 elements are given in Table 4.7.

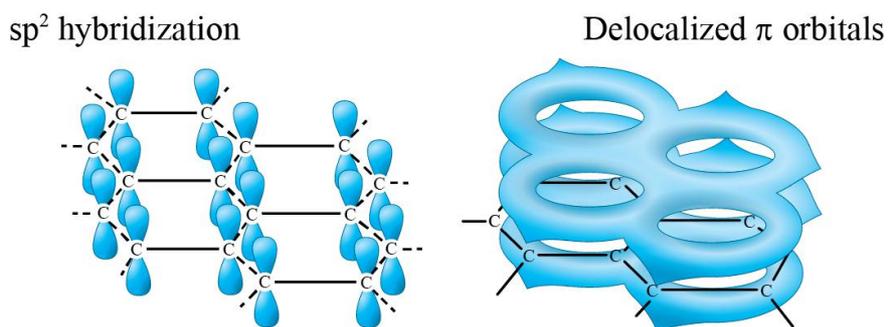
**Table 4.7** Properties of Group 14 elements

	<b>C</b>	<b>**Si</b>	<b>**Ge</b>	<b>**Sn</b>	<b>**Pb</b>
<b>Ground state electronic configuration</b>	$[\text{He}]2s^22p^2$	$[\text{Ne}]3s^23p^2$	$[\text{Ar}]3d^{10}4s^24p^2$	$[\text{Kr}]3d^{10}5s^25p^2$	$[\text{Xe}]4f^{14}5d^{10}6s^26p^2$
<b>Metallic radius/ pm</b>	-	-	-	158	175
<b>Covalent radius/ pm</b>	77	118	122	140	154
<b>Melting point/ °C</b>	3730	1410	937	232	327
<b>Radius of <math>\text{M}^{4+}</math>/ pm</b>	-	-	53	69	78

*\*\*Not a part of current G. C. E. (A/L) Chemistry syllabus*

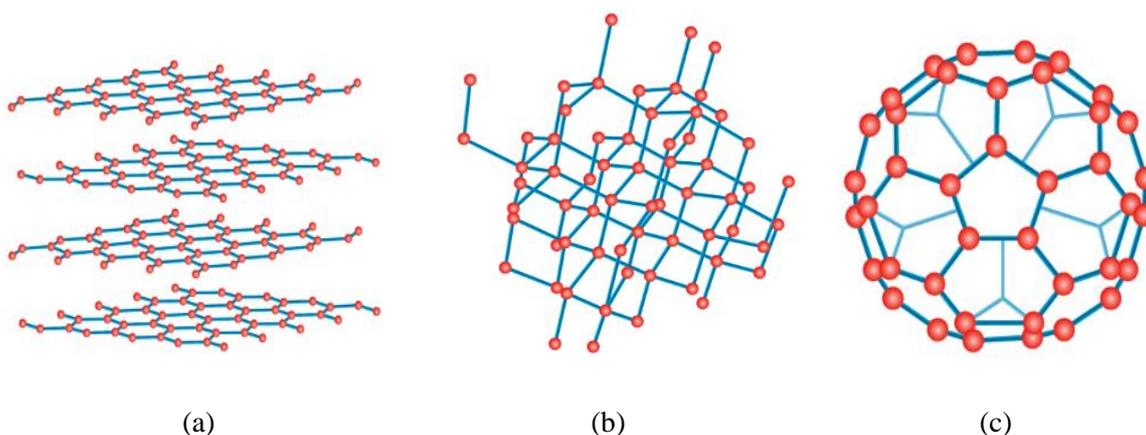
### 4.4.2 Diamond and graphite

Diamond and graphite are composed of homoatomic (same atoms) lattice structures. Diamond ( $sp^3$  hybridized carbon, tetrahedral) has a cubic crystalline structure. Graphite ( $sp^2$  hybridized carbon, trigonal planar) has stacked two-dimensional carbon layers. Carbon-carbon bonds in graphite are shorter than that of diamond (diamond 154 pm and graphite 141 pm) due to the hybridization of carbon atoms. These two crystalline lattice structures are hard however diamond structure is the strongest lattice. Graphite is an electrical and a thermal conductor due to delocalizing  $\pi$  electrons (Figure 4.3). Interactions between layers of carbon in graphite are weak and this makes graphite a good lubricant.



**Figure 4.3** Delocalizing  $\pi$  bonds of graphite

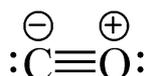
Fullerenes are another series of carbon allotropes. In fullerenes, carbon atoms are connected in a spherical manner. Structures of graphite, diamond and fullerene ( $C_{60}$ ) are shown in Figure 4.4.



**Figure 4.4** Structures of (a) graphite, (b) diamond and (c) fullerene ( $C_{60}$ )

#### 4.4.3 Carbon monoxide and carbon dioxide

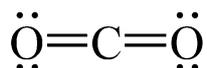
Carbon monoxide is a colourless, odourless, highly poisonous gas. Bond enthalpy of carbon monoxide is more than that of the  $C=O$  double bond. In carbon monoxide,  $CO$  bond length is shorter than that of a typical  $C=O$  double bond. This suggests that the bonding between  $C$  and  $O$  in carbon monoxide is not a typical  $C=O$  double bond. It has a triple bond nature between the two atoms of  $C$  and  $O$ . The Lewis structure of  $CO$  is shown in Figure 4.5.



**Figure 4.5** The Lewis structure of  $CO$

Carbon monoxide is mostly used as a reducing agent in the production of iron. Also, CO plays an important role in many catalytic reactions as a ligand due to the lone pair of electrons on the C atom.

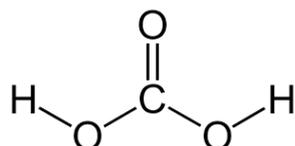
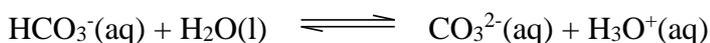
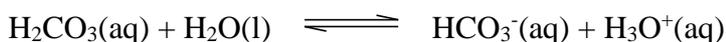
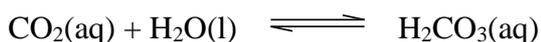
Carbon dioxide (Figure 4.6) solidifies due to London forces at low temperatures and/ or under high pressures. Solid CO<sub>2</sub> (dry ice) sublimates to produce gaseous carbon dioxide under normal atmospheric conditions. It is commonly used as a freezing agent in the food industry and to produce artificial rain.



**Figure 4.6** The Lewis structure of CO<sub>2</sub>

#### 4.4.4 Oxoacid of carbon

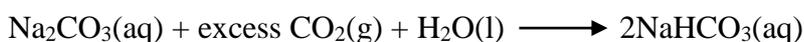
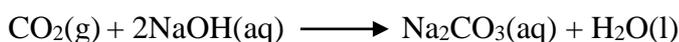
Oxoacid of carbon is referred to as carbonic acid (H<sub>2</sub>CO<sub>3</sub>) which is a weak acid. The bond structure of H<sub>2</sub>CO<sub>3</sub> is given in Figure 4.7. Carbonic acid can be prepared by dissolving CO<sub>2</sub> in water under pressure.



**Figure 4.7** The bond structure of H<sub>2</sub>CO<sub>3</sub>

Hydrogen atom which is directly connected to oxygen atom can be released as a proton to the solution by exhibiting the acidic property of carbonic acid.

Carbon dioxide reacts with bases to produce carbonates showing its acidic property. In the presence of excess CO<sub>2</sub> thus formed carbonates of Group 1 and 2 produce hydrogen carbonates.



## 4.5 Group 15 elements

### 4.5.1 Group trends

The first element, nitrogen of Group 15 shows different properties from the other elements in this group (Table 4.8). Metallic character of the Group 15 elements increases down the group. Nitrogen and phosphorous are nonmetals and show oxidation numbers -3 to +5. Nitrogen can achieve +5 oxidation state with oxygen and fluorine. Dinitrogen, N<sub>2</sub> is greatly stable (inert) under normal conditions due to strong triple bond (942 kJ mol<sup>-1</sup>). Except nitrogen, all the other elements exist as solids. The higher electronegativity, the smaller atomic radius and the absence of *d* orbitals make nitrogen different from the other elements in the group.

**Table 4.8** Properties of Group 15 elements

	N	**P	**As	**Sb	**Bi
Ground state electronic configuration	[He]2s <sup>2</sup> 2p <sup>3</sup>	[Ne]3s <sup>2</sup> 3p <sup>3</sup>	[Ar]3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>3</sup>	[Kr]3d <sup>10</sup> 5s <sup>2</sup> 5p <sup>3</sup>	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>3</sup>
Metallic radius/ pm	-	-	-	-	182
Covalent radius/ pm	75	110	122	143	152
Melting point/ °C	-210	44 (white) 590 (red)	613	630	271
Pauling electronegativity	3.0	2.2	2.2	2.0	2.0

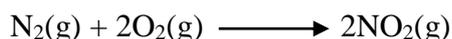
*\*\*Not relevant to the current G. C. E. (A/L) Chemistry syllabus*

### 4.5.2 Chemistry of nitrogen

Nitrogen (boiling point is 195.8 °C) is slightly soluble in water under atmospheric pressure, but the solubility greatly increases with pressure. Nitrogen does not form allotropes. Dinitrogen shows only a few reactions and one of them is given below.



Since nitrogen is an inert gas its chemical reactions occur under strong conditions. For an instance nitrogen gas reacts with oxygen in the presence of external energy from an electrical spark. This reaction naturally occurs in lightening.



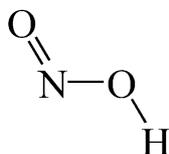
Nitrogen shows oxidation states from -3 to +5. Compounds with these oxidation states are shown in Table 4.9.

Table 4.9 Oxidation states of nitrogen

Oxidation state	Compound	Formula	Bond structure
-3	Ammonia	NH <sub>3</sub>	$\begin{array}{c} \text{H} \\   \\ \text{N}-\text{H} \\   \\ \text{H} \end{array}$
-2	Hydrazine	N <sub>2</sub> H <sub>4</sub>	$\begin{array}{c} \text{H} \qquad \text{H} \\   \qquad   \\ \text{N}-\text{N} \\   \qquad   \\ \text{H} \qquad \text{H} \end{array}$
-1	Hydroxylamine	NH <sub>2</sub> OH	$\begin{array}{c} \text{H} \\   \\ \text{N}-\text{O} \\   \qquad   \\ \text{H} \qquad \text{H} \end{array}$
0	Dinitrogen	N <sub>2</sub>	N≡N
+1	Dinitrogen monoxide	N <sub>2</sub> O	$\text{N}^{\ominus}=\text{N}^{\oplus}=\text{O} \leftrightarrow \text{N}\equiv\text{N}^{\ominus}-\text{O}^{\oplus}$
+2	Nitrogen monoxide	NO	$\cdot\text{N}=\text{O}$
+3	Dinitrogen trioxide	N <sub>2</sub> O <sub>3</sub>	$\begin{array}{c} \text{O}^{\ominus} \\   \\ \text{O}=\text{N}^{\oplus}-\text{N}=\text{O} \end{array}$
+4	Nitrogen dioxide	NO <sub>2</sub>	$\begin{array}{c} \text{O}^{\ominus} \\   \\ \text{O}=\text{N}^{\oplus}-\text{O}^{\ominus} \end{array}$
+4	Dinitrogen tetroxide	N <sub>2</sub> O <sub>4</sub>	$\begin{array}{c} \text{O}^{\ominus} \qquad \text{O}^{\ominus} \\   \qquad   \\ \text{O}=\text{N}^{\oplus}-\text{N}^{\oplus}=\text{O} \\   \qquad   \\ \text{O}^{\ominus} \qquad \text{O}^{\ominus} \end{array} \leftrightarrow \begin{array}{c} \text{O}^{\ominus} \qquad \text{O}^{\ominus} \\   \qquad   \\ \text{O}=\text{N}^{\oplus}-\text{N}^{\oplus}=\text{O} \\   \qquad   \\ \text{O}^{\ominus} \qquad \text{O}^{\ominus} \end{array}$
+5	Nitric acid	HNO <sub>3</sub>	$\begin{array}{c} \text{O}^{\ominus} \\   \\ \text{HO}-\text{N}^{\oplus}=\text{O} \end{array}$
+5	Dinitrogen pentoxide	N <sub>2</sub> O <sub>5</sub>	$\begin{array}{c} \text{O}^{\ominus} \qquad \text{O}^{\ominus} \\   \qquad   \\ \text{O}=\text{N}^{\oplus}-\text{O}-\text{N}^{\oplus}=\text{O} \\   \qquad   \\ \text{O}^{\ominus} \qquad \text{O}^{\ominus} \end{array} \leftrightarrow \begin{array}{c} \text{O}^{\ominus} \qquad \text{O}^{\ominus} \\   \qquad   \\ \text{O}=\text{N}^{\oplus}-\text{O}-\text{N}^{\oplus}=\text{O} \\   \qquad   \\ \text{O}^{\ominus} \qquad \text{O}^{\ominus} \end{array}$

### 4.5.3 Oxoacids of nitrogen

Nitrous acid which is unstable under normal atmospheric conditions is a weak acid. The bond structure of nitrous acid is given in Figure 4.8.

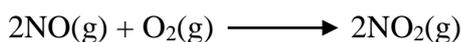


**Figure 4.8** The bond structure of nitrous acid

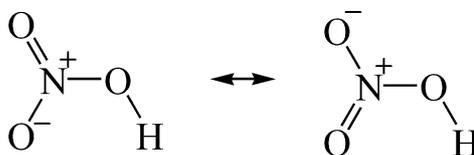
Nitrous acid can undergo disproportionation to produce nitric acid and nitrogen monoxide which is a colourless gas.



Further reaction of nitrogen monoxide with oxygen forms nitrogen dioxide which is redish brown in colour.



Nitric acid (Figure 4.9) is an oily and hazardous liquid. This acid is a strong oxidizing agent and can undergo vigorous chemical reactions.



**Figure 4.9** The bond structure of nitric acid

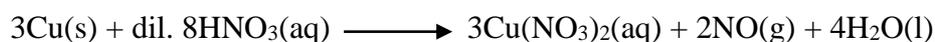
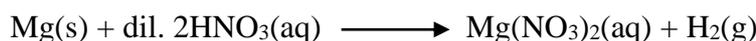
Due to the light-induced decomposition, nitric acid produces oxygen and nitrogen dioxide.



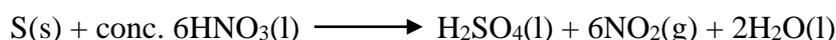
Due to this reason concentrated nitric acid is stored in brown colour glass bottles in laboratories.

### Oxidizing and reducing reactions of nitric acid

Dilute nitric acid reacts with metals to produce metal nitrate and hydrogen gas. In these reactions nitric acid acts as an oxidizing agent with respect to hydrogen. When magnesium and copper reacts with concentrated nitric acid it acts as an oxidizing agent with respect to nitrogen.



The reactions of conc.  $\text{HNO}_3$  acting as an oxidizing agent with non metals such as carbon and sulphur are given below.

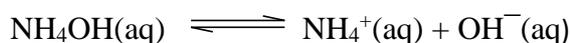


#### 4.5.4 Ammonia and ammonium salts

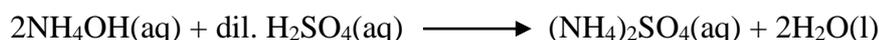
Ammonia is a colourless gas with a strong characteristic smell. Ammonia is a basic gas which is readily soluble in water.



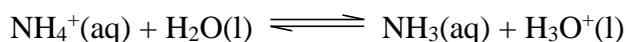
Ammonium hydroxide is a weak base and partially dissociates to produce ammonium ions and hydroxide ions.



Like any other base it reacts with dilute acids to produce aqueous salts.



Hydrolysis of the ammonium ion in aqueous solution produces the conjugate base, ammonia.



All ammonium salts reacts with alkali to liberate ammonia.

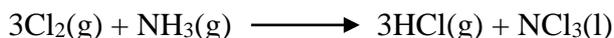


#### Reactions of ammonia

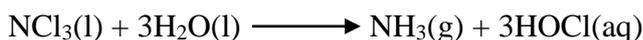
Ammonia acts as a reducing agent with chlorine, and the products vary with the amount of ammonia and chlorine used. In the presence of excess ammonia, chlorine produces nitrogen gas as one of the products. However, with excess chlorine, nitrogen trichloride is produced as one of the products, which is used for water disinfection.



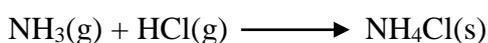
The formed HCl further reacts with unreacted ammonia to form  $\text{NH}_4\text{Cl}$ , excess chlorine,



Nitrogen trichloride is a covalent chloride. It reacts with water to produce ammonia and hypochlorous acid. Due to the ability to produce hypochlorous acid, nitrogen trichloride is used as a water disinfecting agent.



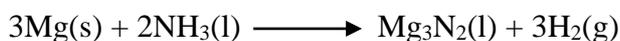
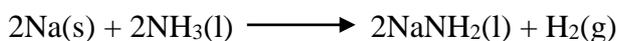
Gaseous ammonia reacts with hydrogen chloride to produce a white smoke of solid ammonium chloride. This can be used as a confirmation test for ammonia.



Ammonia acts as a weak reducing agent with CuO and  $\text{Cl}_2$ .



Ammonia can act as an oxidizing agent as well as an acid with metals under dry condition.



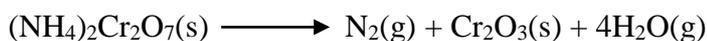
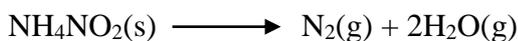
### Thermal decomposition of ammonium salts

Some ammonium salts decompose upon heating to ammonia gas and to the acidic gas.



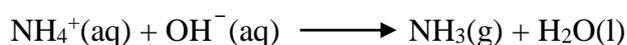
\*Products of this reaction can vary with conditions.

However, anions in some ammonium salts can oxidize the ammonium ion to produce many products upon heating.

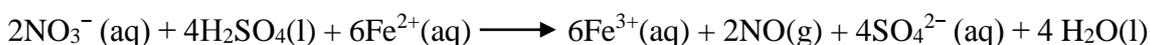


**Identification of ammonium salts**

All ammonium salts produce ammonium gas with NaOH on warming. This gas produces white fumes of ammonium chloride when a glass rod moistened with concentrated hydrochloric acid.

**Reactions of nitrate**

Reaction of nitrate with iron(II)/ conc. sulphuric acid can be used to identify nitrate ion. This test is known as brown ring test. The brown coloured  $[\text{Fe}(\text{NO})]^{2+}$  ring formed in the test tube, confirms the presence of nitrate.



Nitrate reacts with Al/ NaOH to produce ammonia.

**4.6 Group 16 elements****4.6.1 Group trends**

First element, oxygen of Group 16 shows different properties to the other elements in the group. Metallic nature increases going down the group. However, none of the Group 16 elements behaves as true metals. Both oxygen and sulphur are non-metals and other elements in the group show metallic and nonmetallic properties. Only oxygen exists as a gas, and other elements in the group are solids. Except for oxygen, other elements in the group can form even-numbered oxidation states from +6 to -2. Stability of +6 and -2 oxidation states decreases down the group whereas the stability of the +4 oxidation state increases.

**Table 4.10** Properties of Group 16 elements

	O	S	**Se	**Te	**Po
Ground state electronic configuration	[He]2s <sup>2</sup> 2p <sup>4</sup>	[Ne]3s <sup>2</sup> 3p <sup>4</sup>	[Ar]3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>4</sup>	[Kr]4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>4</sup>	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>4</sup>
Ionic radius X <sup>2-</sup> / pm	140	184	198	221	-
Covalent radius/ pm	73	103	117	137	140
Melting point/ °C	-218	113(α)	217	450	254
Pauling electronegativity	3.4	2.6	2.6	2.1	2.0
1 <sup>st</sup> electron gain enthalpy/ kJ mol <sup>-1</sup> X(g) + e → X <sup>-</sup> (g)	-141	-200	-195	-190	-183
2 <sup>nd</sup> electron gain enthalpy/ kJ mol <sup>-1</sup> X <sup>-</sup> (g) + e → X <sup>2-</sup> (g)	844	532	-	-	-

*\*\* Not a part of the current G. C. E. (A/L) Chemistry syllabus*

#### 4.6.2 Hydrides of Group 16

Group 16 elements form simple hydrides with hydrogen. All of them are covalent hydrides. The variation of selected properties down the group of hydrides are shown in Table 4.11.

**Table 4.11** Selected properties of Group 16 hydrides

	H <sub>2</sub> O	H <sub>2</sub> S	H <sub>2</sub> Se	H <sub>2</sub> Te
Melting point/ °C	0.0	-85.6	-65.7	-51
Boiling point / °C	100.0	-60.3	-41.3	-4
Bond length/ pm	96	134	146	169
Bond angle/ °	104.5	92.1	91	90

Due to the extensive hydrogen bonding, H<sub>2</sub>O shows abnormally high boiling and melting points than the other hydrides of the group. Water is the only non-poisonous hydride among all the other hydrides of the group.

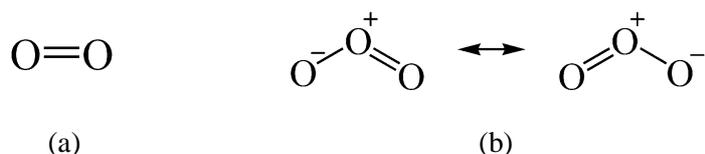
The observed variation in bond length of covalent hydrides is due to the increase of size of the central atom. Therefore, bond length increases down the group.

The covalent bond angle decreases as you come down in the group due to the less repulsion of the bonding electrons as a result of electronegativity of the central atom

decreases down the group. In  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{Te}$  the bond angles become close to  $90^\circ$ . This may also suggest that almost pure  $p$  orbitals on selenium and tellurium especially are used for binding with hydrogen.

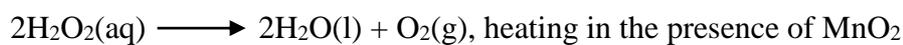
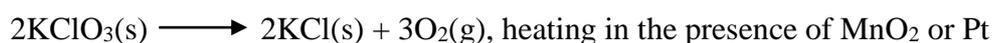
### 4.6.3 Oxygen

Oxygen has two allotropes, dioxygen ( $\text{O}_2$ ) and trioxygen (ozone,  $\text{O}_3$ ). Dioxygen is a colourless and an odourless gas which is slightly soluble in water. Ozone has a pungent odour. Ozone has a bond angle of  $111.5^\circ$ . Structure of these two allotropes are shown below.



**Figure 4.10** Structure of oxygen and ozone

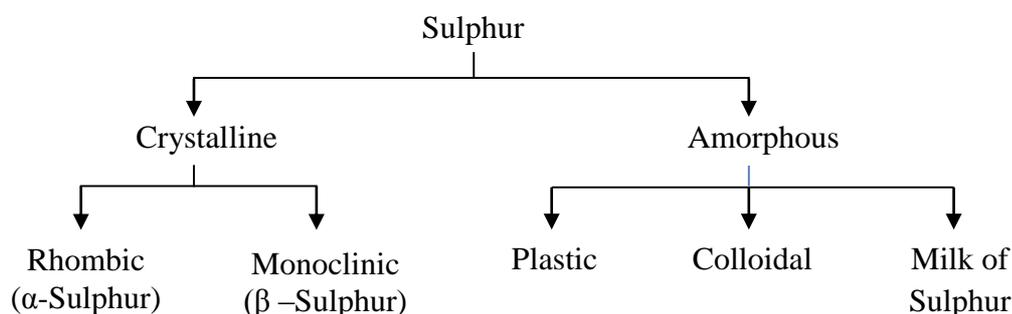
Catalytic decomposition of potassium chlorate and hydrogen peroxide can be used to produce oxygen.



Metals react with dioxygen to produce metal oxides. Ozone is a powerful oxidizing agent stronger than dioxygen. Ozone is used to disinfect water in many developed countries to kill pathogens. Unlike chlorine, ozone does not produce any harmful byproducts in the disinfection process.

### 4.6.4 Sulphur

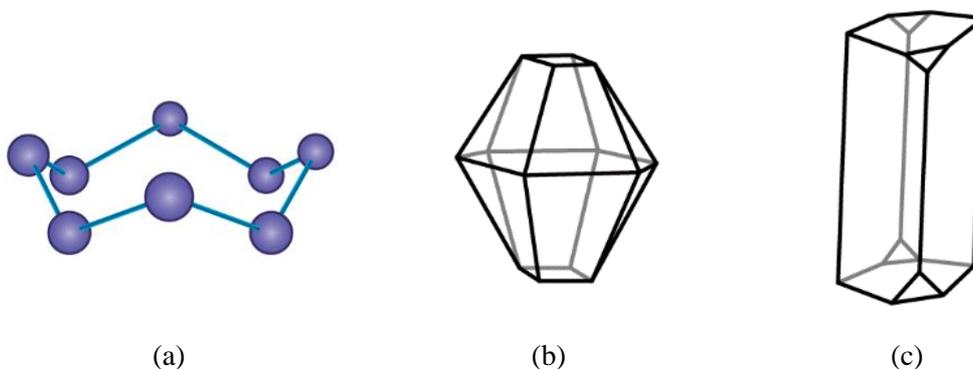
Sulphur can be classified as it is explained below.



**Figure 4.11** Classification of sulphur

Unlike oxygen, sulphur forms single bonds with itself rather than double bonds. The most commonly occurring allotrope is rhombic sulphur which is referred to as  $\alpha$ -sulphur ( $\alpha$ -

$S_8$ ). It has a crown shape with eight-membered ring that has a cyclic zigzag arrangement as shown below. When heated above  $93\text{ }^\circ\text{C}$ ,  $\alpha$ - $S_8$  changes its packing arrangement to the other commonly found form of monoclinic sulphur,  $\beta$ -sulphur ( $\beta$ - $S_8$ ). These two forms are allotropes of each other.



**Figure 4.12** (a) crown form of  $S_8$  (b) Rhombic sulphur (c) Monoclinic sulphur

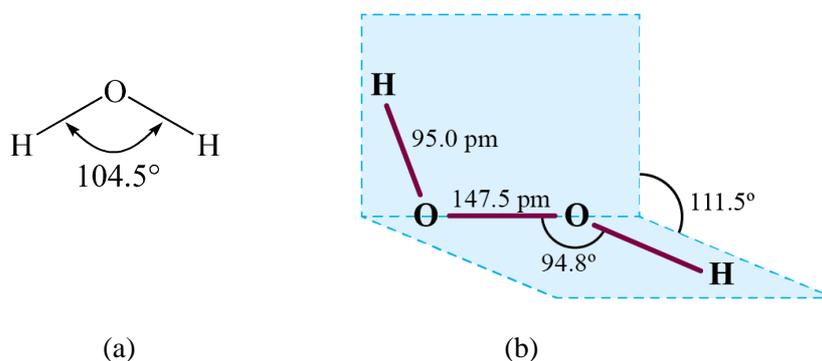
Crystalline form of rhombic and monoclinic sulphur consist of  $S_8$  rings in the shape of crown. These can be packed together in two different ways to form rhombic crystals and to form needle shaped monoclinic crystals as shown above. Below  $95\text{ }^\circ\text{C}$  the rhombic form is the most stable allotropic form of sulphur.

Amorphous sulphur is an elastic form of sulphur which is obtained by pouring melted sulphur into water. Sudden cooling of molten sulphur with open chains converts liquid sulphur to amorphous sulphur with open chains. With time, amorphous sulphur converts to crystalline sulphur. The amorphous form of sulphur is malleable but it is unstable.

#### 4.6.5 Oxygen containing compounds

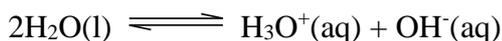
##### Water and hydrogen peroxide

Structures of  $H_2O$  and gaseous  $H_2O_2$  are shown in the figures below.



**Figure 4.13** Structures of (a)  $H_2O$  and (b)  $H_2O_2$

Water is the most widely used solvent. Water ionizes as follows. This is referred to as self-ionization of water.



An amphiprotic molecule can either donate or accept a proton. Therefore, it can act as an acid or a base. Water is an amphiprotic compound since it has the ability to accept and release a proton. The amphoteric nature of water is shown below

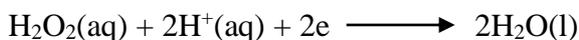


#### 4.6.6 Hydrogen peroxide

Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is a nonplanar molecule. The  $\text{H}_2\text{O}_2$  molecule contains two OH groups which do not lie in the same plane and have a bent molecular shape with the bond angle in the gaseous phase for H-O-O as  $94.8^\circ$ . The structure shown in Figure 4.13 is the one that reduces with a minimum repulsion between the lone pairs found on the 'O' atoms. The two H-O groups have a dihedral angle of  $111.5^\circ$  between each other as indicated above in Figure 4.13.

Due to the extensive hydrogen bonding,  $\text{H}_2\text{O}_2$  is a viscous liquid.  $\text{H}_2\text{O}_2$  can act as an oxidizing as well as a reducing agent. It oxidizes to oxygen and reduces to water.

Reducing half-reaction;



Oxidizing half-reaction;

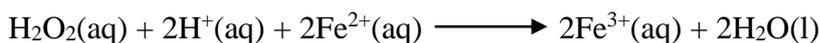
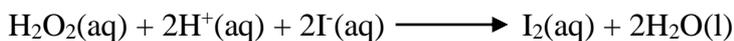


Disproportionation;

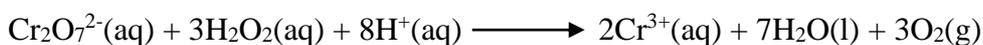
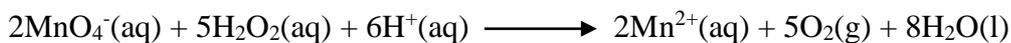


#### Reactions of $\text{H}_2\text{O}_2$

$\text{H}_2\text{O}_2$  as an oxidizing agent;



$\text{H}_2\text{O}_2$  as a reducing agent;

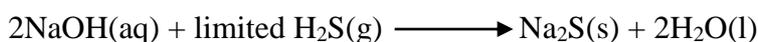
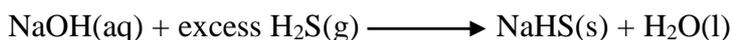


**4.6.7 Sulphur containing compounds****Hydrogen sulphide**

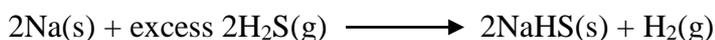
Hydrogen sulphide, H<sub>2</sub>S is a colourless, toxic and acidic gas with the odour of “rotten eggs”. H<sub>2</sub>S can be produced by reacting metal sulphides with strong acids. It dissolves in water to produce weak acidic solutions.

**Reactions of hydrogen sulphide**

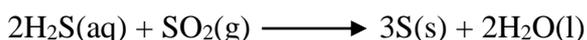
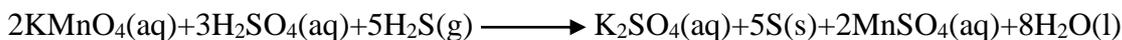
H<sub>2</sub>S as an acid with strong bases;



H<sub>2</sub>S reacts with metals as an acid as well as an oxidizing agent;



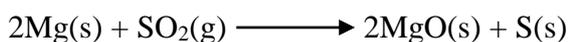
H<sub>2</sub>S as a reducing agent;

**Sulphur dioxide**

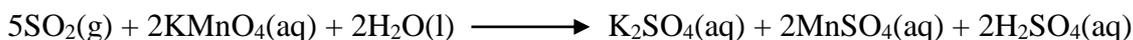
Sulphur dioxide is a colourless gas and soluble in water. Sulphur dioxide can act as an oxidizing and a reducing agent.

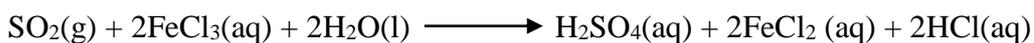
**Reactions of sulphur dioxide**

As an oxidizing agent;



As a reducing agent;



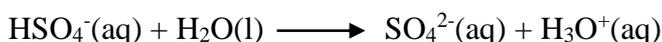
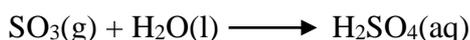


#### 4.6.8 Oxoacids of sulphur

Common oxidation numbers of sulphur are -2, 0, +2, +4 and +6.

##### Sulphuric acid

Sulphuric acid is a strong diprotic acid. Sulphur trioxide reacts with water to produce sulphuric acid.



Concentrated sulphuric acid can act as a dehydrating agent.

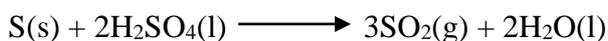


Concentrated hot sulphuric acid can act as an oxidizing agent.

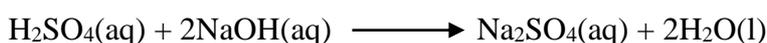
With metals,



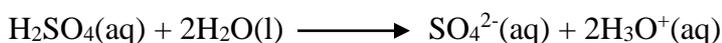
With nonmetals,

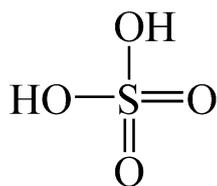


Dilute  $\text{H}_2\text{SO}_4$  act as an acid.



Dilute sulphuric acid is a strong acid which can protonate to give two  $\text{H}^+$  ions to water as shown below.

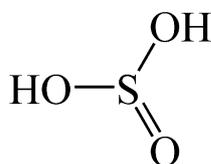




**Figure 4.14** Structure of sulphuric acid

### Sulphurous acid

Due to the air oxidation of sulphurous acid, it always contains a small amount of sulphuric acid. The reaction of gaseous sulphur dioxide and water produces sulphurous acid. The sulphurous acid reacts with dissolved oxygen in water to produce sulphuric acid. Structure of the sulphurous acid is shown below. This acid is a weaker acid than sulphuric acid.



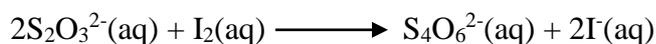
**Figure 4.15** Structure of sulphurous acid

### Thiosulphuric acid

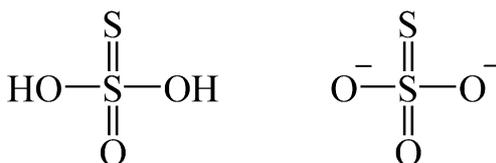
Only the salts of thiosulphuric acid are stable and thiosulphate ion can oxidize as well as reduce to give sulphur and sulphur dioxide as its products. Thiosulphuric is a weak acid. In aqueous solutions, thiosulphuric acid can decompose to produce a mixture of sulphur containing products.



Thiosulphate ion can act as a reducing agent.



Structures of thiosulphuric acid and thiosulphate ion are shown below. The oxidation state of the central sulphur atom is +4 whereas the terminal sulphur is zero in both structures.



**Figure 4.16** Thiosulphuric acid and thiosulphate ion

## 4.7 Group 17 elements

### 4.7.1 Group trends

Halogens are reactive and can only be found naturally as compounds. Fluorine is the most electronegative element and exhibits -1 and 0 oxidation states. The halogens other than fluorine form stable compounds corresponding to nearly all values of the oxidation numbers from -1 to +7. However, compounds of bromine with the oxidation state of +7 are unstable. Due to the smaller atomic radius, fluorine can stabilize higher oxidation states of other elements.

Oxidizing ability of halogens decreases down the group. Fluorine is a powerful oxidizing agent. The reactivity of halogens decreases down the group. This can be explained by using the displacement reactions of halogens.



Fluorine and chlorine are gases with pale yellow and pale green colours respectively at room temperature. Bromine is a red-brown fuming liquid and iodine is a violet-black solid with lustrous effect.

The bond energy of  $\text{F}_2$  ( $155 \text{ kJ mol}^{-1}$ ) is less than that of  $\text{Cl}_2$  ( $240 \text{ kJ mol}^{-1}$ ) due to repulsion between the non-bonded electron pairs of fluorine atoms. This is a reason for the high reactivity of fluorine gas. Down the Group 17 bond energies show a gradual decrease ( $\text{Cl}_2 = 240 \text{ kJ mol}^{-1}$ ,  $\text{Br}_2 = 190 \text{ kJ mol}^{-1}$  and  $\text{I}_2 = 149 \text{ kJ mol}^{-1}$ ).

Table 4.12 Properties of Group 17 elements

	F	Cl	Br	I	**At
Ground state electronic configuration	[He]2s <sup>2</sup> 2p <sup>5</sup>	[Ne]3s <sup>2</sup> 3p <sup>5</sup>	[Ar]3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>5</sup>	[Kr]4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>5</sup>	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>5</sup>
van der Waals radius/ pm	135	180	195	215	-
Ionic radius X <sup>-</sup> / pm	133	181	196	220	-
Covalent radius/pm	71	99	114	133	-
Melting point/ °C	-220	-101	-7.2	114	-
Boiling point/ °C	-188	-34.7	55.8	184	-
Pauling electronegativity	4.0	3.2	3.0	2.7	-
Electron gain enthalpy/ kJ mol <sup>-1</sup>	-328	-349	-325	-295	-
X(g) + e $\longrightarrow$ X <sup>-</sup> (g)					

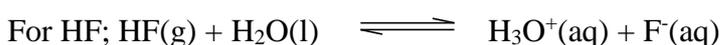
\*\*Not relevant to the current G. C. E. (A/L) Chemistry Syllabus

#### 4.7.2 Simple compounds of Group 17

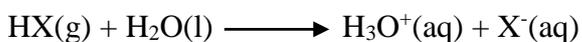
##### Hydrogen halides

Hydrogen halides are acidic in water. HF has the ability to produce extensive hydrogen bonding, however, HF is a gas (boiling point 20 °C) at room temperature and under atmospheric pressure.

##### Acidic nature of hydrogen halides in aqueous solutions



For other hydrogen halides (HCl, HBr and HI);



HF is a weak acid whereas the other hydrogen halides are strong acids in the aqueous medium. HF has the high bond energy (strongest covalent bond), which makes it difficult to dissociate in water to produce H<sup>+</sup> ions readily. The acidic strength of hydrogen halides increases down the Group 17. This can be explained using the same fact mentioned above. Some selected properties of Group 17 hydrogen halides are shown in Table 4.13.

**Table 4.13** Selected properties of group 17 hydrogen halides

	HF	HCl	HBr	HI
Melting point/ °C	-84	-114	-89	-51
Boiling point / °C	20	-85	-67	-35
Bond length/ pm	92	127	141	161
Bond dissociation energy/ kJ mol <sup>-1</sup>	570	432	366	298

**Silver halides**

Silver halides can be used to identify the halides (chloride, bromide, and iodide) using the colour of the precipitate. Few selected properties are shown below.

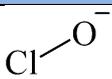
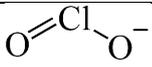
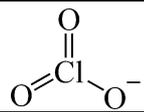
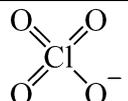
**Table 4.14** Silver halides of Group 17 elements

Silver halide	Colour	Solubility in ammonia
AgCl	White	Dissolves in dil. aqueous ammonia
AgBr	Pale yellow	Dissolves in conc. aqueous ammonia
AgI	Yellow	Insoluble in both dil. and conc. aqueous ammonia

**Oxides and oxoacids of chlorine**

Chlorine forms several oxides and oxoanions with variable oxidation states. Some oxoanions are strong oxidizing agents. Selected oxides of chlorine are shown in Table 4.15.

**Table 4.15** Selected oxides and oxoanions of chlorine

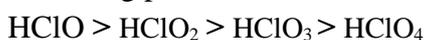
Oxidation state	Formula of oxide	Formula of oxoanion	Structure of oxoanion
+1	Cl <sub>2</sub> O	ClO <sup>-</sup>	
+3		ClO <sub>2</sub> <sup>-</sup>	
+5		ClO <sub>3</sub> <sup>-</sup>	
+6	ClO <sub>3</sub> and Cl <sub>2</sub> O <sub>6</sub>		
+7	Cl <sub>2</sub> O <sub>7</sub>	ClO <sub>4</sub> <sup>-</sup>	

Chlorine forms four types of oxoacids. The acidic strength increases with the increasing oxidation number of the chlorine atom. The structures and the oxidation states of oxoacids are given in the Table 4.16.

**Table 4.16** Structures of oxoacids of chlorine

	HClO	HClO <sub>2</sub>	HClO <sub>3</sub>	HClO <sub>4</sub>
<b>Oxidation state</b>	+1	+3	+5	+7
<b>Structure</b>				

Oxidizing power of oxoacids of chlorine changed as follows.

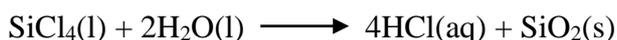


The oxidation state of chlorine in HClO, HClO<sub>2</sub>, HClO<sub>3</sub>, HClO<sub>4</sub> respectively are +1, +3, +5 and +7. The higher the oxidation state the stronger the acid will be. Therefore the variation of acidic strength is HClO < HClO<sub>2</sub> < HClO<sub>3</sub> < HClO<sub>4</sub>.

### Halides

Most covalent halides react vigorously with water. But CCl<sub>4</sub> does not hydrolyze. Most fluorides and some other halides are inert.

Chlorides of group 14 and 15 elements react with less water as follows.



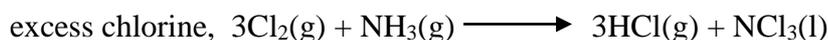
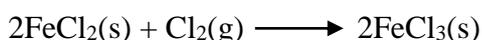
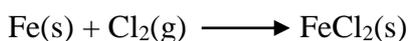
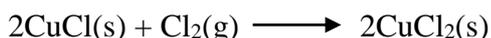
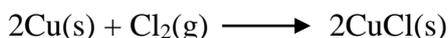
Chlorides of group 14 and 15 elements react excess water as follows.





### 4.7.3 Reactions of chlorine

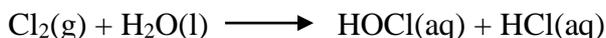
Chlorine is less reactive than fluorine. Chlorine gas is a strong oxidizing agent. Some reactions of chlorine act as a strong oxidizing agent are given below.



### Disproportionation reactions of chlorine

Chlorine is simultaneously reduced and oxidized when it reacts with water and bases.

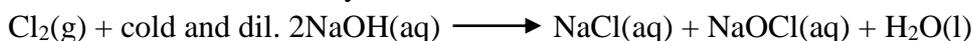
Reaction of chlorine with water;



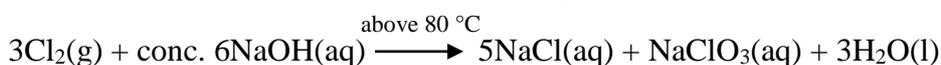
In this reaction, zero oxidation state of chlorine ( $\text{Cl}_2$ ) oxidize to +1 ( $\text{HOCl}$ ) and reduce to -1 ( $\text{Cl}^-$ ).

Reaction with sodium hydroxide;

With cold dilute sodium hydroxide



With hot concentrated/ hot dilute sodium hydroxide

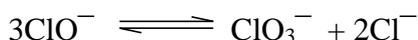


### Reactions of oxoanions

$\text{ClO}^-$  is stable at low temperatures and disproportionates at high temperature to produce  $\text{Cl}^-$  and  $\text{ClO}_3^-$ . However, both  $\text{BrO}^-$  and  $\text{IO}^-$  are not stable even at low temperatures and undergo disproportionation.

**Disproportionation reactions of hypochlorite**

Disproportionation of hypochlorite to produce chlorate and chloride can be written as;



Under acidic conditions, HOCl is more stable than  $\text{ClO}^-$ , which makes disproportionation predominant under basic conditions.

**4.8 Group 18 elements****4.8.1 Group trends**

All group 18 elements are unreactive monoatomic gasses. Only Xe forms a significant range of compounds. All group 18 elements have positive electron gain enthalpy because an incoming electron needs to occupy an orbital belonging to a new shell.

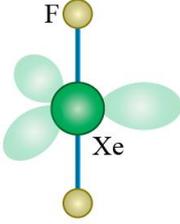
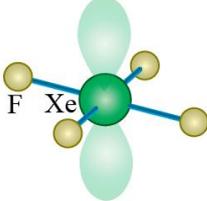
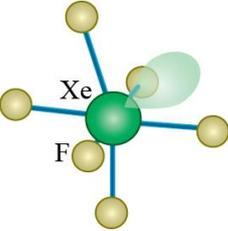
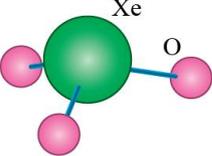
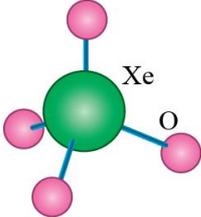
**Table 4.17** Properties of Group 18 elements

	He	Ne	Ar	Kr	Xe
Ground state electronic configuration	$1s^2$	$[\text{He}]2s^22p^6$	$[\text{Ne}]3s^23p^6$	$[\text{Ar}]3d^{10}4s^24p^6$	$[\text{Xe}]4d^{10}5s^25p^6$
Atomic radius/ pm	99	160	192	197	240
1 <sup>st</sup> ionization energy/ $\text{kJ mol}^{-1}$	2373	2080	1520	1350	1170
Electron gain enthalpy/ $\text{kJ mol}^{-1}$	48.2	115.8	96.5	96.5	77.2

**4.8.2 Simple compounds of group 18 elements**

Compounds of xenon have oxidation numbers of +2, +4, +6 and +8. Xenon reacts directly with fluorine. Some Xe compounds are shown in Table 4.18.

Table 4.18 Some selected compounds of Xe

Oxidation state	Compounds	Structure
+2	XeF <sub>2</sub>	
+4	XeF <sub>4</sub>	
+6	XeF <sub>6</sub>	
+6	XeO <sub>3</sub>	
+8	XeO <sub>4</sub>	

## 4.9 Periodic trends shown by s and p block elements

### 4.9.1 The valence electron configuration

The valence electron configuration of an element can be predicted from their position in the periodic table.

Group number	1	2	13	14	15	16	17	18
Valance shell electron configuration	$ns^1$	$ns^2$	$ns^2np^1$	$ns^2np^2$	$ns^2np^3$	$ns^2np^4$	$ns^2np^5$	$ns^2np^6$

### 4.9.2 Metallic character

Metals have lower ionization energies compared to the other elements. Hence, metals can easily release electrons to produce cations. The atomic radii increase and ionization energy decreases when going down a group. Therefore, the metallic nature increases down the group. Also, across a period, atomic radii decrease and ionization energy increases. Therefore, the metallic nature decreases.

The third period shows a gradual increase in melting point and then a decrease across the period. Most abundant elemental form, type of bonding between similar atoms and the melting point of the third period elements are shown below.

**Table 4.19** Most abundant elemental form, type of bonding between similar atoms and the melting point of the third period elements

	Na	Mg	Al	Si	P <sub>4</sub>	S <sub>8</sub>	Cl <sub>2</sub>	Ar
Melting point/ °C	98	649	660	1420	44	119	-101	-189
Bonding type	M	M	M	NC	C	C	C	-

*Metallic – M, Network covalent – NC, Covalent – C*

### Acid, base and amphoteric nature of oxides

Across the third period variation of type of bonding in oxides in which the elements are at their highest oxidation number are given below.

**Table 4.20** Comparison of the third period oxides

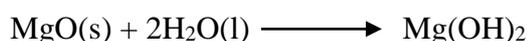
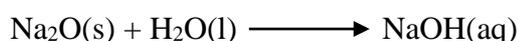
	Na <sub>2</sub> O(s)	MgO(s)	Al <sub>2</sub> O <sub>3</sub> (s)	SiO <sub>2</sub> (s)	P <sub>4</sub> O <sub>10</sub> (s)	SO <sub>3</sub> (g)	Cl <sub>2</sub> O <sub>7</sub> (l)
Oxidation number	+1	+2	+3	+4	+5	+6	+7
Bonding type	I	I	I	NC	C	C	C
Nature	Strongly B	B	Am	Very weakly A	Weakly A	A	Strong A

*Ionic – I, Network covalent – NC, Covalent – C  
Basic – B, Amphoteric – Am, Acidic – A*

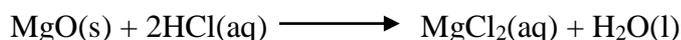
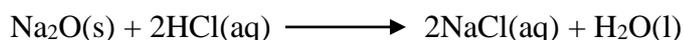
Oxides with the highest oxidation number are considered to compare the chemical nature. The nature from strong basic on the left to strong acidic to the right can be seen. Amphoteric nature can be seen in the middle of the series.

### 4.9.3 Reactions of third period oxides with water, acids and bases

Oxides of sodium and magnesium react with water to produce hydroxides.



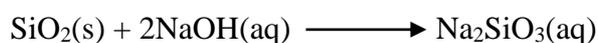
As these two oxides are basic, they react with acids to produce salt and water.



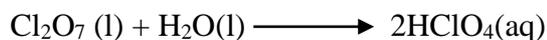
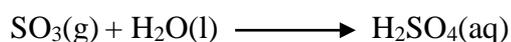
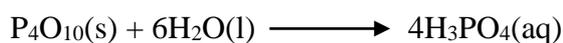
Aluminum oxide is amphoteric and it reacts with acids as well as with bases to produce salts.



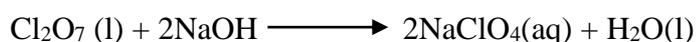
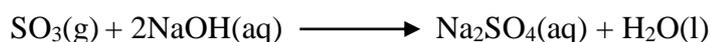
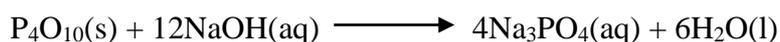
$\text{SiO}_2$  is weakly acidic and reacts with strong bases. Also,  $\text{SiO}_2$  shows no reaction with water.



$\text{P}_4\text{O}_{10}$ ,  $\text{SO}_3$ , and  $\text{Cl}_2\text{O}_7$  are acidic and produce acids when dissolved in water. Those reactions are shown below.



These oxides also react with bases to produce salts and water.



#### 4.9.4 Acid, base and amphoteric nature of hydroxides and hydrides

Hydroxides of the third period show a trend similar to oxides of the same period. The following table shows a comparison of the third period hydroxides.

**Table 4.21** Comparison of the third period hydroxides

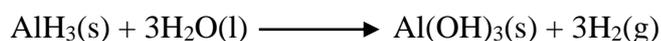
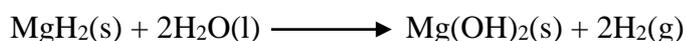
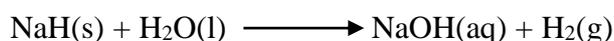
	NaOH	Mg(OH) <sub>2</sub>	Al(OH) <sub>3</sub>	Si(OH) <sub>4</sub>	P(OH) <sub>5</sub>	S(OH) <sub>6</sub>	Cl(OH) <sub>7</sub>
Stable form				H <sub>2</sub> SiO <sub>3</sub>	H <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> SO <sub>4</sub>	HClO <sub>4</sub>
Oxidation number	+1	+2	+3	+4	+5	+6	+7
Bonding type	I	I	C	C	C	C	C
Nature	Strongly B	B	Am	Very weakly A	Weakly A	Strongly A	Very strongly A
<i>Ionic – I, Network covalent – NC, Covalent – C</i>							
<i>Basic – B, Amphoteric – Am, Acidic – A</i>							

Nature of hydrides of third period varies from strong bases to strong acids across the period. Amphoteric nature can be seen in the middle of the series.

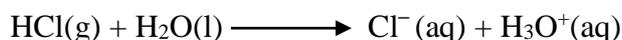
**Table 4.22** Comparison of the third period hydrides

	NaH(s)	MgH <sub>2</sub> (s)	(AlH <sub>3</sub> ) <sub>x</sub> (s)	SiH <sub>4</sub> (g)	PH <sub>3</sub> (g)	H <sub>2</sub> S(g)	HCl(g)
Oxidation number	+1	+2	+3	-4	-3	-2	-1
Nature of the aqueous solution	Strongly B	Weakly B	Am	Very weakly A	N	Weakly A	Very strongly A
Bonding type	I	I	NC	C	C	C	C
<i>Ionic – I, Network covalent – NC, Covalent – C</i>							
<i>Basic – B, Amphoteric – Am, Acidic – A, Neutral – N</i>							

Hydrides of sodium and magnesium react with water to produce basic solutions.



PH<sub>3</sub> is weakly soluble in water and produces a neutral solution. H<sub>2</sub>S and HCl are acidic and aqueous solutions are also acidic.



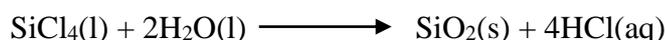
### 4.9.5 Nature of the halides across the third period

As the electronegativity of elements increases across the period from left to right, the ability of hydrolyzation of chlorides increases accordingly. Corresponding reactions are given below. Chlorides of *s* block elements in the third period are ionic and the *p* block elements are covalent.

**Table 4.23** Comparison of the third period chlorides

	NaCl(s)	MgCl <sub>2</sub> (s)	AlCl <sub>3</sub> (s)	SiCl <sub>4</sub> (l)	PCl <sub>5</sub> (g)	SCl <sub>2</sub> (g)
Oxidation number	+1	+2	+3	+4	+5	+2
Bonding type	I	I	C	C	C	C
Nature of the aqueous solution	N	Very weakly A	A	A	A	A
<i>Ionic – I, Covalent – C</i>						
<i>Basic – B, Amphoteric – Am, Acidic – A, Neutral – N</i>						

Reactions with water of third period covalent chlorides are,



Group 15 can be used to understand the variation of properties down the group. Down a group the ionization energy decreases, and the metallic nature increases. Use the information given for the Group 15 and correlate the variation in ionization energies with the increase of metallic properties down the group. Both N and P are nonmetals and produce acidic oxides. However, As and Sb oxides are amphoteric and bismuth oxide is basic.

Reactions with water of group 15 halides are given in the respective section under the halides of group 17.

### *d* Block Elements

Elements in Groups 3 to 12 are collectively classified as *d* block elements. In *d* block elements the last electron gets filled into a *d* orbital. These elements can be categorised into two categories namely transition and non-transition.

#### 4.10 Transition elements

*d* block elements contain incompletely filled *d* subshell at elemental state or with the ability to form at least one stable ion with incompletely filled *d* subshell are called transition elements. Therefore, *d* block elements producing ions only with  $d^{10}$  configurations are considered as non-transition elements.

e.g.: Electronic configurations of Zn :  $[\text{Ar}]3d^{10}4s^2$

Electronic configurations of  $\text{Zn}^{2+}$ :  $[\text{Ar}]3d^{10}4s^0$

Electronic configuration of Sc :  $[\text{Ar}]3d^14s^2$

Electronic configuration of  $\text{Sc}^{3+}$  :  $[\text{Ar}]3d^04s^0$

Both Zn and Sc are *d* block elements (last electron is filled to a *3d* orbital). However, Zn is considered as a non-transition element due to the absence of a partially filled *d* subshell at the elemental stage and  $\text{Zn}^{2+}$  ion. Sc can be considered as a transition element since Sc contains partially filled *d* subshell at the elemental stage.

**Table 4.24** Comparison of the properties of *d* block elements in fourth period

Group	3	4	5	6	7	8	9	10	11	12
Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Pauling electronegativity	1.3	1.5	1.6	1.6	1.5	1.9	1.9	1.9	1.9	1.6
Atomic radius/pm	162	147	134	128	127	126	125	125	128	137
Covalent radius/pm	144	132	122	118	117	117	116	115	117	125
Ionic radius ( $M^{2+}$ )/pm	-	100	93	87	81	75	79	83	87	88

Transition metal ions have less variation in atomic radii across a period than that of the main group elements. Across the period of the transition metals shown in Table 4.23, the atomic radii decrease slightly and then increase. Across the period, to each *d* electron added nuclear charge is also increased by one. The decrease of the atomic radii at the middle of the period (from Sc to Ni) occurs due to the predominance of attraction power of nuclear charge increase than the repulsion among the electrons. However, at the end of the period (Cu and Zn), radii of the atoms increase due to greater repulsion among electrons as electrons are paired in *d* orbitals.

**4.10.1 Occurrence**

Elements on the left of the 3*d* series (fourth period *d* block elements) exist commonly in the nature as metal oxides and cations combined with anions.

Few examples are shown below.

**Table 4.25** Occurrence of some fourth period *d* block elements

Element	Example
Ti	FeTiO <sub>3</sub> (Ilmenite) and TiO <sub>2</sub> (Rutile)
Fe	Fe <sub>2</sub> O <sub>3</sub> (Haematite), Fe <sub>3</sub> O <sub>4</sub> (Magnetite) and FeCO <sub>3</sub> (Siderite)
Cu	CuFeS <sub>2</sub> (Copper Pyrite)

**4.10.2 Properties of fourth period *d* block elements****Oxidation states and ionization energies**

Except Sc and Zn in the fourth period *d* block elements, others can form stable cations with multiple oxidation states. The multiplicity of the oxidation state is due to the varying number of *d* electrons participate in bonding. Both Zn (+2) and Sc (+3) only produce ions with a single oxidation state, and these ions do not contain partially filled *d* orbitals. Electron configuration and the oxidation states of *d* block elements are shown in Table 4.26. Sc forms only Sc<sup>3+</sup> ions. Except in Sc, +2 oxidation number can be seen in all the other elements since electrons in 4*s* orbital get removed due to ionization before electrons in 3*d* orbitals. Reason for this is that the 4*s* orbital with two electrons in the outermost shell experiences a lesser effective nuclear charge than that of electrons in the 3*d* orbital.

As a result of the 3*d*<sup>10</sup>4*s*<sup>1</sup> configuration, Cu can form +1 oxidation number commonly. However, Cr<sup>+</sup> is extremely rare and unstable even though Cr has 3*d*<sup>5</sup>4*s*<sup>1</sup> configuration.

The highest possible oxidation number that a *d* block element can show is the sum of 4*s* and 3*d* electrons. Transition metals are also capable of producing variable oxidation states similar to *p* block elements and show the ability to interconvert among their oxidation states. Therefore, they can act as oxidizing as well as reducing agents.

First five elements achieve the maximum possible oxidation state by losing all 4*s* and 3*d* electrons. With the filling of more 3*d* electrons, towards the right end of the period, the 3*d* orbitals become greater in energy as the nuclear charge of the atom increases. This makes *d* electrons are harder to remove. The most common oxidation state for these elements is +2 due to the loss of 4*s* electrons.

**Reactivity**

*d* block elements do not react with the water while *s* block elements react with water vigorously. The 4*s* electrons of the *d* block elements are tightly bound to the nucleus due

to the higher nuclear charge than that of the *s* block elements. First ionization energy of *d* block elements lies between the values of those of *s* and *p* block elements.

**Table 4.26** Electronic configuration and oxidation states of *d* block elements

Element	Ground state configuration	3d		4s	Oxidation states
Sc	[Ar]3d <sup>1</sup> 4s <sup>2</sup>	↑		↑↓	+3
Ti	[Ar]3d <sup>2</sup> 4s <sup>2</sup>	↑	↑	↑↓	(+2), +3, +4
V	[Ar]3d <sup>3</sup> 4s <sup>2</sup>	↑	↑	↑	(+2), (+3), +4, +5
Cr	[Ar]3d <sup>5</sup> 4s <sup>1</sup>	↑	↑	↑	+2, +3, (+4), (+5), +6
Mn	[Ar]3d <sup>5</sup> 4s <sup>2</sup>	↑	↑	↑	+2, +3, +4, (+5), (+6), +7
Fe	[Ar]3d <sup>6</sup> 4s <sup>2</sup>	↑↓	↑	↑	+2, +3, (+4), (+5), (+6)
Co	[Ar]3d <sup>7</sup> 4s <sup>2</sup>	↑↓	↑	↑	+2, +3, (+4)
Ni	[Ar]3d <sup>8</sup> 4s <sup>2</sup>	↑↓	↑	↑	+2, (+3), (+4)
Cu	[Ar]3d <sup>10</sup> 4s <sup>1</sup>	↑↓	↑↓	↑	+1, +2, (+3), (+4)
Zn	[Ar]3d <sup>10</sup> 4s <sup>2</sup>	↑↓	↑↓	↑↓	+2

\*Less common states are shown in brackets.

Ionization energies of fourth period *d* block elements are higher than that of the *s* block elements in the same period. The first ionization energies of *d* block elements are increase slightly across the period when move from left to the right of the period. Variation of the first ionization energy across the *d* block is less than that of *s* and *p* block elements. Increase in the nuclear charge across the fourth period *d* block elements expect to be increase the first ionization energies due to the greater attraction towards the 4s electrons. However, in all *d* block elements, extra electrons are inserted in to the 3d orbital moving from left to right across the period, and these *d* electrons shield the 4s electrons from the inward attraction of the nucleus. Because of these two counter effects, the ionization energy of *d* block elements increases slightly across the period. Successive ionization energies of the fourth period *d* block elements are shown in the table given below.

**Table 4.27** Successive ionization energies of fourth period *d* block metals, K and Ca.\*\*

Element	1 <sup>st</sup> ionization energy/ kJ mol <sup>-1</sup>	2 <sup>nd</sup> ionization energy/ kJ mol <sup>-1</sup>	3 <sup>rd</sup> ionization energy/ kJ mol <sup>-1</sup>
K	418	3052	
Ca	589	1145	4912
Sc	631	1235	2389
Ti	658	1310	2652
V	650	1414	2828
Cr	653	1496	2987
Mn	717	1509	3248
Fe	759	1561	2957
Co	758	1646	3232
Ni	737	1753	3393
Cu	746	1958	3554
Zn	906	1733	3833

\*\* For K, only first and second ionization energies are given to understand the energy increase due to removal of an electron from an inner orbital.

First ionization energies of *d* block elements are higher than those of *s* block elements in the same period. This explains the less reactivity of *d* block elements than the *s* block elements.

All *d* block elements are metals because 4*s* electrons in *d* block elements can be released easily to form cations. Metallic character of the *d* block elements increases down the group.

All *d* block elements in the fourth period are solids with high melting and boiling points. Melting and boiling points of *d* block elements are extremely high as compared to those of *s* and *p* block elements. *d* block elements are moderately reactive.

Except metal ions with  $3d^0$  and  $3d^{10}$  configurations, *d* block metal compounds produce characteristic colours. This means transition metal ion complexes can produce coloured compounds. Most *d* block metal ions form complex compounds.

### Electronegativity

Table below provides the electronegativity of *d* block elements and can be used to understand the variation of electronegativity of *d* block elements in the fourth period. Electronegativity increases with the atomic number. However, Mn and Zn are deviated from the trend due to their stable electron configuration. Due to the higher nuclear charge, *d* block elements have higher electronegativity than that of the *s* block elements.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Electronegativity	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9	1.6

When an atom exhibits variable oxidation states, the higher oxidation state has higher electronegativity.

### Catalytic properties

Most transition metals and compounds can act as catalysts due to the presence of partially filled and empty  $d$  orbitals. This makes  $d$  orbitals to accept or donate electrons. This property makes them effective components of catalysts. Pd for hydrogenation, Pt/Rh for oxidation of ammonia to nitrogen oxide, and  $V_2O_5$  for oxidation of  $SO_2$  to  $SO_3$  and  $TiCl_3/Al(C_2H_5)_6$  for the polymerization of ethene are some examples for the use of  $d$  block element and its compound as a catalyst. Some popular organic reactions such as alkylation and acylation are done in the presence of transition metal ion as the catalyst.

### Colours of transition metal ions

Aqueous solutions of many transition metal ions can absorb radiation in the visible region of the electromagnetic spectrum to produce various colours. This ability is due to the presence of partially filled  $d$  subshells. In contrast, metal ions of  $s$  block are colourless because these ions have completely filled subshells. The following Table shows some of the colours of transition metal ions and oxoanions in aqueous solutions. For example,  $[Co(H_2O)_6]^{2+}$  is pink,  $[Mn(H_2O)_6]^{2+}$  pale pink. In contrast, aqueous solutions of  $Sc^{3+}$  and  $Zn^{2+}$  are colourless due to the unavailability of partially filled  $d$  orbitals. Also, ions with  $d^0$  or  $d^{10}$  configuration are colourless when in an aqueous solution. Colours of  $MnO_4^-$  and  $CrO_4^{2-}$  are not due to the electron transition of electrons among the  $d$  orbitals. Colours of some selected oxoanions are given in **Table 4.28**.

**Table 4.28** Colours of  $d$  block metal ions and oxoanions in aqueous solutions. The number of  $3d$  and  $4s$  electrons are shown in brackets next to the metal ion.

Ion	Colour	Ion	Colour
$Sc^{3+}(d^0 s^0)$	Colourless	$Fe^{3+}(d^5 s^0)$	Brown yellow
$Ti^{4+}(d^0 s^0)$	Colourless	$Fe^{2+}(d^6 s^0)$	Pale green
$Cr^{3+}(d^3 s^0)$	Violet	$Co^{2+}(d^7 s^0)$	Pink
$Mn^{2+}(d^5 s^0)$	Pale pink	$Ni^{2+}(d^8 s^0)$	Green
		$Cu^{2+}(d^9 s^0)$	Blue
		$Cu^+(d^{10} s^0)$	Colourless
		$Zn^{2+}(d^{10} s^0)$	Colourless
Oxoanion	Colour	Oxoanion	Colour
$MnO_4^-$	Purple	$CrO_4^{2-}$	Yellow
$MnO_4^{2-}$	Green	$Cr_2O_7^{2-}$	Orange

**4.10.3 Oxides of *d* block elements**

First four elements form oxides by removing all valence electrons. Unlike main group elements, transition elements produce different oxidation states. Some *d* block elements can form oxides in which metal atom presence with two different oxidation numbers. Both  $\text{Mn}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  are examples for binary oxides (which are formed with two oxidation numbers).  $\text{Mn}_3\text{O}_4$  is a mixture of Mn(II) and Mn(III). Also,  $\text{Fe}_3\text{O}_4$  is a mixture of Fe(II) and Fe(III).

**4.10.4 Chemistry of some selected *d* block oxides****Chromium and manganese oxides**

Properties of an oxide depend on the oxidation number. The bonding type depends on the oxidation number. The change in the bonding type explains the basis in the acid-base behaviour of metal oxides. For the compounds with high oxidation numbers have covalent bonding characteristics are acidic and the compounds with low oxidation numbers have ionic bonding characteristics are basic.

**Table 4.29** Acid-base nature of chromium oxides

Oxide	Acid-base nature	Oxidation number	
CrO	Weakly basic	+2	low oxidation state
Cr <sub>2</sub> O <sub>3</sub>	Amphoteric	+3	moderate oxidation state
CrO <sub>2</sub>	Weakly acidic	+4	
CrO <sub>3</sub>	Acidic	+6	high-oxidation state

Generally, if the metal is in a lower oxidation state, the oxide is basic. Also, if the metal is in a moderate oxidation state, the oxide is amphoteric and metal oxides with higher oxidation state are acidic. This explains why the compounds in **Tables 4.29** and **4.30** with lower oxidation states are more metallic while compounds with higher oxidation states are more non-metallic in properties.

**Table 4.30** Acid-base nature of manganese oxides

Oxide	Acid-base nature	Oxidation number	
MnO	Basic	+2	Low oxidation state
Mn <sub>2</sub> O <sub>3</sub>	Weakly basic	+3	moderate oxidation state
MnO <sub>2</sub>	Amphoteric	+4	
MnO <sub>3</sub>	Weakly acidic	+6	high-oxidation state
Mn <sub>2</sub> O <sub>7</sub>	Acidic	+7	

**Reactions of some selected oxoanions of chromium**

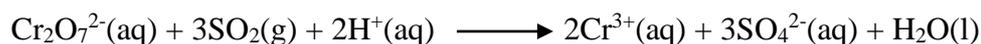
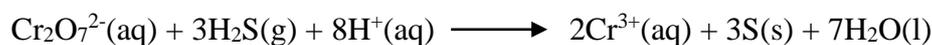
The yellow coloured chromate ion exists in neutral or basic conditions. Under the acidic conditions, it is converted to the orange coloured dichromate ion.



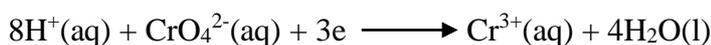
Even without partially filled *d* subshells (Cr at +6 oxidation state), both chromate and dichromate produce colours due to the electron charge transfer between Cr and O ligands. However, the explanation of this phenomena is not a part of the current syllabus.

The reduction of  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$  happens only in acidic medium. In acidic medium,  $\text{CrO}_4^{2-}$  ions will dimerized and converted into  $\text{Cr}_2\text{O}_7^{2-}$  ions. Therefore in acidic medium  $\text{Cr}^{6+}$  present only as  $\text{Cr}_2\text{O}_7^{2-}$ .

Some important redox reactions of chromium oxoanions are given below.



In  $\text{CrO}_4^{2-}$ , oxidation number Cr is +6. Therefore it can act as an oxidizing agent. Under acidic conditions, Cr(IV) can be reduced to Cr(III).

**Reactions of manganese oxides and oxoanions**

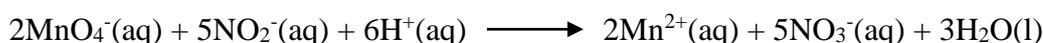
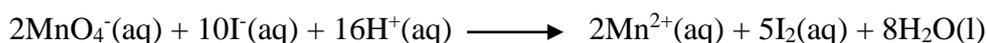
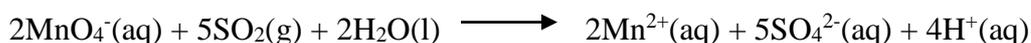
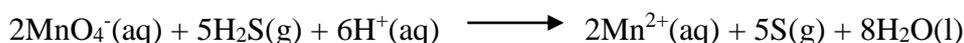
$\text{KMnO}_4$  is a purple solid. Colour of  $\text{MnO}_4^-$  is due to the electron transfer process between central Mn atom and O ligands. Under acidic conditions, permanganate ion can act as a strong oxidizing agent. Colours of  $\text{MnO}_2$  and  $\text{KMnO}_4$  are given below.

**Table 4.31** Colours of  $\text{MnO}_2$  and  $\text{KMnO}_4$

Compound	Colour
$\text{MnO}_2$	Dark brown/black
$\text{KMnO}_4$	Purple

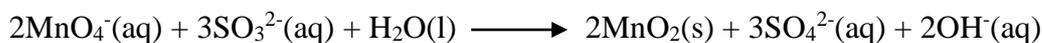
Some important redox reactions of  $\text{MnO}_4^-$  are given below.

Under acidic conditions:



In all these reactions, under acidic conditions,  $\text{MnO}_4^-$  reduces to  $\text{Mn}^{2+}$ .

Under dilute alkaline conditions:



#### 4.10.5 Coordination compounds of transition metal ions

Transition metal ions typically form coordination compounds. These coordination compounds consist of complex ions. These complex ions are built with a central metal ion and two or more surrounding monodentate ligands (there are ligands that form more than one bond with the central metal ion). For example,  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$  consists of the complex ion of  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  and the counter ion of  $\text{Cl}^-$  (Figure 4.17).

Ligands (Lewis bases) can donate electrons to the central metal ion (Lewis acid) to form dative bonds with it.



**4.10.6 Nomenclature of simple complex ions and compounds**

Name of a metal complex provides information about the complex such as oxidation state of the central metal ion, types of ligands and the number. The rules used to write the name of a complex ion is proposed by IUPAC are given below.

**Naming of ligands**

Name of an anion acting as a ligand in the complex ion can be obtained by removing the last letter of the anion name and adding 'o' letter to the end. Neutral molecules acting as ligands are usually given the name of the molecule. However, there are some exceptions and those are not discussed in the current G. C. E. (A/L) Chemistry syllabus.

**Anionic ligands**

$\text{Cl}^-$	chlorido
$\text{Br}^-$	bromido
$\text{CN}^-$	cyanido
$\text{OH}^-$	hydroxido

**Neutral ligands**

$\text{NH}_3$	ammine
$\text{H}_2\text{O}$	aqua
$\text{CO}$	carbonyl

Number of a particular ligand is indicated by prefixes. The used prefixes are *di* – two, *tri* – three, *tetra* – four, *penta* – five, *hexa* – six, etc.

**Naming of complex cations**

Name of the complex ion must be written as a single word with no space and must only be written using lower case English letters. The oxidation number of the metal ion is indicated by Roman numerals within parentheses at the end of the metal name.

e.g.: $[\text{Ni}(\text{NH}_3)_6]^{2+}$	hexaamminenickel(II) ion
$[\text{Cu}(\text{NH}_3)_4]^{2+}$	tetraamminecopper(II) ion
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	hexaaquachromium(III) ion

**Complex anions**

For negatively charged complex ions (complex anions) the suffix 'ate' must be used after the name of the metal.

e.g.: $[\text{CuCl}_4]^{2-}$	tetrachloridocuprate(II) ion
$[\text{CoCl}_4]^{2-}$	tetrachloridocobaltate(II) ion

**Table 4.32** Names used for metals in anionic complexes

Metal	Name used in anionic complexes	Metal	Name used in anionic complexes
Cr	chromate	Co	cobaltate
Cu	cuprate	Fe	ferrate
Mn	manganate	Ni	nickelate
Ag	argentate	Hg	mercurate
Au	aurate		

Name of a complex compound must have the name of the cation first and the anion name second. These two names must be separated by a space.

e.g.:  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$  - hexaamminenickel(II) chloride

$\text{Na}_2[\text{CoCl}_4]$  - sodium tetrachlorocobaltate(II)

### Coordination number

The number of coordination bonds formed between the central metal ion and ligands is defined as coordination number. Since some ligands can form more than one coordination bond with the central metal ion, it is incorrect to define the coordination number as the number of ligands coordinated to the central metal ion. The coordination number depends on the size, charge, nature of ligands and the electronic configuration of the central metal ion.

**Table 4.33** Common coordination numbers of *d* block ions

$\text{M}^+$	Coordination number	$\text{M}^{2+}$	Coordination number	$\text{M}^{3+}$	Coordination number
$\text{Cu}^+$	2, 4	$\text{Mn}^{2+}$	4, 6	$\text{Sc}^{3+}$	6
		$\text{Fe}^{2+}$	6	$\text{Cr}^{3+}$	4,6
		$\text{Co}^{2+}$	4, 6	$\text{Co}^{3+}$	4,6
		$\text{Ni}^{2+}$	4, 6		
		$\text{Cu}^{2+}$	4, 6		
		$\text{Zn}^{2+}$	4, 6		

### 4.10.7 Factors affecting the colour of the complexes

Transition metal atoms and ions can produce coloured complexes. Colour of these complexes depends on the following factors. Examples which reflect the effect these factors are given in Table 4.34.

1. Central metal ion
2. The oxidation state of the central metal ion
3. Nature of the ligands

**Table 4.34** Colours of transition metal ion complexes depends on the factors

1. Central metal ion

Mn(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)
$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
Pink	Pale-green	Pink	Green	Pale-blue

2. The oxidation state of the central metal ion

Mn(II)	Mn(III)	Fe(II)	Fe(III)
$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	$[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
Pale-pink	Violet	Pale-green	Yellow

Colour of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is depend on the anion

3. Nature of the ligand

$\text{H}_2\text{O}$	$\text{OH}^-$	$\text{NH}_3$	$\text{Cl}^-$
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	$[\text{Co}(\text{OH})_4]^{2-}$	$[\text{Co}(\text{NH}_3)_6]^{2+}$	$[\text{Co}(\text{Cl})_4]^-$
Pink	Deep-blue	yellowish-brown	Blue

Ability to form coloured compounds is a unique property of the transition metal elements. Colours of some common metal complexes are given in Table 4.33.

Table 4.33 Metal complexes and colours

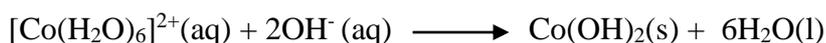
Metal	Nature of the ligand			
	H <sub>2</sub> O(l)	OH <sup>-</sup> (aq)	NH <sub>3</sub> (aq)	Cl <sup>-</sup> (aq)
Cr	[Cr(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> Violet	Cr(OH) <sub>3</sub> Blue-green ppt (precipitate)	Cr(OH) <sub>3</sub> Blue-green ppt	[CrCl <sub>6</sub> ] <sup>3-</sup> Blue-violet
Mn	[Mn(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> Pale pink	Mn(OH) <sub>2</sub> White/ cream colour ppt	Mn(OH) <sub>2</sub> White/ cream colour ppt	[MnCl <sub>4</sub> ] <sup>2-</sup> Greenish yellow
Fe	[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> Pale-green	Fe(OH) <sub>2</sub> Dirty green ppt	Fe(OH) <sub>2</sub> Dirty green ppt	
	[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> Yellow-brown	Fe(OH) <sub>3</sub> Reddish-brown ppt	Fe(OH) <sub>3</sub> Reddish-brown ppt	[FeCl <sub>4</sub> ] <sup>-</sup> Yellow
Co	[Co(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> Pink	Co(OH) <sub>2</sub> Pink ppt	[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup> yellowish-brown	[CoCl <sub>4</sub> ] <sup>2-</sup> Blue
		With excess OH <sup>-</sup> [Co(OH) <sub>4</sub> ] <sup>2-</sup> Deep-blue	[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> Brownish-red	
Ni	[Ni(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> Green	Ni(OH) <sub>2</sub> Green ppt	[Ni(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup> Blue	[NiCl <sub>4</sub> ] <sup>2-</sup> Yellow
Cu	[Cu(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> Pale blue	Cu(OH) <sub>2</sub> Blue ppt	[Cu(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup> Deep blue	[CuCl <sub>4</sub> ] <sup>2-</sup> Yellow
Zn	[Zn(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> Colourless	Zn(OH) <sub>2</sub> White ppt	[Zn(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup> Colourless	[ZnCl <sub>4</sub> ] <sup>2-</sup> Colourless
		With excess OH <sup>-</sup> [Zn(OH) <sub>4</sub> ] <sup>2-</sup> Colourless		

**Reactions of  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$** 

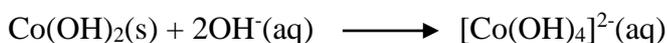
With aqueous  $\text{NH}_3$ , the violet colour  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  aqueous solution will be turned into a blue-green gelatinous precipitate.

**Reactions of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$** 

With strong base ( $\text{NaOH}$ ); the pink colour  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  aqueous solution turns into pink precipitate.



$\text{Co}(\text{OH})_2$  is a pink precipitate. With excess concentrated hydroxide ion solutions, a deep blue solution is formed.

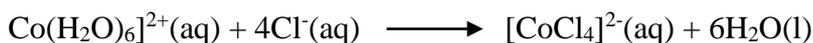


With  $\text{NH}_3$

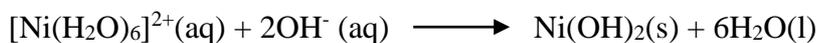


Initially, the pink colour  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  forms a pink colour  $\text{Co}(\text{OH})_2$  precipitate with limited amount of concentrated  $\text{NH}_3$  and on further addition of concentrated  $\text{NH}_3$  it forms a yellow colour  $[\text{Co}(\text{NH}_3)_6]^{2+}$  complex ion. However due to the auto-oxidation,  $[\text{Co}(\text{NH}_3)_6]^{2+}$  complex convert to a brown colour  $[\text{Co}(\text{NH}_3)_6]^{3+}$ . Because of this, the solution appears as yellowish-brown solution.

With conc.  $\text{HCl}$ , pink colour solution turns into a blue colour solution.

**Reactions of  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$** 

With a strong base, the green colour  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  aqueous solution turns into a green precipitate.



With excess  $\text{NH}_3(\text{aq})$ , the green colour  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  solution turns into a deep blue solution.

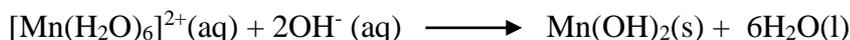


With concentrated  $\text{HCl}$ , green colour solution turns into a yellow colour solution.



**Reactions of  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$** 

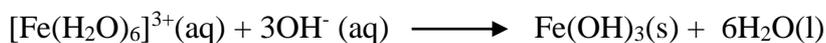
With strong base, pale pink colour  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  aqueous solution turns to a white/ cream colour precipitate.



With aqueous  $\text{NH}_3$ , the pale pink colour solution turns into a white/ cream colour precipitate.

**Reactions of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$** 

With strong base, yellow colour  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  aqueous solution turns into a reddish-brown precipitate.



With aqueous  $\text{NH}_3$ , yellow colour  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  aqueous solution turns into a reddish-brown precipitate.

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

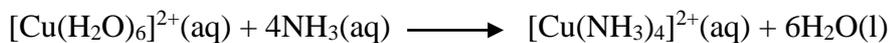
With strong base, the blue colour  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  aqueous solution turns into a blue precipitate.



With a limited amount of aqueous  $\text{NH}_3$ , blue colour solution turns into a blue precipitate.



With excess aqueous  $\text{NH}_3$ , blue colour solution turns into a deep blue colour complex.

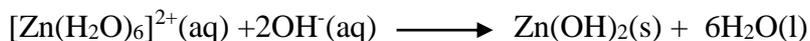


With concentrated  $\text{HCl}$ , blue colour solution turns into a yellow colour solution.

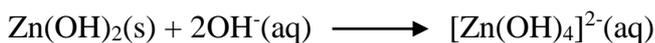


**Reactions of  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$** 

With limited amount of strong base, colourless  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$  aqueous solution turns into a white precipitate.



With excess strong base; white precipitate turns into a colourless clear solution.



The colourless solution turns into a white precipitate, then with excess base, the precipitate dissolves to form a colourless solution.

**4.10.8 Importance of *d* block elements**

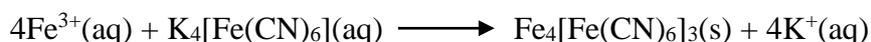
1. Transition metals are good conductors (Au, Ag and Cu), and are also malleable, ductile, and lustrous. Transition metals can be mixed together to produce alloys since they have similar atomic sizes. These alloys are used since the ancient time for various purposes. Production of alloys can change the properties of metals.
2. Cobalt isotope  $^{60}\text{Co}$  is widely used as a radiation source in radiotherapy.
3. Transition metal atoms and ions are used to develop compounds with catalytic properties that are widely used in different industries as catalyst.
4. Since transition metals can form various coloured compounds, they are used as pigments for the production of paint. They are also used to produce coloured glasses and glass bottles.
5. *d* block elements such as Ni and Cd are used to produce rechargeable batteries.
6. They are used in the production of compounds such as cadmium telluride (CdTe) and copper indium diselenide in photovoltaic cells. The solar cell is an example for a photovoltaic cell.

**4.10.9 Identification tests for selected cations of *d* block elements**

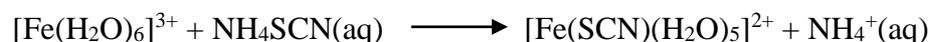
1.  $\text{Fe}^{2+}$   
Formation of  $\text{KFe}[\text{Fe}(\text{CN})_6]$ , a dark-blue precipitate of with  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , can be used to identify  $\text{Fe}^{2+}$ .



2.  $\text{Fe}^{3+}$   
Formation of  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ , Prussian-blue complex of with  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , can be used to identify  $\text{Fe}^{3+}$ .



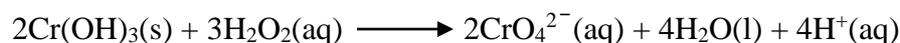
Formation of red colour,  $[\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}$  complex with a slightly acidic  $\text{NH}_4\text{SCN}$  solution, can be used to identify  $\text{Fe}^{3+}$ .



3.  $\text{Cr}^{3+}$

Oxidation of  $\text{Cr}^{3+}$  to yellow colour solution of  $\text{CrO}_4^{2-}$

Addition of excess of sodium hydroxide to a  $\text{Cr}^{3+}$  solution followed by a few milliliters of 6% hydrogen peroxide form a yellow colour solution of  $\text{CrO}_4^{2-}$ .



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