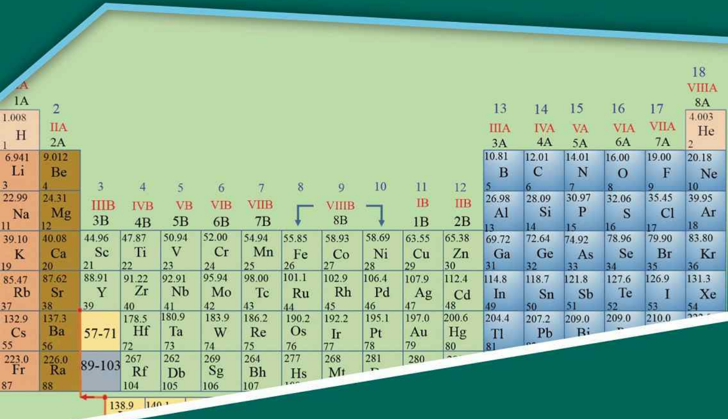
Inorganic Chemistry

for Advanced Level Secondary Schools

Student's Book

Form Five and Six



Tanzania Institute of Education

Inorganic Chemistry

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Student's Book
Form Five and Six

THE UNITED REPUBLIC OF TANZANIA
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Preface

This book, Inorganic Chemistry for Advanced Level Secondary Schools, is written specifically for Form Five and Six students in the United Republic of Tanzania. The book is prepared according to the 2009 Chemistry Syllabus for Advanced Level Secondary Education Form V-VI, issued by the Ministry of Education and Vocational Training.

The book consists of four chapters, which are: Periodic classification, Selected compounds of metals, Extraction of metals, and Transition elements. In addition to the content, each chapter contains illustrations, exercises, revision questions, and some practical work. Learners are encouraged to do all activities and answer all questions so as to enhance their understanding, and promote acquisition of the intended knowledge, skills, and attitudes.

Tanzania Institute of Education

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Chapter One

Periodic classification

Introduction

Periodic classification is the process of arranging elements in a tabular display called a *periodic table*. The arrangement of the elements is based on the similarities and differences in physical and chemical properties. The primary objective of the classification is to arrange the known facts about the elements so that they can be learnt easily. An understanding of the concept of periodic classification simplifies the study of the physical and chemical properties of the elements as well as their uses. In this chapter, you will learn about the concept of periodicity, periodic trends in the properties of the elements, and the diagonal relationships of the elements in the periodic table.

1.1 Concept of periodicity

Periodicity is a tendency of a particular property of an element to appear every after a certain specific interval in a given arrangement. In this section, you will learn about the efforts of different scientists in trying to classify elements, main features of the modern periodic table, and comparison of the Periodic Law in terms of atomic masses and atomic numbers.

1.1.1 Development of the modern periodic table

The modern periodic table is a result of efforts of some prominent scientists who utilised their time to learn how best they could arrange the elements based on similar physical and chemical properties. The development of the modern periodic table is therefore associated with several ideas of scientists described as follows:

Johann Wolfgang Döbereiner (1780-1849)

In 1829, a German chemist Johann Wolfgang Döbereiner noticed that many of the known elements could be grouped in a set of three elements that have similar properties. These sets of elements were called *triads*. Examples of the Döbereiner's triads are shown in Table 1.1.

Table 1.1 Döbereiner's triads

Element	Relative atomic mass	Element	Relative atomic mass	Element	Relative atomic mass	Element	Relative atomic mass
Li	7	Ca	40	Cl	35.5	S	32
Na	23	Sr	88	Br	80	Se	79
K	39	Ba	137	I	127	Te	128

Johann Wolfgang Döbereiner suggested that all the elements could be grouped in forms of triads, but later attempts to expand the Döbereiner's concept were unsuccessful. However, it is currently known that some portions of the periodic table, for example sulphur, selenium, and tellurium in group VIA, or aluminium, gallium, and indium in group IIIA have a significant similarity in their chemistry. Döbereiner also discovered that the relative atomic mass of the middle element in each triad, was close to the average of the relative atomic masses of the other two elements. This discovery provided a significant clue to other scientists on the importance of relative atomic masses when arranging the elements.

John Alexander Newlands (1837–1898)

In 1863, a British chemist John Alexander Newlands observed that, if elements are arranged in the order of increasing atomic masses, the eighth element starting from a given one was almost a repetition of the first in terms of structure and chemical properties. This finding was comparable to the eighth note of the music notes, hence the use of the word octave. Newlands called it the *Law of Octaves*. The Newlands' arrangement of the elements in the order of increasing relative atomic masses is shown in Table 1.2.

Table 1.2 Parts of the Newlands' arrangement of elements into "octaves"

H	Li	Be	B	C	N	O
F	Na	Mg	Al	Si	P	S
Cl	K	Ca	Cr	Ti	Mn	Fe
Co, Ni	Cu	Zn	Y	In	As	Se

The Newlands' arrangement of the elements worked well for the first 17 elements. Thus, the Law of Octaves was not well received and was ignored for years. The chemical society only acknowledged the significance of the Newlands' discoveries five years after they credited Mendeleev.

The first periodic table

The increasing number of known elements was a motivation for scientists working hard towards the stable periodic table based on arranging the elements according to their properties. As a result, Julius Lothar Meyer and Dmitri Ivanovich Mendeleev created the first periodic table at almost the same time while working independently. Both Meyer and Mendeleev focused on the relationships between atomic masses and various physical and chemical properties. These two scientists can be considered as the co-creators of the modern periodic table, though Mendeleev received more credits. The contribution of each of these scientists is described below.

Julius Lothar Meyer (1830-1895)

In 1864, Julius Lothar Meyer, a German chemist produced the first periodic table of only 28 elements, organised by their valences. The table showed that, elements with similar properties often shared the same valence. Between 1864 and 1870, Meyer produced several versions of the periodic table. In 1869, Meyer compiled a periodic table which consisted of 56 elements based on regular repeating patterns of physical properties such as molar volume. The periodic table according to Julius Lothar Meyer is shown in Table 1.3. The question marks in some elements indicate that those elements are likely to exist, they just hadn't been discovered yet.

Table 1.3 The periodic table as suggested by Julius Lothar Meyer

I	II	III	IV	V	VI	VII	VIII	IX
	B (11)	Al (27.3)	–	–	–	? In (113.2)	Tl (202.7)	
				–				
	C (11.97)	Si (28)				Sn (117.8)		Pb (206.4)
			Ti (48)		Zr (89.7)			
	N (14.01)	P (30.9)		As (74.9)		Sb (122.1)		Bi (207.5)
			V (51.2)		Nb (93.7)		Ta (182.2)	
	O (15.96)	S (31.98)		Se (78.0)		Te (128?)		
			Cr (52.4)		Mo (95.6)		W (183.5)	
	F (19.1)	Cl (35.38)		Br (79.85)		I (126.5)		
			Mn (54.8)		Ru (103.5)		Os (198.6?)	
			Fe (55.9)		Rh (104.1)		Ir (196.7)	
			Co & Ni (58.9)		Pd (106.2)		Pt (196.7)	
Li (7.01)	Na (22.96)	K (39.04)		Rb (85.2)		Cs (132.7)		
			Cu (63.3)		Ag (107.66)		Au (196.2)	
Be (9.3)	Mg (23.9)	Ca (39.9)		Sr (87.0)		Ba (136.8)		
			Zn (64.9)		Cd (111.6)		Hg (199.8)	

The molar volume or atomic volume was obtained by dividing the molar mass (atomic mass) in grams per mole by the density of the elements in grams per cubic centimetre as shown in the following formula:

$$\text{Molar volume (cm}^3\text{/mol)} = \frac{\text{Molar mass (g/mol)}}{\text{Density}\,(\text{g/cm}^3)}$$

The variations in molar volumes against atomic numbers as per Meyer's plot are shown in Figure 1.1. Alkali metals appear to have the highest molar volumes. Non-metals appear in the rising parts of the graph, while metals appear at the top, bottom, and on the down slope.

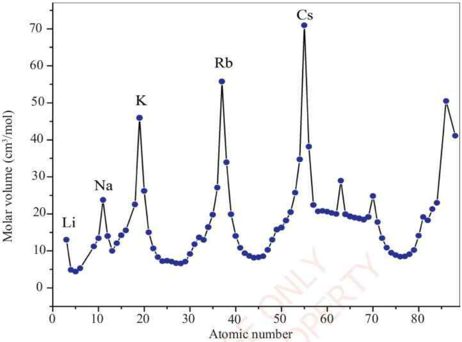


Figure 1.1 A graph of molar volumes of atoms (cm^{3}mol^{-1}) against atomic numbers

Although Julius Lothar Meyer failed to classify the elements correctly, he made a very significant contribution towards the development of the modern periodic table.

Dmitri Ivanovich Mendeleev (1834 – 1907)

In 1869, a Russian chemist Dmitri Ivanovich Mendeleev compiled the periodic table of the known elements in ascending order of their atomic weights. Mendeleev developed the Newlands' idea by placing elements with similar properties into groups and periods. He put forward the Periodic Law which states that *the properties of the elements are a periodic function of their atomic weights.* Mendeleev predicted the existence and properties of new elements and left the gaps for unknown elements. For instance, Mendeleev left a gap below silicon and called the yet undiscovered element as eka-silicon. Similarly, this scholar named scandium as eka-boron and gallium as eka-aluminium. Most of the Mendeleev's predictions were proved correct when the elements in question were subsequently discovered. Table 1.4 shows the Mendeleev's periodic table based on the original table of 1871. In this table, the spaces marked with dash lines represent the elements that Mendeleev deduced their existence but were not known by that time, so he left spaces where they can best fit. The question marks before symbol indicate the uncertainty in the name of some elements.

Table 1.4 The Mendeleev`s 1871 periodic table

Period	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
1	H = 1							
2	Li = 7	Be = 9.4	B = 11	C = 12	N = 14	O = 16	F =19	
3	Na = 23	Mg = 24	Al = 27.3	Si = 28	P = 31	S = 32	Cl = 35.5	
4	K = 39	Ca = 40	--- = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59,
5	(Cu = 63)	Zn = 65	--- = 68	--- = 72	As = 75	Se = 78	Br = 80	Ni = 59, Cu = 63.
6	Rb = 85	Sr = 87	?Yt = 88	Zr = 90	Nb = 94	Mo = 96	--- = 100	Ru =104, Rh = 104,
7	(Ag =108)	Cd = 112	In = 133	Sn =118	Sb = 122	Te = 125	J = 127	Pd =106, Ag = 108.
8	Cs = 133	Ba = 137	?Di =138	?Ce=140	---	---	---	--- --- --- ---
9	(---)	---	---	---	---	---	---	
10	---	---	?Er =178	?La=180	Ta = 182	W = 184	---	Os = 195, Ir = 197
11	(Au = 199)	Hg = 200	Ti = 204	Pb = 207	Bi = 208	---	---	Pt = 198, Au = 199
12	---	---	---	Th = 231	---	U = 240	---	--- --- --- ---

Features of Mendeleev's periodic table

The Mendeleev's periodic table of elements consists of twelve horizontal rows of elements called *periods*, and eight vertical columns called *groups*. The Mendeleev's work is summarised in the following statements:

(a) If the elements are arranged according to their atomic weights, they exhibit an apparent periodicity of properties.

(b) Elements which are similar in chemical properties have atomic weights which are similar in values or which increase regularly.

(c) The arrangement of the elements or groups of the elements in the order of their atomic weights corresponds to their valences.

(d) Elements with small atomic weights diffuse widely and the magnitude of their atomic weights determines their properties.

(e) It was expected that, there could be discoveries of new elements that were not yet known, for example, elements that are analogous to aluminium and silicon whose atomic weights would be between 65 and 75.

(f) The atomic weight of an element may sometimes be amended based on the knowledge of the closely related elements.

Usefulness of Mendeleev's periodic table

The Mendeleev's classification of elements was useful in various ways. Elements with similar chemical properties appeared in the same group. For example, the groups for halogens, alkali metals, and alkaline earth metals were already identified. Also, the table was useful in predicting the existence and properties of the elements which were not yet discovered. The positions of such elements in the table were left empty. The table was also useful in checking the relative atomic masses of the elements. Although some elements had more than one valence, particular valences were associated with particular groups. The valences and the equivalent weights were used to check the correctness of several doubtful atomic masses.

Shortcomings of Mendeleev's periodic table

The following are the shortcomings of the Mendeleev's periodic table:

(a) Mendeleev failed to assign a correct position for hydrogen in his periodic table because it resembles the elements of group IA as well as elements of group VIIA.

(b) The 14 rare earth metals were placed in the same group (group VIII) even though they have different atomic weights.

(c) Some pairs of elements had to be included in inverse order of their relative atomic masses so as to maintain the correct relationships of the elements. Examples of these pairs were argon (39.9) and potassium (39.1), cobalt (58.9) and nickel (58.7), tellurium (128) and iodine (127).

These shortcomings called for modifications that resulted into the development of the modern periodic table.

Henry Gwyn Moseley (1887 – 1915)

Henry Gwyn Moseley was a British physicist who developed the application of x-ray spectra to study atomic structure. The Moseley's discoveries resulted in a more accurate positioning of the elements in the periodic table by atomic numbers. In 1913, Moseley published the results which showed that the ordering of the wavelengths of the x-ray emissions of the elements corresponded to the ordering by their atomic numbers. This discovery revealed that, the properties of the elements in the periodic table varied periodically with atomic numbers and not atomic weights as proposed by Mendeleev, Meyer, and others. The arrangements of the elements in the order of increasing atomic numbers eliminated the shortcomings of the Mendeleev's periodic table. The Moseley's work led to the formulation of the modern periodic table and the Periodic Law based on the atomic numbers. The Modern Periodic Law states that, *the chemical and physical properties of elements are the periodic functions of their atomic numbers*.

1.1.2 Features of the modern periodic table

The periodic table consists of seven horizontal rows called *periods* and eighteen vertical columns called *groups*. A group in the periodic table is a set of elements which have the same numbers of electrons in their outermost shells and hence have similar properties. On the basis of Table 1.5, the first group (group IA) consists of elements known as *alkali metals* which have one electron in their outermost shells. The second group (group IIA) consists of elements known as *alkaline earth metals* which have two electrons in their outermost shells. The elements in groups IIIA, IVA, VA, and VIA have three, four, five, and six electrons, respectively in their outermost shells. The group VIIA consists of elements which have seven electrons in their outermost shells. These elements are known as *halogens*. The elements in group VIIIA have eight electrons in their outermost shells and are collectively known as *noble gases*. The elements in groups IA, IIA to VIIIA are called main group elements. The elements from group 3 (group IIIB) to group 12 (group IIB) are called *transition elements*.

A period in the periodic table is a set of elements which have the same number of electron shells and whose atomic numbers increase by one unit from one atom to another. In the period, elements are arranged in order of increasing atomic numbers. The number of electron shells increases from one period to another down the group. Within the period, the number of protons and electrons increase by one when moving from one group to another.

In the modern periodic table, the first period is the shortest with only two elements which are hydrogen and helium. The second and third periods consist of eight elements each, which start from Li to Ne and Na to Ar, respectively. The fourth and the fifth periods are long with 18 elements each, which start from K to Kr and Rb to Xe, respectively. The sixth and seventh periods are incomplete periods of elements which are radioactive, including rare earth elements (atomic numbers 57 to 71). Elements with atomic numbers from 93 to 105 are only synthetic, discovered during atomic researches. The structure of the modern periodic table is presented in Table 1.5.

Table 1.5 The modern periodic table

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
1.008 H 1																	4.003 He 2
6.941 Li 3	9.012 Be 4											10.81 B 5	12.01 C 6	14.01 N 7	16.00 O 8	19.00 F 9	20.18 Ne 10
22.99 Na 11	24.31 Mg 12											26.98 Al 13	28.09 Si 14	30.97 P 15	32.06 S 16	35.45 Cl 17	39.95 Ar 18
39.10 K 19	40.08 Ca 20	44.96 Sc 21	47.87 Ti 22	50.94 V 23	52.00 Cr 24	54.94 Mn 25	55.85 Fe 26	58.93 Co 27	58.69 Ni 28	63.55 Cu 29	65.38 Zn 30	69.72 Ga 31	72.64 Ge 32	74.92 As 33	78.96 Se 34	79.90 Br 35	83.80 Kr 36
85.47 Rb 37	87.62 Sr 38	88.91 Y 39	91.22 Zr 40	92.91 Nb 41	95.94 Mo 42	98.00 Tc 43	101.1 Ru 44	102.9 Rh 45	106.4 Pd 46	107.9 Ag 47	112.4 Cd 48	114.8 In 49	118.7 Sn 50	121.8 Sb 51	127.6 Te 52	126.9 I 53	131.3 Xe 54
132.9 Cs 55	137.3 Ba 56	57-71	178.5 Hf 72	180.9 Ta 73	183.9 W 74	186.2 Re 75	190.2 Os 76	192.2 Ir 77	195.1 Pt 78	197.0 Au 79	200.6 Hg 80	204.4 Tl 81	207.2 Pb 82	209.0 Bi 83	209.0 Po 84	210.0 At 85	222.0 Rn 86
223.0 Fr 87	226.0 Ra 88	89-103	267 Rf 104	262 Db 105	263 Sg 106	264 Bh 107	277 Hs 108	268 Mt 109	281 Ds 110	280 Rg 111	285 Cn 112	286 Nh 113	289 Fl 114	286 Mc 115	292 Lv 116	294 Ts 117	294 Og 118

138.9 La 57	140.1 Ce 58	140.9 Pr 59	144.2 Nd 60	145 Pm 61	150.4 Sm 62	152.0 Eu 63	157.3 Gd 64	158.9 Tb 65	162.5 Dy 66	164.9 Ho 67	167.3 Er 68	168.9 Tm 69	173.04 Yb 70	175.0 Lu 71
227.0 Ac 89	232.0 Th 90	231.0 Pa 91	238.0 U 92	237 Np 93	244 Pu 94	243 Am 95	247 Cm 96	247 Bk 97	251 Cf 98	252 Es 99	257 Fm 100	258 Md 101	259 No 102	262 Lr 103

🟧 Alkali metals (*s*-**block**)

🟫 Alkaline earth metals (*s*-**block**)

🟦 ***p*-block** elements

🟩 Transition elements (***d*-block**)

🟨 Lanthanides (***f*-block**)

⬜ Actinides (***f*-block**)

Blocks of the modern periodic table

Depending on the types of orbitals occupied by the electrons in the outermost shells, the periodic table is divided into four main blocks, namely, *s*-block, *p*-block, *d*-block, and *f*-block. The letters *s*, *p*, *d,* and *f* were coined from the properties of spectral lines observed from the hydrogen atom which were sharp (*s*), principal (*p*), diffuse (*d*), and fundamental (*f*). The division of periodic table into blocks is shown in Figure 1.2.

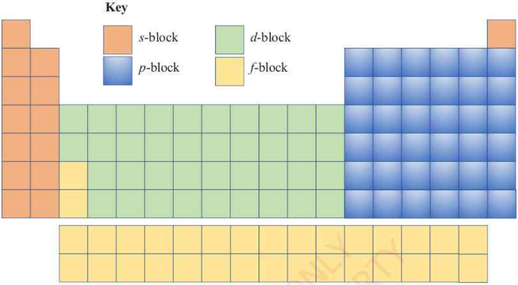


Figure 1.2 A sketch of the periodic table to locate the *s*, *p*, *d,* and *f*-blocks

The *s*-block consists of elements whose outermost electrons occupy the *s*-orbitals and constitute the elements in groups IA and IIA, and helium (He), which is found in group VIIIA. The *p*-block consists of elements whose outermost electrons occupy the *p*-orbitals and constitute the elements in groups IIIA to VIIIA with the exception of helium (He).

The *s* and *p*-blocks collectively form the main group elements whose general outer electronic configurations are $ns^{1\text{ to }2}$ and $ns^2np^{1\text{ to }6}$, respectively. Groups IB to VIIIB form *d*-block elements whose outermost electrons occupy the *d*-orbitals. These elements have the general outer electronic configuration of $(n\text{-}1)\,d^{1\text{ to }10}\,ns^{1\text{ to }2}$.

Similarly, *f*-block consists of elements whose outermost electrons occupy the *f* orbitals. Elements in the *f*-block elements include lanthanides (atomic numbers 57 to 71) and actinides (atomic number 89 to 103) whose general outermost electronic configuration is $(n\text{-}2)f^{1\text{to}14}(n\text{-}1)\,d^{1\text{ to }10}\,ns^{1\text{ to }2}$. The *d* and *f*-block elements are collectively known as *transition elements* as they exhibit transition behaviour between *s* and *p*-block elements. Transition elements can further be classified into outer transition (*d*-block) and inner transition elements (*f*-block).

1.1.3 Comparison between Mendeleev's and modern period tables

The arrangements of elements using atomic masses and atomic numbers resulted into differences and similarities in the study of elements in the periodic table. The use of atomic weights in arranging the elements resulted into the Mendeleev's periodic table and the modern periodic table arose due to the placement of the elements by considering their atomic numbers. The following are the similarities between the Mendeleev's and modern periodic tables:

(a) Both used columns and rows to classify elements.

(b) Both tables aimed at simplifying the study of the elements.

(c) Both tables indicated periodicity properties of the elements.

The differences between the Mendeleev's and modern periodic tables are presented in Table 1.6.

Table 1.6 Differences between the Mendeleev's and modern periodic tables

Mendeleev's periodic table	Modern periodic table
Elements were arranged in order of increasing atomic weights.	Elements are arranged in order of increasing atomic numbers.
Table consisted of gaps for unknown elements.	There are no gaps in the modern periodic table
Elements with different properties were placed together.	Elements with different properties are placed in different groups and periods.
Rows of inner transition elements were not included.	Rows of inner transition elements are included.
Failed to locate the position of hydrogen.	Hydrogen is placed on top of group one.
Elements with higher atomic masses were placed before the elements with lower atomic masses. For example, argon (atomic mass 39.9) was placed before potassium (atomic mass 39.1).	The anomalies of having higher atomic masses of elements before elements with lower atomic masses are resolved.
Isotopes of the same elements were placed differently.	Isotopes of the same element are placed together.

Activity 1.1 **Designing a modern periodic table**

Requirements: Manila sheets, maker pens, rulers, and pencils.

Procedure

1. Prepare 30 small cards from manila sheets.
2. Label the cards with respective element symbols starting from the first to the 30th.
3. Design the periodic table using another manila sheet by fixing the cards on their appropriate positions on the manila sheet.

Question

How is your design useful in explaining the physical and chemical properties of elements?

Exercise 1.1

1. State the Law of Octaves as given by John Alexander Newlands.
2. Describe the Meyer's classification of elements.
3. State the Mendeleev's Periodic Law and give its merits and demerits.
4. (a) State the Modern Periodic Law.
   (b) What is the difference between the Mendeleev's periodic table and the modern periodic table?
5. Explain the correctness of using the term *periodic* in the construction of the periodic table.
6. Outline the general features of the modern periodic table?
7. Describe the basis for classifying the elements into the blocks in the modern periodic table.

1.2 Periodic trends in properties of elements

Periodic trend is a regular variation in the properties of elements with increasing atomic number, caused by regular variations in the atomic structures of the elements. The arrangement of elements using the atomic numbers in the modern periodic table makes it easy to study the trends of the physical and chemical properties of the elements. In this section, the general periodic trends of elements across the periods and down the groups of the periodic table will be covered.

1.2.1 Periodic trends in physical properties of elements

The major periodic trends in physical properties include atomic size, ionisation energy (IE), electron affinity (EA), electronegativity, metallic character, melting points (mp), and boiling points (bp). The following are trends of the physical properties of elements down the group and across the period:

Atomic size

Atomic size is determined by the atomic radius, which is one-half the distance between the nuclei of two covalently bonded atoms. For monoatomic elements such as noble gases, the atomic size is simply the diameter of the whole atom, which is equal to two times the radius of the isolated atom (also called van der Waals radius). In general, the atomic radius is determined by two factors which are the effect of the nuclear charge and the screening effect.

Effect of nuclear charge

The nuclear charge is the attractive force that pulls all the electrons closer to the nucleus. The higher the nuclear charge, the smaller the atomic radius. The atomic radii decrease from left to right of the period due to the increase in effective nuclear charge caused by an increase in the number of protons while the number of shells remains the same. Down the group, the atomic radii increase due to the decrease in the effective nuclear charge caused by an increase in the number of shells.

Screening (shielding) effect

Screening effect is the tendency of the innermost electrons to prevent the outermost electrons from receiving full influence of proton from the nucleus. The shielding effect is caused by the repulsion force between the electrons in the inner shell and those in the outer shell. This effect lowers the effective nuclear charge to the outermost shell, causing the increase in the atomic radius. The higher the number of shells, the stronger the screening effect and vice versa.

Generally, the atomic sizes decrease from left to right across the period (Figure 1.3). This is due to an increase in the number of electrons and protons, and hence the effective nuclear charge which then pulls the outer electrons closer. Despite the fact that, the number of protons increases proportionally to the number of electrons across the periods, the sizes of the atoms decrease because the number of shells remains constant. This in turn increases the effective nuclear charge which outweighs the screening effect. Appendix 1 shows both the empirical and calculated atomic radii for most of the element.

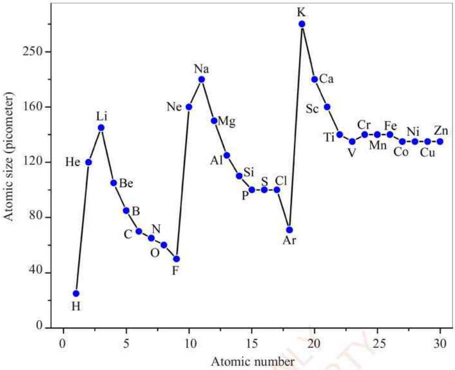


Figure 1.3 Periodic trend in atomic size across the periods and down the groups

On the other hand, the atomic sizes increase down the group because an increase in the number of shells makes the outer electrons to be far away from the nucleus. Atomic sizes increase down the group due to the increase in the number of shells. The increase in the number of shells increases both the distance between the outer electrons and the nucleus as well as the number of inner electrons. The increased number of electrons causes an increase in the screening effect to the outer electrons which decreases the effective nuclear charge and therefore increasing the atomic sizes.

Ionic radii

The ionic radius is half the distance between two ions that are barely touching each other. Depending on the electronic charge of an ion, the ionic radius may be larger or smaller than the atomic radius (the radius of a neutral atom). Neutral atoms have larger atomic radii than their corresponding cations because electrons are removed and the remaining fewer electrons in cation experience stronger nuclear attractive forces.

For the atoms that consist of only one electron in the outermost shell, the removal of one electron during ionisation is accompanied by the loss of the shell, hence smaller ionic radii. Additionally, when an electron is removed from the outermost shell, the remaining fewer electrons experience a weaker electron-electron repulsion, and therefore are strongly attracted to the nucleus. An anion has a larger ionic size than a neutral atom because the addition of electron increases the size of the electron cloud.

Also in anions, the nuclear attractive force is distributed to a larger number of electrons. As a result, the electrons experience weaker nuclear attractive forces compared to a neutral atom. These weaker nuclear attractive forces are also attributed to an increase in the electron-electron repulsion due to the additional electrons. Therefore, the general trend in ionic radii is the same as that of the atomic radii which decrease across the period due to the increased effective nuclear charge, and increases down the group because of an increase in the number of shells.

Ionisation energy

In order to remove an electron from an atom, energy must be applied to overcome the electrostatic forces of attraction between the electron and the nucleus. This energy is called *ionisation energy* (IE). The ionisation energy is the minimum amount of energy required to completely remove one mole of the electron from one mole of a gaseous atom or ion. It is expressed in kilojoules per mole (kJ/mol). The lower the ionisation energy, the more easily the atom becomes a cation and vice versa. Ionisation energy is determined by the atomic size, nuclear charge, screening or shielding effect, electron locality in orbitals, and electronic configuration.

Atomic size

As the size of an atom increases, the distance between the nucleus and valence electrons also increases. As a result, the force of attraction between the nucleus and valence electrons decreases. This makes the valence electrons to be loosely held and therefore require smaller energy to remove an electron. Thus, the ionisation energy decreases with increase in the atomic sizes (down the group) and increases with the decrease in the atomic sizes (along the period).

Nuclear charge

An increase in the nuclear charge causes an increase in the force of attraction between the nucleus and valence electrons. This makes it difficult to remove an electron from a valence shell. Therefore, an increase in the nuclear charge causes the ionisation energy to increase.

Screening or shielding effect

Electrons that are present in the shells between the nucleus and the valence shell reduce the electrostatic attraction between the nucleus and the outermost electrons. The larger the number of electrons in the inner shells, the greater the screening effect and hence the easier the removal of an electron (lower ionisation energy).

Electron locality in orbitals

Within the same energy level, the *s*-electrons are closer to the nucleus than the *p*-electrons, *d*-electrons, and lastly *f*-electrons. Hence, electrons in *s*-orbitals experience more attraction from the nucleus than those in the *p, d*, and *f*-orbitals. Therefore, ionisation energy within a certain energy level decreases in the trend: $s > p > d > f$. This means that the *s*-electrons have the highest ionisation energies and the *f*-electrons have the lowest ionisation energies.

Electronic configuration

Atoms whose orbitals are full-filled or half-filled with electrons have stable electronic configurations. Therefore, these atoms have a low tendency of losing electrons, hence high ionisation energies. It is important to note that, it is possible to remove more than one electron from an atom. In this case, there are different types of ionisation energies starting from the 1st, 2nd, 3rd to the nth ionisation energy depending on the valence of an atom.

First ionisation energy (1st IE) is the energy which is required to remove one mole of the most loosely held electrons from one mole of a gaseous atom to produce one mole of gaseous ion with a charge of positive one (+1).

$$X(g) \longrightarrow X^{+}(g) + e^{-} \qquad 1^{st}\ \text{IE}$$

Second ionisation energy (2nd IE) is the energy which is needed to remove a second electron from one mole of a unipositive gaseous ion to form a *di*-positive gaseous ion.

$$X^{+}(g) \longrightarrow X^{2+}(g) + e^{-} \qquad 2^{nd}\ \text{IE}$$

If an atom has two or more electrons in the valence shell, the amount of energy needed to remove the 2nd, 3rd and nth electrons increases steadily. That is, the 1st ionisation energy is always lower than the 2nd and subsequent ionisation energies. This is because when the first electron is removed (1st IE), the remaining fewer electrons experience stronger nuclear attractive effects. Also, the attractive effects between the electrons in the valence shell and the positive charge created by the 1st ionisation make it difficult for the second electron to be removed, and hence higher second ionisation energy (2^{nd} IE). The first and the other successive ionisation energies for Na, Mg, and Al are shown in Table 1.7.

Table 1.7 The first and the other successive IEs for Na, Mg, and Al in kJ mol^{-1}

Element	**1^{st} IE**	**2^{nd} IE**	**3^{rd} IE**	**4^{th} IE**
Na	496	4565	6912	9540
Mg	738	1450	7732	10550
Al	577	1816	2744	11580

For sodium (Na), the 1^{st} IE involves the removal of one electron from the outer 3*s*-orbital but the second should be removed from the full-filled inner 2*p*-orbitals which have a stable configuration. In magnesium, the 2^{nd} IE involves the removal of an electron from the charged magnesium ion (Mg^{+}), which has an extra nuclear charge, hence higher ionisation energy. To remove a third electron (3^{rd} IE) is even more difficult because the electron should come from the full-filled inner 2*p*-orbitals. The same argument holds during the formation of aluminium ion (Al^{3+}).

Periodic trends in the ionisation energies

Generally, the ionisation energies (IEs) increase from left to right across a period due to the increase in the effective nuclear charge which holds the electrons tightly. The IEs decrease down the group due to the increase in the number of shells and hence the electron distance from the nucleus which lowers the attraction for the electrons. Despite this general trend, there is a large discrepancy in the IEs for the various elements in the periodic table. Figure 1.4 shows a sketch of the 1^{st} IEs against the atomic numbers. The discrepancy in the trends of the IEs is observed between beryllium (Be) and boron (B), and nitrogen (N) and oxygen (O) in period 2, and between magnesium (Mg) and aluminium (Al), and phosphorus (P) and sulphur (S) in period 3.

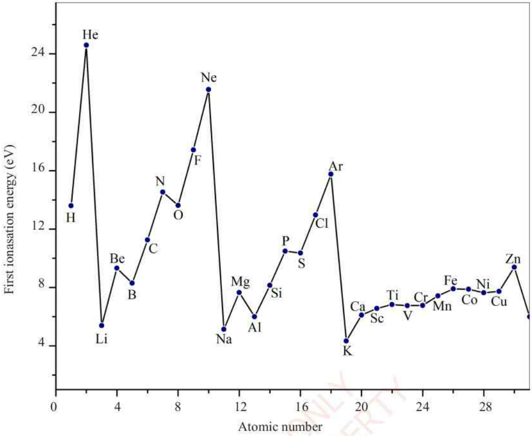


Figure 1.4 A graph of first ionisation energies against atomic numbers for some elements

Beryllium and boron

The decrease in IEs across the period from beryllium (Be) to boron (B) is observed not to follow the general trend of increasing the IEs across the period from left to right. The 1st IE of Be involves the removal of an electron from the 2*s*-orbital that is full-filled with electrons. Meanwhile, the 1st IE of B involves the removal of an electron from the 2*p*-orbital that is partially filled (with one unpaired electron). Therefore, the higher IE of Be relative to that of B can be explained by two factors. First, the electrons in the 2*s*-orbital are closer to the nucleus than the electrons in the 2*p*-orbital, therefore they experience stronger nuclear attractive forces. Secondly, the electronic configuration of Be is full-filled with 2 electrons in 2*s*-orbitals and therefore is stable, while B is partially filled with only one electron in 2*p*-orbitals, which makes it easier to lose one electron and acquire stability leading to its low IE.

Nitrogen and oxygen

The decrease in the 1st IEs across the period from nitrogen to oxygen is also observed not to follow the general trend of increasing IEs across the period from left to right. Nitrogen consists of 3 unpaired electrons in the 2*p*-orbital, which is a half-filled configuration and therefore stable. To remove an electron from this stable configuration needs a higher energy, hence higher IE. In oxygen, the outer 2*p*-orbital consists of 2 unpaired electrons and one pair of electrons. This configuration is unstable as it is neither half-filled nor full-filled. Therefore, it requires less energy to remove an electron due to the lower stability causing its low first IE.

Magnesium and aluminium

The decrease in the 1st IE across the period is also observed when moving from magnesium (Mg) to aluminium (Al). This does not follow the general trend of the increase in 1st IEs across the period. In Mg, the 1st IE involves the removal of an electron from a set of paired electrons from 3*s*-orbital which is full-filled hence more stable. Also, this orbital experiences high nuclear attractive forces because it is closer to the nucleus than 3*p*, therefore it requires higher energy to remove the electron leading to higher 1st IE. For the case of Al, the 1st IE involves the removal of an electron from the 3*p*-orbital which is partially filled with only one electron in 3*p*-orbital, and is higher in energy than the 3*s*-orbital. As a result, the electron is removed more easily, leaving a stable configuration hence low 1st IE.

Phosphorus and sulphur

Phosphorus has higher IE than sulphur due to its half-filled electronic configuration which is stable, hence to remove an electron from phosphorus, high IE is needed contrary to sulphur which has unstable electronic configuration caused by single and double occupancy of electrons in the degenerate 3*p*-orbitals which makes it easy to remove electrons.

Electron affinity

The electron affinity (EA) of an atom or molecule is the amount of energy change when one mole of electrons is added to one mole of a gaseous atom or ion to form one mole of gaseous ions. EA is expressed in units of kJ/mol and is represented by the following general equation:

$$X(g) + ne^- \longrightarrow X^{n-}(g) \qquad EA = \text{...... kJ/mol}$$

Just like IE, electron affinity can be first, second, third up to the nth electron affinity depending on the valence of an atom. The first EA is the energy released when one mole of electrons is added to one mole of gaseous atom to form one mole of negative monovalent ions. For example addition of one mole of electrons to one mole of gaseous oxygen atom:

$$O(g) + e^- \longrightarrow O^-(g) \qquad EA = -142 \text{ kJ/mol}$$

The second EA is the energy absorbed when one mole of electrons is added to one mole of negative monovalent ion to form one mole of negative divalent ions.

Example:

$$O^-(g) + e^- \longrightarrow O^{2-}(g) \qquad EA = +791 \text{ kJ/mol}$$

It is important to note that the first electron affinity is always negative because the electron is attracted to the atom's nuclear charge. The second and subsequent electron affinities are always positive because the energy must be absorbed in order to overcome electrostatic repulsion and add another electron to a negative ion. In general, the electron affinity depends on the atomic size, screening or shielding effect and electronic configuration.

Atomic size

As the sizes of atoms increase, the effective nuclear charge or the nuclear attraction for adding electron decreases. As a result, the tendency of an atom to attract additional electron towards itself decreases. Therefore, electron affinity is inversely related to the size of the atom and directly related to the effective nuclear charge.

Screening or shielding effect

Electrons closer to the nucleus of an atom hinder the nuclear attraction for the incoming electron. Therefore, the larger the number of electrons around the nucleus the lower the electron affinity (more negative). This means that, electron affinity is inversely related to the shielding effect.

Electronic configuration

Electron affinities are largely influenced by electronic configurations of the elements. If an atom has a full-filled or half-filled configuration of orbitals, its electron affinity will be low. This is because, these configurations are stable and have less tendency to accept the incoming electrons, hence the lower the values of the electron affinity. If an atom has an electronic configuration that is neither half-filled nor full-filled, its electron affinity will be relatively higher because the atom is less stable and easily accepts an incoming electron to acquire stability.

Periodic trends in electron affinity

Generally, electron affinities increase (become more negative) across the period from left to right due to decrease in atomic sizes as a result of increase in the effective nuclear charge. This decrease in atomic sizes makes it possible for the nucleus to pull the incoming electrons more readily. The electron affinities decrease down the group due to an increase in the atomic sizes, which causes the decrease in the electron attraction to the nucleus.

However, the changes in electron affinities down the group are not as large as observed across the period because, the lower electron-nucleus attraction is counter-balanced by the lower electron-electron repulsion. This low electron-electron repulsion is caused by a large electron-electron distance due to a larger valence shell. Beside the general trend in electron affinities across the periods and down the groups, there are some observed discrepancies (Figure 1.5). Elements in group IA, namely Li, Na, K, Rb, and Cs have unexpected higher electron affinities than the corresponding elements in group IIA within the same period which are Be, Mg, Ca, Sr, and Ba, respectively. Group IA elements have one electron in the outermost *s*-orbitals, while group IIA elements have two electrons in the outermost *s*-orbitals (full-filled). Therefore, the incoming electron in group IA elements will be filled in the outermost *s*-orbital having one electron, hence higher electron affinity (becomes more negative). For the case of group IIA elements, which have a full-filled outermost *s*-orbital, the incoming electron will move to the empty *p*-orbital, which is higher in energy and therefore energetically unfavourable. As a result, these elements have lower electron affinities.

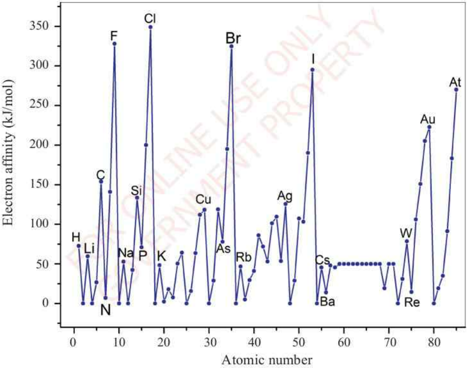


Figure 1.5 Periodic trends in the electron affinities for main group elements as function of atomic numbers

Another discrepancy is observed between group IVA elements, namely C, Si, Ge, and Sn and the corresponding group VA elements which are N, P, As, and Sb, respectively within the same period. Group IVA elements have two unpaired electrons in the outermost *p*-orbitals, and one empty *p*-orbital while group VA have three unpaired electrons in the *p*-orbitals (half–filled), and therefore stable. Group IVA elements need one electron to acquire half–filled configurations which are stable, and therefore have higher electron affinities. For the case of group VA elements, the addition of one electron creates the first paired electrons in the *p*-orbital. Due to the electron-electron repulsion, this atom becomes less stable and therefore energetically unfavourable. As a result, group VA elements have low electron affinities (less negative or more positive).

For the case of group VIIA, a discrepancy is observed between fluorine and chlorine. Electron affinity of fluorine is unexpectedly lower than that of chlorine; this is because fluorine has small size that makes electrons to accumulate within a small region of an atom (increased electron density). The incoming electrons will experience more repulsion; thus some amount of energy must be absorbed to overcome repulsion hence energy released becomes smaller than expected.

Electronegativity

Electronegativity is the ability of an atom in a molecule to attract a bonding pair of electrons towards itself. An atom with high electronegativity has a strong tendency to attract electrons towards itself (high electron affinity) while resisting its electrons from being taken (high ionisation energy). Similarly, an atom with a positive electron affinity and a low ionisation energy has a very low electronegativity because it does not want more electrons and can willingly give away its valence electrons. Therefore, electronegativity is closely related to ionisation energy and electron affinity.

Generally, the electronegativity increases from left to right across the period due to an increase in the effective nuclear charge. This increase in the effective nuclear charge makes it difficult for an atom to lose electrons hence high ionisation energy and an increase in the electron affinity. Down the group, the electronegativity decreases due to a decrease in the effective nuclear charge. This decrease in the effective nuclear charge accounts for the decrease in the ionisation energy and a small decrease in the electron affinity. Just like other periodic properties, the trend in electronegativity shows some discrepancies. However, these discrepancies are not observed in the main group elements but only in the transition elements. The periodic trend in electronegativity as a function of atomic numbers is shown in Figure 1.6.

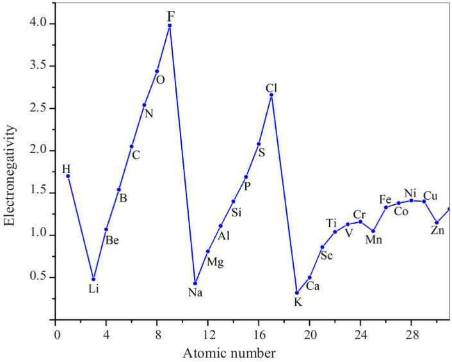


Figure 1.6 Periodic trend in electronegativity

Metallic character

Metallic character is referred to as a set of chemical properties that are associated with the elements classified as metals in the periodic table. This character depends on the ability of an element to lose its valence electrons. Generally, metals tend to lose electrons to form cations while non-metals have a tendency of gaining electrons to form anions. Metals are also easily oxidised and are strong reducing agents. Metallic character can also be accounted for in terms of various physical properties such as high density, high thermal conductivity, high electrical conductivity, shiny appearance, and malleability.

Periodic trends in metallic characters

Metallic characters decrease across the period from left to right. This is because, the number of electrons in the valence shell increases. Therefore, the tendency of atoms to gain electrons and fill the valence shell increases relative to lose electrons and remove the unfilled shell. Metallic characters increase down the group from top to bottom. This is because when moving down the group, the number of shells increases resulting into low attraction between the nucleus and valence electrons. Therefore, the ability of an element to lose its valence electrons increases.

Periodic trends in melting and boiling points

Melting point is the temperature required to break bonds and change the physical state of a substance from solid to liquid. The stronger the bond, the higher the melting point. The trend in the melting points across the period in the periodic table is not consistent. Generally, metals have higher melting points as compared to non-metals.

Boiling point is the temperature at which the vapour pressure of a substance is equal to the atmospheric pressure. The trend in the boiling points is closely related to that of the melting points, but the values of boiling points are generally higher than those of the melting points.

Periodic trends in physical properties across period 3

The physical properties of period 3 elements are similar to those discussed in the general trends except density, melting, and boiling points which show greater variations. The densities of period 3 elements increase from sodium to aluminium due to closely packed atoms, high atomic masses, and small atomic radii. The density decreases for silicon because the structure of silicon has more open spaces than closed packed aluminium structure making it to have lower density. Other elements of period 3 have lower densities because they exist as molecules. The densities decrease from S_8, P_4 to Cl_2. Sulphur has relatively larger molecules than P_4 and Cl_2.

Generally, the melting points increase from sodium to silicon followed by a decrease towards argon with a slight increase from phosphorus to sulphur. Similarly, the boiling points increase from sodium to aluminium, then decrease towards argon with a slight increase from phosphorus to sulphur. The melting points and boiling points of period 3 elements are presented in Figure 1.7.

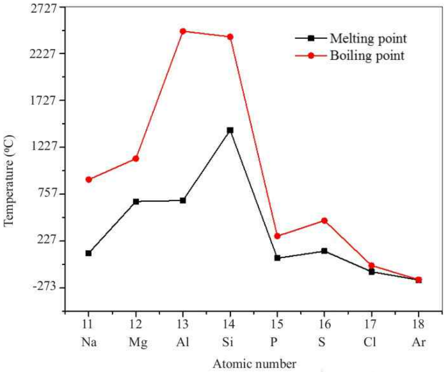


Figure 1.7 Variation in melting and boiling points of period 3 elements

Explanation of the observed trends

Sodium, magnesium, and aluminium are metals with a metallic bonding in which metal ions are attracted to the delocalised sea of electrons. The charges on the metal ions increase across the period from sodium (+1) to aluminium (+3). Since the number of delocalised electrons increases, the strength of metallic bonding also increases and hence an increase in the melting and boiling points. Although aluminium ionises by losing three electrons due to its high total ionisation energies (1st IE, 2nd IE, and 3rd IE), it contributes only two electrons during formation of metallic crystal, hence this accounts for the close melting point to that of magnesium which also contributes two electrons in the metallic crystal.

Silicon, which is a metalloid that possesses non-metallic and metallic properties, has a strong covalent bonding whereby each silicon is bonded to four other silicon atoms forming a three dimensional giant molecule. Therefore, silicon has very high melting and boiling points because of the strong covalent bonds that need a large amount of energy to be broken.

On the other hand, phosphorus, sulphur, and chlorine are non-metals, which exist as small and separate molecules. Their atoms are held together by the van der Waals forces of attraction. Argon which is also a non-metal exists as separate atoms (monoatomic). These elements have low melting and boiling points because the melting and boiling processes involve breaking the weak van der Waals forces which require little energy.

Sulphur has higher melting and boiling points than phosphorus, chlorine, and argon because it exists as S_8 molecules followed by phosphorus which exists as P_4 molecules, then chlorine which exists as Cl_2 and lastly the monoatomic argon (Ar) atoms. The strengths of the van der Waals forces decrease as the sizes of the molecules decrease and hence decreasing the melting and boiling points in the order of $S_8 > P_4 > Cl_2 > Ar$.

Exercise 1.2

1. (a) What is the atomic radius of an atom?

   (b) Explain the trend in atomic radii across a period and down a group.

2. Rank the following ionisation energies in the order of increasing values. Briefly explain your answer.

   (a) First IE of Be

   (b) First IE of Li

   (c) Second IE of Be

   (d) Second IE of Na

   (e) First IE of K

3. (a) Why does the electronegativity generally decrease down the group?

   (b) Explain the variations of the IEs and EAs with respect to the following:

      (i) Atomic size

      (ii) Effective nuclear charge

4. Briefly explain each of the following terms as applied in periodic classification of elements:
   - (a) Electronegativity
   - (b) Electron affinity
   - (c) Screening effect
5. Arrange the following elements in the order of decreasing atomic sizes: Al, B, C, K, and Na.
6. Arrange the following atoms in the order of increasing ionisation energy: Si, K, As, and Ca.
7. Compare the elements Na, Mg, O and P.
   - (a) Which element has the largest atomic radius?
   - (b) Which element has the highest electron affinity?
   - (c) Arrange the elements in order of increasing ionisation energy.
8. Why is the first ionisation energy of magnesium greater than that of sodium?

Periodic trends in physical properties of the elements in groups IA, IIA, and IIIA

Group IA

Group IA consists of metallic elements which are lithium, sodium, potassium, rubidium, caesium, and francium. These elements are soft and silvery white with lustre. They have low melting and boiling points due to their large atomic sizes and low charges which lead to formation of weak metallic bond. They have low densities due to lower molar masses and large atomic radii. The group IA elements have relatively lower densities than other elements of the same periods.

Group IIA

Group IIA elements consist of metallic elements which are beryllium, magnesium, calcium, strontium, barium, and radium. These elements have small atomic sizes and high charges compared to those of group IA. They have higher melting and boiling points than those of group IA elements. The trends of melting and boiling points decrease down the group. Group IIA elements are more closely packed in their lattices making them to have strong metallic bond. They have lower densities but relatively higher than those of group IA.

Group VII (Halogens)

Group VIIA consists of fluorine, chlorine, bromine, iodine, and astatine elements. These elements have low melting and boiling points which increase down the group. The trend is opposite to that of groups IA and IIA elements whose trends in melting and boiling points decrease down the groups. This is because the halogens exist as diatomic molecules that interact through van der Waals forces which increase the strength as the atoms become large.

1.2.2 Periodic trends in chemical properties (chemical periodicity)

Chemical periodicity considers how the elements in the periodic table react. This section covers the reactions in groups IA, IIA, and VIIA and trends in chemical properties along period 3.

Reactions of group IA elements with oxygen

Group IA elements react with oxygen to form metal oxides and their reactions are called oxidation. Group IA elements are very reactive and they easily undergo oxidation when they come in contact with air. To prevent them from oxidation, they are stored in liquid oils, sealed glass tube, vacuum or in an inert gas. The reactivity of group IA elements increases down the group. Depending on the period of the metal and hence the reactivity, different types of oxides are formed when the metals are burnt in oxygen. The reactions of group IA elements in air are the same as in oxygen except that oxygen reacts violently.

Lithium

Lithium burns strongly with red flame when heated in air to form white lithium monoxide.

$$4Li(s) + O_2(g) \longrightarrow 2Li_2O(s)$$

Lithium is unique among the group IA elements as it reacts with nitrogen in the air to form lithium nitride.

$$6Li(s) + N_2(g) \longrightarrow 2Li_3N(s)$$

Sodium

Sodium burns in air with a bright yellow or golden yellow flame to form a white solid mixture of sodium oxide. However, if oxygen is present in excess, sodium peroxide is formed.

$$4Na(s) + O_2(g) \longrightarrow \underset{\text{Sodium oxide}}{2Na_2O(s)}$$

$$2Na(s) + O_2(g) \longrightarrow \underset{\text{Sodium peroxide}}{Na_2O_2(s)}$$

Potassium

Potassium burns in air to form a mixture of potassium peroxide and potassium superoxide. If small pieces of potassium are used, no flame is observed and if large pieces are used, a lilac flame is observed.

$$2K(s) + O_2(g) \longrightarrow \underset{\text{Potassium peroxide}}{K_2O_2(s)}$$

$$K(s) + O_2(g) \longrightarrow \underset{\text{Potassium superoxide}}{KO_2(s)}$$

Rubidium and caesium

Both rubidium and caesium burn in air with orange or yellow flame to form superoxides. Rubidium also shows a dark brown flame.

$$Rb(s) + O_2(g) \longrightarrow RbO_2(s)$$
$$Cs(s) + O_2(g) \longrightarrow CsO_2(s)$$

Reactions of group IA elements with water

All group IA elements react violently or explosively with water to form aqueous metal hydroxides and hydrogen gas, as shown in the following general equation:

$$2M(s) + 2H_2O(l) \longrightarrow 2MOH(aq) + H_2(g)$$

where, M represents any group IA metal.

Examples:

$$2Li(s) + 2H_2O(l) \longrightarrow 2LiOH(aq) + H_2(g)$$
$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$
$$2K(s) + 2H_2O(l) \longrightarrow 2KOH(aq) + H_2(g)$$

Reactions of group IA elements with hydrochloric acid

Lithium

Lithium reacts violently with dilute hydrochloric acid to form lithium chloride salt and hydrogen gas.

$$2Li(s) + 2HCl(aq) \longrightarrow 2LiCl(aq) + H_2(g)$$

Sodium

Sodium reacts with dilute hydrochloric acid to form sodium chloride salt and hydrogen gas. The reaction is violent and finishes quickly. The sodium ignites, producing a bright flame.

$$2Na(s) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2(g)$$

Potassium

Potassium reacts violently with dilute hydrochloric acid to produce potassium chloride salt and hydrogen gas. The reaction is very fast due to its position in the periodic table compared to Li and Na though it can be affected by the strength of the acid. Potassium ignites when in contact with acid producing a bright lilac flame.

$$2K(s) + 2HCl(aq) \longrightarrow 2KCl(aq) + H_2(g)$$

Reactions of group IA elements with sulphuric acid

Lithium

Lithium reacts with dilute sulphuric acid to form lithium sulphate and hydrogen gas. When lithium is added to the dilute sulphuric acid effervescence occurs as hydrogen gas is released. The colour of sulphuric acid turns yellowish as it is converted to lithium sulphate. As the reaction proceeds, the heat generated ignites the hydrogen gas which is released and produces a reddish flame.

$$4Li(s) + 2H_2SO_4(aq) \longrightarrow 2Li_2SO_4(s) + 2H_2(g)$$

Sodium

Sodium reacts with dilute sulphuric acid to give sodium sulphate and hydrogen gas.

$$2Na(s) + H_2SO_4(aq) \longrightarrow Na_2SO_4(s) + H_2(g)$$

Potassium

Potassium reacts explosively with dilute sulphuric acid to give potassium sulphate and hydrogen gas.

$$2K(s) + H_2SO_4(aq) \longrightarrow K_2SO_4(s) + H_2(g)$$

Reactions of group IA elements (alkali metals) with dilute nitric acid

Lithium

Lithium reacts with dilute nitric acid to form lithium nitrate, ammonium nitrate and water.

$$8Li(s) + 10HNO_3(aq) \longrightarrow 8LiNO_3(aq) + NH_4NO_3(aq) + 3H_2O(l)$$

Sodium

Sodium reacts with dilute nitric acid to produce sodium nitrate, nitrogen monoxide, dinitrogen monoxide, and water.

$$11Na(s) + 14HNO_3(aq) \longrightarrow 11NaNO_3(aq) + NO(g) + N_2O(g) + 7H_2O(l)$$

Potassium

Potassium reacts with dilute nitric acid to produce potassium nitrate, nitrogen monoxide, dinitrogen monoxide, nitrogen gas, and water.

$$21K(s) + 26HNO_3(aq) \longrightarrow 21KNO_3(aq) + NO(g) + N_2O(g) + N_2(g) + 13H_2O(l)$$

Reactions of group IIA elements

Group IIA elements exhibit similar chemical and physical properties because they consist of two electrons in their outermost shells. The group IIA elements are strong reducing agents, because they strongly cause other species to be reduced (addition of electrons) and themselves become oxidised (lose electrons).

Reactions of group IIA elements with air or oxygen

All group IIA elements burn in air or oxygen to form metal oxides. Their reactions in pure oxygen are violent and produce white ionic oxides. The general equation for combustion is given as follows:

$$2M(s) + O_2(g) \longrightarrow 2MO(s)$$

where M represents any group IIA metal.

Examples:

$$2Ca(s) + O_2(g) \longrightarrow 2CaO(s)$$

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

$$2Sr(s) + O_2(g) \longrightarrow 2SrO(s)$$

The burning of barium in air forms a peroxide (BaO_2).

$$Ba(s) + O_2(g) \longrightarrow BaO_2(s)$$

The burning of calcium in air produces a brick red flame and magnesium burns with a brilliant white flame (no colour). Strontium and barium burn with bright-red and pale-green flames, respectively.

Reactions of group IIA elements with water

When group IIA elements react with water they form hydroxides ($M(OH)_2$) and hydrogen gas (H_2). The general equation for the reactions of group IIA elements with water is

$$M(s) + 2H_2O(l) \longrightarrow M(OH)_2(aq) + H_2(g)$$

where M represents any group IIA metal.

The reactivity of group IIA elements increases down the group. Moving down the group, the reactions become more vigorous. Therefore, calcium, strontium, and barium elements react with cold water to form hydroxides and hydrogen gas.

$$Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + H_2(g)$$

$$Sr(s) + 2H_2O(l) \longrightarrow Sr(OH)_2(aq) + H_2(g)$$

$$Ba(s) + 2H_2O(l) \longrightarrow Ba(OH)_2(aq) + H_2(g)$$

Magnesium reacts slowly with cold water, but when the steam is passed over heated magnesium the reaction becomes violent and magnesium oxide is formed.

$$Mg(s) + H_2O(l) \longrightarrow MgO(s) + H_2(g)$$

Beryllium forms an oxide when it reacts with water at room temperature.

$$Be(s) + H_2O(l) \longrightarrow BeO(s) + H_2(g)$$

Reactions of group IIA elements with hydrochloric acid

Generally, group IIA elements react with hydrochloric acid to form metal chloride salts and hydrogen gas,

$$M(s) + 2HCl(aq) \longrightarrow MCl_2(aq) + H_2(g)$$

where M represents any group IIA metal. For example, magnesium reacts vigorously with hydrochloric acid to form magnesium chloride and hydrogen gas.

$$Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$$

Similar reactions may occur between group IIA elements with dilute sulphuric acid to form corresponding salts and hydrogen gas. This is because these elements are highly electropositive and can easily displace hydrogen from acid solutions. Dilute nitric acid reacts with only magnesium to liberate hydrogen gas.

Reactions of group IIA elements with sodium hydroxide

All the elements of group IIA do not react with alkalis, except beryllium. Beryllium reacts with sodium hydroxide to form beryllates and hydrogen gas.

$$Be(s) + 2NaOH(aq) \longrightarrow \underset{\text{Sodium beryllate}}{Na_2BeO_2(aq)} + H_2(g)$$

Activity 1.2 **Investigation of the reactions of Na, Mg, and Ca with HCl and H_2O**

Requirements: Na, Mg and Ca metals, dilute HCl, distilled water, beakers (100 mL), and measuring cylinder (100 mL).

Procedure

1. Measure 50 mL of HCl using a measuring cylinder and put it in a beaker.
2. Add 2 g of sodium metal and record your observations.
3. Repeat step 2 using Mg and Ca metals and record your observations.
4. Repeat steps 1 to 3 using 50 mL of water.

Questions

1. What happens when the pieces of the metals (Na, Mg, and Ca) are added to dilute HCl and water?
2. What can you comment about the reactivity of the three metals with HCl and water?

Reactions of group VIIA elements

These elements are called *halogens* and they exist as diatomic molecules, with weak intermolecular forces of attractions. Halogens consist of seven electrons in their outermost shells which is one electron less than the next noble gas electronic configuration. This property makes them to be good oxidising agents, because they tend to remove electrons from other substances during reactions. The reactivity of the halogens decreases down the group because of the increase in atomic radii and the shielding effect. Even though the nuclear charge increases down the group, its effects are largely cancelled out by the shielding effect and increased atomic radii.

Reactions of group VIIA elements with air

Halogens react with oxygen to form oxides. For example, fluorine reacts with oxygen to form oxygen difluoride (OF_2) and dioxygen difluoride (O_2F_2).

$$4F(g) + O_2(g) \longrightarrow 2OF_2(g)$$

$$2F(g) + O_2(g) \longrightarrow O_2F_2(g)$$

The oxides of chlorine, namely dichlorine monoxide (Cl_2O) and chlorine dioxide (ClO_2) are unstable, hence not prepared directly from oxygen. The dichlorine monoxide is prepared by passing chlorine gas in the hydrated sodium carbonate at 20-30 °C.

$$2Cl_2(g) + 2Na_2CO_3(s) + H_2O(l) \longrightarrow Cl_2O(g) + 2NaHCO_3(aq) + 2NaCl(aq)$$

Reactions of group VIIA elements with water

Fluorine reacts violently with water vapour to form hydrogen fluoride and oxygen or ozone.

$$2F_2(g) + 2H_2O(g) \longrightarrow 4HF(g) + O_2(g)$$

$$3F_2(g) + 3H_2O(g) \longrightarrow 6HF(g) + O_3(g)$$

Chlorine disproportionates in water to form hypochlorous acid and hydrochloric acid.

$$Cl_2(g) + H_2O(l) \rightleftharpoons HClO(aq) + HCl(aq)$$

Hypochlorous acid decomposes slowly to give oxygen unless sunlight is present to accelerate the decomposition.

$$2HClO(g) \longrightarrow 2HCl(aq) + O_2(g)$$

Disproportionation is a reaction in which a substance is simultaneously oxidised and reduced giving two different products.

Bromine reacts with water to form hypobromous acid and hydrobromic acid, also disproportionate in water.

$$Br_2(g) + H_2O(l) \longrightarrow HBrO(aq) + HBr(aq)$$

Iodine reacts slowly with water to form hypoiodous acid and hydroiodic acid.

$$I_2(g) + H_2O(l) \longrightarrow HIO(aq) + HI(aq)$$

These hypohalous acids are also called *oxo-acids*.

Reactions of group VIIA elements with sodium hydroxide

Fluorine gas reacts with dilute sodium hydroxide to form oxygen fluoride, sodium fluoride, and water.

$$2F_2(g) + 2NaOH(aq) \longrightarrow 2NaF(aq) + OF_2(g) + H_2O(l)$$

But when fluorine gas reacts with concentrated sodium hydroxide, oxygen is formed instead of OF_2.

$$2F_2(g) + 4NaOH(aq) \longrightarrow 4NaF(aq) + O_2(g) + 2H_2O(l)$$

Chlorine gas reacts with cold dilute sodium hydroxide solution to form colourless solution of sodium chloride, sodium hypochlorite and water.

$$Cl_2(g) + 2NaOH(aq) \longrightarrow NaCl(aq) + NaOCl(aq) + H_2O(l)$$

Bromine liquid reacts with dilute sodium hydroxide to form sodium bromide, sodium hypobromite, and water.

$$Br_2(l) + 2NaOH(aq) \longrightarrow NaBr(aq) + NaOBr(aq) + H_2O(l)$$

This reaction is less reactive compared to the reaction between chlorine and sodium hydroxide. A solid iodine reacts slowly with dilute sodium hydroxide to form sodium iodide, sodium hypoiodite and water.

$$I_2(s) + 2NaOH(aq) \longrightarrow NaI(aq) + NaOI(aq) + H_2O(l)$$

This reaction is the least reactive compared with that of fluorine, chlorine, and bromine. If hot concentrated NaOH is reacted with other halogens (Br, Cl, and I), the general equation is given in the following equation:

$$3X_2(g) + 6NaOH(aq) \xrightarrow{60\ ^{o}C} 5NaX(aq) + NaXO_3(aq) + 3H_2O(l)$$

where X stands for Br, Cl, and I.

Reactions of halogens with acids

Fluorine reacts with dilute hydrochloric acid to form hydrogen fluoride and chlorine gas at room temperature.

$$F_2(g) + 2HCl(aq) \longrightarrow 2HF(aq) + Cl_2(g)$$

Fluorine reacts with sulphuric acid to form hydrogen fluoride and sulphuryl peroxide. The reaction occurs at a temperature near 0 ^{o}C.

$$F_2(g) + H_2SO_4(aq) \longrightarrow 2HF(aq) + \underset{\text{Sulphuryl peroxide}}{SO_2(O_2)(aq)}$$

Unique properties of fluorine

Fluorine differs in chemical and physical properties from other elements of group VIIA. These differences are due to its small atomic size, highest electronegativity, low bond dissociation energy, and the absence of *d*-orbitals in the valence shell. These differences in properties are described below.

(a) *High chemical reactivity*

Fluorine is the most reactive element of all the halogens, because the F–F bond is weak and hence has low bond dissociation energy. The reason for the weakness of the F–F bond is that the F atom is small, with short F–F bond which causes repulsion between the lone pairs of neighbouring F atoms. Fluorine is a very strong oxidising agent, which tends to oxidise other halogens lower in the group as shown in the following general equation.

$$F_2(g) + X_2(g) \longrightarrow 2XF(g)$$

where X represents halogens other than fluorine.

(b) *Strong hydrogen bonding in HF*

Hydrogen fluoride undergoes strong hydrogen bonding while other halogen acids do not. This is because of the small atomic size and high electronegativity of fluorine. The following are the consequences of the strong hydrogen bonding in HF:

(i) HF is the weakest haloacid among all the halogen acids because of the strength of the H–F bond (does not easily dissociate).

(ii) HF is a liquid at room temperature while other halogen acids are gases at room temperature, due to strong H–F bond that holds the molecules close to each other.

(iii) Due to strong hydrogen bonding, HF can form acidic salts of the type MHF_2; where M is a metal such as potassium (K), that is, $K^+[H–F–F]^-$. Other halogens do not form such kinds of salts.

(c) *Maximum ionic character*

Fluorides have the maximum ionic characters, for example, AlF_3 is ionic while other halides of Al are covalent. Due to high reactivity, HF cannot be stored in a glass bottle because it tends to react with silicates to form fluorosilicates. Other hydrogen halides do not react with silicates; hence they can be stored in glass bottles.

$$Na_2SiO_3(g) + 6HF(l) \longrightarrow \underset{\text{Sodium fluorosilicate}}{Na_2SiF_6(aq)} + 3H_2O(l)$$

(d) *Solubility in water*

Fluoride of silver (AgF) is soluble in water while other halides of silver such as AgCl and AgBr are insoluble in water.

(e) *Reaction of fluorine with water*

Fluorine reacts violently with water to form hydrogen fluoride and oxygen.

$$2F_2(g) + 2H_2O(l) \longrightarrow 4HF(aq) + O_2(g)$$

Other halogens such as Cl_2 and Br_2 undergo disproportionation reactions with water and form hydrogen halides (HX) and hypohalous acids (HXO).

Periodic trends in chemical properties along period 3

Periodic trends in chemical properties along period 3 will be discussed by considering the reactions of hydrides, chlorides, hydroxides, and oxides of the elements in period 3. Period 3 includes the following elements: sodium, magnesium, aluminium, silicon, phosphorus, sulphur, chlorine, and argon.

The reaction of hydrides of period 3 elements with water

The hydrides are formed when elements react with hydrogen gas. Sodium and magnesium react with hydrogen to form ionic hydrides which have basic characteristics. Many electronegative elements such as sulphur and chlorine react with hydrogen to form covalent acidic hydrides. The hydrides of sodium, magnesium, and aluminium are ionic. They react with water to form metal hydroxides and hydrogen gas.

$$NaH(s) + H_2O(aq) \longrightarrow NaOH(aq) + H_2(g)$$

$$MgH_2(s) + 2H_2O(l) \longrightarrow Mg(OH)_2(aq) + 2H_2(g)$$

Aluminium hydride, also called *alane* or *alumane,* reacts with water to form hydroxide and hydrogen gas.

$$AlH_3(s) + 3H_2O(l) \longrightarrow Al(OH)_3(aq) + 3H_2(g)$$

Lithium aluminium hydride, dissolves in water to form lithium hydroxide, aluminium hydroxide and hydrogen gas.

$$LiAlH_4(s) + 4H_2O(l) \longrightarrow LiOH(aq) + Al(OH)_3(aq) + 4H_2$$

The hydride of silicon (SiH_4), which is known as *silane,* is partially ionic. The partial charges on the atoms are relatively small, hence it dissolves in water to form silicon hydroxide and hydrogen gas in the presence of strong base as a catalyst.

$$SiH_4(s) + 4H_2O(l) \xrightarrow{NaOH} Si(OH)_4(aq) + 4H_2(g)$$

The hydride of phosphorus (PH_3), which is known as *phosphine*, does not react with water because the electronegativities of phosphorus and hydrogen are the same. Therefore, the partial charges on phosphine molecules are absent.

The hydrides of sulphur and chlorine are partially ionic, because sulphur and chlorine are more electronegative than hydrogen hence they attract electrons from hydrogen. These hydrides react with water reversibly to form acidic solutions.

$$H_2S(g) + 2H_2O(l) \rightleftharpoons 2H_3O^+(aq) + S^{2-}(aq)$$

$$HCl(g) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

Reactions of chlorides of period 3 elements with water

The chlorides of sodium and magnesium are ionic or strong electrovalent compounds. They are not hydrolysed by water, they just ionise completely to form neutral solutions. This is because they have large ionic sizes and low charges compared to the other elements in the same period. They can also conduct electricity and undergo electrolysis when fused. Sodium chloride dissolves readily in water with a negligible heat change to form a colourless solution which contains Na^+ and Cl^- ions. The reaction does not involve hydrolysis.

$$NaCl(s) + H_2O(l) \longrightarrow Na^+(aq) + Cl^-(aq)$$

Magnesium chloride dissolves in water with a slightly heat change to form colourless solution which contains Mg^{2+} and Cl^- ions.

$$MgCl_2(s) + H_2O(l) \longrightarrow Mg^{2+}(aq) + 2Cl^-(aq)$$

In a hydrated form, magnesium chloride partially hydrolysed to form basic chloride Mg(OH)Cl.

$$MgCl_2 \cdot 6H_2O(s) \xrightarrow{heat} Mg(OH)Cl(s) + HCl(g) + 5H_2O(l)$$

Aluminium chloride ($AlCl_3$) has characteristics of covalent compounds and does not conduct electricity. It reacts vigorously with water to form a colourless solution containing $[Al(H_2O)_5(OH)]^{2+}$ and Cl^-. They undergo hydrolysis to form an acidic solution which turns blue litmus paper to red.

$$Al_2Cl_6(s) + 12H_2O(l) \longrightarrow 2[Al(H_2O)_6]^{3+}(aq) + 6Cl^-(aq)$$

$$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \longrightarrow [Al(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq)$$

Phosphorus chloride (PCl_3), silicon chloride ($SiCl_4$), and disulphur dichloride (S_2Cl_2) also undergo hydrolysis in water to form acidic solutions.

$$PCl_3(s) + 3H_2O(l) \longrightarrow H_3PO_3(aq) + 3HCl(aq)$$

$$SiCl_4(s) + 3H_2O(l) \longrightarrow H_2SiO_3(aq) + 4HCl(aq)$$

$$S_2Cl_2(s) + 3H_2O(l) \longrightarrow H_2S(aq) + 2HCl(aq) + H_2SO_3(aq)$$

Reactions of hydroxides of period 3 elements with water

In all the hydroxides of period 3, oxygen is more electronegative than the other period 3 elements. In sodium and magnesium hydroxides, hydrogen is more electronegative than a particular metal. In the hydroxide, oxygen attracts the bonding electrons more away from the metals than how it attracts the bond electron pair from hydrogen. As a result, dipole moment is formed between oxygen and the metal of period 3 but not between oxygen and hydrogen.

Therefore, when sodium and magnesium hydroxides are dissolved in water, they form metal and hydroxyl ions making their solutions basic.

$$NaOH(aq) + H_2O(l) \longrightarrow Na^+(aq) + OH^-(aq)$$

$$Mg(OH)_2(aq) + H_2O(l) \longrightarrow Mg^{2+}(aq) + 2OH^-(aq)$$

Aluminium hydroxide is amphoteric because it has both basic and acidic properties. When dissolved in water, it acts as a base by generating hydroxyl and aluminium ions.

$$Al(OH)_3(aq) + H_2O(l) \longrightarrow Al^{3+}(aq) + 3OH^-(aq)$$

This reaction occurs in a series of three steps with hydroxide ion being released in each step.

$$Al(OH)_3(aq) + H_2O(l) \longrightarrow Al(OH)_2^+(aq) + OH^-(aq) \qquad \text{Step 1}$$

$$Al(OH)_2^+(aq) + H_2O(l) \longrightarrow Al(OH)^{2+}(aq) + OH^-(aq) \qquad \text{Step 2}$$

$$Al(OH)^{2+}(aq) + H_2O(l) \longrightarrow Al^{3+}(aq) + OH^-(aq) \qquad \text{Step 3}$$

Aluminium hydroxide as an acid, generates hydroxonium ions when dissolved in water. This reaction occurs in a series of steps as follows:

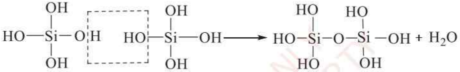
$$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq)$$

$$[Al(OH)(H_2O)_5]^{2+}(aq) + H_2O(l) \rightleftharpoons [Al(OH)_2(H_2O)_4]^{+}(aq) + H_3O^+(aq)$$

$$[Al(OH)_2(H_2O)_4]^{+}(aq) + H_2O(l) \rightleftharpoons [Al(OH)_3(H_2O)_3](s) + H_3O^+(aq)$$

Silicon, phosphorus, sulphur, and chlorine in their hydroxides are electronegative and can withdraw electrons from O-H bond thus polarising it and facilitating the release of hydrogen as proton (H^+).

Silicic acid ($Si(OH)_4$) has a tendency of polymerising by releasing water molecules as by-products. The polymerisation process occurs when a molecule of $Si(OH)_4$ acts as an acid releasing H^+ ion and another molecule acts as a base releasing OH^- ions. The process occurs when silicon hydroxide is dissolved in water. The formation of silicic acid polymer is shown as follows:



$$HO{-}Si(OH)_2{-}OH + HO{-}Si(OH)_2{-}OH \longrightarrow HO{-}Si(OH)_2{-}O{-}Si(OH)_2{-}OH + H_2O$$

Other oxo-acids have acidities in the order $HClO_4 > H_2SO_4 > H_3PO_4$. Phosphoric(V) acid molecule ($OP(OH)_3$) has only one oxygen atom hence its electronegativity effect has to be shared by the three hydroxyl groups. This makes the phosphoric(V) acid weaker than sulphuric acid, which has two singly attached oxygen atoms. The chloric(VII) acid ($HClO_4$), commonly known as perchloric acid, has three oxygen atoms to one hydroxyl group hence it is stronger than sulphuric and phosphoric(V) acids.

The oxides of period 3 elements

Sodium and magnesium are strong metallic in properties whose oxides are ionic. Thus, their crystal structures are held strongly by ionic bonds which lead into their high melting and boiling points. Sodium and magnesium oxides are strong bases, aluminium oxide (Al_2O_3) is amphoteric, and the oxides of the remaining metals are acidic. Silicon dioxide (SiO_2) and phosphorus pentoxide (P_2O_5) are covalent solids while sulphur dioxide (SO_2) and chlorine(VII) oxide (Cl_2O_7) are gases.

The following are the reactions which show the amphoteric nature of aluminium oxide:

As a base: $Al_2O_3(s) + 6HF(aq) \longrightarrow \underset{\text{Aluminium fluoride}}{2AlF_3(s)} + 3H_2O(l)$

As an acid: $Al_2O_3(s) + 2NaOH(aq) \longrightarrow \underset{\text{Sodium aluminate}}{2NaAlO_2(aq)} + H_2O(l)$

Reactions of the oxides of period 3 elements with water

Sodium oxide (Na_2O) and magnesium oxide (MgO) are basic oxides as they react with water to form basic solutions.

$$Na_2O(s) + H_2O\ (l) \longrightarrow 2NaOH(aq)$$

$$MgO(s) + H_2O(l) \longrightarrow Mg(OH)_2(aq)$$

Aluminium oxide reacts with water to form aluminium hydroxide ($Al(OH)_3$).

$$Al_2O_3(s) + 3H_2O(l) \longrightarrow 2Al(OH)_3(aq)$$

The $Al(OH)_3$ formed behaves as an acid or a base.

$Al(OH)_3(aq) + 3H^+(aq) \longrightarrow Al^{3+}(aq) + 3H_2O(l)$ As a base

$Al(OH)_3(aq) + OH^-(aq) \longrightarrow [Al(OH)_4]^-(aq)$ As an acid

Silicon dioxide (SiO_2) does not react with water, because it is difficult to break up the giant covalent structure. It reacts with hot concentrated solution of NaOH.

$$SiO_2(s) + 2NaOH(aq) \xrightarrow{\text{heat}} Na_2SiO_3(s) + H_2O(l)$$

Phosphorus pentoxide reacts with water to form phosphoric acid.

$$2P_2O_5(s) + 6H_2O(l) \longrightarrow 4H_3PO_4(aq)$$

Sulphur dioxide (SO_2) and sulphur trioxide (SO_3) react with water to form sulphurous acid (H_2SO_3) and sulphuric acid (H_2SO_4), respectively.

$$SO_2(g) + H_2O(l) \longrightarrow H_2SO_3(aq)$$

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$

Exercise 1.3

1. Describe the acid–base characters of the oxides of period 3 elements.
2. Explain with equations, the reactivity of the oxides of group IA with water.
3. The metallic characters of the elements change across a period. Illustrate this concept with reference to chlorides and hydrides of the elements of period 3.
4. How do Li, Ca, and F react with water?
5. Briefly explain the following facts:
   (a) BeO is amphoteric. (b) MgO is a weak base.
   (c) CaO is basic. (d) SiO_2 and BaO are extremely basic.

1.3 Diagonal relationships

Every first element in a group exhibits anomalous behaviour from the rest of the group members in the periodic table. Lithium for example, exhibits properties, which distinguish it from other members of group I (Na, K, Rb, and Cs) and has similar properties to the second member of group II (Mg) which is located diagonal to it in period 3. This kind of similarity is called *diagonal relationship.* Diagonal relationship is the resemblance in properties whereby the first element in a particular group has similar properties diagonally with the second element in the next group. Other examples of elements that are related diagonally are Be, and Al, and B and Si. Table 1.8 indicates the positions of the elements in the periodic table and those related diagonally are painted in the same colour. In this section, you will learn about the diagonal relationships between Li and Mg, Be, and Al, and the anomalous behaviour of the first element in a group as compared to the rest of the elements.

Table 1.8 Elements with diagonal relationships

Period	**Group**				
	IA	IIA		IIIA	IVA
2	Li	Be		B	C
3	Na	Mg		Al	Si
4	K	Ca		Ga	Ge

Period 2 elements at the top of the main groups are called the *head elements*. These elements have properties and their corresponding compounds that differ from those of their group members. This is due to the resemblance of atomic size and electronegativity, diagonally with the second element in the next group. For example, lithium has properties that resemble those of magnesium more than those of its members in the group.

1.3.1 Anomalous behaviours of lithium

Lithium differs in its chemical behaviours from other alkali metals (group IA), but it shows similarities with the second elements of the alkali earth metals (group IIA). These differences are due to the following reasons:

(a) Atomic and ionic radii of lithium are relatively smaller than of the other elements in the same group.

(b) Lithium ion (Li^+) due to its small size, has very high polarising power; hence exhibits covalent character in its compounds.

(c) Lithium does not possess *d*-orbitals in its valence shell while other group IA elements have *d*-orbitals. Therefore, lithium differs chemically from the other alkali metals (group IA) as explained in the following aspects:

  (i) It burns in oxygen to form a normal lithium oxide (Li_2O).

$$4\,Li(s) + O_2(g) \longrightarrow \underset{\text{Lithium oxide}}{2Li_2O(s)}$$

  However, the rest of alkali metals form peroxides such as Na_2O_2 or superoxides like KO_2. Other elements which are below Li in the same group form peroxides on combustion.

$$2Na(s) + O_2(g) \longrightarrow Na_2O_2(s)$$

$$K(s) + O_2(g) \longrightarrow KO_2(s)$$

  (ii) It reacts with nitrogen gas to form lithium nitride (Li_3N) while other members in the same group do not. Sodium nitride (Na_3N) does exist, but it is highly unstable such that it cannot be formed by direct reaction between sodium and nitrogen gas.

$$6Li(s) + N_2(g) \longrightarrow 2Li_3N(s)$$

(d) Lithium is harder with higher melting point and boiling point than the rest of the group IA elements, because of strong metallic bond caused by small atomic size.

(e) Lithium nitrate, chloride, bromide, and iodide are more soluble in polar organic solvents such as acetone and ethanol than other alkali metal compounds which are insoluble in polar organic solvents.

(f) Fluoride, carbonate, hydroxide, and phosphate of Li are less soluble in water than those of other alkali metals such as Na and K. This is because Li^+ is very small, highly positive and hence its salts do not easily dissociate into ions in water.

(g) Lithium chloride forms hydrated crystals, $LiCl \cdot H_2O$, when dissolved in water, but chlorides of other group IA elements do not form hydrates. Lithium chloride is deliquescent while chlorides of group IA elements are not.

(h) Lithium is the only alkali metal which forms molecular compounds (called organolithium) with hydrocarbon groups from organic halides, which are important reactants in the synthesis of organic compounds. For example, lithium reacts with ethyl bromide to form ethyl lithium (an organolithium compound).

$$2Li(s) + CH_3CH_2Br(g) \longrightarrow CH_3CH_2Li(s) + LiBr(s)$$

(i) The hydroxide and carbonate of lithium decompose on heating.

$$Li_2CO_3(s) \xrightarrow{heat} Li_2O(s) + CO_2(g)$$

$$2Li(OH)(s) \xrightarrow{heat} Li_2O(s) + H_2O(g)$$

The other hydroxides and carbonates of other elements in a group do not decompose on heating.

(j) On heating, lithium nitrate evolves nitrogen dioxide and oxygen

$$4LiNO_3(s) \xrightarrow{heat} 2Li_2O(s) + 4NO_2(g) + O_2(g)$$

Nitrates of other elements below lithium evolve oxygen gas only on heating.

$$2NaNO_3(s) \xrightarrow{heat} 2NaNO_2(s) + O_2(g)$$

1.3.2 Diagonal relationships between lithium and magnesium

Lithium and magnesium are diagonally related because they have similar chemical properties such as equal electronegativity and polarising power values. The following are other factors that account for the diagonal relationships between Li and Mg:

(a) On combustion, both Li and Mg form normal oxides.

$$4Li(s) + O_2(g) \longrightarrow 2Li_2O(s)$$

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

(b) Both Li and Mg combine directly with nitrogen gas to form nitrides.

$$6Li(s) + N_2(g) \longrightarrow 2Li_3N(s)$$

$$3Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$$

(c) Hydroxides, carbonates, and nitrates of both Li and Mg decompose easily on heating to form oxides.

$$4LiNO_3(s) \xrightarrow{\text{heat}} 2Li_2O(s) + 2N_2O_4(g) + O_2(g)$$

$$2Mg(NO_3)_2(s) \xrightarrow{\text{heat}} 2MgO(s) + 2N_2O_4(g) + O_2(g)$$

$$Li_2CO_3(s) \xrightarrow{\text{heat}} Li_2O(s) + CO_2(g)$$

$$MgCO_3(s) \xrightarrow{\text{heat}} MgO(s) + CO_2(g)$$

(d) Carbonates, phosphates, and fluorides of both Li and Mg are sparingly soluble in water. The corresponding group IIA salts are insoluble and those of group IA elements are soluble in water.

(e) Both halides of Li and Mg are partially covalent in character, hence can dissolve in many organic solvents. But the corresponding halides of groups IA and IIA metals are ionic.

1.3.3 Anomalous behaviours of beryllium

Beryllium in period 2, shows markedly different behaviours from the rest of the alkaline earth metals (group IIA elements). The anomalous behaviours of Be are caused by its extreme small size and high electronegativity. The main chemical differences between beryllium and other group IIA elements are:

(a) Beryllium does not react with water even in hot water, but other alkaline earth metals react with water to form hydroxide and hydrogen gas.

$$Be(s) + H_2O(l) \longrightarrow \text{No reaction}$$

$$Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + H_2(g)$$

(b) The compounds of beryllium with oxygen, nitrogen, sulphur, and chlorine are covalent in nature unlike the corresponding compounds of group IIA elements. In fact, all Be compounds exhibit covalent bonding.

(c) Beryllium dissolves in strong alkalis to form beryllate while other alkali earth metals do not react with alkalis.

$$\mathrm{Be}(s) + 2\mathrm{NaOH}(aq) \longrightarrow \underset{\text{Sodium beryllate}}{\mathrm{Na_2BeO_2}(aq)} + \mathrm{H_2}(g)$$

(d) The oxide and hydroxide of Be are amphoteric and dissolve in acids to form salts while those of other alkaline earth metals are basic in characters. BeO is insoluble in water unlike the oxides of other alkaline earth metals.

(e) Beryllium forms volatile nitride with nitrogen gas, while other alkaline earth metals form non-volatile nitrides with nitrogen gas.

(f) The sulphate of beryllium is soluble in water while the sulphates of other alkaline earth metals are sparingly soluble or insoluble in water.

(g) Beryllium shows a maximum coordination number of four, unlike other alkaline earth metals which have a maximum of six coordination numbers due to the presence of *d*-orbitals.

(h) Beryllium does not liberate hydrogen when reacts with dilute acids, but the corresponding elements in the group react with acids to liberate hydrogen gas. For example, magnesium reacts with dilute hydrochloric acid to liberate hydrogen gas.

$$\mathrm{Mg}(s) + 2\mathrm{HCl}(aq) \longrightarrow \mathrm{MgCl_2}(aq) + \mathrm{H_2}(g)$$

1.3.4 Diagonal relationships between beryllium and aluminium

Beryllium and aluminium are diagonally related because they have similar chemical properties such as polarising power. The following are diagonal relationships between Be and Al:

(a) Both Be and Al do not easily react with acids and water, because these elements react with oxygen to form a thin oxide layer which is inert. This makes Be and Al elements impervious to further attack. But their corresponding elements of group IIA and group IIIA metals react with acids and water as follows:

$$\mathrm{Mg}(s) + 2\mathrm{HCl}(aq) \longrightarrow \mathrm{MgCl_2}(aq) + \mathrm{H_2}(g)$$

$$2\mathrm{Ga}(s) + 6\mathrm{HCl}(aq) \longrightarrow 2\mathrm{GaCl_3}(aq) + 3\mathrm{H_2}(g)$$

$$\mathrm{Mg}(s) + 2\mathrm{H_2O}(l) \longrightarrow \mathrm{Mg(OH)_2}(aq) + \mathrm{H_2}(g)$$

(b) Both Be and Al dissolve in excess alkalis to give beryllate and aluminate ions, respectively and liberate hydrogen gas.

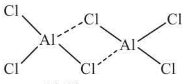
$$Be(s) + 2NaOH(aq) \longrightarrow \underset{\text{Sodium beryllate}}{Na_2BeO_2(aq)} + H_2(g)$$

$$2Al(s) + 2NaOH(aq) + 2H_2O(l) \longrightarrow \underset{\text{Sodium aluminate}}{2NaAlO_2(aq)} + 3H_2(g)$$

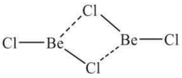
Other elements of group IIA and IIIA do not react with alkalis.

(c) Both Be and Al possess strong tendencies of forming covalent compounds, while other elements in groups IIA and IIIA form ionic compounds.

(d) The chlorides of beryllium (Be_2Cl_4) and aluminium (Al_2Cl_6) are covalent and have bridged polymeric structures.



Al_2Cl_6



Be_2Cl_4

(e) Both Be^{2+} and Al^{3+} ions have strong tendencies of forming complexes due to their similar charge to radius ratios. The following are examples of complexes of Be and Al:

(i) $BeF_4^{2-}(aq)$ (ii) $[Be(C_2O_4)_2]^{2-}(aq)$

(iii) $AlF_6^{3-}(aq)$ (iv) $[Al(C_2O_4)_3]^{3-}(aq)$

But other elements of groups IIA and IIIA do not have a strong tendency of forming complexes.

(f) Both salts of Be and Al hydrolyse in water and precipitate when boiled in hydroxides. The hydroxides and oxides of both Be and Al are amphoteric.

BeO as a base, forms Be^{2+} and $H_2O(l)$.

$$BeO(s) + 2H^+(aq) \rightleftharpoons Be^{2+}(aq) + H_2O(l)$$

BeO as an acid, forms beryllate ion.

$$BeO(s) + 3H_2O(l) \rightleftharpoons [Be(OH)_4]^{2-}(aq) + H_2(g)$$

Al_2O_3 as a base, neutralises the HCl to form salt and water.

$$Al_2O_3(s) + 6HCl(aq) \longrightarrow 2AlCl_3(s) + 3H_2O(l)$$

Al_2O_3 as an acid, reacts with strong alkalis to form aluminate.

$$Al_2O_3(s) + 2NaOH(aq) \longrightarrow 2NaAlO_2(aq) + H_2O(l)$$

Exercise 1.4

1. Illustrate using balanced chemical equations why carbonates of lithium and magnesium readily decompose on heating while the carbonates of other elements below lithium and magnesium in their groups are stable on heating.
2. (a) Give the meaning of diagonal relationship.

   (b) Describe the diagonal relationships between the following pairs of elements:

   (i) Lithium and magnesium

   (ii) Beryllium and aluminium
3. Explain the anomalous behaviours of lithium and beryllium.
4. Complete the following chemical equations:

   (a) $Li_2CO_3(s) \xrightarrow{\text{heat}}$

   (b) $MgCO_3(s) \xrightarrow{\text{heat}}$

   (c) $Be(s) + 2NaOH(aq) \longrightarrow$

   (d) $Al_2O_3(s) + 2NaOH(aq) \longrightarrow$

Revision exercise 1

1. Explain the following phenomena:

   (a) Fluorine has lower electron affinity than chlorine.

   (b) Atomic sizes increase as group one is descended.
2. Describe the ways in which lithium differs in chemical properties from the rest of the group members.
3. Arrange the following atoms in the order of increasing ionisation energies: Li, K, C, and N. Explain your answer.

4. (a) Place the following elements in the order of increasing ionisation energies: F, O, and S.

   (b) Which element has the largest ionisation energy; O, S or Se?

   (c) Which element has the largest electron affinity; Se, Cl or Br?

   (d) Which species has the largest radius; O^{2-}, F, and F^{-}?

5. Give reasons as to why the second ionisation energy of magnesium is higher than its first ionisation energy.

6. Which of the following series of elements is arranged correctly in the order of increasing ionisation energy?

   (a) $C < Si < Li < Ne$
   (b) $Ne < Si < C < Li$
   (c) $Li < Si < C < Ne$
   (d) $Ne < C < Si < Li$

7. Place the following elements and ions in the order of decreasing sizes: Ar, K^{+1}, Cl^{1-}, S^{2-}, and Ca^{2+}.

8. How is the electronic structure of an element related to each of the following?

   (a) Its position in the periodic table.

   (b) Its valence.

9. How is it possible to predict many of the properties of an element from the knowledge of its atomic number?

10. Consider the elements B, Al, C, and Si. Specify the element that has the;

    (a) most metallic character.

    (b) largest atomic radius.

    (c) largest electron affinity.

Chapter Two

Selected compounds of metals

Introduction

A compound is a substance formed by chemical combinations of two or more elements. Metals react with other substances, especially non-metals, to form different useful compounds. Learning about compounds of metals is important because such compounds have numerous applications in daily life, such as in industries, pharmaceuticals, and agriculture. Therefore, in this chapter, you will learn about the classification, preparations, properties, and uses of metal compounds. These compounds include metal oxides, metal hydroxides, metal carbonates, hydrogen carbonates, metal sulphates, metal chlorides, and metal nitrates.

2.1 Metal oxides

An oxide is a chemical compound which is formed by chemical combination of one or more oxygen atoms with another element. Oxides are binary compounds. This means that they contain two elements, one of which must be oxygen. Metal oxides are compounds of metals with oxygen. In this section, you will learn about the classes, methods of preparation, chemical properties, and uses of metal oxides.

2.1.1 Classification of metal oxides

Oxides can be classified as basic oxides, acidic oxides, amphoteric oxides, compound oxides (mixed oxides), peroxides, hyperoxides (superoxides), and neutral oxides depending on how they react with dilute acids, alkalis and water.

The discussion in this section is centred on the first four types of the metal oxides which are basic oxides, acidic oxides, amphoteric oxides, and mixed oxides (compound oxides).

Basic oxides

These are metallic oxides which react with acids to produce salt and water only and if soluble in water, they form alkaline solutions. Examples of basic oxides are CaO and Na_2O which react with acids and water as follows:

Reaction with acid:

$$CaO(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l)$$

$$Na_2O(s) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2O(l)$$

Reaction with water:

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq)$$

$$Na_2O(s) + H_2O(l) \longrightarrow 2NaOH(aq)$$

Other examples of basic oxides are potassium oxide (K_2O), calcium oxide (CaO), and magnesium oxide (MgO). In the periodic table, the basicity of oxides increases with an increase of the atomic numbers down the group. This is because size of atoms increase down the group leading to decrease in a ionisation pontential as a result element in group act as an electron donor which are also proton acceptor. For example, the basicity of group IIA metal oxides increases in the following order:

$$BeO < MgO < CaO < SrO < BaO$$

Acidic oxides

Acidic oxides are oxides of non-metals. They can also be termed as inorganic chemicals that react with water to form acids or react with bases to form salts. Acidic oxides can be formed from metals with high oxidation states. Examples of acidic oxides include carbon dioxide (CO_2), sulphur trioxide (SO_3), sulphur dioxide (SO_2), and silicon dioxide (SiO_2). In the periodic table, the acidity of oxides increases across the period from left to right. This is because across the period more electronegative atoms are associated with strong Brønsted acids. Thus, increase in the electronegativity of the atom that shares an electron pair will decrease basicity; hence acidity increases. The reactions of the acidic oxides with water and bases are described through the following examples:

Reactions with water (H_2O):

$$SO_2(g) + H_2O(l) \longrightarrow \underset{\text{Sulphurous acid}}{H_2SO_3(aq)}$$

$$SO_3(g) + H_2O(l) \longrightarrow \underset{\text{Sulphuric acid}}{H_2SO_4(aq)}$$

$$CO_2(g) + H_2O(l) \longrightarrow \underset{\text{Carbonic acid}}{H_2CO_3(aq)}$$

Reactions with base:

$$SO_2(g) + 2NaOH(aq) \longrightarrow \underset{\text{Sodium sulphite}}{Na_2SO_3(aq)} + H_2O(l)$$

Amphoteric oxides

Amphoteric oxides are metallic oxides which have both basic and acidic properties. These oxides can react with both acids and alkalis to form salt and water only. Some examples of amphoteric oxides are aluminium oxide (Al_2O_3), zinc oxide (ZnO), lead(II) oxide (PbO), tin(II) oxide (SnO), and antimony(III) oxide (Sb_2O_3). The acidic and basic properties of amphoteric oxides are described below with some examples.

Amphoteric properties of ZnO

Acidic property; for example, reaction with sodium hydroxide:

$$ZnO(s) + 2NaOH(aq) \longrightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2(aq)} + H_2O(l)$$

Basic property; for example, reaction with hydrochloric acid:

$$ZnO(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2O(l)$$

Amphoteric properties of Al_2O_3

Acidic property; for example, reaction with sodium hydroxide:

$$Al_2O_3(s) + 2NaOH(aq) \longrightarrow \underset{\text{Sodium aluminate}}{2NaAlO_2(aq)} + H_2O(l)$$

Basic property; for example, reaction with sulphuric acid:

$$Al_2O_3(s) + 3H_2SO_4(aq) \longrightarrow \underset{\text{Aluminium sulphate}}{Al_2(SO_4)_3(aq)} + 3H_2O(l)$$

Mixed oxides (compound oxides)

These are oxides formed by the combination of two oxides of the same metal element, with one having lower oxidation state and another having higher oxidation state. Two common examples of compound oxides are tri-lead tetraoxide (Pb_3O_4)

and tri-iron tetraoxide (Fe_3O_4). The former is commonly known as red lead and the latter is commonly known as *magnetite*.

Red lead: $Pb_3O_4(s) = (2PbO + PbO_2)$ is *di*-lead(II) and lead(IV) oxide

Ferro-ferric oxide: $Fe_3O_4(s) = (FeO + Fe_2O_3)$ is iron(II) and *di*-iron(III) oxide

The oxides Pb_3O_4 and Fe_3O_4 are actually individual substances but they act chemically as though they were mixtures. This fact is revealed when the oxides react with acids, giving a mixture of salts or salt and oxide.

$$Pb_3O_4(s) + 4HNO_3(aq) \longrightarrow 2Pb(NO_3)_2(aq) + PbO_2(aq) + 2H_2O(l)$$

$$Fe_3O_4(s) + 8HCl(aq) \longrightarrow FeCl_2(aq) + 2FeCl_3(aq) + 4H_2O(l)$$

2.1.2 Preparation of metal oxides

There are two methods used to prepare metal oxides, which are *direct* and *indirect methods*.

Direct methods of preparing metal oxides

The direct methods of preparing metal oxides involve direct heating of the metals or metal compounds with oxygen. Many metals or metal compounds produce oxides when heated in oxygen. Sodium burns in air with a persistent yellow flame to form pale yellow solid of sodium peroxide.

$$2Na(s) + O_2(g) \longrightarrow \underset{\text{Pale yellow}}{Na_2O_2(s)}$$

On exposure to air, sodium reacts vigorously with oxygen to form a whitish-grey solid of sodium oxide. This is the reason why sodium is stored under paraffin oil. The sodium oxide can also be formed when sodium is burnt in a limited supply of oxygen.

$$4Na(s) + O_2(g) \longrightarrow \underset{\text{Whitish-grey}}{2Na_2O(s)}$$

Magnesium burns in air with a very brilliant white flame to form a white solid, magnesium oxide.

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

Calcium burns with a red flame in air to form a white solid calcium oxide. Aluminium, iron, and copper also burn in air to form oxides as shown below.

$$2Ca(s) + O_2(g) \longrightarrow 2CaO(s)$$

$$4Al(s) + 3O_2(g) \longrightarrow 2Al_2O_3(s)$$

$$4Fe(s) + 3O_2(g) + 2H_2O(l) \longrightarrow 2Fe_2O_3{\cdot}H_2O$$

$$2Cu(s) + O_2(g) \longrightarrow 2CuO(s)$$

Metal oxides can also be formed when metal compounds react with oxygen at very high temperatures. Sulphides of lead and zinc for example, are usually oxidised when heated with oxygen at high temperatures to form metal oxides and sulphur dioxide gas.

$$2PbS(s) + 3O_2(g) \longrightarrow 2PbO(s) + 2SO_2(g)$$

$$2ZnS(s) + 3O_2(g) \longrightarrow 2ZnO(s) + 2SO_2(g)$$

Activity 2.1 Preparation of metal oxides by direct method

Requirements: Bunsen burner, pair of tongs, deflagrating spoon, spatula, knives, watch glass, measuring cylinder, test tubes, filter papers, magnesium foil/ribbon, phenolphthalein indicator, distilled water, steel wool, and litmus paper.

Procedure

1. Put 5 mL of distilled water in a test tube and add two drops of phenolphthalein indicator.
2. Cut 1 g of magnesium ribbon and clean it with a steel wool and hold it with a deflagrating spoon.
3. Heat the sample of magnesium until it ignites.
4. Note the colour of the flame and allow the sample to keep on burning until the flame goes off.
5. Note the colour of the residue and put it in a test tube in procedure number 1 above.
6. Shake well the mixture and record your observations.

Questions

1. What is observed when magnesium ribbon burns in air?
2. What is the colour of the flame and the residue?
3. What is observed when the residue is put in the distilled water containing the indicator?
4. Write the equation for the reaction that took place when the magnesium sample was heated.

Indirect methods of preparing metal oxides

The indirect methods of preparing metal oxides involve the oxidation of some metals with concentrated acids and thermal decomposition of metal compounds containing oxygen.

Oxidation of some metals with concentrated nitric acid

When copper is dissolved in concentrated nitric acid and the mixture is heated, copper(II) oxide, nitrogen dioxide gas, water, and oxygen gas are produced.

$$2Cu(s) + 8HNO_3(aq) \xrightarrow{\text{heat}} 2CuO(s) + 8NO_2(g) + O_2(g) + 4H_2O(l)$$

The copper(II) oxide is left as a black residue. Nitrogen dioxide is observed as brown fumes.

Thermal decomposition of metal compounds containing oxygen

The decomposition of metal compounds by heat depends on their positions in the reactivity series. The more reactive the metal is, the more difficult to decompose its compounds by heat.

Thermal decomposition of metal hydroxides

The hydroxides of calcium, magnesium, zinc, iron, lead, and copper readily decompose on heat to form metal oxides and water. The hydroxide of sodium is very stable and hence does not decompose on heating. Examples of thermal decomposition of metal hydroxides are:

$$Zn(OH)_2(s) \xrightarrow{\text{heat}} ZnO(s) + H_2O(l)$$

$$Mg(OH)_2(s) \xrightarrow{\text{heat}} MgO(s) + H_2O(l)$$

$$2Al(OH)_3(s) \xrightarrow{\text{heat}} Al_2O_3(s) + 3H_2O(l)$$

Thermal decomposition of metal sulphates

The sulphates of most reactive metals such as sodium and potassium are very stable and do not decompose on heating. The sulphate of calcium exists as a dihydrate ($CaSO_4{\cdot}2H_2O$) and when heated at temperature above 200 °C loses its water of crystallisation to form anhydrous $CaSO_4$. On heating at very high temperature of about 1200 °C, the anhydrous $CaSO_4$ forms calcium oxide, sulphur dioxide, and oxygen gas.

$$CaSO_4{\cdot}2H_2O(s) \xrightarrow[-2H_2O]{280\ ^\circ C} CaSO_4(s) \xrightarrow{1200\ ^\circ C} CaO(s) + SO_2(g) + \tfrac{1}{2}O_2(g)$$

Sulphates of Mg, Zn, Pb, and Cu decompose easily on heating to form metal oxides, sulphur dioxide gas, and oxygen gas.

$$2MgSO_4(s) \xrightarrow{\text{heat}} 2MgO(s) + 2SO_2(g) + O_2(g)$$

$$2ZnSO_4(s) \xrightarrow{\text{heat}} 2ZnO(s) + 2SO_2(g) + O_2(g)$$

$$2PbSO_4(s) \xrightarrow{\text{heat}} 2PbO(s) + 2SO_2(g) + O_2(g)$$

$$2CuSO_4(s) \xrightarrow{\text{heat}} 2CuO(s) + 2SO_2(g) + O_2(g)$$

The sulphate of iron exists as hydrated salt ($FeSO_4{\cdot}7H_2O$) and on heating it loses water to form anhydrous ferrous sulphate ($FeSO_4$). On further heating, the anhydrous $FeSO_4$ decomposes to form ferric oxide (Fe_2O_3), sulphur dioxide (SO_2), and sulphur trioxide (SO_3) as shown in the following equation:

$$2FeSO_4{\cdot}7H_2O(s) \xrightarrow[-7H_2O]{\text{heat}} 2FeSO_4(s) \xrightarrow{\text{heat}} Fe_2O_3(s) + SO_2(g) + SO_3(g)$$

Thermal decomposition of metal carbonates

The carbonates of Ca, Mg, Zn, Fe, Pb, and Cu decompose readily on heating to form metal oxides and carbon dioxide as shown in the following examples:

$$CaCO_3(s) \xrightarrow{\text{heat}} CaO(s) + CO_2(g)$$

$$ZnCO_3(s) \xrightarrow{\text{heat}} ZnO(s) + CO_2(g)$$

$$CuCO_3(s) \xrightarrow{\text{heat}} CuO(s) + CO_2(g)$$

The carbonates of most reactive metals such as sodium and potassium are very stable and therefore do not decompose on heating.
Example:

$$Na_2CO_3(s) \xrightarrow{\text{heat}} \text{No decomposition}$$

Activity 2.2 **Preparation of metal oxides by indirect method**

Requirements: Bunsen burner, spatula, test tubes, test tube racks, delivery tube, spatula, clamps, retort stand, beaker, lime water, and magnesium carbonate (or any available metal carbonate of the selected metal).

Procedure

1. Put a spatulaful of the given metal carbonate in a test tube.
2. Set up the apparatus as shown in Figure 2.1.

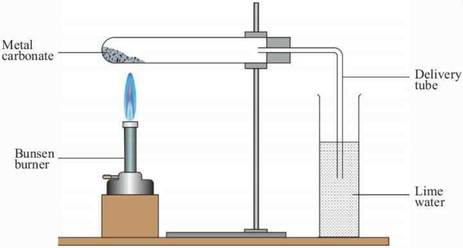


Figure 2.1 Set up for the preparation of metal oxide

3. Heat the carbonate until the residue is formed.
4. Note the colour of the residue left in the test tube when it is hot and after cooling and record your observation(s).
5. Note any change in the lime water and record your observation(s).

Questions

1. What is the name of the residue formed and what led to the change observed in the lime water?
2. Give balanced chemical equations for two reactions taking place in the experiment.

2.1.3 Chemical properties of metal oxides

Metal oxides have many chemical properties. However, in this section only the reactions of metal oxides with water and acids are described.

Reactions of metal oxides with water

Most metal oxides react with water to form basic solutions. The oxides of sodium, magnesium, and calcium are soluble in water. However, MgO is only slightly soluble. When these oxides are dissolved in water, they form metal hydroxides (basic solutions) as shown in the following examples:

$$Na_2O(s) + H_2O(l) \xrightarrow{heat} 2NaOH(aq) \qquad pH \approx 14$$

$$MgO(s) + H_2O(l) \xrightarrow{heat} Mg(OH)_2(aq) \qquad pH \approx 12$$

$$CaO(s) + H_2O(l) \xrightarrow{heat} Ca(OH)_2(aq) \qquad pH \approx 12$$

Oxides of aluminium, zinc, lead(II), copper(II), iron(II), and iron(III) do not react with water, which implies that these oxides are insoluble in water.

Reactions of metal oxides with acids

Most metal oxides react with acids to form salt and water only. This kind of reaction is called *neutralisation reaction*. These include the metal oxides which do not dissolve in water. Magnesium, calcium, and sodium oxides are basic oxides. Aluminium, zinc, and lead oxides are amphoteric oxides, hence react with both acids and alkalis. Dilute hydrochloric acid reacts with metal oxides to give metal chlorides and water. The reaction between lead(II) oxide and dilute hydrochloric acid stops as soon as it starts. This is due to the formation of lead(II) chloride which is insoluble. Lead(II) chloride forms a coating on the lead(II) oxide, thus preventing further reaction.

$$PbO(s) + 2HCl(aq) \longrightarrow PbCl_2(s) + H_2O(l)$$

Dilute sulphuric acid reacts with metal oxides to give metal sulphates and water. The reactions involving calcium oxide and lead(II) oxide with sulphuric acid produce insoluble calcium sulphate and lead(II) sulphate, respectively. The sulphates form coatings on their respective metal oxides, thus preventing further reactions on the metal oxides. The reactions therefore stop as soon as they start.

$$CaO(s) + H_2SO_4(aq) \longrightarrow CaSO_4(s) + H_2O(l)$$

$$PbO(s) + H_2SO_4(aq) \longrightarrow PbSO_4(s) + H_2O(l)$$

The calcium sulphate formed from the reaction of calcium oxide with dilute sulphuric acid is sparingly (slightly) soluble in water. Table 2.1 shows the reactions of the metal oxides with dilute mineral acids.

Table 2.1: The reactions of metal oxides with dilute mineral acids

Metal oxides	Reaction
Dilute nitric acid	
Sodium oxide	$Na_2O(s) + 2HNO_3(aq) \longrightarrow 2NaNO_3(aq) + H_2O(l)$
Calcium oxide	$CaO(s) + 2HNO_3(aq) \longrightarrow Ca(NO_3)_2(aq) + H_2O(l)$
Magnesium oxide	$MgO(s) + 2HNO_3(aq) \longrightarrow Mg(NO_3)_2(aq) + H_2O(l)$
Aluminium oxide	$Al_2O_3(s) + 6HNO_3(aq) \longrightarrow 2Al(NO_3)_3(aq) + 3H_2O(l)$
Iron(II) oxide	$FeO(s) + 2HNO_3(aq) \longrightarrow Fe(NO_3)_2(aq) + H_2O(l)$
Lead(II) oxide	$PbO(s) + 2HNO_3(aq) \longrightarrow Pb(NO_3)_2(aq) + H_2O(l)$
Copper(II) oxide	$CuO(s) + 2HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + H_2O(l)$
Zinc oxide	$ZnO(s) + 2HNO_3(aq) \longrightarrow Zn(NO_3)_2(aq) + H_2O(l)$
Dilute hydrochloric acid	
Sodium oxide	$Na_2O(s) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2O(l)$
Calcium oxide	$CaO(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l)$
Magnesium oxide	$MgO(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2O(l)$
Aluminium oxide	$Al_2O_3(s) + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2O(l)$
Iron(II) oxide	$FeO(s) + 2HCl(aq) \longrightarrow FeCl_2(aq) + H_2O(l)$
Lead(II) oxide	$PbO(s) + 2HCl(aq) \longrightarrow PbCl_2(s) + H_2O(l)$
Copper(II) oxide	$CuO(s) + 2HCl(aq) \longrightarrow CuCl_2(aq) + H_2O(l)$
Zinc oxide	$ZnO(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2O(l)$
Dilute sulphuric acid	
Sodium oxide	$Na_2O(s) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + H_2O(l)$
Calcium oxide	$CaO(s) + H_2SO_4(aq) \longrightarrow CaSO_4(s) + H_2O(l)$
Magnesium oxide	$MgO(s) + H_2SO_4(aq) \longrightarrow MgSO_4(aq) + H_2O(l)$
Aluminium oxide	$Al_2O_3(s) + 3H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 3H_2O(l)$
Iron(II) oxide	$FeO(s) + H_2SO_4(aq) \longrightarrow FeSO_4(aq) + H_2O(l)$
Lead(II) oxide	$PbO(s) + H_2SO_4(aq) \longrightarrow PbSO_4(s) + H_2O(l)$
Copper(II) oxide	$CuO(s) + H_2SO_4(aq) \longrightarrow CuSO_4(aq) + H_2O(l)$
Zinc oxide	$ZnO(s) + H_2SO_4(aq) \longrightarrow ZnSO_4(aq) + H_2O(l)$

Activity 2.3 Investigation of the reactions of metal oxides with acids

Requirements: Test tubes, measuring cylinders, wire gauze, glass rod, spatula, tripod stand, heating source, oxides of magnesium, lead and copper, 0.2 M H_2SO_4, 0.2 M HCl, and 0.2 M HNO_3.

Procedure

1. Label three test tubes with the names of the three oxides.
2. Put 2 g of each of the metal oxides into the respective test tubes.
3. Add 5 mL of 0.2 M H_2SO_4 and record your observations.
4. Repeat the above procedure using the remaining acids. If there is no any reaction, warm the mixture and record your observations.

Question

Write balanced chemical equations for the reactions observed between the mineral acids and the oxides.

2.1.4 Uses of metal oxides

Metal oxides are used as important components in the production of other compounds which are useful in daily life. Their uses can be categorised into industrial and agricultural uses as follows:

Industrial uses of metal oxides

The following are some industrial applications of the metal oxides:

Nanotechnology

Many metal oxides are used in nanotechnology for the production of various important products in agriculture and health. Nanotechnology *is the branch of technology that deals with manipulation of properties of materials (atoms or molecules) whose dimensions are less than 100 nanometres, to obtain various properties for technological applications*. Copper(II) oxide for example, is used in the production of nanoparticles which are used as adsorbents in the removal of heavy metals such as cadmium, arsenic, and mercury from water.

Pharmaceutical industries

Metal oxides such as ZnO are used as components in the production of creams, powders, dental pastes, antiseptic ointments, and enamels. Magnesium oxide is used to manufacture anti-acid drugs for the relief of heartburn and ulcers. It is also used to improve indigestion symptoms. Fe_3O_4, due to its paramagnetic properties, is used in making nanoparticles for biomedical applications.

Production of building materials

Preparing mortar

Calcium oxide reacts with water to make slaked lime ($Ca(OH)_2$). Slaked lime, sand, and water are mixed to make mortar which is used to stick bricks and plaster. Zinc oxide is used as a white pigment in paints, and as a component of ceramic glazes.

Manufacture of cements, glasses, optics, and ceramics

Calcium oxide (lime) or limestone, silicates, and aluminates are mixed together and strongly heated to make cement. Magnesium oxide is used as a component in making magnesia based cements, including oxychloride, oxysulphate, and phosphate based cements. These cements are used in the production of fireproof materials and coatings, wall boards, flooring, and grinding wheels. Sodium oxides are used in the manufacture of glasses, optics, and ceramics. For example, soda lime and glass are made from sodium monoxide.

Manufacture of refractory materials

A refractory material is the one that is physically and chemically stable at high temperatures. Metal oxides which have this property include CaO and MgO. These oxides are used in lining furnaces because they have high melting points of more than 2500 °C making them suitable refractory materials. Magnesium oxide is used as a basic refractory material for crucibles, insulators in industrial cables and as a component of tubular construction heating elements.

Manufacturing of other chemicals

Metal oxides have wide applications in the manufacture of chemicals such as alcohols, alkalis, fertilisers, and many organic solvents. Calcium oxide for example, is used as a drying agent in the preparation of ammonia and ethanol. Metal oxides such as Fe_2O_3 and Fe_3O_4 are used as sources of iron (Fe) in its extraction. In the extraction process of iron, the CaO which is produced from heating $CaCO_3$, combines with SiO_2 to form a molten waste product called *slag*. The role of calcium oxide in this process is to remove the impurities from molten iron and prevent it from being oxidised. Aluminium oxide (Al_2O_3), which is commonly known as *corundum,* is used for cleaning hard surfaces by scratching (an abrasive substance).

Agricultural uses of metal oxides

In agriculture, metal oxides have very wide applications. The lime (CaO) is used to treat soil for raising its pH, hence reducing its acidity. A mixture of CaO and MgO, which is commonly known as *magmax* is also used for improving soil pH, soil porosity, and supplies calcium and magnesium ions for better plant growth. The use of metal oxide-based nanoparticle agrochemicals, such as zinc oxide (ZnO) and silver oxide (AgO) provides a significant promise in the management of insects and pathogens in the protection of plants. These oxides are used to manufacture nanoparticle based insecticides and anti-microbials for the management of pests and microorganisms.

Exercise 2.1

1. Describe with examples, the two common methods used for the preparation of metal oxides.
2. Some oxides are both acidic and basic. Mention their collective name and give examples.
3. Mention the classes of metal oxides based on their reactions with acids or bases, and in each case give two examples with complete balanced equations.
4. Write an equation to show the;
   (a) burning of sodium in air.
   (b) decomposition of metal carbonates by heat.
   (c) dissolving of sodium oxide in dilute acid.
5. Name two metal oxides which are soluble in water and other two which are insoluble in water.
6. Describe five uses of metal oxides.
7. Account for the colour of the following metal oxides when hot or cold:
   (a) Copper oxide (b) Zinc oxide (c) Lead oxide (d) Magnesium oxide
8. Write equations to show how each of the oxides of aluminium, potassium, and copper reacts with;
   (a) water. (b) dilute nitric acid.
   (c) dilute sulphuric acid. (d) dilute hydrochloric acid.
9. Explain with balanced chemical equations, what happens when;
   (a) a piece of sodium metal is dropped in water.
   (b) sodium metal is heated in excess of air that is free of carbon dioxide.

2.2 Metal hydroxides

A hydroxide is any inorganic compound that contains the hydroxide ions (OH^-). Metal hydroxides can be prepared directly by the reactions of metals high in the reactivity series with water and indirectly by the reactions of alkalis with salts such as chlorides, sulphates, and nitrates. In this section, you will learn about classes of hydroxides, methods of preparation, properties and their uses.

2.2.1 Classification of metal hydroxides

Metal hydroxides are classified according to their solubility in water. Therefore, there are soluble and insoluble hydroxides. Metal hydroxides are also classified into basic and amphoteric hydroxides based on their reactions with acids and bases.

Solubility of hydroxides in water

Metal hydroxides of group IA elements, which include lithium hydroxide, sodium hydroxide, potassium hydroxide, rubidium hydroxide, and caesium hydroxide, are soluble in water. Lithium hydroxide is the least soluble hydroxide in group IA, even though it is possible to make a solution of lithium hydroxide with a concentration of 12.8 grams per 100 g of water at 20 °C. The solubilities of the hydroxides increase down the group. Just like group IA hydroxides, the solubilities of the hydroxides of group IIA increase down the group. Beryllium hydroxide is sparingly soluble. Magnesium hydroxide appears as if it is insoluble in water. However, if it is shaken with water and filtered, the pH test of the solution shows that it is slightly alkaline meaning that there are some hydroxide ions in the solution. One litre of water has the ability to dissolve one gram of calcium hydroxide at room temperature. Barium hydroxide is the most soluble hydroxide of group IIA with the ability to dissolve just 3.9 grams per 100 grams of water at 20 °C.

Amphoteric hydroxides

Amphoteric hydroxides are hydroxides that show both acidic and basic properties. Examples of amphoteric hydroxides are $Al(OH)_3$, $Zn(OH)_2$, and $Pb(OH)_2$. When excess sodium hydroxide is added to insoluble metal hydroxides of zinc, lead, and aluminium, they would dissolve to form complex ions. These hydroxides are said to be amphoteric since they react with both acids and bases.

Reactions with acids

Amphoteric hydroxides behave as bases by reacting with acids to form salt and water as shown in the following examples:

$$Zn(OH)_2(s) + H_2SO_4(aq) \longrightarrow ZnSO_4(aq) + 2H_2O(l)$$

$$Pb(OH)_2(s) + 2HNO_3(aq) \longrightarrow Pb(NO_3)_2(aq) + 2H_2O(l)$$

$$Al(OH)_3(s) + 3HCl(aq) \longrightarrow AlCl_3(aq) + 3H_2O(l)$$

Reactions with alkalis

In the presence of strong alkalis such as sodium hydroxide, these hydroxides behave as acids as they react to produce salt and water.

Zinc hydroxide dissolves in excess sodium hydroxide to form sodium zincate and water.

$$Zn(OH)_2(s) + 2NaOH(aq) \longrightarrow Na_2ZnO_2(aq) + 2H_2O(l)$$

Lead(IV) hydroxide dissolves to form sodium plumbate and water.

$$Pb(OH)_4(s) + 2NaOH(aq) \longrightarrow Na_2PbO_3(aq) + 3H_2O(l)$$

Aluminium hydroxide dissolves to form sodium aluminate and water.

$$Al(OH)_3(s) + NaOH(aq) \longrightarrow NaAlO_2(aq) + 2H_2O(l)$$

2.2.2 Preparation of metal hydroxides

Metal hydroxides can be prepared either by direct or indirect methods.

Direct method of preparing metal hydroxides

This method involves direct reactions between metals and water. The method is suitable for the preparation of hydroxides which are soluble in water (alkalis). In the direct method, metals especially those high in the reactivity series are reacted with water to form hydroxides. The direct method for the preparation of metal hydroxides occurs in various ways. Sodium reacts vigorously with water to form an alkaline solution of sodium hydroxide and hydrogen gas.

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$

The resulting solution turns red litmus paper blue, indicating that the solution is basic.

When calcium metal is added to water, a white suspension of calcium hydroxide is formed in the completion of the reaction and hydrogen gas is evolved. This suspension indicates that calcium hydroxide is sparingly soluble.

$$Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + H_2(g)$$

Magnesium reacts slightly with water to form magnesium hydroxide and hydrogen gas.

$$Mg(s) + 2H_2O(l) \longrightarrow Mg(OH)_2(aq) + H_2(g)$$

Indirect method of preparing metal hydroxides

This method is used in the preparation of hydroxides of metals which are below hydrogen in the reactivity series. The method is also called *precipitation method* since it results into the formation of hydroxides which are insoluble in water. The precipitation method involves reacting aqueous solutions of most reactive metal hydroxides with aqueous salts of less reactive metals.

Aqueous solution of copper(II) chloride reacts with dilute sodium hydroxide to form blue precipitates of copper(II) hydroxide.

$$CuCl_2(aq) + 2NaOH(aq) \longrightarrow Cu(OH)_2(s) + 2NaCl(aq)$$

$$Cu^{2+}(aq) + 2OH^-(aq) \longrightarrow Cu(OH)_2(s)$$

Zinc nitrate solution reacts with enough dilute sodium hydroxide to form a white precipitate of zinc hydroxide.

$$Zn(NO_3)_2(aq) + 2NaOH(aq) \longrightarrow Zn(OH)_2(s) + 2NaNO_3(aq)$$

$$Zn^{2+}(aq) + 2OH^-(aq) \longrightarrow Zn(OH)_2(s)$$

If excess sodium hydroxide is used, the zinc hydroxide precipitate will dissolve to form a complex zincate ion.

$$Zn(OH)_2(s) + 2OH^-(aq) \longrightarrow Zn(OH)_4^{2-}(aq)$$

Iron(II) sulphate solution reacts with dilute potassium hydroxide to form iron(II) hydroxide precipitate and potassium sulphate solution.

$$FeSO_4(aq) + 2KOH(aq) \longrightarrow Fe(OH)_2(s) + K_2SO_4(aq)$$

$$Fe^{2+}(aq) + 2OH^-(aq) \longrightarrow Fe(OH)_2(s)$$

Similarly, iron(III) chloride solution reacts with dilute sodium hydroxide to form reddish brown precipitate of iron(III) hydroxide.

$$FeCl_3(aq) + 3NaOH(aq) \longrightarrow Fe(OH)_3(s) + 3NaCl(aq)$$

$$Fe^{3+}(aq) + 3OH^-(aq) \longrightarrow Fe(OH)_3(s)$$

Indirect preparation of sodium hydroxide by electrolysis of brine

Brine *is a concentrated solution of sodium chloride*. During electrolysis of brine, an aqueous solution of sodium hydroxide is produced together with hydrogen and chlorine gases.

$$2NaCl(aq) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g) + Cl_2(g)$$

In the electrolysis of brine, three types of electrolytic cells are used to produce hydroxide.These cells are Castner-kellner cell (mercury process), Nelson diaphragm cell, and membrane cell. In this chapter, the membrane electrolytic cell is discussed. Figure 2.2 shows the setup of the membrane cell for the electrolysis of brine.

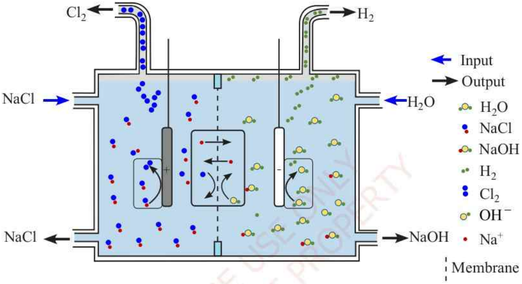


Figure 2.2 Basic membrane cell used in the electrolysis of brine

The anode and cathode compartments are separated by an ion-selective membrane which allows only Na^+ to pass through but prevents OH^- and Cl^- ions from diffusing across. The aqueous solution of sodium chloride is introduced into the anode compartment. The current that is passing through the cell splits the sodium chloride into its constituent components.

$$NaCl(aq) \longrightarrow Na^+(aq) + Cl^-(aq)$$

Pure water is introduced at the cathode compartment. At the cathode, water is reduced to hydroxide and hydrogen gas.

$$2H_2O(l) + 2e^- \longrightarrow 2OH^-(aq) + H_2(g)$$

At the anode, the chloride ions (Cl^-) from sodium chloride are oxidised to form chlorine gas (Cl_2).

$$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$$

The sodium ions (Na^+) penetrate the ion selective membrane to the cathode compartment, which contains OH^- ions. The sodium ions (Na^+) and hydroxide ions (OH^-) then combine to form sodium hydroxide.

$$Na^+(aq) + OH^-(aq) \longrightarrow NaOH(aq)$$

The solution of sodium hydroxide (NaOH) is collected at the bottom of the cathode compartment.

The overall reaction for the electrolysis of brine is summarised by the following equation:

$$2NaCl(aq) + 2H_2O(l) \longrightarrow 2NaOH(aq) + Cl_2(g) + H_2(g)$$

Activity 2.4 Preparation of metal hydroxides by the precipitation method

Requirements: Beakers, droppers, test tubes, measuring cylinder, wash bottle, retort stand, clamp, filter funnel, filter paper, sodium hydroxide (1M NaOH), copper(II) sulphate solution ($CuSO_4$), 1M zinc nitrate solution, and distilled water.

Procedure

1. Label two test tubes **A** and **B** and measure 5 mL of each of the $CuSO_4$ and $Zn(NO_3)_2$ solutions and put into the respective test tube.
2. Add NaOH in each of the test tubes above until precipitates are formed.
3. Filter the precipitates and dry them in the sun.

Questions

1. Give the names of the precipitates formed in each of the test tube.
2. What colours did you observe from each test tube?
3. Write an ionic equation to summarise what happened in each of the test tubes.

2.2.3 Chemical properties of metal hydroxides

Metal hydroxides take part in different chemical reactions. These include thermal decomposition and neutralisation reactions with acids.

Action of heat on metal hydroxides

The hydroxides of metals high in the reactivity series such as potassium and sodium do not decompose on heating. Other metal hydroxides decompose to give metal oxides and water. For example, lead(II) hydroxide decomposes to give lead oxide and water as shown in the following equation:

$$Pb(OH)_2(s) \xrightarrow{\text{heat}} PbO(s) + H_2O(l)$$

Reactions of sodium hydroxide with metals

Concentrated sodium hydroxide reacts with metals such as aluminium, zinc, and lead to form aluminates, zincates and plumbates, respectively.

$$2NaOH(aq) + 2Al(s) + 6H_2O(l) \longrightarrow \underset{\text{Sodium aluminate}}{2NaAl(OH)_4(aq)} + 3H_2(g)$$

$$2NaOH(aq) + Zn(s) + 2H_2O(l) \longrightarrow \underset{\text{Sodium zincate}}{Na_2Zn(OH)_4(aq)} + H_2(g)$$

$$2NaOH(aq) + Pb(s) + 2H_2O(l) \longrightarrow \underset{\text{Sodium plumbate}}{Na_2Pb(OH)_4(aq)} + H_2(g)$$

Reactions of acids with metal hydroxides

Metal hydroxides react with mineral acids in the neutralisation reaction to give salts and water only. For example, sodium hydroxide reacts with hydrochloric acid and sulphuric acid to form sodium chloride and sodium sulphate, respectively.

$$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

$$2NaOH(aq) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O(l)$$

Also, copper hydroxide which is a blue solid reacts with both hydrochloric acid and sulphuric acid to form copper(II) chloride and copper(II) sulphate, respectively.

$$Cu(OH)_2(s) + 2HCl(aq) \longrightarrow CuCl_2(aq) + 2H_2O(l)$$

$$Cu(OH)_2(s) + H_2SO_4(aq) \longrightarrow CuSO_4(aq) + 2H_2O(l)$$

Calcium hydroxide dissolves readily in dilute nitric acid and hydrochloric acid to form calcium nitrate and calcium chloride, respectively.

$$Ca(OH)_2(aq) + 2HNO_3(aq) \longrightarrow Ca(NO_3)_2(aq) + 2H_2O(l)$$

$$Ca(OH)_2(aq) + 2HCl(aq) \longrightarrow CaCl_2(aq) + 2H_2O(l)$$

When the reaction between calcium hydroxide and dilute sulphuric acid occurs, precipitates of calcium sulphate are formed and prevent further reaction. Similarly, the reaction between lead(II) hydroxide and dilute sulphuric acid stops immediately due to the formation of insoluble lead(II) sulphate.

$$Pb(OH)_2(aq) + H_2SO_4(aq) \longrightarrow PbSO_4(s) + 2H_2O(l)$$

Iron(II) hydroxide, which is a green solid, reacts with both hydrochloric acid and sulphuric acid to form iron(II) chloride and iron(II) sulphate, respectively:

$$Fe(OH)_2(aq) + 2HCl(aq) \longrightarrow FeCl_2(aq) + 2H_2O(l)$$

$$Fe(OH)_2(aq) + H_2SO_4(aq) \longrightarrow FeSO_4(aq) + 2H_2O(l)$$

When left to stand for a few minutes, the light green solutions of iron(II) chloride and iron(II) sulphate change to reddish brown solutions due to the oxidation of iron(II) ions to iron(III) ions by air.

$$\underset{\text{Light green}}{Fe^{2+}(aq)} \longrightarrow \underset{\text{Reddish brown}}{Fe^{3+}(aq)} + e^-$$

Reactions of amphoteric hydroxides with acids and bases

Amphoteric hydroxides such as aluminium hydroxide are largely insoluble in neutral water. When HCl is added to $Al(OH)_3$, the acid-base neutralisation reaction occurs.

$$Al(OH)_3(s) + 3HCl(aq) \longrightarrow AlCl_3(aq) + 3H_2O(l)$$

When aluminium hydroxide is added to a strongly basic solution, it picks up hydroxide ions out of solution and thereby acting as a Lewis acid.

$$Al(OH)_3(s) + OH^-(aq) \longrightarrow Al(OH)_4^-(aq)$$

Therefore, aluminium hydroxide can act as either a Brønsted-Lowry base by accepting protons from acidic solution or as a Lewis acid by accepting electrons from hydroxide ions in basic solution. Thus, hydroxides with highly charged central metals can be amphoteric. Other examples of amphoteric hydroxides include zinc, tin, lead, and beryllium hydroxides. The reactions of amphoteric hydroxides in acids and in basic solutions are also discussed under the classification of hydroxides.

Reactions of hydroxides with soluble salts

Sodium hydroxide for example, reacts with soluble salts of some metals such as copper, lead, zinc, and iron to form insoluble hydroxides.

Examples:

$$3NaOH(aq) + FeCl_3(aq) \longrightarrow Fe(OH)_3(s) + 3NaCl(aq)$$

$$2NaOH(aq) + ZnSO_4(aq) \longrightarrow Zn(OH)_2(s) + Na_2SO_4(aq)$$

These reactions which involve the exchange of ions between the reacting substances are known as *double decomposition reactions*. On the other hand, when sodium hydroxide is warmed with ammonium salts it releases ammonia gas.

Examples:

$$NaOH(aq) + NH_4Cl(aq) \xrightarrow{\text{heat}} NaCl(aq) + NH_3(g) + H_2O(l)$$

$$NaOH(aq) + NH_4NO_3(aq) \xrightarrow{\text{heat}} NaNO_3(aq) + NH_3(g) + H_2O(l)$$

Similar reaction is observed when calcium hydroxide is treated with an ammonium salt.

$$Ca(OH)_2(aq) + 2NH_4Cl(aq) \xrightarrow{\text{heat}} CaCl_2(aq) + 2NH_3(g) + 2H_2O(l)$$

2.2.4 Uses of metal hydroxides

Metal hydroxides have a wide range of uses in industrial and agricultural fields. The industrial uses are very significant in the production of various chemical compounds which are useful in our daily life. The following section describes the uses of metal hydroxides.

Soap manufacturing

Alkali metal hydroxides are very useful in making detergents and soaps. A detergent is a water-soluble cleansing agent which combines with dirt and dissolves it. Unlike soaps, detergents do not form scum with the salts in hard water. A detergent can emulsify oils easily because it has a long non-polar tail and a highly polar (negatively charged) head. Sodium lauryl sulphate for example, is a detergent made from the addition of sodium hydroxide into a solution of lauryl hydrogen sulphate.

$$\begin{tikzcd}
CH_3(CH_2)_{10}CH_2OH(l) \arrow[r, "H_2SO_4"] & CH_3(CH_2)_{10}CH_2OSO_3H(l) \arrow[d, "NaOH"] \\
\text{Lauryl alcohol} & CH_3(CH_2)_{10}CH_2OSO_3^- \, Na^+(s) + H_2O(l) \\
 & \text{Sodium lauryl sulphate}
\end{tikzcd}$$

Soap is made up of metal hydroxide salt and fatty acid. Sodium palmitate for example, is the product of the reaction between palmitic acid and NaOH.

$$\underset{\text{Palmitic acid}}{CH_3(CH_2)_{14}COOH(l)} + NaOH(aq) \longrightarrow \underset{\text{Sodium palmitate (soap)}}{CH_3(CH_2)_{14}COO^- Na^+(aq)} + H_2O(l)$$

In the extraction of metals

Sodium hydroxide is used to remove impurities of acidic SiO_2 (sand) in the bauxite during the extraction of aluminium. When bauxite (hydrated Al_2O_3) is treated with boiling NaOH, the SiO_2 dissolves in NaOH to form sodium silicate ($Na_2Si(OH)_6$).

$$SiO_2(s) + 2NaOH(aq) + 2H_2O(l) \longrightarrow \underset{\text{Sodium silicate}}{Na_2Si(OH)_6(aq)}$$

Paper manufacturing

The solution of calcium hydrogen sulphite is prepared by passing sulphur dioxide gas into a solution of calcium hydroxide.

$$Ca(OH)_2(aq) + 2SO_2(g) \longrightarrow Ca(HSO_3)_2(aq)$$

When the solution is applied to a wood it removes the lignin leaving the cellulose. This process is called *bleaching of pulp*. The solution of sodium hydroxide is also used in the paper industry for bleaching of pulp.

Production of building materials

Metal hydroxides play significant roles in the production of building materials. Sodium hydroxide for example, is used in the manufacturing of artificial textile fibres, dyes, and bleaches. Calcium hydroxide ($Ca(OH)_2$) is used in the production of paints, cement, mortar, and whitewashes. The mortar, which is a mixture of slaked lime ($Ca(OH)_2$), sand, and water is used to stick bricks together. The whitewash is a thick suspension of slaked lime. When it is smeared on the walls of buildings, it provides a smooth protective layer.

Production of other chemicals

Metal hydroxides are widely used in the manufacturing of many chemical compounds in small or large scale production. Metal hydroxides are used in the manufacturing of chemicals such as salts, ammonia, phosphates, alcohols, and washing soda. Caustic soda (NaOH) for example, is used as a cleansing agent. Soap of the NaOH is a powerful degreaser on stainless steel, glass, bakeware, and ovens.

Activity 2.5 **Investigation of the cleansing ability of caustic soda**

Requirements: Sodium hydroxide (caustic soda), 20 litres of water, empty bucket, brush, two dirty sinks, and cup.

Procedure

1. Measure 200 g of NaOH on a weighing balance or beam balance.
2. Dissolve 200 g of NaOH in 5 litres of water.
3. Use 5 litres of water to clean one of the dirty sinks.
4. Use the prepared caustic soda to wash the remaining dirty sink.

Question

Compare the cleansing ability between water and caustic soda. Which one is suitable to be used as a cleansing reagent?

Health

Some of the metal hydroxides have medical applications in improving the health of humans. For example, the milk of magnesia ($Mg(OH)_2$) is used as an anti-acid medicine due to its basic nature. It neutralises the excess acid-reflux (indigestion and heartburn). It is also used as an anti-perspirant, arm pit deodorant and for treatment of skin diseases.

Water treatment

Calcium hydroxide is used in removing temporary hardness in salty water.

$$Ca(OH)_2(aq) + Ca(HCO_3)_2(aq) \longrightarrow 2CaCO_3(s) + 2H_2O(l)$$

Magnesium hydroxide is used in industries as non-hazardous alkali to neutralise acidic wastewater. The addition of caustic soda (NaOH) into water supplying centres, raises the water pH and hence making the water less corrosive to plumbing and reduces the amounts of Pb, Cu and other toxic metals that can dissolve into the drinking water.

Agricultural uses of metal hydroxides

Metal hydroxides have a wide range of applications in agriculture. For instance, when slaked lime is mixed with copper(II) sulphate, it forms Bordeaux mixture which is used as a fungicide. This mixture is used to prevent infestations of downy mildew, powdery mildew, and other fungi in vineyards, fruit farms, and gardens. The slaked lime is also used in agriculture to adjust the pH of acidic soil. The metal hydroxide based nanoparticles act as storage and slow release matrices of nutrients and agrochemicals for plant growth. These particles on the soil, slowly release nitrates, phosphates, and agrochemicals which are essentially used as adsorbents for the wastewater treatment.

Exercise 2.2

1. (a) Give three examples of amphoteric hydroxides.

   (b) Write equations to show how each of the hydroxides provided in (a) reacts with;

      (i) dilute nitric acid.

      (ii) excess sodium hydroxide solution.

2. Using balanced chemical equations, explain the direct method of preparing metal hydroxides.

3. Explain the importance of storing hydroxides in containers which are tightly closed.

4. The hydroxides of metals can be classified in terms of their reactions with acids and bases. Name the classes of the hydroxides and in each case, give two examples and provide balanced chemical equations for their reactions.

5. Give two examples of water soluble and insoluble hydroxides. What is the name given to the water soluble hydroxides?

6. Mention five uses of the metal hydroxides.

2.3 Metal carbonates and hydrogen carbonates

A carbonate is a salt of carbonic acid (H_2CO_3) with a polyatomic ion called carbonate ion (CO_3^{2-}). Hydrogen carbonate (bicarbonate) is an intermediate form in the deprotonation of carbonic acid having a polyatomic anion with the chemical formula HCO_3^-. Metal carbonates and hydrogen carbonates are derived from carbonic acid. Carbonic acid is a dibasic compound with two replaceable hydrogen atoms in its molecule.

$$H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$

$$H_2CO_3(aq) \rightleftharpoons CO_3^{2-}(aq) + 2H^+(aq)$$

Metal carbonates are formed when both hydrogen atoms in carbonic acid are replaced by a metal ion. But, when only one hydrogen atom of carbonic acid is replaced by a metal ion, the hydrogen carbonate is formed. In this section, you will learn about the classification of metal carbonates, preparations, non-existence of carbonates of iron and aluminium, effects of heat on carbonates, properties of carbonates and their uses.

2.3.1 Classification of metal carbonates

The classification of carbonates is based on their solubility in water. Carbonates which dissolve in water and form clear solutions are classified as soluble carbonates and those which do not dissolve in water are classified as insoluble carbonates.

Soluble carbonates

The carbonates of very reactive metals such as potassium and sodium are examples of soluble carbonates. However, ammonium carbonate ($(NH_4)_2CO_3$) is the only non-metal carbonate which is also soluble in water.

Insoluble carbonates

The carbonates of less reactive metals such as copper, lead, iron(II), zinc, magnesium, and calcium are insoluble in water, but the carbonate of calcium is slightly soluble. The classification of metal carbonates is summarised in Table 2.2.

Table 2.2 Solubility of various metal carbonates in water

Metal carbonates	Solubility in water
Sodium carbonate	Soluble
Calcium carbonate	Insoluble
Magnesium carbonate	Insoluble
Zinc carbonate	Insoluble
Iron(II) carbonate	Insoluble
Lead carbonate	Insoluble
Copper carbonate	Insoluble

Activity 2.6 **Investigation of the solubility of carbonates in water**

Requirements: Beakers, test tubes, measuring cylinder, carbonates of sodium, magnesium, calcium, iron, copper, zinc, lead, and distilled water.

Procedure

1. Measure about 2 g of each of the carbonates and put it into its respective test tube.
2. In each test tube, add 5 mL of distilled water and shake to dissolve the solid samples.
3. Tabulate the results in a table as shown below. Use ✓ to indicate soluble carbonates and **X** for insoluble carbonates.

Metal carbonate	Na_2CO_3	$MgCO_3$	$CaCO_3$	$CuCO_3$	$ZnCO_3$	$PbCO_3$
solubility						

Question

What general conclusion can you draw based on the solubility of metal carbonates in water?

2.3.2 Preparations of metal carbonates and hydrogen carbonates

The preparation of carbonates depends on whether the carbonates are soluble or insoluble in water.

Preparation of soluble carbonates and hydrogen carbonates

The carbonates and hydrogen carbonates of sodium and potassium are only soluble in water. These metal carbonates are prepared by passing carbon dioxide into the solution of strong alkalis as shown in the following reactions:

$$2NaOH(aq) + CO_2(g) \longrightarrow Na_2CO_3(aq) + H_2O(l)$$

When the colourless aqueous solution of Na_2CO_3 is evaporated, white crystals are formed. This crystalline Na_2CO_3 is known as *washing soda*. Calcium carbonate can also be prepared in the same way.

$$Ca(OH)_2(aq) + CO_2(g) \longrightarrow \underset{\text{Slightly soluble}}{CaCO_3(aq)} + H_2O(l)$$

The solubility of $CaCO_3$ in pure water is very low, but relatively high in rain water which is saturated with carbon dioxide. When an excess of CO_2 gas is passed through a solution of an alkali, hydrogen carbonate is formed. For example:

$$Na_2CO_3(aq) + H_2O(l) + CO_2(g) \longrightarrow 2NaHCO_3(aq)$$

$$CaCO_3(aq) + H_2O(l) + CO_2(g) \longrightarrow Ca(HCO_3)_2(aq)$$

The passing of excess CO_2 gas into a solution of strong alkali, is the easiest and convenient way of producing hydrogen carbonates. All metal hydrogen carbonates are soluble in water. The hydrogen carbonates of Al, Zn, Pb, and Cu do not exist. Ammonium carbonate is a known soluble non-metal carbonate, which is formed by passing carbon dioxide gas into an alkaline solution of ammonia.

$$2NH_3(aq) + H_2O(l) + CO_2(g) \longrightarrow (NH_4)_2CO_3(aq)$$

The carbonates and hydrogen carbonates of metals can be distinguished by using magnesium sulphate solution. When a solution of magnesium sulphate is added to a solution of metal carbonate, a white precipitate of magnesium carbonate is formed.

$$Na_2CO_3(aq) + MgSO_4(aq) \longrightarrow MgCO_3(s) + Na_2SO_4(aq)$$

The addition of magnesium sulphate solution into a solution of metal hydrogen carbonate forms a clear solution of magnesium hydrogen carbonate.

$$2NaHCO_3(aq) + MgSO_4(aq) \longrightarrow Mg(HCO_3)_2(aq) + Na_2SO_4(aq)$$

A clear solution is formed, because magnesium hydrogen carbonate is very soluble in water. However, the heating of magnesium hydrogen carbonate forms a white precipitate of magnesium carbonate.

$$Mg(HCO_3)_2(aq) \xrightarrow{\text{heat}} \underset{\text{white precipitate}}{MgCO_3(s)} + H_2O(g) + CO_2(g)$$

Preparation of insoluble carbonates

Insoluble carbonates of metals are prepared by precipitation reactions. This method involves the addition of a soluble carbonate to a solution of salt of a less reactive metal. The carbonates of calcium, copper, magnesium, zinc, and lead are prepared by this method.

$$CaCl_2(aq) + Na_2CO_3(aq) \longrightarrow CaCO_3(s) + 2NaCl(aq)$$

$$MgCl_2(aq) + Na_2CO_3(aq) \longrightarrow MgCO_3(s) + 2NaCl(aq)$$

$$ZnSO_4(aq) + Na_2CO_3(aq) \longrightarrow ZnCO_3(s) + Na_2SO_4(aq)$$

$$CuCl_2(aq) + K_2CO_3(aq) \longrightarrow CuCO_3(s) + 2KCl(aq)$$

$$PbCl_2(aq) + Na_2CO_3(aq) \longrightarrow PbCO_3(s) + 2NaCl(aq)$$

Activity 2.7 **Preparation of insoluble metal carbonates**

Requirements: Filter funnel, filter paper, retort stand, beakers, measuring cylinder, petri dish, 2 M sodium carbonate solution, 2 M calcium chloride solution, and distilled water.

Procedure

1. Put 10 mL of sodium carbonate solution into a beaker.
2. Add 10 mL of calcium chloride into the beaker containing sodium carbonate solution and shake well the mixture.
3. Filter the precipitates with distilled water, empty the residue into a petri dish and expose to dry it.

Questions

1. What was the colour of the precipitates formed?
2. Give the states and the IUPAC names of the products formed.

2.3.3 Non-existence of iron and aluminium carbonates

Aluminium carbonate ($Al_2(CO_3)_3$) and iron(III) carbonate ($Fe_2(CO_3)_3$) do not exist. For the case of $Al_2(CO_3)_3$, smaller and more charged cations of Al^{3+} have high charge density but easily distort the electron cloud of the carbonate ions (polarisation). The polarisation weakens the C—O bond in the carbonate ion, hence making it highly exposed to water or water vapour and attached to form hydroxide and carbon dioxide gas.

$$Al_2(CO_3)_3(aq) + 3H_2O(l) \longrightarrow 2Al(OH)_3(s) + 3CO_2(g)$$

Similarly, iron(III) carbonate does not exist in a solution because, iron(III) bounds to water molecules and exists as $[Fe(H_2O)_6]^{3+}$. Due to a strong interaction between Fe^{3+} ions and aqua ligand, the complex dissociates into negatively charged complex and H^+ ions. Because carbonate is a base, it captures H^+ ions to form hydroxyl complexes which produce carbonic acid (H_2CO_3) and iron(III) hydroxide, ($Fe(OH)_3$. The weak carbonic acid eventually decomposes into water and carbon dioxide gas.

In solid state, most iron(III) compounds are hygroscopic as they tend to absorb moisture from the air. Then, when water gets involved, the reaction starts to take place as a result, the formed iron(III) carbonate decomposes into iron(III) hydroxide, carbon dioxide and water.

$$Fe_2(CO_3)_3(aq) + 4H_2O(l) \longrightarrow 2Fe(OH)_3(aq) + 3CO_2(g) + H_2O(l)$$

Therefore, iron(III) carbonate is not stable when in solution or solid state.

2.3.4 Effects of heat on carbonates

The carbonates of sodium and potassium are very stable compounds, hence do not decompose on heating. The other metal carbonates decompose on heating to give the metal oxides and carbon dioxide.

$$Na_2CO_3(s) \xrightarrow{\text{heat}} \text{No decomposition}$$

$$CaCO_3(s) \xrightarrow{\text{heat}} CaO(s) + CO_2(g)$$

$$MgCO_3(s) \xrightarrow{\text{heat}} MgO(s) + CO_2(g)$$

$$ZnCO_3(s) \xrightarrow{\text{heat}} ZnO(s) + CO_2(g)$$

$$PbCO_3(s) \xrightarrow{\text{heat}} PbO(s) + CO_2(g)$$

$$CuCO_3(s) \xrightarrow{\text{heat}} CuO(s) + CO_2(g)$$

The degree of heating required to decomposes the metal carbonates varies from one metal to another. Magnesium and calcium carbonates decompose only on strong heating. The other metal carbonates decompose on mild heating.

Activity 2.8 **Investigation of the effects of heat on metal carbonates**

Requirements: Two pyrex test tubes, heat source, spatula, test tube holder, carbonates of zinc and sodium.

Procedure

1. Put two spatulaful of zinc and sodium carbonates into separate test tubes.
2. Heat the samples and observe the colour changes of the residues when hot and after cooling. Observe the evolution of gases.

Questions

1. What was the colour of the residue when hot and after cooling?
2. Explain how you can identify the gases evolved in the above experiment.
3. Summarise each of the observations with a well-balanced equation.

2.3.5 Chemical properties of metal carbonates

Metal carbonates like other compounds have many chemical properties. This part discusses the reactions of acids on metal carbonates.

Reactions of dilute acids with metal carbonates

Metal carbonates react with dilute mineral acids to form carbon dioxide gas. For example, sodium and zinc carbonates react with dilute hydrochloric acid to form colourless chloride solutions, water and carbon dioxide gas.

$$Na_2CO_3(aq) + 2HCl(aq) \longrightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

$$ZnCO_3(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + CO_2(g) + H_2O(l)$$

The reaction of the acid with copper(II) carbonate produces carbon dioxide and a blue solution of copper(II) chloride.

$$CuCO_3(s) + 2HCl(aq) \longrightarrow CuCl_2(aq) + CO_2(g) + H_2O(l)$$

When lead carbonate reacts with dilute hydrochloric acid, effervescence is initially observed, but the reaction stops after a short while. This is due to the formation of lead chloride which is insoluble.

$$PbCO_3(s) + 2HCl(aq) \longrightarrow PbCl_2(s) + CO_2(g) + H_2O(l)$$

The lead chloride forms a coating on the lead carbonate, preventing further action on the carbonate.

Dilute sulphuric acid reacts with metal carbonates to give respective metal sulphates, carbon dioxide, and water. Lead carbonate and calcium carbonate react with dilute sulphuric acid to form insoluble lead sulphate and calcium sulphate, respectively.

$$PbCO_3(s) + H_2SO_4(aq) \longrightarrow PbSO_4(s) + CO_2(g) + H_2O(l)$$

$$CaCO_3(s) + H_2SO_4(aq) \longrightarrow CaSO_4(s) + CO_2(g) + H_2O(l)$$

The insoluble sulphate forms a coating on the carbonates, thus preventing further reaction between the carbonates and the acid.

Dilute nitric acid reacts with all the metal carbonates, including lead and calcium carbonates, to liberate carbon dioxide and soluble metal nitrates. Carbon dioxide forms a white precipitate with lime water. This is used as a confirmatory test for metal carbonates.

$$PbCO_3(aq) + 2HNO_3(aq) \longrightarrow Pb(NO_3)_2(aq) + CO_2(g) + H_2O(l)$$

$$CaCO_3(aq) + 2HNO_3(aq) \longrightarrow Ca(NO_3)_2(aq) + CO_2(g) + H_2O(l)$$

2.3.6 Chemical properties of hydrogen carbonates

The chemical properties discussed in this part include action of heat on hydrogen carbonates and their reactions with acids.

Action of heat on hydrogen carbonates

Hydrogen carbonates, whether in solution or in solid forms, decompose to give carbon dioxide and carbonate when heated. Sodium hydrogen carbonate and calcium hydrogen carbonate decompose to give sodium carbonate and calcium carbonate, respectively, plus carbon dioxide and water.

$$2NaHCO_3(aq) \xrightarrow{\text{heat}} Na_2CO_3(s) + CO_2(g) + H_2O(l)$$

$$Ca(HCO_3)_2(aq) \xrightarrow{\text{heat}} CaCO_3(s) + CO_2(g) + H_2O(l)$$

Reactions of acids with hydrogen carbonates

Hydrogen carbonates react with dilute acids to give salt, water, and carbon dioxide. For example, sodium hydrogen carbonate reacts with dilute sulphuric acid to give sodium sulphate, water, and carbon dioxide.

$$2NaHCO_3(s) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + 2CO_2(g) + 2H_2O(l)$$

When dilute hydrochloric acid is added to sodium hydrogen carbonate, some effervescence is observed. This is due to the production of carbon dioxide which forms white precipitates with the lime water. A colourless solution of sodium chloride is also formed.

$$NaHCO_3(s) + HCl(aq) \longrightarrow NaCl(aq) + CO_2(g) + H_2O(l)$$

Calcium hydrogen carbonate reacts with dilute hydrochloric acid in the same way.

$$Ca(HCO_3)_2(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + 2CO_2(g) + 2H_2O(l)$$

The hydrogen carbonate of magnesium also reacts with hydrochloric acid in a similar way to give metal chlorides, carbon dioxide and water.

$$Mg(HCO_3)_2(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + 2CO_2(g) + 2H_2O(l)$$

Test for soluble carbonates and hydrogen carbonates

Soluble carbonates form white precipitates with magnesium sulphate solution while the hydrogen carbonates do not. This test is used to distinguish soluble carbonates from hydrogen carbonates. For example, sodium carbonate and sodium hydrogen carbonate can be distinguished using this test.

Sodium carbonate reacts with magnesium sulphate to form an insoluble salt of magnesium carbonate and sodium sulphate.

$$Na_2CO_3(aq) + MgSO_4(aq) \longrightarrow \underbrace{MgCO_3(s)}_{\text{White precipitates}} + Na_2SO_4(aq)$$

Sodium hydrogen carbonate reacts with magnesium sulphate to form soluble magnesium hydrogen carbonate and sodium sulphate.

$$2NaHCO_3(aq) + MgSO_4(aq) \longrightarrow Mg(HCO_3)_2(aq) + Na_2SO_4(aq)$$

2.3.7 Uses of metal carbonates

Metal carbonates are salts which have broad uses in the industrial, agricultural and health fields. The manipulations of carbonates into various chemical compounds in industry have impacts and values to our daily life. The following section describes the uses of metal carbonates.

Production of building and construction materials

Carbonates are used in the production of glasses. For example, when a mixture of calcium carbonate, sodium carbonate, and sand (SiO_2) is strongly heated at a temperature between 1300 and 1400 °C, it produces a clear melt. When this melt is cooled down, it hardens to form glass. Carbon dioxide gas is given off during this process leaving a mixture of sodium silicate and calcium silicate.

$$CaCO_3(s) + SiO_2(s) \xrightarrow{\text{heat}} \underbrace{CaSiO_3(s)}_{\text{Calcium silicate}} + CO_2(g)$$

$$Na_2CO_3(s) + SiO_2(s) \xrightarrow{\text{heat}} \underbrace{Na_2SiO_3(s)}_{\text{Sodium silicate}} + CO_2(g)$$

The carbonate which is extensively used in the construction industry is limestone ($CaCO_3$). When limestone powder is roasted with clay soil and then the product ground into very fine powder, forms cement. Marble is used on the walls of houses and other buildings to make them look attractive. It is also used in bonding bricks, concrete blocks, and stones, roofing shingles, rubber compounds and tiles. Due to their high refractive properties, metal carbonates such as zinc and magnesium carbonates are used as fire proofing materials for rubber, components of fire extinguishers, and plastic materials and in the equipment such as porcelains and pottery which are exposed to high temperature.

Manufacturing of pigment, colourants and paints

The mixture of copper carbonate and alkaline components is used to make paints and varnishes. Lead carbonate (white lead) has also been used as a pigment in colouring paint, plastic fabric materials. However, it has been phased out in many countries because of its high toxicity.

Medical industry

Magnesium carbonate and sodium hydrogen carbonate are used as anti-acids for treating heartburn and other disorders of the stomach and kidneys. Calcium and magnesium carbonates are used in making toothpaste. Calcites, which are crystals of calcium carbonate, are very valuable to a number of optical applications due to their double refraction property. The fine powdery form of calcium carbonate known as ground calcium carbonate (GCC) has many applications in pharmaceutical industries.

Metal carbonates such as zinc carbonate are used as additive pigments in cosmetics, lotions, fungicides, and antiseptic creams. The ferrous carbonate is a very essential dietary supplement for anaemic people. However, the salt is moderately toxic with lethal dosage ranging from 0.5 to 5 g/kg for a 70-kg weighed person. Ammonium bicarbonate is medically applied as a key component of the expectorant cough syrup. Carbonates are also used in the laboratories to prevent damage caused by strong acids. When applied on areas of potential acid leakage, the carbonate powder neutralises the acids.

Food industries

Hydrogen carbonates of sodium and ammonium are widely used to raise the flat baked foods such as breads and cakes. When the sodium hydrogen carbonate (baking soda) is mixed with dough and heated, the sodium hydrogen carbonate decomposes to give off carbon dioxide which makes the dough expand.

$$2NaHCO_3(s) \xrightarrow{\text{heat}} Na_2CO_3(s) + CO_2(g) + H_2O(l)$$

To improve the taste of the baked food, the baking soda is mixed with organic acids such as citric acid or tartaric acid. The use of ammonium bicarbonate as a baking agent has the advantage of producing more gas compared to the baking soda. It decomposes completely into water and the gaseous products that evaporate during baking leaving no any salty or soapy taste in the food products. However, ammonium bicarbonate cannot be used for moist, bulky baked foods, because some ammonia gas may be trapped inside the food and cause unpleasant taste.

Water purification

Temporary hard water contains large amounts of bicarbonate (HCO_3^-) ions of divalent cations, such as Ca^{2+}, Mg^{2+}, and Fe^{2+}. These cations combine with the anions of fatty acids in soap to produce an insoluble product called *scum* which deposits on clothes, sinks, washing machines, and utensils.

$$Ca^{2+}(aq) + \underset{\text{Soap}}{2C_{17}H_{35}COONa(aq)} \xrightarrow{\text{heat}} 2Na^{+}(aq) + \underset{\text{Scum}}{(C_{17}H_{35}COO)_2Ca(s)}$$

The hard water cations cause a deposition of insoluble carbonate within water pipes, boilers, and damage plumbing systems.

$$Ca^{2+}(aq) + 2HCO_3^-(aq) \xrightarrow{\text{heat}} CaCO_3(s) + CO_2(g) + H_2O(l)$$

The permanent hard water contains large amounts of sulphate and chloride ions of Ca^{2+}, Mg^{2+}, and Fe^{2+}. Both permanent and temporary hardness of water can be removed by addition of washing soda. The addition of washing soda in hard water precipitates the carbonates of bivalent cations (Ca^{2+}, Mg^{2+} or Fe^{2+}) which can further be filtered off easily.

$$CaSO_4(aq) + Na_2CO_3(aq) \longrightarrow CaCO_3(s) + Na_2SO_4(aq)$$

Agricultural uses of metal carbonates

Copper carbonate is used as fertiliser and in a variety of animal feeds. It also plays a big role in the manufacturing of pesticides, fungicides, and weed killers.

Calcium carbonate when spread on farms with acidic soil neutralises the acidity and supplies calcium into the soil for better plant growth. Calcium carbonate is a source of lime, which is also used as fertiliser.

The ammonium carbonate, a non-metal carbonate, is commonly used as an inexpensive nitrogen fertiliser. But its application is now being phased out in favour of urea for stability and quality.

Exercise 2.3

1. Explain how sodium carbonate can be prepared in the laboratory.
2. Use chemical equations to show the reaction between:
   (a) Potassium hydrogen carbonate and zinc chloride
   (b) Sodium hydrogen carbonate and lead(II) nitrate
   (c) Sodium hydrogen carbonate and copper(II) sulphate
3. Use chemical equations to show the effects of heat on the carbonates of sodium, magnesium, and zinc.
4. Explain using an equation, what happens when dilute hydrochloric acid is added to powdered lead carbonate in a beaker.
5. Describe how you can distinguish a hydrogen carbonate from a soluble carbonate.
6. Explain five uses of metal carbonates.
7. Dilute nitric acid is added to a green solid **P.** A blue solution **Q** is formed and a gas **R** that forms a white precipitate with lime water is formed. The blue solution is evaporated to dryness and then strongly heated in a crucible. A black solid **S**, brown fumes of gas **T** and a gas that relights a glowing splint are formed.
   (a) Identify the:
      (i) solids **P** and **S** (ii) gases **R** and **T**
   (b) Write an equation for the;
      (i) reaction between solid **P** and dilute nitric acid.
      (ii) formation of solid **S.**
8. Baking powder contains sodium hydrogen carbonate mixed with an acid. When water is added, the baking powder releases carbon dioxide.
   (a) How could you test the gas to show that it is carbon dioxide?
   (b) Write a balanced chemical equation for the reaction of sodium hydrogen carbonate with sulphuric acid.

2.4 Metal sulphates

A sulphate ion is a polyatomic anion with the empirical formula SO_4^{2-}. Metal sulphates are salts of sulphuric acid and many are prepared from that acid. Sulphates occur widely in everyday life. The metal sulphates can be classified into soluble and insoluble sulphates. Most metal sulphates are soluble in water.

The sulphates that are insoluble in water are lead sulphate ($PbSO_4$), barium sulphate ($BaSO_4$), silver sulphate (Ag_2SO_4), and strontium sulphate ($SrSO_4$). Calcium sulphate ($CaSO_4$) is sparingly soluble in water. All the remaining metal sulphates dissolve in water. In this section, you will learn about the preparations, properties, effects on heating, and uses of metal sulphates.

2.4.1 Preparation of metal sulphates

The methods used to prepare metal sulphates depend on whether the sulphate is soluble or insoluble in water.

Preparation of soluble sulphates

Soluble sulphates can be prepared by reacting a metal, a metal carbonate, a metal hydroxide or a metal oxide with dilute sulphuric acid.

Reaction of sulphuric acid with metal

Dilute sulphuric acid reacts with granulated zinc to give a colourless solution of zinc sulphate and hydrogen gas. White crystals of zinc sulphate are formed when the solution is heated to saturation and then cooled. The granulated zinc contains impurities which act as catalysts. The impurities make the gas produced to have a chocking smell. With pure zinc, the reaction would be very slow.

$$Zn(s) + H_2SO_4(aq) \longrightarrow ZnSO_4(aq) + H_2(g)$$

Other metal sulphates such as magnesium, copper, and iron(III) sulphates can also be prepared using this method. This type of reaction in which metals react with sulphuric acid to form metal salt and hydrogen gas is called a *displacement reaction*.

Reaction of sulphuric acid with metal carbonates

Zinc carbonate reacts with dilute sulphuric acid to give a colourless solution of zinc sulphate, water, and carbon dioxide gas.

$$ZnCO_3(s) + H_2SO_4(aq) \longrightarrow ZnSO_4(aq) + CO_2(g) + H_2O(l)$$

The sulphates of magnesium, copper, calcium, and iron(III) can also be prepared by using this method.

Activity 2.9 Preparation of sulphates from metal carbonates

Requirements: Bunsen burner, beaker, tripod stand, wire gauze, glass rod, measuring cylinder, evaporating dish, filter funnel, filter paper, zinc carbonate powder, and 2 M sulphuric acid.

Procedure

1. Put 20 mL of 2 M sulphuric acid in a beaker.
2. Add some zinc carbonate little by little until the reaction stops with the excess zinc carbonate in the reaction mixture.
3. Filter the solution into the evaporating dish.
4. Heat the solution to saturation and then leave it to cool, crystallise and dry.

Question

Using balanced chemical equations, give an account for the observations made during the experiment.

Reactions of sulphuric acid with metal hydroxides

Zinc hydroxide reacts with dilute sulphuric acid in a neutralisation reaction to form zinc sulphate and water.

$$Zn(OH)_2(s) + H_2SO_4(aq) \longrightarrow ZnSO_4(aq) + 2H_2O(l)$$

Zinc sulphate solution is colourless but forms white crystals of zinc sulphate when heated to saturation and then cooled. Other sulphates that can be prepared using the same method include copper sulphate, magnesium sulphate, sodium sulphate, and aluminium sulphate.

Reactions of sulphuric acid with metal oxides

A metal oxide, such as copper(II) oxide reacts with dilute sulphuric acid to form a blue solution of copper(II) sulphate.

$$CuO(s) + H_2SO_4(aq) \longrightarrow CuSO_4(aq) + H_2O(l)$$

This reaction in which copper(II) oxide reacts with dilute sulphuric acid is called a *neutralisation reaction*. Copper oxide acts as a base, therefore the products formed are salt and water just like in the normal acid base reactions. The blue solution of copper sulphate forms blue crystals when heated to saturation and then cooled.

Preparation of insoluble sulphates

Insoluble metal sulphates are best prepared by the precipitation method. That is, the corresponding salts of metals that are soluble in water such as nitrates and chlorides are reacted with dilute sulphuric acid to form metal sulphate precipitates.

$$BaCl_2(aq) + H_2SO_4(aq) \longrightarrow BaSO_4(s) + 2HCl(aq)$$

$$Ba(NO_3)_2(aq) + H_2SO_4(aq) \longrightarrow BaSO_4(s) + 2HNO_3(aq)$$

$$Pb(NO_3)_2(aq) + H_2SO_4(aq) \longrightarrow PbSO_4(s) + 2HNO_3(aq)$$

2.4.2 Chemical properties of metal sulphates

Effects of heat on metal sulphates

Sulphates are generally stable on heating than the corresponding nitrates. They only decompose under very strong heating. Even sulphates of the least reactive metals in the reactivity series must be strongly heated to decompose. The sulphates of alkali metals and those of alkaline earth metals do not decompose on heating. When the crystals of hydrated copper(II) sulphate are heated, the colour changes from blue to white due to the formation of anhydrous copper(II) sulphate.

$$\underset{\text{Blue}}{CuSO_4{\cdot}5H_2O(s)} \xrightarrow{\text{heat}} \underset{\text{White}}{CuSO_4(s)} + 5H_2O(g)$$

On further strong heating, the anhydrous copper(II) sulphate decomposes to copper(II) oxide and sulphur trioxide gas.

$$CuSO_4(s) \xrightarrow{\text{heat}} CuO(s) + SO_3(g)$$

The sulphur trioxide gas, which is liberated, turns a wet blue litmus paper red (acidic gas). Zinc sulphate ($ZnSO_4$) also decomposes in the same way on strong heating.

$$ZnSO_4(s) \xrightarrow{\text{heat}} ZnO(s) + SO_3(g)$$

Similarly, when hydrated iron(II) sulphate is gently heated, it gives up its water of crystallisation and forms anhydrous iron(II) sulphate.

$$\underset{\text{Light green}}{FeSO_4{\cdot}7H_2O(s)} \xrightarrow{\text{heat}} \underset{\text{White}}{FeSO_4(s)} + 7H_2O(g)$$

The colour of iron(II) sulphate changes from light green to white. On strong heating, the anhydrous iron(II) sulphate decomposes to form a reddish brown iron(III) oxide, sulphur trioxide, and sulphur dioxide. The reddish brown colour indicates that iron(III) oxide (and not iron(II) oxide) is formed. This means that the decomposition of iron(II) sulphate is accompanied with oxidation of Fe^{2+} to Fe^{3+}.

$$\underset{\text{White}}{2FeSO_4(s)} \xrightarrow{\text{heat}} \underset{\text{Reddish brown}}{Fe_2O_3(s)} + SO_2(g) + SO_3(g)$$

Also, strong heating of anhydrous iron(III) sulphate forms a reddish brown iron(III) oxide and sulphur trioxide.

$$Fe_2(SO_4)_3(s) \xrightarrow{\text{heat}} Fe_2O_3(s) + 3SO_3(g)$$

The sulphur trioxide turns a wet blue litmus paper red.

Hydrated sodium sulphate is stable to heat such that when heated it loses just the water of crystallisation and forms anhydrous sodium sulphate.

$$Na_2SO_4{\cdot}10H_2O(s) \xrightarrow{\text{heat}} Na_2SO_4(s) + 10H_2O(l)$$

Reactions of sulphates with barium chloride or lead chloride

All metal sulphates form white precipitates when reacted with aqueous solutions of barium chloride or lead chloride or any other aqueous solution of barium or lead.

$$BaCl_2(aq) + Na_2SO_4(aq) \xrightarrow{\text{heat}} BaSO_4(s) + 2NaCl(aq)$$

$$Pb(NO_3)_2(aq) + Na_2SO_4(aq) \xrightarrow{\text{heat}} PbSO_4(s) + 2NaNO_3(aq)$$

The white precipitates are formed because $BaSO_4$ and $PbSO_4$ are insoluble in water.

Activity 2.10 **Investigation of the effects of heat on metal sulphates**

Requirements: $CuSO_4{\cdot}5H_2O$ crystals, iron(II) sulphate ($FeSO_4{\cdot}7H_2O$), test tubes, heat source, litmus paper, filter paper, potassium dichromate, and barium chloride solution.

Procedure

1. Put one spatulaful of the hydrated $CuSO_4{\cdot}5H_2O$ crystals into a test tube and heat the salt gently at first and then strongly.

2. Observe any gas produced and test it with a wet litmus paper and potassium dichromate solution.
3. Observe the colour change for the residue.
4. Prepare separate solutions of the given sulphates in respective test tubes and to each solution add 2 to 3 drops of barium chloride followed by hydrochloric acid. Shake well and record the observations.

Questions

1. Summarise the observations in each of the tests and provide the names of the gases and residues formed.
2. Write ionic equations for the reactions of the sulphates with barium chloride solution.

Chemical test for sulphates

The barium ions (Ba^{2+}) and lead ions (Pb^{2+}) are used to test for the presence of sulphate ions in a solution where white precipitates are formed (insoluble sulphates). For example, if hydrochloric acid is added to a test solution which contains sulphate, no effervescence is observed and no precipitates are formed, this shows that the solution does not contain a carbonate, but it is not sufficient to conclude that the solution is sulphate. However, if on adding barium chloride to the solution a precipitate is formed, then the tested solution is a sulphate.

2.4.3 Uses of metal sulphates

Sulphates have wide applications in industries as well as in agricultural fields. In industries, they are used to produce various chemicals which are useful to human beings and domestic animals. The following section describes some uses of metal sulphates.

Production of building materials

Hydrated calcium sulphate also known as *gypsum* ($CaSO_4{\cdot}2H_2O$) is a very essential raw material in the manufacturing of cement, moulds, wall plasters, wallboards and other art works. Together with sulphates such as iron(II) sulphate, barium sulphate and copper sulphate, calcium sulphates are used as pigments in making different paints, colouring glass, cement, ceramic wares and plasters. The sulphates of zinc and copper are used in the preservation of timber and in the preparation of other wood preservatives such as oil based copper naphthenates and water based copper arsenic which prevent wood worms and wood rots.

Production of dyes and leather tannings

Hydrated zinc sulphate ($ZnSO_4 \cdot 7H_2O$), aluminium sulphate ($Al_2(SO_4)_3$), iron(II) sulphate ($FeSO_4$), and alums such as potash alum ($K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 2H_2O$) (colourless) and iron(III) alum $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 2H_2O$ (purple) are used as mordant in the dyeing industry. A mordant is an inorganic substance that combines with a dye or stain and thereby fixes it in the material. These sulphates are also used as reagents in tanning processes in leather industries.

Manufacturing of other chemicals

Metal sulphates can be used in the preparation of other chemical substances in large or small scale production. For instance, copper(II) sulphate is used in the preparation of cuprous chloride which is used in the purification of organic compounds, a catalyst used in chlorinating rubber latex and in the preparation of ethanol.

Paper manufacturing

In paper industry, aluminium sulphate is used to size the paper during paper making process. It reduces the tendency of a paper to absorb moisture. The prepared wood pulp for making paper is treated with copper sulphate to prevent it from wood rot. The salt is also impregnated in fruit wrapping papers to prevent them from storage rot.

Pharmaceutical industry

Plaster of Paris, which is the form of calcium sulphate, is used in medical centres to make plaster casts that are used for repairing broken limbs. Iron(II) sulphate ($FeSO_4$) is commonly used to make tablets that supplement iron deficiency in human bodies while the hydrated sodium sulphate ($Na_2SO_4 \cdot 10H_2O$), known as *Glauber's salt* and magnesium sulphate ($MgSO_4 \cdot 7H_2O$) known as *Epsom salt* are used as medicines or agents for relieving constipation in patients. Zinc sulphate and its hydrated salt known as *white vitriol* ($ZnSO_4 \cdot 7H_2O$) are used for the preparation of eye lotions, deodorants, cosmetics, mouth washes and in the treatment of skin diseases and wounds.

Water treatments

Water for human consumption needs to be free from any contaminations. Sulphates such as iron(II) sulphate, aluminium sulphate, and zinc sulphate are important chemicals in the water and sewage treatments. When water is treated with these chemical substances, they precipitate the colloidal matters and kill microorganisms.

Agricultural uses of metal sulphates

Metal sulphates have wide applications in improving the health of crops and domestic animals. Aluminium sulphate ($Al_2(SO_4)_3$) and non-metallic sulphate, ammonium sulphate ($(NH_4)_2SO_4$) are used as fertilisers. Sulphates are used to control fungal diseases which interfere with crop production. For instance, copper(II) sulphate is used in making Bordeaux and Burgundy mixtures which are sprayed on potatoes and vines farms to control fungal diseases. Other sulphates which are used as fungicides include iron(II) sulphate, hydrated copper sulphate ($CuSO_4 \cdot 5H_2O$). Copper sulphate and iron(II) sulphates are used in making insecticides and weed killers (herbicides). The mixing of sulphates with animal feeds stimulates growth in animals. For example, copper(II) sulphate is used as a growth stimulant in pigs and broiler chickens. Copper(II) sulphate is used as molluscicide for the destruction of slugs and snails, particularly the one which is a host of liver flukes.

Exercise 2.4

1. (a) List four methods that can be used to prepare soluble metal sulphates in the laboratory.
   (b) Give one example of a metal sulphate that can be prepared using each of the methods you have listed above.
2. Describe the preparation of barium sulphate in the laboratory, starting with barium nitrate and sulphuric acid.
3. When metal sulphates are heated, they decompose to form metal oxides and sulphur trioxides. Explain with reasons, which of the sulphates of group IIA is expected to be the least stable (easily decomposed) and which is expected to be the most stable.
4. Using balanced equations, describe the following reactions:
   (a) Hydrolysis of an aqueous solution of aluminium sulphate. Explain whether the resulting solution is neutral, acidic, or basic.
   (b) Thermal decomposition of an aqueous solution of aluminium sulphate.
5. Describe using chemical equation(s), a chemical test that can be used to identify sulphates in solution.
6. Describe with balanced equation(s) what would be observed when a piece of magnesium ribbon is dropped into a test tube containing copper sulphate solution.

7. Anhydrous copper(II) sulphate can be turned into hydrated copper sulphate. What would you need to add? Apart from the change in colour, what could you observe?
8. Explain five uses of the metal sulphates.

2.5 Metal chlorides

Metal chlorides are compounds formed between metals and chloride ions or atoms. Chlorides are generally among the most important and common compounds. In this section, you will learn about the preparations, properties, special characteristics of iron(III) chloride and aluminium chloride and the uses of the chlorides.

2.5.1 Preparation of metal chlorides

Metal chlorides can be prepared by direct or indirect methods.

Direct method

When metals are heated directly in chlorine gas, chlorides are produced. This is the direct method of preparing metal chlorides. For example, when iron is heated in chlorine gas, a reddish brown solid of iron(III) chloride is formed.

$$2Fe(s) + 3Cl_2(g) \xrightarrow{\text{heat}} \underset{\text{Reddish brown}}{2FeCl_3(s)}$$

The iron(III) chloride sublimes on heating and is collected in the conical flask. During the preparation, iron(II) chloride is formed first.

$$3Fe(s) + 3Cl_2(g) \xrightarrow{\text{heat}} 3FeCl_2(s)$$

Chlorine being a strong oxidising agent, oxidises iron(II) chloride to iron(III) chloride.

$$2FeCl_2(s) + Cl_2(g) \longrightarrow \underset{\text{Reddish brown}}{2FeCl_3(s)}$$

Iron(III) chloride is a deliquescent substance which on exposure to air, it absorbs water vapour to form a solution. The chlorides of other metals such as zinc and aluminium can also be prepared by this method.

$$Zn(s) + Cl_2(g) \longrightarrow ZnCl_2(s)$$

$$2Al(s) + 3Cl_2(g) \longrightarrow 2AlCl_3(s)$$

Indirect methods

Precipitation reactions

Insoluble metal chlorides are prepared by indirect methods through the precipitation processes. For example, silver and lead chlorides are insoluble in water. The two chlorides are prepared using the precipitation methods. Silver nitrate solution precipitates silver chloride when it reacts with dilute hydrochloric acid.

$$AgNO_3(aq) + HCl(aq) \longrightarrow AgCl(s) + HNO_3(aq)$$

In the same way, lead chloride is precipitated out when dilute hydrochloric acid reacts with lead nitrate.

$$Pb(NO_3)_2(aq) + 2HCl(aq) \longrightarrow PbCl_2(s) + 2HNO_3(aq)$$

Silver chloride and lead chloride are white solids when exposed to light. Silver chloride changes colour from white to purple because of the conversion of silver chloride to silver and chlorine which takes place in the presence of light.

$$2AgCl(s) \xrightarrow{\text{light}} 2Ag(s) + Cl_2(g)$$

Reactions of alkalis with dilute hydrochloric acid

Sodium hydroxide reacts with dilute hydrochloric acid in a neutralisation reaction to form sodium chloride and water. Calcium hydroxide and potassium hydroxide also react with dilute hydrochloric acid to give respective chlorides and water.

$$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

$$Ca(OH)_2(aq) + 2HCl(aq) \longrightarrow CaCl_2(aq) + 2H_2O(l)$$

The sodium chloride, calcium chloride, and potassium chloride are soluble in water.

Reactions of metal oxides with hydrochloric acid

The reaction between metal oxide and dilute hydrochloric acid is also a neutralisation reaction. For example, zinc oxide reacts with hydrochloric acid to give a colourless solution of zinc chloride.

$$ZnO(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2O(l)$$

White crystals of zinc chloride are formed when the solution is boiled to saturation and cooled.

Iron(III) oxide, which is reddish brown in colour, reacts with dilute hydrochloric acid to give a reddish brown solution of iron(III) chloride.

$$Fe_2O_3(s) + 6HCl(aq) \longrightarrow 2FeCl_3(aq) + 3H_2O(l)$$

Copper(II) oxide reacts with dilute hydrochloric acid to form a green solution of copper(II) chloride.

$$CuO(s) + 2HCl(aq) \longrightarrow CuCl_2(aq) + H_2O(l)$$

Calcium oxide reacts with dilute hydrochloric acid to form a colourless solution of calcium chloride.

$$CaO(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l)$$

2.5.2 Chemical properties of metal chlorides

The chemical properties of metal chlorides include reactions with water, acid/base characters, action of heat, and chemical test.

Reactions of metal chlorides with water

Sodium chloride and magnesium chloride have no chemical reaction with water. When these salts are dissolved in water they form aqueous solutions in which ions are hydrated by water molecules.

$$NaCl(s) + H_2O(l) \longrightarrow NaCl(aq)$$

$$MgCl_2(s) + H_2O(l) \longrightarrow MgCl_2(aq)$$

Other chlorides react with water in different ways and the reaction is known as *hydrolysis*. Aluminium chloride reacts with water by first forming hexaaquaaluminium ions.

$$AlCl_3(s) + 6H_2O(l) \longrightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$$

Further reaction with water forms hydroxonium ions which make the solution acidic.

$$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq)$$

Zinc chloride reacts with water to form zinc hydroxychloride and hydrogen chloride.

$$ZnCl_2(s) + H_2O(l) \longrightarrow ZnOHCl(aq) + HCl(aq)$$

Copper chloride reacts with water to form dichlorodiaquacopper(II).

$$CuCl_2(s) + 2H_2O(l) \longrightarrow [Cu(H_2O)_2Cl_2](aq)$$

Acid/base characters of chlorides

Sodium chloride and magnesium chloride are neutral; have neither acidic nor basic characters. Magnesium chloride in hydrated form is weakly acidic. Other chlorides of period 3 elements are acidic.

Action of heat on metal chlorides

Most metal chlorides do not decompose on heating. However, hydrated chlorides undergo hydrolysis when heated strongly. For example, when hydrated magnesium chloride is heated gently, it is partially hydrolysed to form a basic salt, hydrogen chloride and water vapour.

$$MgCl_2{\cdot}7H_2O(s) \xrightarrow{\text{heat}} Mg(OH)Cl(s) + HCl(g) + 6H_2O(g)$$

When strongly heated, the basic salt formed decomposes to form magnesium oxide and hydrogen chloride gas.

$$Mg(OH)Cl(s) \xrightarrow{\text{heat}} MgO(s) + HCl(g)$$

When hydrated crystals of aluminium chloride are heated, they are hydrolysed to form an oxide.

$$2AlCl_3{\cdot}6H_2O(s) \xrightarrow{\text{heat}} Al_2O_3(s) + 6HCl(g) + 9H_2O(g)$$

When an anhydrous aluminium chloride salt is heated, it sublimes to form a dimeric molecule.

$$2AlCl_3(s) \xrightarrow{\text{heat}} Al_2Cl_6(g)$$

When hydrated copper(II) chloride ($CuCl_2{\cdot}2H_2O$) is heated to 150 °C in a stream of dry hydrogen chloride, the anhydrous brownish yellow copper(II) chloride is formed.

$$CuCl_2{\cdot}2H_2O(s) \longrightarrow \underset{\substack{\text{Anhydrous}\\ \text{brownish yellow}}}{CuCl_2(s)} + 2H_2O(g)$$

Anhydrous iron(III) chloride is dark red covalent solid that exists as a dimer in gaseous state. On heating, the molecule dissociates to $FeCl_3$ and on further heating forms iron(II) chloride and chlorine gas.

$$Fe_2Cl_6(g) \xrightleftharpoons{\text{heat}} 2FeCl_2(g) + Cl_2(g)$$

$$Fe_2Cl_6(g) \xrightleftharpoons{\text{heat}} 2FeCl_3(g)$$

On heating, hydrated zinc chloride forms anhydrous zinc chloride and water.

$$\mathrm{ZnCl_2{\cdot}2H_2O}(s) \xrightarrow{\text{heat}} \mathrm{ZnCl_2}(s) + \mathrm{2H_2O}(g)$$

Chemical test for chloride ions

To test if a substance contains chloride ions, silver nitrate solution can be used. When a solution containing chloride ions is added to a silver nitrate solution, white precipitates of silver chloride (AgCl) are formed.

$$\mathrm{AgNO_3}(aq) + \mathrm{Cl^-}(aq) \longrightarrow \underset{\substack{\text{White}\\ \text{precipitates}}}{\mathrm{AgCl}(s)} + \mathrm{NO_3^-}(aq)$$

2.5.3 Special characteristics of iron(III) chloride and aluminium(III) chloride

Chlorides of iron(III) and aluminium(III) exhibit peculiar properties which differentiate them from chlorides of other elements as explained below.

(a) They are typical covalent compounds as shown by their volatility, poor electrical conductivity in their molten states and their solubility in organic solvents. Iron(III) chloride has a narrow liquid range when anhydrous; it can exist in liquid form at temperature ranging from only 303 °C to 313 °C. Similarly, aluminium chloride melts at 193 °C under a pressure of 2 atmospheres, but vaporises and sublimes at 183 °C under normal pressure. Pure anhydrous $\mathrm{FeCl_3}$ and $\mathrm{AlCl_3}$ are covalent compounds which in their molten states show poor conductivity of electricity. This is because they exist as molecules and not ions. The two salts are soluble in organic solvents. For example, iron(III) chloride dissolves in methanol, ethanol and acetone. Aluminium chloride dissolves in benzene and carbon disulphide.

(b) When pure, anhydrous iron(III) chloride boils at 315 °C giving vapour which consists of the dimer $\mathrm{Fe_2Cl_6}$. Further increase in temperature results into the dissociation of the dimer molecules into monomeric $\mathrm{FeCl_3}$; and at higher temperatures, the monomeric $\mathrm{FeCl_3}$ decomposes to give iron(II) chloride and chlorine gas as shown in the following equations:

$$\begin{tikzcd}
2\mathrm{FeCl_3}(s) \arrow[r, shift left, "315\ ^\circ\mathrm{C}"] & \mathrm{Fe_2Cl_6}(g) \arrow[l, shift left] \arrow[r, shift left, ">315\ ^\circ\mathrm{C}"] & 2\mathrm{FeCl_3}(s) \arrow[l, shift left] \arrow[d, shift left, "\text{strong heating}"] \\
 & & 2\mathrm{FeCl_2}(g) + \mathrm{Cl_2}(g) \arrow[u, shift left]
\end{tikzcd}$$

When heated to about 350 °C, aluminium chloride, like iron(III) chloride, gives vapour consisting of dimeric Al_2Cl_6 molecules. As in the case of iron(III) chloride, further heating produces monomeric $AlCl_3$ molecules.

$$2AlCl_3(s) \xrightarrow{350\,^{\circ}C} Al_2Cl_6(g) \xrightarrow{\text{strong heating}} 2AlCl_3(g)$$

(c) In aqueous solutions, both $FeCl_3$ and $AlCl_3$ salts hydrolyse to give acidic solutions as depicted by the following chemical equations:

(i) $FeCl_3(s) + 6H_2O(l) \longrightarrow [Fe(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

$[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq)$

(ii) $AlCl_3(s) + 6H_2O(l) \longrightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq)$

(d) Anhydrous iron(III) chloride and aluminium chloride exhibit catalytic properties. This is associated with the small size, high charge of their cations and vacant d^2sp^3 and sp^3 hybrid orbitals in Fe^{3+} and Al^{3+}, respectively.

Activity 2.11 Identification of chlorides of unknown solution

Requirements: Dropper, measuring cylinder, beaker, 2 M HNO_3, unknown chloride test solution and 0.05 M $AgNO_3$.

Procedure

1. Measure 5 mL of the test solution into a beaker.
2. Add 3 to 4 drops of 2 M HNO_3.
3. Add 3 drops of 0.05 M of acidified $AgNO_3$ and then add three more drops of HNO_3.
4. Record the observations.

Questions

1. Why did you add HNO_3 to the test solution?
2. Give the equations for the reactions.
3. What can you conclude from this experiment?

2.5.4 Uses of metal chlorides

Metal chlorides have many uses with a wide range of applications in the industrial and agricultural fields. The following are some of the uses of metal chlorides:

Production of building and construction materials

Hygroscopic and deliquescent chlorides, for example, calcium chloride, are used for dust control and road base stabilisation. Because of its hygroscopic and deliquescence properties, calcium chloride draws moisture from the air and resists its evaporation. Hence, when it is spread on haulage roads or mining centres, apart from minimising the dust levels, it also reduces the overall road maintenance costs. The use of calcium chloride in concrete mix accelerates hydration rate of cement, facilitating its early strength and protect freshly placed concrete in cold weather. Ready mixed concrete containing calcium chloride has significant economic benefits to the contractors by reducing operation costs. Chlorides can also be used in metal castings. For instance, sodium chloride is used as a corrosive flux ingredient in the welding and soldering processes. Zinc chloride and ammonium chloride are also used as flux in the soldering process.

Anti-freezing agent

Metal chlorides such as sodium chloride and calcium chloride are used as anti-freezing agents. Calcium chloride for example, is used as an anti-freezing agent in the storage and transportation of minerals that contain substantial amounts of moisture, such as coal. Sodium chloride is used as an anti-freezing agent in the de-icing processes and as a secondary coolant in the heat transferring machinery.

Drying agents

Chlorides are used in the industries to remove moistures from the manufactured products. In refineries and petrochemical industries for example, calcium chloride is used to remove the dissolved and free the water from hydrocarbons and liquefied petroleum gases (LPGs).

Water treatment

Chlorides of metals are very useful in the detection of the levels of faecal contamination in water bodies (rivers, lakes, ponds, and underground water). Calcium chloride effectively removes fluoride ions from effluents. This treatment can be done to the source of drinking water and make it safe for public consumption. Sodium hypochlorite is also used to disinfect water, removes harmful microorganisms and hence reducing the spread of diseases to the community. The hypochlorite is effective in lower concentrations and it is also inexpensive.

Pharmaceutical industry

Chlorides have broad uses in pharmaceutical industries. Sodium chloride for example, is used as a component in many cosmetics such as hair tonics, toilet soaps, body polishes, and cleaners. Ammonium chloride, a non-metal salt, is commonly used as an ingredient in many cough medications such as expectorants. It is also used as a dietary supplement to improve the blood pH levels of patients. A mixture of zinc chloride and zinc oxide is used as dental cement.

Food industry

Many chlorides are used as important ingredients in food products. Calcium chloride, for instance is used in increasing the size and strength of the curds in cheese. In beverages, calcium chloride is used to remove sodium alkalinity from water used in making soft drinks and beers. Calcium chloride is also used as a refrigerant in moulds used in making ice cream and frozen dessert products. Chloride salts such as sodium chloride (table salt) are commonly used in the preservation of food.

Agricultural uses of metal chlorides

Chlorides are used as fertilisers in supplementing the deficiency of important plant nutrients in the soil. Potassium chloride, known as *muriate of potash (MoP)* for example, is a natural, rich source of potassium ions in the soil. When the salt is directly used to the soil, it increases crop yields and quality, and increases the crop resistance against diseases. The post-harvest spray of calcium chloride in peas and grapes reduces brown core, cork spot, superficial scald and fruit rot. It also controls physiological disorders of plants.

The spray of calcium chloride can be done before the harvest, which also improves crop yields when applied on crop foliage, fruits and vegetables. Magnesium chloride fertilisers provide magnesium and chloride ions which are essential nutrients in the photo-chemical reactions in photosynthesis and in the maintenance of plant health. Excessive applications of chlorides in the soil as fertilisers may cause necrotic spots or bronzing on the plant leaves. Chloride ion deficiency in plants causes plant wilting.

Ammonium chloride and non-metal fertilisers are commonly used to supply nitrogen and chloride ions for better plant growth and prevent plant diseases. When supplemented in cattle and dairy sheep, magnesium chloride flakes prevent the animals from grass tetany. The grass tetany is magnesium deficiency in ruminants.

Exercise 2.5

1. Using balanced chemical equations, compare the hydrolysis of sodium chloride and calcium chloride.
2. Explain how you would distinguish iron(II) chloride from iron(III) chloride.
3. Write a balanced chemical equation for the reaction between iron(II) chloride and metallic sodium.
4. Arrange the following in the order of increasing ionic characters: KCl, $MgCl_2$, and $CaCl_2$. Explain your answer.
5. Describe using chemical equation(s), the chemical test that can be used to identify the presence of chlorides in a solution.
6. Iron(II) chloride in water forms a light green solution. When exposed in air and left to stand for some time, the colour changes to reddish brown solution. Explain what leads to the change of colour. Give the balanced equation.
7. Under certain conditions, iron reacts with chlorine to give anhydrous iron(III) chloride.
    (a) Why is excess chlorine used?
    (b) Why should moisture not be allowed into the apparatus during the reaction?
    (c) Explain why iron(II) chloride is not formed.
8. Explain any five uses of the metal chlorides.

2.6 Metal nitrates

Metal nitrates are polyatomic compounds formed between metal cations and a polyatomic ion with the molecular formula NO_3^-. They are simply the salts derived from nitric acid. All metal nitrates are soluble in water and cannot be prepared by precipitation. Nitric acid is the common reagent in the preparation of the metal nitrates. In this section, you will learn about preparations, properties, effects of heat on metal nitrates, and the uses of metal nitrates.

2.6.1 Preparation of metal nitrates

There are different methods of preparing metal nitrates, which include the direct methods that involve the reaction between a metal with nitric acid, and the indirect methods that involve the reactions between nitric acid with metal hydroxide, metal carbonate or metal oxide.

Reactions of metals with nitric acid

When metals react with nitric acid, they usually reduce hydrogen ions to hydrogen gas. The elemental metal is oxidised to metal cations in the process. However, the nitrate ions are easily reduced to nitrogen monoxide and nitrogen dioxide. Therefore, metals reacting with nitric acid tend to produce oxides of nitrogen rather than metal nitrate and hydrogen gas, except for magnesium and calcium when the acid is very dilute. For some metals, the reaction with dilute nitric acid relatively produces nitrogen monoxide, although this immediately reacts with atmospheric oxygen, forming nitrogen dioxide. If concentrated nitric acid is used, nitrogen dioxide is formed directly. This experiment should be carried out in a fume cupboard.

$$Mg(s) + 2HNO_3(aq) \longrightarrow Mg(NO_3)_2(aq) + H_2(g)$$

Similar reaction is observed when calcium metal is dissolved in dilute nitric acid.

$$Ca(s) + 2HNO_3(aq) \longrightarrow Ca(NO_3)_2(aq) + H_2(g)$$

Also sodium nitrate can be prepared from dilute nitric acid.

$$11Na(s) + 14HNO_3(aq) \longrightarrow 11NaNO_3(aq) + NO(g) + N_2O(g) + 7H_2O(g)$$

When a metal reacts with concentrated nitric acid, it gives a nitrate of the metal among other products, as well as nitrogen dioxide as the main gas is given off. The nitrogen dioxide gas is brown in colour. Magnesium reacts with concentrated nitric acid to form a solution of magnesium nitrate and nitrogen(IV) oxide gas.

$$Mg(s) + 4HNO_3(aq) \longrightarrow Mg(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

When the solution evaporates followed by cooling, white crystals of magnesium nitrate are formed. Zinc does not form nitrogen dioxide with concentrated nitric acid. Instead, ammonium nitrate is formed.

$$4Zn(s) + 10HNO_3(aq) \longrightarrow 4Zn(NO_3)_2(aq) + NH_4NO_3(aq) + 3H_2O(l)$$

When the solution is evaporated to saturation and cooled, white crystals of zinc nitrate are formed. Copper reacts with concentrated nitric acid to give a blue solution of copper nitrate and brown fumes of nitrogen(IV) oxide.

$$Cu(s) + 4HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

When moderately concentrated nitric acid is used, nitrogen monoxide gas (NO) is formed instead of nitrogen(IV) oxide.

$$3Cu(s) + 8HNO_3(l) \longrightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$$

The solution should not be evaporated to dryness because nitrates will undergo thermal decomposition. The reaction of nitric acid with aluminium and iron stops soon after starting due to the formation of oxide layers on the metals' surfaces. The oxide layers prevent further reactions between the acid and the metals.

Reactions of dilute nitric acid with metal hydroxides

Dilute nitric acid reacts with metal hydroxides in a neutralisation reaction to give salt and water. For example, dilute nitric acid reacts with sodium hydroxide to form sodium nitrate and water.

$$NaOH(aq) + HNO_3(aq) \longrightarrow NaNO_3(aq) + H_2O(l)$$

When the solution of sodium nitrate is heated to saturation then cooled, white crystals of sodium nitrate are formed. Similar reactions occur with other metal hydroxides such as $Ca(OH)_2$, $Al(OH)_3$, and $Cu(OH)_2$.

$$Ca(OH)_2(aq) + 2HNO_3(aq) \longrightarrow Ca(NO_3)_2(aq) + 2H_2O(l)$$

$$Al(OH)_3(s) + 3HNO_3(aq) \longrightarrow Al(NO_3)_3(aq) + 3H_2O(l)$$

$$Cu(OH)_2(s) + 2HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2H_2O(l)$$

Reactions of dilute nitric acid with metal carbonates

Dilute nitric acid reacts with metal carbonates to form metal nitrates, carbon dioxide, and water. For example, dilute nitric acid reacts with copper carbonate to form a blue solution of copper nitrate.

$$CuCO_3(s) + 2HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + CO_2(g) + H_2O(l)$$

When the solution of copper nitrate is heated to saturation and cooled, blue crystals of copper nitrate are formed. For sodium carbonate, the reaction with dilute nitric acid forms a colourless solution of sodium nitrate.

$$Na_2CO_3(s) + 2HNO_3(aq) \longrightarrow 2NaNO_3(aq) + CO_2(g) + H_2O(l)$$

When the solution is heated to saturation and cooled, white crystals of sodium nitrate are formed.

Reactions of dilute nitric acid with metal oxides

The reactions between dilute nitric acid and metal oxides are neutralisation reactions in which salt and water are formed. For example, zinc oxide forms a colourless solution of zinc nitrate when is reacted with dilute nitric acid.

$$ZnO(s) + 2HNO_3(aq) \longrightarrow Zn(NO_3)_2(aq) + H_2O(l)$$

When zinc nitrate solution is heated to saturation and cooled, white crystals of zinc nitrate are formed.

$$Zn(NO_3)_2(aq) + H_2O(l) \xrightarrow{\text{heat}} \underset{\text{White crystals}}{Zn(NO_3)_2(s)} + H_2O(g)$$

Copper(II) oxide reacts with dilute nitric acid to form a blue solution of copper nitrate.

$$CuO(s) + 2HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + H_2O(l)$$

The heating of the copper nitrate solution to saturation followed by cooling, forms blue crystals.

$$Cu(NO_3)_2(aq) + H_2O(l) \xrightarrow{\text{heat}} \underset{\text{Blue crystals}}{Cu(NO_3)_2(s)} + H_2O(g)$$

Calcium oxide forms a colourless solution of calcium nitrate.

$$CaO(s) + 2HNO_3(aq) \longrightarrow Ca(NO_3)_2(aq) + H_2O(l)$$

The solution forms white crystals when heated to saturation and cooled.

$$Ca(NO_3)_2(aq) + H_2O(l) \xrightarrow{\text{heat}} \underset{\text{White crystals}}{Ca(NO_3)_2(s)} + H_2O(g)$$

Magnesium oxide forms a colourless solution of magnesium nitrate when reacted with dilute nitric acid.

$$MgO(s) + 2HNO_3(aq) \longrightarrow Mg(NO_3)_2(aq) + H_2O(l)$$

Being hygroscopic, the magnesium nitrate absorbs water and quickly forms the crystals of magnesium nitrate hexahydrate.

$$Mg(NO_3)_2(s) + 6H_2O(l) \longrightarrow Mg(NO_3)_2 \cdot 6H_2O(s)$$

2.6.2 Chemical properties of metal nitrates

The chemical properties of metal nitrates are discussed in this section.

Effects of heat on nitrates

Metal nitrates decompose when heated; however, the nitrates of the most reactive metals such as potassium and sodium melt first to form colourless liquids. On strong heating, they slowly decompose to give nitrites and oxygen gas.

Example:

$$2NaNO_3(s) \xrightarrow{\text{heat}} 2NaNO_2(s) + O_2(g)$$

When hydrated copper nitrate is heated, it first releases its water of crystallisation and then it dissolves in the water to form a blue solution. On further heating, the water evaporates.

$$2Cu(NO_3)_2{\cdot}xH_2O(s) \xrightarrow{\text{heat}} 2Cu(NO_3)_2(s) + (2x)H_2O(g)$$

When most of it has evaporated, decomposition starts. The nitrate decomposes to form copper(II) oxide, a reddish brown gas (nitrogen dioxide) and oxygen gas.

$$2Cu(NO_3)_2(s) \xrightarrow{\text{heat}} 2CuO(s) + 4NO_2(g) + O_2(g)$$

Lead nitrate decomposes with a characteristic cracking sound to form lead(II) oxide, nitrogen dioxide gas and oxygen gas.

$$2Pb(NO_3)_2(s) \xrightarrow{\text{heat}} 2PbO(s) + 4NO_2(g) + O_2(g)$$

The cracking sound is produced as a result of the air inside the crystals expanding and breaking the crystals.

Nitrates of zinc, magnesium, and iron decompose to form metal oxides, nitrogen dioxide, and oxygen.

$$2Zn(NO_3)_2(s) \xrightarrow{\text{heat}} 2ZnO(s) + 4NO_2(g) + O_2(g)$$

Magnesium nitrate and iron(III) nitrate decompose in the same way.

$$2Mg(NO_3)_2(s) \xrightarrow{\text{heat}} 2MgO(s) + 4NO_2(g) + O_2(g)$$

$$Fe(NO_3)_3(s) \xrightarrow{\text{heat}} FeO(s) + 3NO_2(g) + O_2(g)$$

Nitrates of metals that are low in the reactivity series such as silver nitrate, decompose to give the metal, nitrogen dioxide and oxygen gas. For example;

$$2AgNO_3(s) \xrightarrow{\text{heat}} 2Ag(s) + 2NO_2(g) + O_2(g)$$

Activity 2.12 Preparation of metal nitrate by using metal hydroxide

Requirements: Measuring cylinder, source of heat, tripod stand, wire gauze, glass rod, evaporating dish, 2 M NaOH, 2 M HNO_3, and two beakers of 250 mL.

Procedure

1. Measure 20 mL of 2 M NaOH and put it into the first beaker.
2. Add 20 mL of 2 M HNO_3 into the second beaker and stir using a glass rod.
3. Pour the content of the first beaker into the second and stir using a glass rod.
4. Measure 20 mL of the mixture and put into an evaporating dish, then heat it to saturation.
5. Leave the solution to cool, crystallise, and record your observations.

Question

Give the name and chemical formula of the crystals formed when the reaction is heated to saturation then allowed to cool.

Chemical tests for nitrates

Various tests are used to identify metal nitrates in solution or in solid forms. These tests include the action of heat on nitrates. When any metal nitrate, except nitrates of sodium and potassium is heated, reddish brown fumes of nitrogen dioxide are observed.

$$2Ca(NO_3)_2(s) \xrightarrow{\text{heat}} 2CaO(s) + 4NO_2(g) + O_2(g)$$

Other tests for nitrates include the *brown ring* test and solubility in water followed by heating.

Brown ring test

The brown ring test for nitrate ion is performed by adding iron(II) sulphate to the test solution followed by slow addition of sulphuric acid while watching for a brown ring on the test tube. The formation of brown ring indicates the presence of the nitrate ion. Consider zinc nitrate as a solution being tested for the presence of nitrate ions. This will react with sulphuric acid and form zinc sulphate and nitric acid.

$$Zn(NO_3)_2(aq) + H_2SO_4(aq) \longrightarrow ZnSO_4(aq) + 2HNO_3(aq)$$

The nitric acid formed reacts with sulphuric acid and iron(II) sulphate. The sulphuric acid oxidises the iron(II) sulphate to iron(III) sulphate.

$$6FeSO_4(aq) + 3H_2SO_4(l) + 2HNO_3(aq) \rightarrow 3Fe_2(SO_4)_3(aq) + 4H_2O(l) + 2NO(g)$$

Then a brown ring is formed when iron(II) sulphate reacts with water and nitrogen monoxide.

$$FeSO_4(aq) + 5H_2O(l) + NO(g) \rightarrow \underset{\text{Brown ring}}{[Fe(NO)(H_2O)_5]SO_4}$$

Therefore, formation of the brown ring indicates the presence of nitrates in solution. The brown ring forms between the layer of concentrated sulphuric acid and the mixture of the solution and iron(II) sulphate.

Test for identifying a metal nitrate in an unknown solid

Any metal nitrate will readily dissolve in water to form a solution. The production of brown fumes of nitrogen dioxide gas on heating indicates the presence of a metal nitrate.

2.6.3 Uses of metal nitrates

Metal nitrates have different uses such as, manufacturing of explosives, drugs, food preservatives, and in agriculture.

Manufacturing of explosives

Nitrates are used as the main components in the manufacturing of explosives. Ammonium nitrate fuel oil (ANFO) for example, contains 94% of ammonium nitrate and 6% of fuel oil. ANFO is used in making many explosives because of its low cost and high stability. Ammonium nitrate is also used as improvised explosive devices (IEDs), homemade bombs and explosives in mining industry.

Potassium nitrate (KNO_3), also known as *saltpeter* or *niter,* is a component of gunpowder which is used as an explosive. The salt is also used in artillery-shell primers, hand grenade fuses and in fireworks. Other famous bomb making nitrate based chemicals include nitroglycerin, nitrocellulose, C_4 plastics and trinitrotoluene (TNT). The explosion in nitrogen compounds is caused by the rapid release of excess energy when nitrogen atoms move from a less stable high energy state (such as NO_3^-, NO_2^- or NH_4^+) to a very stable, low energy state (such as in N_2).

Manufacturing of drugs

Some nitrates have antiseptic properties; for example, silver compounds such as silver nitrate and silver sulfadiazine, have been used to prevent infections on the skin, eyes, and destroy small, rough, and hard growths of skin called *warts*. Nitrates are also used in the manufacturing of medicines used for the treatment or prevention of heart pains caused by heart diseases. Nitroglycerin is an example of the nitrate based drugs, which is used to treat and relieve symptoms of *angina* and prevents its onset during strenuous activities. Angina is the condition that is marked by severe pains in the chest that often spread to the shoulders, arms and neck regions caused by an inadequate blood supply from the heart.

Food preservations

Nitrates and nitrites are used in preserving and curing foods such as meat, fish and in the manufacturing of solid, semi-solid and mould cheeses. Potassium and sodium nitrates are examples of sources of nitrites. In the cured foods, nitrites produce a good flavour, give a characteristic pink colour and inhibit the growth of food spoilage bacteria such as *Clostridium botulinum*. However, due to the potential risk of the formation of carcinogenic *N*-nitroso compounds such as nitrosamine in the cured foods and in the human body, many countries have reduced the applications of nitrates in food preservation.

Production of photographic films

Silver nitrate is a precursor to many silver compounds such as those used in photography, stain in scanning electron microscopy and other staining purposes. In photographic films, a solution of silver nitrate reacts with potassium bromide to form silver bromide.

$$AgNO_3(aq) + KBr(aq) \longrightarrow AgBr(s) + KNO_3(aq)$$

Photographic films and plates contain an emulsion in the form of silver bromide, which decomposes to small amounts of silver on exposure to light. The photochemical change equation is expressed as,

$$2AgBr(s) \xrightarrow{\text{light}} 2Ag(s) + Br_2(g)$$

The photochemical change involving silver bromide is a key reaction in black and white photographs.

Agricultural uses of metal nitrates

Nitrogenous fertilisers are mainly nitrates. The nitrogenous fertilisers which are used are made of the nitrates of ammonium (NH_4^+), sodium (Na^+), potassium (K^+) and calcium (Ca^{2+}) salts. Nitrate fertilisers provide nitrogen and metal ions required for the plant development. Ammonium nitrate (NH_4NO_3) for example, has high content of nitrogen which is an important plant nutrient for various plant metabolic processes. However, due to the hygroscopic character of ammonium nitrate, it is mixed with powdered calcium carbonate to prevent hardening of salt and reduces its ability to explode. The mixture of ammonium nitrate and calcium carbonate is commercially sold as *nitro chalk*, also called *calcium ammonium nitrate*. All nitrogenous fertilisers are cheap, soluble and biodegrade easily leaving a safe environment. But, since they are easily hydrolysed to form acidic solutions, nitrogenous fertilisers are not suitable for acidic soil.

Exercise 2.6

1. Using balanced chemical equations, explain four methods that can be used to prepare metal nitrates in the laboratory.
2. Using chemical equations, describe the decomposition of the following compounds when heated:
   (a) Potassium nitrate (b) Aluminium nitrate
   (c) Silver nitrate
3. Describe using chemical equation(s), the chemical tests that can be used to identify the presence of nitrates in a solution.
4. Explain the chemical reagents and the tests that can be used to distinguish potassium nitrate from magnesium nitrate.
5. Copper(II) nitrate salt can be prepared by reacting a metallic copper with nitric acid.
   (a) Write a balanced equation for the process when a moderate concentrated nitric acid is used.
   (b) Explain why the resulting aqueous solution should not be evaporated to dryness.
6. When heated, sodium nitrate and lead nitrate decompose to their respective products. Write balanced chemical equations for the decomposition of these nitrates.
7. Explain the uses of the metal nitrates.

Revision exercise 2

1. You are provided with the following chemicals: ammonium hydroxide, chlorine gas, copper oxide, iron, lead nitrate, and dilute sulphuric acid. Using only chemicals from this list, write balanced chemical equations for the preparation of a;

(a) salt by direct combination.

(b) soluble salt by neutralisation of alkali.

(c) soluble salt from an insoluble base.

(d) salt by double decomposition (precipitation).

(e) soluble salt from a metal.

2. Given the following list of reagents: dilute sulphuric acid, copper, lead, dilute nitric acid, dilute hydrochloric acid, copper oxide, lead carbonate, sodium carbonate, sodium and zinc. Which of these would you use to prepare each of the following salts?

   (a) Lead sulphate (b) Copper(II) sulphate

   (c) Sodium sulphate (d) Zinc sulphate

3. (a) Describe the steps necessary to convert lead carbonate into lead chloride.

   (b) Name a soluble lead salt and write the equation for the action of heat on this salt.

4. How would you distinguish the following pairs of compounds?

   (a) Lead nitrate from copper nitrate

   (b) Zinc oxide from calcium oxide

   (c) Sodium carbonate from sodium nitrate

5. Explain using chemical equations, how magnesium, zinc, iron, lead carbonate, copper oxide, and copper hydroxide can be converted to their respective chlorides, sulphates and nitrates.

6. Using a balanced chemical equation, explain what happens when dilute hydrochloric acid is added to each of the following: lead nitrate solution, calcium oxide and sodium hydroxide solutions.

7. Giving reasons, explain the similarities or differences in thermal stability between the following pairs of compounds:

   (a) Sodium carbonate and magnesium carbonate

   (b) Magnesium carbonate and calcium carbonate

8. In the preparation of magnesium carbonate, sodium hydrogen carbonate is reacted with hot magnesium sulphate.

   (a) Explain why sodium carbonate is not used in this reaction.

   (b) Explain why under these conditions, magnesium hydrogen carbonate is not produced.

9. Using balanced chemical equations, explain the differences in the thermal decomposition products among sodium nitrate, lead nitrate and silver nitrate.

10. Complete the following word equations and then write the corresponding balanced chemical equations for each reaction:

    (a) Zinc + Lead nitrate solution ⟶

    (b) Lead + Copper nitrate solution ⟶

    (c) Magnesium + Zinc chloride solution ⟶

    (d) Copper + Sodium chloride solution ⟶

    (e) Zinc + Iron(II) sulphate solution ⟶

11. Using balanced chemical equations for the reactions, describe the effects of heat on the following compounds:

    (a) Magnesium chloride hexahydrate

    (b) Magnesium sulphate heptahydrate

    (c) Calcium carbonate

12. (a) Give the importance of limestone, cement and plaster of Paris in everyday life.

    (b) Describe two important uses of each of the following:

    (i) Quicklime (ii) Caustic soda

13. (a) Identify substances **A**, **B**, and **C** and explain the reactions involved in the following:

    When nitric acid is added to a bright red powder **B** and warmed gently, it changes to a dark brown solid **A.** On filtration, washing and adding concentrated hydrochloric acid to the brown substance, chlorine gas is evolved on warming, leaving behind a yellowish-white residue **C** on cooling. When tested, **C** is found to contain lead.

    (b) Two metals **P** and **Q** are derived from the *s*-block of the periodic table. The metal **P** forms an insoluble oxide and a soluble sulphate and the metal **Q** forms a soluble oxide and an insoluble sulphate. Both metals form a hydroxide of the formula $M(OH)_2$, where **M** = **P** or **Q**. The hydroxide $P(OH)_2$ dissolves in alkalis but $Q(OH)_2$ does not. Predict the probable positions of the metals **P** and **Q** in the periodic table and indicate which one of the two forms a thermally more stable carbonate.

Chapter Three

Extraction of metals

Introduction

The importance of metals to humans cannot be overemphasised. Metals are found in the earth's crust, and exist in combination with other elements like oxygen, sulphur, and carbon. To make these metals useful, they have to be extracted from whatever materials they are mixed with, and be purified. In this chapter, you will learn about metal ores, metal extraction, and occurrence, extraction, properties, and uses of selected metals.

3.1 Metal ores

An ore *is a naturally occurring solid material from which metals can be extracted*. Metal ores which are composed of mixed proportions of metals, impurities and anions are found in combined forms. Alongside the metals of interest, ores or mineral concentrates contain small quantities of other metals that may not be appreciable for extraction. For instance, mineral concentrates from Geita Gold mine in Tanzania have been found to contain varying amounts of copper, silver, sulphur, and iron. Pure metals are obtained from their ores through a process known as *extraction of metals*. This process is a stepwise process through which impurities present in the metal ores are removed followed by refinery processes in order to obtain pure metals. The extraction and refinery processes are generally known as *metallurgy*.

3.1.1 Natural occurrence of metals

Metals occur in nature either in combined forms or as free elements. The forms in which a metal exists depend on its ability to react with the available free elements or anions in air, water, or the earth's crust. Some metals have low reactivity with air, moisture, or anions present in nature, and therefore exist in their pure forms. Such elements are said to be noble metals since they tend to remain in unreactive forms. Examples are gold, mercury, silver, and platinum.

To a large extent, they remain in uncombined forms. Moderately reactive metals such as aluminium, zinc, lead, and iron are found in combined states in the earth's crust. They react with air, carbon dioxide, moisture or non-metals such as oxygen, sulphur or halogens to form their corresponding oxides, carbonates, hydroxides, sulphides, and halides.

Metals of group I and group II in the periodic table are very reactive. They exist as halides and carbonates in the earth's crust or the sea. Tin, copper, and aluminium belong to the group of moderately reactive metals. They naturally occur in combined forms as oxides, carbonates, sulphides or silicates.

3.2 Metal extraction

Metal ores exist in different compositions of active metals and impurities. The ore is also embedded in a gangue or matrix which must be separated in the process of extraction. Since metals have different reactivities, the choice of a method to be used is governed by the nature and the reactivity of the metal. The stages towards the extraction of the metals are determined by the types of impurities to be removed from the ores and the nature of the metals. The common stages for the extraction of metals arranged sequentially include; crushing and pulverisation, concentration or dressing of the ore, calcination or roasting of the ore, reduction of metal oxide to a free metal and finally purification and refining of the metal as depicted by Figure 3.1.

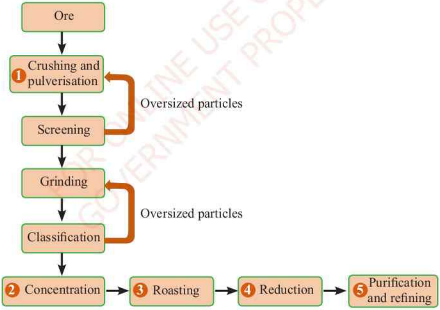


Figure 3.1 A simple flow diagram of the stages for extraction of metals

3.2.1 Crushing and pulverising

Metal ores are obtained from large pieces of rocks or sediments that contain sufficient minerals, impurities, and the gangue or matrix. The metal ore has to be ground and pulverised so that the components are converted into powder. This process goes through the following stages:

Crushing

The crude mineral ores are first crushed using jaw crushers or grinders to form small sized ore particles which are easy to use. The crushed ore particles are further processed through screening.

Screening

Under this stage, the granulated ores from the crushing stage are screened to separate the particles into the required size. Particles with larger sizes than the required ones are screened out and taken back to the crushing stage while particles with the required size are carried to the grinding stage.

Grinding

This stage involves breaking the particles from the screening stage into fine particles by the use of grinders. Essentially, grinders consist of two rotating hard metallic drums which upon rotation they break the granulated ore materials into fine particles by compression. The obtained fine particles are transported to the classification stage for further processing.

Classification

Under this stage, the ground particles undergo further separation into very fine particles in the machines called *classifiers*. The particles are separated by the classifiers to get particles of the size required for the next stage. Classifiers can be cyclones, hydraulic classifiers, or mechanical classifiers. Oversized particles are recycled back to be reground.

3.2.2 Concentration or dressing of the ore

The ground powder in the above steps contains metals and the earthly impurities such as sand, clay, and lime. The impurities are commonly known as *gangue* or *matrix*. They are removed from the mixture before the chemical reduction of the metal ore. The process of removing the impurities from the powdered metal ore is known as *concentration or dressing of the ore*. The concentration of the ore is done by considering the properties of the impurities and the metal of interest.

The commonly used concentration methods are the gravity method, magnetic separation, and the froth floatation.

Gravity method

Under this method, the metal ore and the gangue are separated based on the differences in densities between the two. During separation process, the classified powder is washed with water and heavier particles settle at the bottom and lighter ones float on the surface of water. Based on these arrangements, the components are then separated from each other (Figure 3.2).

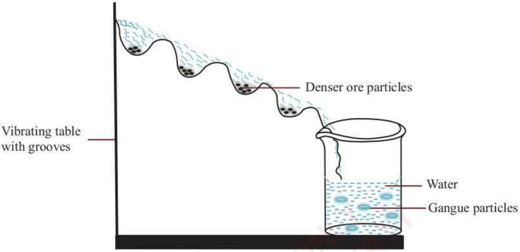


Figure 3.2 Gravity method for concentration of metal ores

Magnetic separation

This method is used to separate the classified powder when there is a significant difference in magnetic properties between the gangue or matrix and the metal ore. During the concentration process, the classified powder is passed over a magnetic wheel where the matrix or metal ore is attracted by the magnet and separated from each other. A good example of the application of this method is the separation of iron ore from its impurities.

Froth floatation

In this method, the different surface properties such as the wetting ability between the metal ore and the gangue is employed to separate the components. The method is used to separate ores containing sulphides like ZnS, CuS, and PbS. The gangue particles are hydrophilic in nature and therefore, they are wetted by water. Conversely, the sulphides' ores are hydrophobic in nature and therefore, they are wetted by oil. In the froth floatation process, fine powder of the ore is mixed with water followed by the addition of pine oil. The emulsion is agitated by passing compressed air causing oil and froth to float on the surface along with the ore. The froth is removed and allowed to settle down. The mineral which is rich in froth is collected for further processing. The froth floatation process for concentration of mineral ores is shown in Figure 3.3.

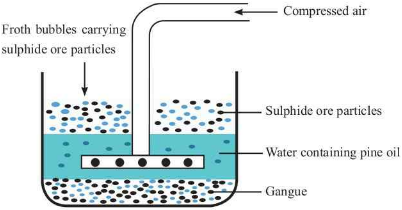


Figure 3.3 Froth floatation process for the concentration of mineral ores

After concentrating the ore, the gangue is completely removed from the mixture leaving behind a metal ore and other impurities with close wetting property. At this point, the ore is subjected to calcination or roasting processes.

3.2.3 Calcination or roasting

The concentrated metal ore may contain moisture, volatile substances, and water of hydration. These substances must be driven out of the ore before roasting. The removal of the moisture, water of hydration, and volatile substances is known as *calcination*. This is done under a limited supply of oxygen where the impurities become gaseous and escape. Calcination is then followed by roasting in which the calcinated concentrate is roasted in excess air below the fusion temperature of the ore. Roasting is done in order to dry the ore, remove the volatile substances and transform it into an oxide. It is important to note that if the ore is in the form of oxide, roasting process should not be done. After roasting, the ore is ready for reduction to metal.

3.2.4 Reduction of metal ore

In this stage, the roasted or calcinated metal ore is converted to metal through reduction process. The process is done by heating the metal ore (thermal reduction), self-reduction, precipitation, electrolytic reduction or by using a reducing agent (chemo-reduction) depending on the reactivity of the metal of interest. During this process, other impurities that were not removed during the roasting and calcination processes are removed. These reduction methods are discussed in the following sub-sections:

Thermal reduction

This method is used to reduce oxides of metals which are present at the bottom of the reactivity series by action of heat alone. For example, mercury oxide is reduced to mercury metal by burning it to around 300 °C.

$$2HgO(s) \xrightarrow{300\ ^\circ C} 2Hg(l) + O_2(g)$$

Self-reduction process

Self-reduction process can be applied in the reduction of Cu_2S, HgS, and PbS. Part of the ore is roasted in air to form an oxide which then reduces the rest of the metal ore to metal. That is;

$$2Cu_2S(s) + 3O_2(g) \longrightarrow 2Cu_2O(s) + 2SO_2(g)$$

$$2Cu_2O(s) + Cu_2S(s) \longrightarrow 6Cu(s) + SO_2(g)$$

Reduction by precipitation

In this method, a complex solution of metal ions is precipitated using an appropriate substance. The precipitate is then drawn off and dried. Precipitation of silver using dilute solution of sodium cyanide is a representative example of the precipitation reduction.

$$Ag_2S(s) + 4NaCN(aq) \longrightarrow 2Na[Ag(CN)_2](aq) + Na_2S(aq)$$

$$2Na[Ag(CN)_2](aq) + Zn(s) \longrightarrow Na_2[Zn(CN)_4](aq) + 2Ag(s)$$

Reduction by electrolysis

Electrolytic reduction *is convenient for reactive metals that cannot be reduced by chemical reducing agents or thermal reduction*. Common metals extracted by electrolysis include potassium from a molten potassium chloride, sodium from sodium chloride (brine), calcium from calcium chloride and aluminium from molten alumina. The mechanism for electrolytic reduction involves the process of oxidation and reduction of metals. The fused or molten chlorides are electrolysed where metals are collected at the cathode. Example is the electrolysis of sodium chloride (brine).

Reaction: $NaCl(l) \longrightarrow Na^+(l) + Cl^-(l)$

Reaction at the anode: $2Cl^-(l) \longrightarrow Cl_2(g) + 2e^-$

Reaction at the cathode: $Na^+(l) + e^- \longrightarrow Na(s)$

Overall reaction: $2Na^+(l) + 2Cl^-(l) \longrightarrow 2Na(s) + Cl_2(g)$

During electrolysis, the cathode acts as a reducing agent by supplying electrons to the metallic ions in the molten electrolyte, resulting in the deposition of the free metal at the cathode. The electrolyte is usually a salt of the metal such as chloride or an oxide, with a high melting point.

Reduction using a reducing agent

Under this method, roasted or calcinated ores of metals like zinc, iron, copper, nickel, tin or lead are mixed with carbon or carbon monoxide as a reducing agent. The resulting mixture is heated at high temperature in the furnace. During the heating process, coke reduces the metal ore to free metal. The following reactions indicate what happens when an iron ore is heated with carbon monoxide or carbon in the furnace:

$$Fe_2O_3(s) + 3C(s) \longrightarrow 2Fe(s) + 3CO(g)$$

$$Fe_2O_3(s) + CO(g) \longrightarrow 2FeO(s) + CO_2(g)$$

$$FeO(s) + CO(g) \longrightarrow Fe(s) + CO_2(g)$$

It is important to note that, if this method is used to extract manganese or chromium, aluminium is used instead of carbon or carbon monoxide in the process called *thermite reduction*.

$$Cr_2O_3(s) + 2Al(s) \longrightarrow 2Cr(s) + Al_2O_3(s)$$

Choice of the reduction method for extracting metals

In order to choose which method is suitable for the extraction of a particular metal from its ore, the knowledge of reactivity of the metal is required. Reactivity of the metal depends on its tendency to lose electron(s), that is, the tendency to form cations (M^{n+}); where n is a variable number of ions, for example 1, 2, and 3. This tendency depends on the magnitude of its standard reduction potential. Metals with high negative values (or smaller positive values) of standard reduction potentials readily lose electron(s). Such metals are said to be chemically active. When metals are arranged in the order of their decreasing reactivity (*i.e.*, with the most reactive metal at the top and the least reactive metal at the bottom), a reactivity series shown in Table 3.1 is obtained. The most reactive metal lithium is at the top of the series and has the highest negative reduction potential, while the least reactive metal gold is at the bottom and has the highest positive reduction potential. Note that, the reactions in Table 3.1 are written in oxidation forms and hence the potentials are oxidation potentials.

Table 3.1 Reactivity series of metals in aqueous solutions

Metal	Oxidation reaction	E°
Lithium	$\mathrm{Li}(s) \longrightarrow \mathrm{Li}^{+}(aq) + e^{-}$	+3.05
Potassium	$\mathrm{K}(s) \longrightarrow \mathrm{K}^{+}(aq) + e^{-}$	+2.92
Barium	$\mathrm{Ba}(s) \longrightarrow \mathrm{Ba}^{2+}(aq) + 2e^{-}$	+2.90
Calcium	$\mathrm{Ca}(s) \longrightarrow \mathrm{Ca}^{2+}(aq) + 2e^{-}$	+2.76
Sodium	$\mathrm{Na}(s) \longrightarrow \mathrm{Na}^{+}(aq) + e^{-}$	+2.71
Magnesium	$\mathrm{Mg}(s) \longrightarrow \mathrm{Mg}^{2+}(aq) + 2e^{-}$	+2.37
Aluminium	$\mathrm{Al}(s) \longrightarrow \mathrm{Al}^{3+}(aq) + 3e^{-}$	+1.66
Manganese	$\mathrm{Mn}(s) \longrightarrow \mathrm{Mn}^{2+}(aq) + 2e^{-}$	+1.18
Zinc	$\mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq) + 2e^{-}$	+0.76
Chromium	$\mathrm{Cr}(s) \longrightarrow \mathrm{Cr}^{3+}(aq) + 3e^{-}$	+0.73
Iron	$\mathrm{Fe}(s) \longrightarrow \mathrm{Fe}^{2+}(aq) + 2e^{-}$	+0.44
Nickel	$\mathrm{Ni}(s) \longrightarrow \mathrm{Ni}^{2+}(aq) + 2e^{-}$	+0.23
Tin	$\mathrm{Sn}(s) \longrightarrow \mathrm{Sn}^{2+}(aq) + 2e^{-}$	+0.14
Lead	$\mathrm{Pb}(s) \longrightarrow \mathrm{Pb}^{2+}(aq) + 2e^{-}$	+0.13
Hydrogen	$\mathbf{H_2(g) \longrightarrow H^{+}(aq) + e^{-}}$	**0.00**
Copper	$\mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2e^{-}$	−0.34
Silver	$\mathrm{Ag}(s) \longrightarrow \mathrm{Ag}^{+}(aq) + e^{-}$	−0.80
Mercury	$2\mathrm{Hg}(l) \longrightarrow \mathrm{Hg}_2^{2+}(aq) + 2e^{-}$	−0.79
Gold	$\mathrm{Au}(s) \longrightarrow \mathrm{Au}^{3+}(aq) + 3e^{-}$	−1.50

Metals at the top of the reactivity series (potassium, sodium, calcium, magnesium, and aluminium) are extracted by electrolysis. They have high oxidation potentials and therefore, they are the strongest reducing agents. These metals form too stable compounds that are difficult to be reduced using simple reducing agents like carbon monoxide; thus, they have to be extracted by the most powerful reducing agent which is none other than the cathode of the electrochemical cell. Since they are also electropositive, they cannot be displaced from aqueous solutions of their salts by other metals. However, other metals such as zinc, iron, tin, and copper can be extracted from their ores using electrolysis, but if simple reduction is possible, electrolysis is preferred to because it is cost effective. The more active (or reactive) a metal is, the more stable the compound it forms and the greater the energy required to produce the metal from its ore. Therefore, the stability of the metal in its reduced form is related to its position in the electrochemical series of metals. This makes aluminium with a relative higher negative reduction potential value to be extracted from its ores by electrolytic reduction. At the same time, tin and copper are extracted using thermal reduction process because of their low reduction potential values.

3.2.5 Purification and refining of metals

The final stage of metal extraction is purification or refinery process. This process differs from others such as smelting and calcining because they involve chemical changes to the raw materials, whereas in refining, the final materials are usually chemically identical to the original ones. Most of the metals such as copper, silver, gold, zinc, and chromium are refined electrolytically. The impure metal is made the anode and a thin sheet of the pure metal as the cathode. In the electrolytic vessel, a solution of a salt of the metal serves as the electrolyte.

Exercise 3.1

1. Describe the natural occurrence of metal ores.
2. Describe the stages of metal extraction.
3. Identify the factors which influence the choice of the methods for extracting metals from their ores.
4. With examples, explain the self-reduction process.
5. Describe the electrolysis of fused NaCl.

3.3 Occurrence, extraction, properties, and uses of selected metals

A few metals have been selected to represent the rest, since most of them undergo more or less similar methods of extraction. In this section, you will learn about occurrence, extraction, properties, and uses of tin, copper, and aluminium metals.

3.3.1 Tin

Natural occurrence of tin

Tin occurs in nature in combined forms with oxygen, sulphides of iron, copper, and native tin. The ores have varying amounts of tin that can be extracted to a useful tin. The most abundant ore is cassiterite or stannic oxide (SnO_2) with a significant amount of tin. Other ores contain small amounts of tin that can make its production costs insignificantly high, rendering it uneconomical. An example of such ores is a stannite (Cu_2FeSnS_4).

Extraction of tin

Tin ore contains foreign materials such as soil, sulphur, carbon, and oil; hence it has to be concentrated mainly by froth floatation method. The concentration process starts by crushing and grinding raw materials to get fine powder which is then put in water containing pine oil. The obtained mixture is agitated using compressed air to separate unwanted solid matters such as soil which settles down the tank and leaves tin ore floating on the surface of the emulsion. The concentrate is collected and roasted to take away foreign matters such as carbon, sulphur, and oil.

Being a less reactive metal, tin can easily be reduced from its oxide by using the cheap thermal reduction method because the electrolytic reduction process is expensive in terms of installation and maintenance. An electrolytic reduction is used only when chemical or thermal reduction method is not possible. The thermal reduction of tin is done in a furnace as shown in Figure 3.4.

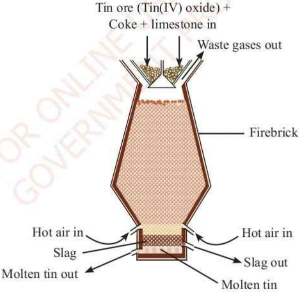


Figure 3.4 Thermal reduction of tin ore

The concentrate, SnO_2, is mixed with coke or carbon monoxide and the mixture heated in a reverberatory furnace at high temperature (above 232 °C). In the furnace, SnO_2 is thermally reduced to Sn by carbon or carbon monoxide as the reducing agent.

$$SnO_2(s) + 2C(s) \longrightarrow Sn(s) + 2CO(g)$$

$$SnO_2(s) + 2CO(g) \longrightarrow Sn(s) + 2CO_2(g)$$

The molten ore is tapped from the furnace leaving behind the less fusible impurities. Higher purity tin may be obtained by electrolytic methods (compare with copper purification).

Purification and refinery of tin

Refinery of impure tin blocks is done through electrolytic methods whereby impure tin is made an anode while pure tin is made the cathode. These are suspended in an electrolytic tank containing hydrofluorosilicic acid (H_2SiF_6), tin(II) sulphate ($SnSO_4$), and sulphuric acid (H_2SO_4). During the electrolysis, the anode dissolves pure tin (99.9% purity) and is deposited on the cathode while other impurities settle down on the bottom of the tank as anode sludge/mud. The reactions that occur at the electrodes are:

At the anode: $Sn(s) \longrightarrow Sn^{2+}(l) + 2e^-$

At the cathode: $Sn^{2+}(l) + 2e^- \longrightarrow Sn(s)$

Physical properties of tin

Tin is a white lustrous metal which melts at about 232 °C. It exists in two allotropic forms called *white tin* and *grey tin* with the transition temperature of 13.2 °C between them. While the grey allotrope of tin is stable below 13.2 °C, the white allotrope is stable above 13.2 °C.

Chemical properties of tin

(a) At ordinary temperature, tin does not react with air or water. When tin is heated strongly in air, tin(IV) oxide (SnO_2) is formed.

$$Sn(s) + O_2(g) \xrightarrow{heat} SnO_2(s)$$

(b) Tin reacts slowly with dilute (non-oxidising) acids, such as HCl and H_2SO_4 liberating hydrogen gas.

$$Sn(s) + 2HCl(aq) \longrightarrow SnCl_2(aq) + H_2(g)$$

$$Sn(s) + H_2SO_4(aq) \longrightarrow SnSO_4(aq) + H_2(g)$$

(c) Tin combines directly with chlorine to form tin(IV) chloride.

$$Sn(s) + 2Cl_2(g) \longrightarrow SnCl_4(s)$$

(d) Tin reacts with dilute nitric acid to form a complex mixture of products. The most important components of the mixture are tin(II) nitrate and ammonium nitrate

$$4Sn(s) + 10HNO_3(aq) \longrightarrow 4Sn(NO_3)_2(aq) + NH_4NO_3(aq) + 3H_2O(l)$$

(e) With concentrated mineral acids, tin reacts as described below.

(i) Reaction with concentrated sulphuric acid

Tin reacts with hot concentrated sulphuric acid to form tin(IV) sulphate, sulphur dioxide, and water.

$$Sn(s) + 4H_2SO_4(aq) \longrightarrow Sn(SO_4)_2(aq) + 2SO_2(g) + 4H_2O(l)$$

(ii) Reaction with concentrated nitric acid

Concentrated nitric acid oxidises tin to the hydrated oxide, which readily decomposes on heating to tin(IV) oxide and water.

$$Sn(s) + 4HNO_3(aq) \longrightarrow SnO_2(s) + 4NO_2(g) + 2H_2O(l)$$

(f) Hot concentrated alkalis react slowly with tin to form the complex ion, hexahydroxostannate(IV), $[Sn(OH)_6]^{2-}$.

$$Sn(s) + 4H_2O(l) + 2OH^-(aq) \longrightarrow [Sn(OH)_6]^{2-}(aq) + 2H_2(g)$$

Preparations of tin compounds

The common existing compounds of tin include tin(II) oxide, tin(IV) oxide, and tin halides. The preparation methods for these compounds are discussed below.

Preparation of tin(IV) oxide, (SnO_2)

This oxide occurs naturally as tin stone or cassiterite. It can be prepared by using the following ways:

(a) Heating tin with oxygen:

$$Sn(s) + O_2(g) \xrightarrow{heat} SnO_2(s)$$

(b) Reaction of tin with concentrated nitric acid:

$$Sn(s) + 4HNO_3(l) \longrightarrow SnO_2(s) + 4NO_2(g) + 2H_2O(l)$$

Preparation of tin(II) oxide (SnO)

The best way to prepare this oxide is by thermal decomposition of tin(II) oxalate, SnC_2O_4.

$$SnC_2O_4(s) \xrightarrow{heat} SnO(s) + CO(g) + CO_2(g)$$

Preparation of tin(IV) chloride ($SnCl_4$)

This is a colourless liquid which is formed when dry chlorine is passed over hot metallic tin.

$$Sn(s) + 2Cl_2(g) \longrightarrow SnCl_4(l)$$

Preparation of tin(II) chloride ($SnCl_2$)

The anhydrous tin(II) chloride may be formed by passing dry hydrogen chloride over hot tin wire.

$$Sn(s) + 2HCl(g) \longrightarrow SnCl_2(s) + H_2(g)$$

The hydrated tin(II) chloride is obtained when tin is reacted with concentrated hydrochloric acid.

$$Sn(s) + 2HCl(l) + 2H_2O(l) \xrightarrow{heat} SnCl_2.2H_2O(s) + H_2(g)$$

Uses and applications of tin compounds

Tin is mostly used in tin-plating of iron to protect it from rusting. Tin-plated iron cans are used as containers for foodstuffs. The tin plate may be deposited on the iron surface electrolytically. Although zinc has a more protective action on iron than tin, tin-plated iron cans are preferred over galvanised iron cans for food storage. Galvanised iron cans are not used for food storage because some elements that are used in galvanisation might leach and cause food poisoning.

Tin is also used in the production of alloys such as bronze (76% Cu and 24% Sn), and solder (50% Pb and 50% Sn). In addition, SnF_4 is sometimes used in toothpastes, although tin(II) fluoride is more common.

Exercise 3.2

1. Describe the natural occurrence of metal ores of tin.
2. Describe the processes involved in thermal reduction of metal ores.
3. Explain the chemical reactions involved in the thermal reduction of tin.
4. Explain why some metals cannot be extracted by thermal reduction method.

3.3.2 Copper

Natural occurrence of copper

Copper is found in combined forms in various ores such as chalcopyrite or copper pyrites ($CuFeS_2$), cuprite (Cu_2O), malachite ($Cu_2CO_3(OH)_2$), and azurite ($Cu_2CO_3{\cdot}Cu(OH)_2$). Extraction of copper is mainly done using chalcopyrites ($CuFeS_2$), since the ore contains a significant amount of copper and hence more economical than using other ores.

Extraction of copper

Copper is a less electropositive metal, therefore is extracted by thermal reduction method. However, if pure copper is required, the obtained blister copper is purified electrolytically. Before reduction process, the impure ore of copper is first concentrated using froth floatation method. In this method, the ore is crushed and mixed with vegetable oil. Air is blown through the mixture, so that copper-containing particles float as froth and are separated out. The copper concentrate obtained by froth floatation is then mixed with lime and roasted. Earthy materials separate out as slag. Some impurities are volatilised at this stage, for instance, antimony, and arsenic impurities. Further roasting is done in air to convert all the iron present to iron(II) oxide.

$$2CuFeS_2(s) + 4O_2(g) \xrightarrow{\text{heat}} Cu_2S(s) + 3SO_2(g) + 2FeO(s)$$

Silica (SiO_2) is added and the mixture is heated in the absence of air to convert iron(II) oxide to iron(II) silicate ($FeSiO_3$), which is poured out.

$$SiO_2(s) + FeO(s) \xrightarrow{\text{heat}} FeSiO_3(l)$$

Under controlled air supplies, the following reaction takes place in the reverberatory furnace:

$$2Cu_2S(s) + 3O_2(g) \xrightarrow{\text{heat}} 2Cu_2O(s) + 2SO_2(g)$$

Copper metal is then liberated by the following self-reduction reaction:

$$Cu_2S(s) + 2Cu_2O(s) \xrightarrow{\text{heat}} 6Cu(l) + SO_2(g)$$

or the obtained washed Cu_2S is heated in a limited supply of oxygen.

$$Cu_2S(s) + O_2(g) \xrightarrow{\text{heat}} 2Cu(l) + SO_2(g)$$

The metal separates out as a liquid, which is allowed to solidify in moulds to form blister copper. The blister copper is impure and can be purified electrolytically (Figure 3.5). The anode is a large block of the impure copper and the cathode is a very thin sheet of extremely pure copper. The electrolyte used is a 15% solution of $CuSO_4$ mixed with 5% solution of H_2SO_4. On electrolysis, copper dissolves from the anode and it is deposited on the cathode. Metallic silver and gold, which are commonly present as impurities, are left behind as an anode deplete. Similarly, lead sulphate and the insoluble basic salts of tin, antimony and bismuth are also left behind.

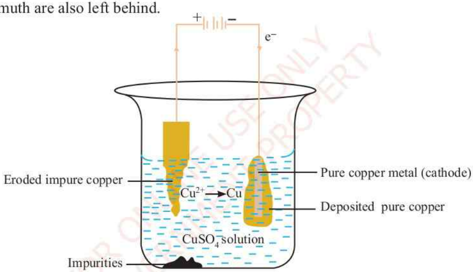


Figure 3.5 Electrolytic purification of copper

Activity 3.1 **Extracting copper from copper carbonate**

Requirements Bunsen burner, 1 g of copper(II) carbonate, 2 g of powdered wood charcoal, eye protection glass, crucible, crucible tongs, heat resistant mat, tripod stand, gauze, water, beaker (250 mL or larger), and spatula.

Procedure

1. Put one spatula measure of powdered copper(II) carbonate, into a crucible.
2. Heat the crucible and contents, slowly at first, then strongly until there is no further change in appearance of the mixture.
3. Allow the crucible and contents to cool for a few minutes.
4. Add two spatula measures of powdered charcoal (carbon) to the contents of the crucible, then mix them using the spatula whilst holding the crucible with tongs. Note that, do not attempt to grip around the body of the crucible because it is likely to slip out. Grip the edge of the crucible with the tongs.
5. Add a thin layer of powdered charcoal over the surface of the mixture.
6. Heat the crucible and its contents strongly on the tripod and gauze for a few minutes then allow the mixture to cool.
7. Half fill the beaker with water and then use tongs to tip the contents from the crucible into the water.
8. Swirl the contents of the beaker around so that any heavy material falls to the bottom, and then pour off the water and charcoal suspension.
9. Add more water and keep on pouring and swirling so that only the heavy material is left at the bottom of the beaker.

Questions

1. Give balanced chemical equations for any two reactions that took place in the experiments.
2. Why was the thin layer of charcoal added on the surface of the mixture?
3. Identify the heavy material formed in steps 8 and 9. Give reason(s) to support your answer.

Physical properties of copper

Copper is a hard metal, reddish in colour and takes a bright metallic lustre. It is malleable and ductile with a relatively high conductivity of heat and electricity. Its melting point is 1083 °C and has density of 8.92 g cm^{-3}.

Chemical properties of copper

(a) At room temperature, copper is stable in air but in the presence of moisture, oxygen, and CO_2 gas it reacts to form a basic carbonate, $CuCO_3 \cdot Cu(OH)_2$ which appears as a green solid mass on the surface of the metal.

(b) When heated in air (oxygen) at a temperature above 1100 °C, copper combines with oxygen to form copper(II) oxide.

$$2Cu(s) + O_2(g) \xrightarrow{\text{heat}} 2CuO(s)$$

(c) Dilute sulphuric acid and dilute hydrochloric acid have no action on copper. But dilute nitric acid reacts with copper slowly giving nitrogen monoxide (nitric oxide).

$$3Cu(s) + 8HNO_3(aq) \longrightarrow 3Cu(NO_3)_2(aq) + 4H_2O(l) + 2NO(g)$$

(d) With concentrated mineral acids, copper reacts as follows:

(i) Reaction with concentrated nitric acid

Copper reacts with concentrated nitric acid to form copper(II) nitrate, water, and nitrogen dioxide gas.

$$Cu(s) + 4HNO_3(l) \longrightarrow Cu(NO_3)_2(l) + 2H_2O(l) + 2NO_2(g)$$

(ii) Reaction with concentrated sulphuric acid

Copper reacts with hot concentrated sulphuric acid to form copper sulphate, water, and sulphur dioxide

$$Cu(s) + 2H_2SO_4(l) \longrightarrow CuSO_4(l) + 2H_2O(l) + SO_2(g)$$

(e) When copper metal is heated strongly in an atmosphere of pure dry ammonia, copper(II) nitride is formed.

$$3Cu(s) + 2NH_3(g) \xrightarrow{\text{heat}} Cu_3N_2(s) + 3H_2(g)$$

(f) Copper reduces Fe^{3+} compounds to Fe^{2+} compounds according to the following chemical equation:

$$Cu(s) + 2Fe^{3+}(aq) \longrightarrow Cu^{2+}(aq) + 2Fe^{2+}(aq)$$

Uses of copper

Like the other *d*-block elements, copper and its compounds have many uses. It is used to make domestic utensils, pipes, electric cables, and wires which are used in the winding of dynamos and motors. Copper is used to make alloys such as brass, silver coinage, and bronze. Alloying with other metals improves the properties of copper. Copper is an important constituent of a number of enzymes and it is required for the synthesis of haemoglobin. It is also used to activate enzymes in plants.

Exercise 3.3

1. Give the composition of copper pyrites and describe how copper is extracted from copper pyrites.
2. Explain why sulphide ores of copper are roasted first before reduction.
3. What is meant by concentration of copper ores? List the stages involved in the concentration of copper ores.
4. Write all the possible chemical equations representing reduction of copper in the reverberatory furnace.
5. Describe the process of obtaining pure copper from blister copper.

3.3.3 Aluminium

Natural occurrence of aluminium

Aluminium is one of the moderately reactive metals found in combined forms. It exists as a free oxide, hydrated oxide, fluoride, silicate, and sulphate. The ores have varying percentage of aluminium from which aluminium can be extracted. The common ores of aluminium is free oxide called *corundum* (Al_2O_3), hydrated oxides namely bauxite ($Al_2O_3{\cdot}2H_2O$), and diaspore ($Al_2O_3{\cdot}H_2O$), fluorides such as cryolite (Na_3AlF_6), silicates such as kaolin ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$), potash feldspar ($K_2O{\cdot}Al_2O_3{\cdot}6SiO_2$), potash mica ($K_2O{\cdot}Al_2O_3{\cdot}6SiO_2{\cdot}2H_2O$), and sulphates such as alunite ($K_2SO_4{\cdot}Al_2(SO_3)_3{\cdot}4Al(OH)_3$). However, bauxite is the mainly ore from which aluminium can be economically extracted because other ores contain insignificant amounts of aluminium and the process of extraction is not economical.

Extraction of aluminium

Aluminium like other *s*-block metals has more negative reduction potential. Therefore, it cannot be obtained by electrolysis of its aqueous solutions. It is obtained in large scale by the electrolysis of bauxite ($Al_2O_3{\cdot}2H_2O$). The melting point of bauxite (2050 °C) is too high for the electrolytic process. Therefore, the ore is dissolved in molten cryolite which lowers the melting point to 1000 °C. Bauxite ore is usually found to contain iron(II) oxide, silicon dioxide (SiO_2), and titanium(IV) oxide as impurities. Before the electrolysis, the impurities present in the bauxite must be removed. The methods of purification of bauxite depend on the nature of the impurities present in the bauxite ore. Three commonly used methods of purification are described below.

Bayer's method

Bayer's method *is the principal industrial means of refining bauxite to alumina*. Bauxite ore containing iron(II) oxide as the main impurity is purified by the Bayer's process. In this process, the finely ground ore is roasted to convert iron(II) oxide to iron(III) oxide. The roasted ore is then digested with sodium hydroxide solution at 200-250 °C under pressure where alumina (Al_2O_3) and SiO_2 are dissolved. Iron(III) oxide, titanium(IV) oxide and others are left behind as solid masses. The mixture is agitated and filtered to separate the solution from the undissolved mass. The sodium aluminate from the filtrate is extracted with water followed by heating up at 50-60 °C in the presence of CO_2 to precipitate aluminium hydroxide.

$$Al_2O_3(s) + 2NaOH(aq) \xrightarrow[35\text{ atm}]{(200-250\ ^\circ C)} 2NaAlO_2(aq) + H_2O(l)$$

$$2Na[Al(OH)_4](aq) + CO_2(g) \xrightarrow{50-60\ ^\circ C} \underset{\text{White gelatinous ppt}}{2Al(OH)_3(s)} + Na_2CO_3(aq) + H_2O(l)$$

Another way of precipitating the aluminate to $Al(OH)_3$ is by *seeding* with a freshly prepared $Al(OH)_3$ as follows:

$$2Na[Al(OH)_4](aq) \xrightarrow{\text{seeding}} 2Al(OH)_3(s) + 2NaOH(aq)$$

The precipitate, $Al(OH)_3$ is filtered, dried, and heated at 1200 °C to give pure Al_2O_3 as in the following chemical reaction:

$$2Al(OH)_3(s) \xrightarrow{1200\ ^\circ C} Al_2O_3(s) + 3H_2O(g)$$

Hall's method

The Hall's method *is used for purifying bauxite ore which contains iron oxide as the major impurity*. In this process, the bauxite ore is fused with sodium carbonate to form sodium meta-aluminate.

$$Al_2O_3 \cdot 2H_2O(s) + Na_2CO_3(s) \xrightarrow{\text{heat}} 2NaAlO_2(s) + 2H_2O(g) + CO_2(g)$$

As for the Bayer's process, the soluble sodium meta-aluminate is extracted with water and iron oxide (impurity) remains behind as the residue. The water extract of sodium meta-aluminate is heated to about 50 °C in the presence of carbon dioxide and the precipitated aluminium hydroxide is filtered, dried, and ignited to get pure alumina.

Serpeck's method

Serpeck's method *is another means of extraction of aluminium*. This method is used when the bauxite ore contains silica (SiO_2) as the major impurity. The ore is heated with carbon at about 1000 °C under nitrogen. The following reactions take place:

$$Al_2O_3(s) + 3C(s) + N_2(g) \xrightarrow{1000\ ^\circ C} 2AlN(s) + 3CO(g)$$

$$SiO_2(s) + C(s) \xrightarrow{1000\ ^\circ C} Si(g) + CO_2(g)$$

The silica gets reduced to silicon and carbon dioxide. Volatile silicon and carbon dioxide escape leaving behind aluminium nitride (AlN). On hydrolysis, aluminium nitride gives $Al(OH)_3$ according to the following chemical equation:

$$AlN(s) + 3H_2O(l) \longrightarrow Al(OH)_3(s) + NH_3(g)$$

The obtained $Al(OH)_3$ precipitate is then dried and ignited to obtain Al_2O_3.

$$2Al(OH)_3(s) \xrightarrow{1200\ ^\circ C} Al_2O_3(s) + 3H_2O(g)$$

Mechanism of electrolytic reduction of Al_2O_3

Pure aluminium oxide obtained from bauxite ore is melted in a steel container in the presence of cryolite (Na_3AlF_6) and fluorspar (CaF_2). Cryolite and fluorspar serve two purposes: To reduce the melting point of bauxite, and to make the alumina good conductor for the passage of electricity. The process of electrolysis is conducted in a steel electrolytic cell lined from inside with a sheet of graphite acting as cathode. The anode is also made of carbon rods. When an electric current passes through the molten electrolyte containing Al_2O_3 (2 – 8%), Na_3AlF_6 (80 – 85%), CaF_2 (5 – 7%), and AlF_3 (5 – 7%), aluminium gets liberated on the surface of the cathode. Molten aluminium collects at the bottom of the cell and is tapped from time to time. Oxygen is liberated at the carbon anodes. At high temperature of the cell, oxygen reacts with the carbon anodes to form carbon monoxide and carbon dioxide, therefore, the carbon anodes gradually vanish because each molecule of carbon monoxide or carbon dioxide which is given off, takes a little carbon away with it. Thus, the anode has to be replaced after sometime. The process of electrolytic reduction of fused alumina is summarised in Figure 3.6.

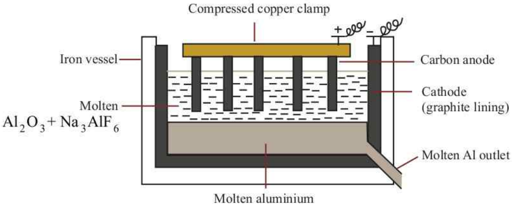


Figure 3.6 Extraction of aluminium by electrolysis of fused alumina

In the electrolytic cell, the chemical reactions occurring during the electrolysis are complicated but could be approximately equivalent to the electrolysis of Al_2O_3. The cathode reaction is the reduction of the aluminium ion and the anode reaction is the oxidation of the oxide ion.

At cathode: $4Al^{3+}(l) + 12e^- \longrightarrow 4Al(s)$

At anode: $6O^{2-}(l) \longrightarrow 3O_2(g) + 12e^-$

Overall reaction: $4Al^{3+}(l) + 6O^{2-}(l) \longrightarrow 4Al(s) + 3O_2(g)$

The aluminium obtained by this process is not pure. To obtain pure aluminium, the product of the electrolytic reduction of Al_2O_3 has to be refined by the Hoop's electrolytic process.

The Hoop's process *is an electrolytic process for the purification of aluminium*. Its electrolytic cell is made of iron, which is lined with carbon at the bottom. It consists of a lower layer of an alloy of impure aluminium with copper which serves as an anode. The middle layer contains a solution of cryolite (Na_3AlF_6) and barium fluoride (BaF_2). The upper layer consists of pure aluminium which serves as a cathode. These three layers are separated from each other due to the differences in their specific gravities (Figure 3.7). During electrolysis, Al^{3+} ions from the middle layer migrate to the upper layer where they are reduced to aluminium. Equal numbers of Al^{3+} ions are produced in the lower layer. These ions migrate to the middle layer making the process continuous. Pure aluminium of about 99.99% is tapped off from time to time.

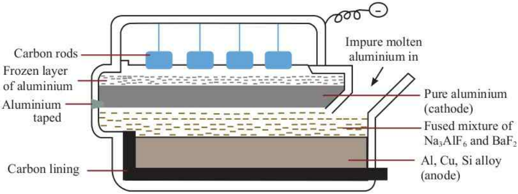


Figure 3.7 Hoop's cell for purification of aluminium

Physical properties of aluminium

Aluminium is a bluish-light metal with a density of 2.7 g cm^{-3}. The metal is malleable and ductile. It shows good conductivity of electricity and heat. Aluminium melts at 560 °C and has a boiling point of 2450 °C.

Chemical properties of aluminium

(a) At ordinary temperature and moist air, a thin protective layer of aluminium oxide forms on its surface. When heated to redness, it burns with a brilliant white flame and with evolution of heat energy.

$$4Al(s) + 3O_2(g) \xrightarrow{\text{strong heat}} 2Al_2O_3(s)$$

(b) Aluminium reacts with steam only when it is amalgamated or finely powdered.

$$2Al(s) + 6H_2O(g) \xrightarrow{\text{high temperature}} 2Al(OH)_3(s) + 3H_2(g)$$

(c) With dilute mineral acids, aluminium reacts as follows:

(i) Reaction with dilute HCl

Aluminium reacts with dilute HCl to liberate hydrogen gas.

$$2Al(s) + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2(g)$$

(ii) Reaction with dilute H_2SO_4

Aluminium does not react with dilute H_2SO_4. The acid makes aluminium passive by forming a resistant oxide layer on its surface which prevents the metal from further chemical attack by the acid.

(iii) Reaction with dilute HNO_3

Aluminium does not react with dilute nitric acid. Like H_2SO_4, nitric acid makes aluminium passive due to the formation of a protective layer of Al_2O_3 on its surface.

(d) With concentrated mineral acids, aluminium reacts as described in the following accounts:

(i) Reaction with concentrated HCl

Aluminium only reacts with concentrated HCl when heated to liberate hydrogen gas.

$$2Al(s) + 6HCl(l) \xrightarrow{\text{heat}} 2AlCl_3(l) + 3H_2(g)$$

(ii) Reaction with concentrated H_2SO_4

With hot concentrated H_2SO_4, aluminium is oxidised to liberate SO_2.

$$2Al(s) + 6H_2SO_4(l) \xrightarrow{\text{heat}} Al_2(SO_4)_3(aq) + 3SO_2(g) + 6H_2O(l)$$

(iii) Reaction with concentrated HNO_3

Aluminium is made passive by concentrated nitric acid and therefore, it does not react with the acid.

(e) With aqueous alkali solutions, aluminium reacts to form aluminate and hydrogen gas is liberated.

$$2Al(s) + 2NaOH(aq) + 6H_2O(l) \longrightarrow 2Na[Al(OH)_4](aq) + 3H_2(g)$$

(f) With non-metals such as halogens, sulphur, nitrogen, and carbon, aluminium reacts as follows:

(i) Reactions with halogens

When heated with halogens, aluminium reacts to form its halide. For example, with chlorine, it forms aluminium chloride.

$$2Al(s) + 3Cl_2(g) \xrightarrow{\text{heat}} 2AlCl_3(s)$$

(ii) Reaction with sulphur

When it is heated with sulphur, aluminium reacts to form aluminium sulphide.

$$2Al(s) + 3S(s) \xrightarrow{\text{heat}} Al_2S_3(s)$$

(iii) Reaction with nitrogen

Aluminium nitride is formed when aluminium is heated in nitrogen.

$$2Al(s) + N_2(g) \xrightarrow{heat} 2AlN(s)$$

(iv) Reaction with carbon

Aluminium reacts with carbon when heated to form aluminium carbide.

$$4Al(s) + 3C(s) \xrightarrow{heat} Al_4C_3(s)$$

(g) Aluminium also shows reducing property. This is due to its strong affinity to oxygen, thus acts as a reducing agent. Aluminium can reduce iron(II) and chromium(III) oxides to their respective metals.

$$Fe_2O_3(s) + 2Al(s) \xrightarrow{heat} 2Fe(s) + Al_2O_3(s)$$

$$Cr_2O_3(s) + 2Al(s) \xrightarrow{heat} 2Cr(s) + Al_2O_3(s)$$

Uses of aluminium

Aluminium is applicable in various areas. Some uses of aluminium are summarised below.

(a) It is used to make domestic appliances such as cooking pans, electric kettles, and storage containers.

(b) Aluminium is used to make building materials such as roofing sheets, windows, and door frames.

(c) Aluminium powder is used to make paints and varnishes.

(d) Aluminium is used to make electric cables and poles for power transmission.

(e) When fused with other elements such as copper, magnesium, manganese, and silicon, aluminium forms very strong, tough, and light alloys. These are used in the aviation industry for the construction of aeroplanes and for making vehicle parts such as piston heads. Some aluminium/magnesium alloys are resistant to sea water and air oxidation/corrosion, and thus, they are used in ship building.

Exercise 3.4

1. Describe the process of extracting aluminium from bauxite.
2. Describe the chemical reactions involved in aluminium extraction by specifying anodic and cathodic reactions.

3. With the aid of chemical equations, explain the reactions occurring in each stage of the concentration of bauxite ore.
4. Why is it necessary for the bauxite ore to be roasted before treating it with aqueous solution of sodium hydroxide?

Revision exercise 3

1. Describe how the following metals are extracted from their important ores:
   (a) Tin (b) Copper (c) Aluminium
2. Explain two uses of each of the following metals:
   (a) Tin (b) Copper (c) Aluminium
3. With examples, give reasons as to why some metals cannot be extracted by the thermal reduction method.
4. Write the chemical equations involved in the electrolytic reduction of aluminium and copper metals.
5. With examples, explain why some metals are not extracted by the electrolytic reduction method.
6. Explain the following:
   (a) Although nitric acid is a strong oxidising agent, it is transported by using aluminium containers.
   (b) Common chemical reducing agents have no action on aluminium ore.
7. Write a chemical equation which shows the reducing property of tin.
8. Aluminium is obtained from alumina (Al_2O_3) by electrolysis. Explain why direct reduction of aluminium oxide with coke is not used.
9. The principal ore used for the extraction of tin is cassiterite. Give the name and formula of the tin compound present in cassiterite. Give the names of the two common impurities usually present in cassiterite.
10. In the electrolytic extraction of aluminium from a fused mixture of aluminium oxide and cryolite, about 80 kg of cryolite are lost when one ton of aluminium is produced.

    (a) What happens to this cryolite?

    (b) Why is aluminium being reduced instead of sodium in this electrolysis?

Chapter Four Transition elements

Introduction

The periodic table of elements is made up of four blocks namely *s, p, d*, and *f*-blocks. The transition elements are metallic elements that are found in the *d*-block and serve as a bridge between the two sides of the periodic table; *s* and *p*-blocks. These elements have many uses, including making alloys, ornaments, and being used as catalysts in many chemical reactions. In this chapter, you will learn about the general concepts on transition elements, characteristics of transition elements, as well as ligands and formation of complexes.

4.1 General concepts on transition elements

Chemical elements in the periodic table are classified according to their groups or periods. Based on electronic configurations, the periodic table can be divided into blocks denoting which sublevel is in the process of being filled. If the electrons are filled in an *s*-orbital, the elements belong to the *s*-block. If the last electrons are filled in *p*, *d* or *f*-orbitals, the elements belong to the *p*, *d* or *f*-blocks, respectively. The *s*-block is comprised of groups 1 and 2. The *p*-block includes groups 13 to 18 except helium. The *d*-block is situated between *s*-block and *p*-block (Chapter one, Table 1.5). The *d*-block elements are further classified into four series as follows:

(a) The first series consists of elements from scandium, Sc (Z = 21) to zinc, Zn (Z = 30) where *Z* is the atomic number. These elements lie in the fourth period of the periodic table.

(b) The second series consists of elements from yttrium Y (Z = 39) to cadmium, Cd (Z = 48). These elements lie in the fifth period of the periodic table.

(c) The third series consists of elements from lanthanum, La (Z = 57) to lutetium, Lu (Z = 71) and from hafnium, Hf (Z = 72) to mercury, Hg (Z = 80). These elements lie in the sixth period of the periodic table.

(d) The fourth series consists of elements from actinium, Ac (Z = 89) and those beyond rutherfordium, Rf (Z = 104). These elements lie in the seventh period of the periodic table.

The *f*-block includes the lanthanides (Z = 57 to 71) and the actinides (Z = 89 to 103). These are the inner transition metals.

The *d*-block elements are called *transition elements* because they exhibit transition behaviours between the highly reactive ionic-compounds forming *s*-block elements (electropositive elements) on one side and *p*-block elements (electronegative elements) on the other side. For an element to be considered as a transition element, it must have at least one electron in the *d*-orbital or forms at least one ion which has 1 to 9 electrons in the *d*-orbitals (partially filled *d*-orbitals). This chapter considers only the first series of the transition elements which include scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, and zinc. Zinc does not qualify to be a transition element because it has full-filled *d*-orbitals. It also forms compounds in which the *d*-orbitals are full-filled. However, since zinc is the last element of the first row of transition elements, its chemistry is discussed along with that of the first row transition elements for comparison purposes.

The *d*-block elements contain two electrons in their *ns*-orbitals while the differentiating electron enters an available (n-1) d orbital. Copper and chromium show exceptions by having one electron in the *ns*-orbital. Table 4.1 shows the electronic configurations of the first transition series for the atoms and ions.

Table 4.1 Electronic configuration of atoms and corresponding ions of the first series of transition elements

Element symbol	Atomic number	Electronic configuration of atoms	Electronic configuration of ions (M^{2+})	Electronic configuration of ions (M^{3+})	Number of unpaired *d*-electrons in M
Sc	21	[Ar]$3d^{1}4s^{2}$	[Ar]$3d^{1}$	[Ar]	1
Ti	22	[Ar]$3d^{2}4s^{2}$	[Ar]$3d^{2}$	[Ar]$3d^{1}$	2
V	23	[Ar]$3d^{3}4s^{2}$	[Ar]$3d^{3}$	[Ar]$3d^{2}$	3
Cr	24	[Ar]$3d^{5}4s^{1}$	[Ar]$3d^{4}$	[Ar]$3d^{3}$	5
Mn	25	[Ar]$3d^{5}4s^{2}$	[Ar]$3d^{5}$	[Ar]$3d^{4}$	5
Fe	26	[Ar]$3d^{6}4s^{2}$	[Ar]$3d^{6}$	[Ar]$3d^{5}$	4
Co	27	[Ar]$3d^{7}4s^{2}$	[Ar]$3d^{7}$	[Ar]$3d^{6}$	3
Ni	28	[Ar]$3d^{8}4s^{2}$	[Ar]$3d^{8}$	[Ar]$3d^{7}$	2
Cu	29	[Ar]$3d^{10}4s^{1}$	[Ar]$3d^{9}$	[Ar]$3d^{8}$	0
Zn	30	[Ar]$3d^{10}4s^{2}$	[Ar]$3d^{10}$	[Ar]$3d^{9}$	0

The unexpected electronic configurations of chromium and copper are the results of the extra stability acquired from their half-filled or full-filled sub-shells. For chromium, the expected configuration, [Ar]$3d^{4}4s^{2}$ is less stable compared to chromium with a configuration [Ar]$3d^{5}4s^{1}$ (half-filled structure).The [Ar]$3d^{5}$ is slightly stable than the [Ar]$3d^{4}$. Conversely, copper has a stable electronic configuration of $3d^{10}4s^{1}$ instead of $3d^{9}4s^{2}$. A full-filled $3d^{10}$ results into a more stable structure compared to the partially filled $3d^{9}$.

Example 4.1

Although zinc and scandium belong to the *d*-block elements of the periodic table, they are not transition elements. Justify this statement with reference to the definition of transition element.

Solution

By definition, a transition element is the one which forms at least one compound in which its *d*-orbitals are partially filled. Zinc forms compounds in which it exhibits only one oxidation state of +2 (Zn^{2+}, [Ar] $3d^{10}4s^{0}4p^{0}$) and scandium forms compounds in which it exhibits only one oxidation state of +3 (Sc^{3+}, [Ar] $3d^{0}4s^{0}4p^{0}$). Looking at the electronic configurations of Zn^{2+} and Sc^{3+}, it is clear that the *d*-orbitals in Zn^{2+} are full-filled while the *d*-orbitals in Sc^{3+} are empty. Hence, based on the definition of the transition elements, zinc and scandium do not qualify as transition elements.

4.2 Characteristics of transition elements

4.2.1 Physical properties of transition elements

Transition elements are metals with good mechanical properties which make them useful for many industrial applications. The following are some of the physical properties of the transition elements:

(a) They have high tensile strengths; that is, they can withstand high stresses and loads without fracturing, hence can be used in construction.

(b) They are ductile, thus, they can be drawn into wires.

(c) They are malleable, therefore, can be pressed to form sheets.

(d) They have high melting and boiling points; consequently, they can withstand high temperatures.

(e) They are good conductors of heat and electricity; therefore, they are used to make electric cables.

Other physical properties of the first–row *d*-block elements are summarised in Table 4.2.

Table 4.2 Selected properties of the first- row *d*-block elements

Element symbol	Atom number	Atomic radius, Å	Ionic radius, Å	Boiling point, °C	Melting point, °C	Density, g cm^{-3}
Sc	21	1.44	0.81	2830	1539	2.99
Ti	22	1.32	0.76	3260	1680	4.49
V	23	1.22	0.74	3450	1710	5.96
Cr	24	1.17	0.69	2642	1890	7.20
Mn	25	1.17	0.66	2100	1247	7.43
Fe	26	1.16	0.64	3000	1528	7.86
Co	27	1.16	0.63	2900	1490	8.90
Ni	28	1.15	0.63	2730	1452	8.90
Cu	29	1.17	0.73	2600	1083	8.92
Zn	30	1.24	0.74	906	419	7.14

4.2.2 Chemical properties of transition elements

Transition elements exhibit peculiar chemical properties which are not shown by other elements. The properties of these elements are attributed by the splitting of the *d*-orbitals (d_{z^2}, $d_{x^2-y^2}$, d_{xy}, d_{xz}, and d_{yz}) into the upper and lower sets with slightly different energies. The upper set is known as e_g set while the lower is called t_{2g} set. The e_g set is slightly high in energy compared to the t_{2g} set (Figure 4.1). In this section, the common characteristics of the transition elements will be described.

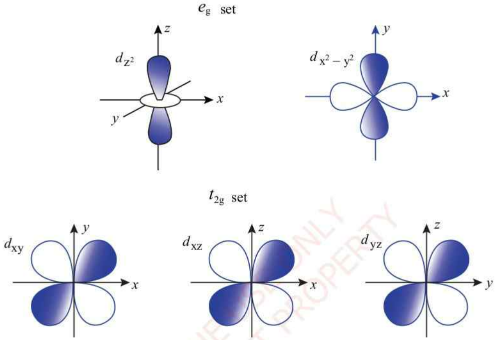


Figure 4.1 *d*-orbitals in e_g set and t_{2g} set

Variable oxidation states

The *d*-block elements show a wide range of oxidation states. Usually, the highest oxidation state of a metal corresponds to its group number in the periodic table. The variable valences are due to the ability of the transition elements to lose electrons from both the outer *quantum shell* and the *penultimate shell* to form ions. The 4*s* and 3*d* orbitals have very little energy differences and hence can be used for valence purposes. Table 4.3 shows the most common oxidation states of the first series of the transition elements.

Table 4.3 Common oxidation states shown by the transition elements of the first series

Element symbol	Common oxidation states						
Sc			+3				
Ti		+2		+4			
V		+2	+3	+4	+5		
Cr		+2	+3			+6	
Mn		+2	+3	+4		+6	+7
Fe		+2	+3				
Co		+2	+3				
Ni		+2					
Cu	+1	+2					
Zn		+2					

As indicated in Table 4.3, the most common oxidation state is +2 which is acquired by losing two electrons. Oxidation states higher than +2 can be obtained upon subsequent removal of electrons from the 3*d*-orbital. Manganese compared with the other first-row transition elements has the greatest number of oxidation states.

Example 4.2

Give the oxidation states of manganese in MnO_4^-, MnO_2, and $MnCl_2$ and account for the observed differences.

Solution

The oxidation state of manganese in MnO_4^- is +7, in MnO_2 is + 4, and in $MnCl_2$ is +2. It is therefore concluded that, manganese exhibits a property of variable oxidation states. This property is attributed to its ability to lose electrons from both the outer quantum shell and the penultimate shell.

Catalytic properties

Most of the transition elements and their compounds, particularly oxides, have good catalytic properties. The catalytic properties of the transition elements and their compounds are associated with the presence of vacant *d*-orbitals, the tendency to exhibit variable oxidation states, the tendency to form reaction intermediates with reactants, and the presence of defects (irregular arrangements of atoms) in their crystal lattices. Moreover, the catalytic properties of the transition elements are associated with their ability to provide surfaces where reacting molecules can temporarily attach to allow rearrangement of atoms. Commonly used catalysts in various industries are nickel, iron, vanadium, manganese, and platinum. Nickel or platinum are used in catalytic hydrogenation, iron is used in the Haber process, and vanadium pentoxide is used in the contact process. Examples of the reactions in which the transition elements exhibit catalytic properties are presented below.

(a) Iron and nickel play the roles of catalysts in the Haber process and in the hydrogenation reaction, respectively, by providing contact surface areas to facilitate the reactions.

(i) $N_2(g) + 3H_2(g) \xrightleftharpoons{Fe} 2NH_3(g)$

(ii) $CH_2{=}CH_2 + H_2(g) \xrightarrow{Ni} CH_3CH_3(g)$

In reactions (i) and (ii), Fe and Ni possess vacant low-lying 3*d*-orbitals which act as electron acceptors to form temporary bonds between the catalyst and reactant. This process brings the reactant particles closer enough to result into successful reaction.

(b) V_2O_5 and Fe^{3+} exhibit catalytic properties by varying their oxidation states to alter the rates of chemical reactions. When gaseous sulphur dioxide is passed together with air over a solid vanadium pentoxide catalyst, V_2O_5 oxidises SO_2 to SO_3 and itself gets reduced to V_2O_4 as shown in the first chemical equation (i) below. The V_2O_4 is then oxidised by oxygen to V_2O_5 as shown in the second chemical equation (ii). The net reaction equation can be represented as,

$$2SO_2(g) + O_2(g) \xrightleftharpoons{V_2O_5} 2SO_3(g)$$

with catalytic steps;

(i) $SO_2(g) + V_2O_5(s) \rightleftharpoons SO_3(g) + V_2O_4(s)$

(ii) $2V_2O_4(s) + O_2(g) \longrightarrow 2V_2O_5(s)$

(c) Similarly, in the reaction between I^- and $S_2O_8^{2-}$, Fe^{3+} ions catalyse the reaction by changing its oxidation state. The net reaction equation is,

$$2I^-(aq) + S_2O_8^{2-}(aq) \xrightleftharpoons{Fe^{3+}} I_2(aq) + 2SO_4^{2-}(aq)$$

with catalytic steps;

(i) $2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(g)$

Then, the produced Fe^{2+} reacts with $S_2O_8^{2-}$ according to the following reaction:

$$\text{(ii) } 2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \longrightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$$

In the given catalytic steps (i) and (ii), the transition elements vanadium in V_2O_5 and iron in Fe^{3+} allow electron transfer between the reactants and the products by means of the catalytic interchange between the two oxidation states, thus facilitating a redox cycle.

The formation of coloured compounds

Generally, the compounds of the transition elements are coloured. For example, hydrated copper(II) sulphate is blue, potassium permanganate is purple, and hydrated iron(II) sulphate is light green. The colours are characteristics of their hydrated salts or solutions. The cations of the transition elements become coloured only when they interact with other chemical species such as ions or molecules. The colours of the compounds depend on the types of the chemical species (ligands) which the transition metal cations interact with. The concept of colour formation in transition metals is explained by the Crystal Field Theory (CFT).

In the Crystal Field Theory, the transition metals form colour as a result of the splitting of the degenerate *d*-orbitals. The splitting of the *d*-orbitals of the central metal is a result of the electrostatic attraction between the ion pair electrons of the ligand and the nucleus of the central metal. Besides the electrostatic attraction between the ligand and the nucleus of the central metal, repulsion occurs between the ion pair electrons and the electrons of the central metal. This results into the splitting of the degenerate *d*-orbitals into the two sets. The splitting raises two of the *d*-orbitals, d_{z^2} and $d_{x^2-y^2}$ to a higher energy level (the e_g set) while the remaining orbitals, d_{xy}, d_{xz}, and d_{yz} occupy a lower energy level (the t_{2g} set) as shown in Figure 4.2.

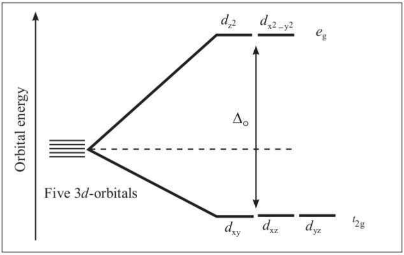


Figure 4.2 The splitting of *d*-orbitals in octahedral complex

The extent to which the orbitals are separated depends on the nature of the ligand. The stronger the ligand, the bigger the splitting effect and vice versa. The energy difference between the e_g and t_{2g} is known as the *Crystal Field Stabilisation Energy* (CFSE). It is a characteristic physical quantity that depends on the strength of the ligand.

The spatial distribution of the degenerate orbitals depends on the geometry of the complex formed between the central metal and the ligand. Stronger splitting results into a greater energy difference (Δ_o) between the e_g and the t_{2g} sets. If the energy difference is large, the electrons will absorb more energy and transmit radiations of higher wavelength and lower frequency (colours of visible light are given in terms of wavelengths or frequencies). The electron movements between the two groups of the *d*-orbitals absorb energy and transmit radiations of specific wavelengths corresponding to the specific colours that are observed.

Compounds of some of the 1st series of the *d*-block elements are colourless when no electrons are present in the *d*-orbitals as for Sc^{3+} or when all the *d*-orbitals are filled, as for Cu^+ and Zn^{2+}. Only complexes of the transition elements having partially filled *d*-orbitals form coloured compounds. Examples of ionic complexes of the transition elements which form colours are given in Table 4.4.

Table 4.4 Coloured complexes of some transition elements

Ionic complex	Colour
$[Co(H_2O)_6]^{2+}$	Pinkish-red
$[Fe(CN)_6]^{4-}$	Greenish-yellow
$[Fe(H_2O)_6]^{2+}$	Pale-green
$[Fe(H_2O)_6]^{3+}$	Brownish-yellow
$[Cu(NH_3)_4]^{2+}$	Deep-blue
$[Cu(H_2O)_4]^{2+}$	Pale-blue

Consider the different colours of the complexes of cobalt in which H_2O, NH_3, and CN^- are ligands. The complex $[Co(H_2O)_6]^{3+}$ is blue, $[Co(NH_3)_6]^{3+}$ is orange, and $[Co(CN)_6]^{3-}$ is yellow. The effects of the different ligands on the colours of the cobalt complexes can be explained as follows: The aqua ligand (H_2O) induces a small energy difference in Co^{3+} and low energy photons are absorbed; thus $[Co(H_2O)_6]^{3+}$ appears blue. The ammine ligand (NH_3) induces a larger energy difference and high energy photons are absorbed; thus $[Co(NH_3)_6]^{3+}$ appears orange. The cyano ligand (CN^-) induces the largest energy difference and highest energy photons are absorbed; thus $[Co(CN)_6]^{3-}$ appears yellow. Table 4.5 gives the summary of the effects produced by different ligands on the colours of the cobalt complexes.

Table 4.5 Effects of different ligands on the colours of the cobalt complexes

Ion	**$[Co(CN)_6]^{3-}$**	**$[Co(NH_3)_6]^{3+}$**	**$[Co(H_2O)_6]^{3+}$**
Colour of ion	Yellow	Orange	Blue
Colour absorbed	Violet	Blue	Orange
Energy difference	Largest	Intermediate	Smallest
Ligand involved	Cyano, CN^-	Ammine, NH_3	Aqua, H_2O
Splitting ability of the ligands	Strongest	Intermediate	Weakest

Magnetic properties

Magnetic properties explain how a material behaves when placed in magnetic field. The magnetic properties of an element or ion are due to the presence of unpaired electrons in the *d*-orbitals. If unpaired electrons are present in the *d*-orbital of an atom, ion or molecule, the material will be weakly attracted by a magnet and is classified as a *paramagnetic material*. If the unpaired electrons are many, the material is more strongly attracted by a magnet and is classified as *ferromagnetic material*. If an atom contains no unpaired electrons, the material will not respond to magnetism and is classified as a *diamagnetic material*.

Unpaired electrons spin about their own axis and in so doing create a small magnet (movement of charge creates magnetism). The small magnets of spinning electrons have north and south poles. If an external magnet is introduced, these small magnets will be attracted and the material will show magnetic properties. Paired electrons spin in opposite directions and their small magnets have opposite orientations, thus cancelling each other. Materials with paired electrons do not respond to external magnetism. Table 4.6 shows box electronic configurations of the first transition metal series.

The number of unpaired electrons determines the strength of the magnetic moment. The higher the number of unpaired electrons, the higher the magnetic moment and the greater the magnetic behaviour of the substance. Furthermore, the magnetic properties of the compounds are affected by the types of ligands surrounding the central atom in a complex compound. This is because when the ligands approach the central atom, they cause repulsion of the *d*-electrons of the central atom; thus, the orbitals split into sublevels. The extent to which the *d*-orbitals split depends on the strength of the external electric field of the ligands.

Table 4.6 Arrangement of valence shell electrons of the first transition metal series

Element symbol	Electronic configuration						
		3*d*					4*s*
Sc	[Ar]	↑					↑↓
Ti	[Ar]	↑	↑				↑↓
V	[Ar]	↑	↑	↑			↑↓
Cr	[Ar]	↑	↑	↑	↑	↑	↑
Mn	[Ar]	↑	↑	↑	↑	↑	↑↓
Fe	[Ar]	↑↓	↑	↑	↑	↑	↑↓
Co	[Ar]	↑↓	↑↓	↑	↑	↑	↑↓
Ni	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑↓
Cu	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Zn	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

Taking the complexes of Fe^{2+} as examples, when the ligands approach the cation (Fe^{2+}) along its six axes, the energy of d_{z^2} and $d_{x^2-y^2}$ will be raised above that of d_{xy}, d_{xz}, and d_{yz}. Ligands such as NH_3, H_2O, F^-, Cl^-, Br^-, and I^- have low external electric fields. The split caused by these ligands is always small and therefore, electrons are distributed according to the Hund's Rule of maximum multiplicity. Therefore, since Fe^{2+} has six electrons in the five *d*-orbitals, the spread will be as shown in Figure 4.3. Each of the unpaired electrons in the split *d*-orbital will exhibit a magnetic moment. This compound will strongly be paramagnetic and it is said to be of high spin.

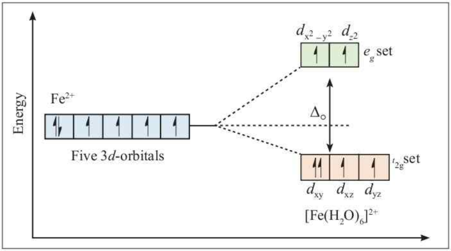


Figure 4.3 Splitting of *d*-orbitals of Fe^{2+} caused by weak field ligands

Conversely, when the Fe^{2+} is coordinated by ligands having a high external electric field such as CN^- and ethylenediamine (en), the split is so large that the electrons are forced to form pairs in the lower t_{2g} orbitals as shown in Figure 4.4. Pairing of electrons results into disappearance of the paramagnetic property, thus $[Fe(CN)_6]^{4-}$ is a diamagnetic low spin complex.

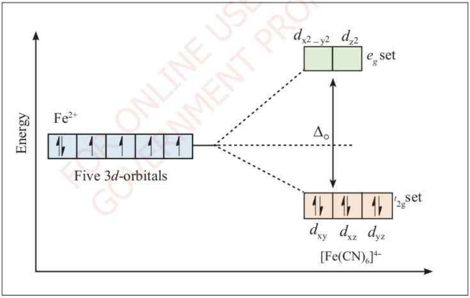


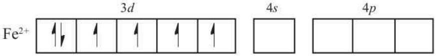
Figure 4.4 Splitting of *d*-orbitals of Fe^{2+} caused by strong field ligands

Example 4.3

Account for the fact that $[Fe(CN)_6]^{4-}$ is diamagnetic whereas $[FeCl_4]^{2-}$ is paramagnetic.

Solution

In both complexes, the central metal oxidation state is +2 (Fe^{2+}) with the valence shell electronic configuration of $3d^6 4s^0 4p^0$ and the electrons are arranged as follows:



When chloride ligands approach Fe^{2+}, they cause splitting of the d-orbitals but to a lesser extent as they are weak field ligands. As a result, the arrangements of the electrons in the d-orbitals remain unchanged in e_g and t_{2g} sets as shown in Figure 4.5.

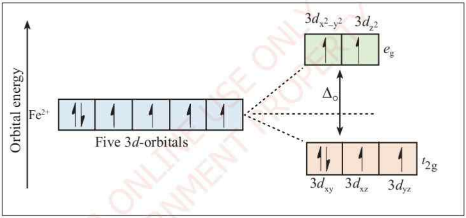


Figure 4.5 Splitting of d-orbital of Fe^{2+} caused by weak field ligands leading to paramagnetism

Conversely, CN^- ligands which are strong field ligands cause large splitting of d-orbitals. The large energy gap between the e_g and t_{2g} sets, prevents electrons from being distributed to the higher energy level and they fall back from e_g to t_{2g} as shown in Figure 4.6.

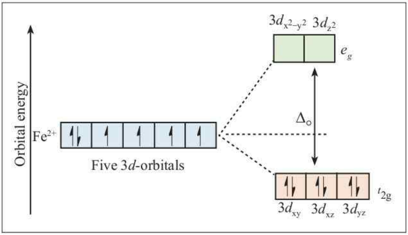


Figure 4.6 Splitting of *d*-orbital of Fe^{2+} caused by strong field ligands leading to diamagnetism

The electron pairing leads to the loss of the paramagnetic property of the material and hence $[Fe(CN)_6]^{4-}$ is diamagnetic, whereas $[FeCl_4]^{2-}$ is paramagnetic.

Alloy formation

When transition metals are fused with other metals, they form alloys. An *alloy* is a solid mixture obtained by fusing a metal with another metal(s) or non-metal. Transition elements form alloys with other metals which are not transition metals or with other transition metals. For example, steels are alloys of iron with metals such as chromium, vanadium, molybdenum, tungsten, and manganese or with other elements such as carbon. Alloys of transition elements have desired properties compared to the pure elements. Looking at the atomic radii of the first series of the transition elements (Table 4.2), it can be noted that they are not much different from each other. Because of this property, they can very easily replace each other in the lattice and form solid mixtures over an appreciable composition range, attributed to their ability to form alloys.

4.3 Ligands and formation of complexes

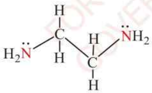
One of the most important chemical properties of the *d*-block elements is their ability to form complexes. A complex *is a molecule or ion composed of a central metal atom or ion surrounded by negative, positive, or neutral ligands*. Ligands *are ions or molecules which bind to the central atom in a complex*. They are either polar molecules such as H_2O, NH_3 or anions such as Cl^- and CN^- which have at least one lone pair of electrons to be shared with a central metal atom or ion.

4.3.1 Ligands

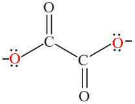
Ligands are attached to the central metal ion by a coordinate bond. The atom in a ligand that is bound directly to the central metal atom or ion is known as the *donor atom*. The number of the donor atoms surrounding the central metal atom or ion in a complex is called the *coordination number*. For example, in $[Cu(NH_3)_4]^{2+}$, the coordination number is four and the donor atom is nitrogen. Depending on the number of the donor atoms present in the ligand, ligands are classified as monodentate, bidentate or polydentate (Table 4.7).

Monodentate ligands have only one donor atom per ligand. Examples of monodentate ligands are H_2O, NH_3, and Cl^-. H_2O donates electrons through oxygen atom, O; NH_3 donates through the nitrogen atom, N; and Cl^- donates through the electron pairs present on the chlorine atom. Ambidentate is a monodentate ligand which uses one atom at a time to form coordinate bonds with the central metal atom or ion. For example, the nitrite ion (NO_2^-) can bind to the central metal atom/ion at either the nitrogen atom or one of the oxygen atoms. The thiocyanate ion (SCN^-) can bind to the central metal at either the sulphur or the nitrogen, while the CN^- binds to the central metal at either the carbon or nitrogen.

Bidentate ligands have two donor atoms per ligand molecule. Atoms in red are donor atoms. Examples of the bidentate ligands are:



Ethylenediamine (en)



Oxalate ion (oxalato)

Ligands with more than two donor atoms are referred to as *polydentate ligands*. An example of the polydentate ligands is ethylenediaminetetraacetic acid (EDTA).

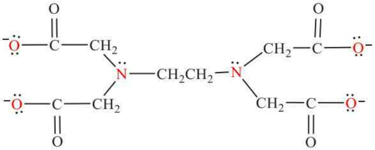
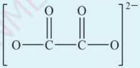
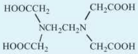


Table 4.7 Examples of some common ligands

Ligand name	Ligand formula	Classification
Bromo	Br^-	Monodentate
Iodo	I^-	Monodentate
Chloro	Cl^-	Monodentate
Thiocyanato	SCN^-	Monodentate
Aqua	H_2O	Monodentate
Nitro	ONO^-	Monodentate
Fluoro	F^-	Monodentate
Ammine	NH_3	Monodentate
Hydroxo	OH^-	Monodentate
Cyano	CN^-	Monodentate
Carbonyl	CO	Monodentate
Nitrosyl	NO	Monodentate
Methylamine	CH_3NH_2	Monodentate
Ethylenediamine (en)	$H_2NCH_2CH_2NH_2$	Bidentate
Oxalato	 $\left[O-\overset{\overset{O}{\Vert}}{C}-\overset{\overset{O}{\Vert}}{C}-O\right]^{2-}$	Bidentate
Diethylenetriamine	$H_2N(CH_2)_2NH(CH_2)_2NH_2$	Polydentate
Ethylenediaminetetraacetic acid (EDTA)		Polydentate

4.3.2 Formation of complexes

The transition elements differ in their ability to form complex compounds. This is attributed by the sizes of the cations and the presence of empty or vacant *d*-orbitals.

Ionic radii

The term ionic radius *refers to half the distance between two bonded ions*. It indicates the distance from the nucleus of an ion to a point where it has an influence on its electron cloud. Ionic radius is important in determining the polarising power of a cation or the polarisability of anions. It is a measure of charge density of the ion which is given by the ratio of the ionic charge to the ionic radius. The ionic radii for the *d*-block transition metals are shown in Table 4.2.

The effect of ionic size on complex compound formation is explained in terms of the polarising power of the central metal ion. *Polarising power* refers to the ability of a central metal ion to deform a ligand. The smaller the size of a central metal ion, the higher the polarising power. The more a central metal ion polarises a ligand, the higher the chance for complex compound formation.

Vacant *d*-orbitals

The atom with vacant *d*-orbitals acts as an electron pair acceptor; therefore, it is a Lewis acid. The central metal atom or ion together with all the coordinated ligands form what is known as the *coordination sphere*. Looking at the coordination sphere of a complex compound or ion, it becomes possible to classify complexes into neutral, anionic and cationic. Negatively charged complexes such as $[Fe(CN)_6]^{3-}$, $[CoCl_4]^{2-}$ and $[Al(H_2O)_2(OH)_4]^-$ are called *anionic complexes*. They have a net negative charge outside the coordination sphere. On the other hand, complexes that carry a net positive charge outside the coordination sphere such as $[Cu(H_2O)_6]^{2+}$, and $[Co(NH_3)_6]^{3+}$ are called *cationic complexes*. Complexes whose coordination spheres have no charge outside their coordination sphere are called *neutral complexes*. Therefore, $[Ni(CO)_4]$ and $[Pt(NH_3)_2Cl_4]$ are neutral complexes.

Example 4.4

Choose one complex cation of cobalt and one complex anion of nickel and complete the following table to show the formula of the complex ion, type of ligand(s), and oxidation state of the central metal.

Element	Formula of the selected complex	Ligand(s)	Type of ligand	Oxidation state
Cobalt				
Nickel				

Solution

Element	Formula of the selected complex	Ligand (s)	Type of ligand	Oxidation state
Cobalt	$[Co(en)_2(H_2O)CN]^{2+}$	en H_2O CN^-	Bidentate Monodentate Monodentate	+3
Nickel	$[Ni(CN)_4]^{2-}$	CN^-	Monodentate	+2

Exercise 4.1

1. (a) Define the following terms:

   (i) Transition element (ii) Oxidation state

   (iii) Coordination number (iv) Ligand

   (b) Complete the following statements for the complex ion $[Co(en)_2(H_2O)CN]^{2+}$

   (i) en is the abbreviation for _______________

   (ii) The oxidation state of Co is___________

   (iii) The coordination number of Co is_________

   (iv) _________is a bidentate ligand.

2. Account for the following observations:

   (a) Hydrated copper(II) salts are coloured but the anhydrous salts are colourless or white.

   (b) Chromium is less reactive than its standard reduction potential.

(c) $[FeF_6]^{3-}$ has stronger magnetic field than $[Fe(CN)_6]^{3-}$.

(d) A concentrated aqueous copper(II) chloride solution is bright green in colour. When diluted with water, the solution becomes light blue.

3. Transition elements and their compounds are used as catalysts. Briefly, explain the attributes of the transition elements which are responsible for their catalytic activity.

4. Which is a stronger oxidising agent in aqueous solution, Mn^{3+} or Cr^{3+}? Explain your choice.

Coordination number and geometry of complexes

Complex compounds are formed by a central metal atom or ion directly coordinated to the ligands. The ligands donate an electron pair to the empty *d*-orbitals of the central metal. The number of ligands which is directly coordinated to the central metal ion is the coordination number of that atom in the complex. The most frequent coordination numbers for the complexes of the first transition metal series are 6, 5, and 4. The coordination numbers depend on the relative sizes of the central metal atoms or ions, the ligands surrounding, and the charges of the ligands. Large ligands favour low coordination numbers, while small ligands favour high coordination numbers. Neutral ligands favour high coordination numbers, while anionic ligands favour low coordination numbers. For example, on complexing with iron(II) ion the chloride ion (a large ion) forms $[FeCl_4]^{2-}$, while the fluoride ion (a small ion) forms $[FeF_6]^{4-}$. On complexing with nickel(II), ammonia (neutral ligand) forms $[Ni(NH_3)_6]^{2+}$, while the chloride ion (an anionic ligand) forms $[NiCl_4]^{2-}$ ion.

The coordination number is usually very much associated with the geometry of the complex. Considering the most common coordination numbers 4 and 6, the coordination number of 4 forms two types of geometries, namely a *square planar* and a *tetrahedral,* while coordination number 6 has an *octahedral geometry*. The illustration is given by Valence Bond Theory which predicts the use of unoccupied orbitals.

Square planar complexes such as $[Ni(CN)_4]^{2-}$ and $[Pt(NH_3)_4]^{2+}$, have central metal atoms or ions surrounded by four ligands at the four corners of the square making an angle of 90°. The square planar geometry is commonly formed when the ions with electronic configuration of $(n\text{-}1)d^8$ form dsp^2 hybridised orbitals. This is illustrated by the formation of $[Ni(CN)_4]^{2-}$ in Figure 4.7.

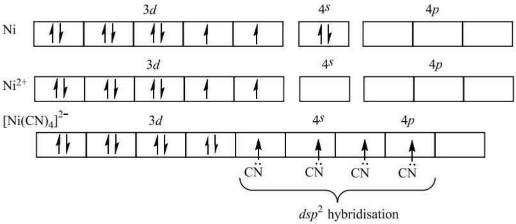


Figure 4.7 The dsp^2 hybridisation in $[Ni(CN)_4]^{2-}$

The outermost electronic configuration of Ni^{2+} is $3d^84s^04p^0$. In the formation of $[Ni(CN)_4]^{2-}$, two unpaired 3*d* electrons pair in one orbital and the vacant 3*d* orbital mixes with the 4*s* and two 4*p*-orbitals forming four dsp^2 hybrid orbitals lying in the same plane with their four lobes directed to the four corners of the square (Figure 4.8).

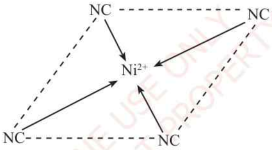


Figure 4.8 Square planar complex ion of $[Ni(CN)_4]^{2-}$

Tetrahedral complexes, such as $[CoCl_4]^{2-}$, $[CuCl_4]^{2-}$, and $[Cu(H_2O)_4]^{2+}$, have a central metal atom or ion at the centre of a regular tetrahedron with ligands making the angle of around 109.5°. The formation of tetrahedral geometry in $[Cu(H_2O)_4]^{2+}$ can be described by using the illustration shown Figure 4.9.

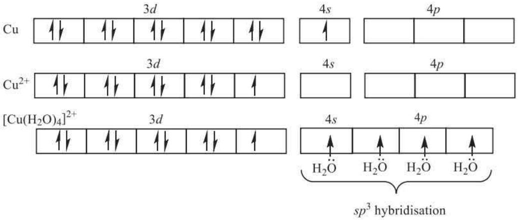


Figure 4.9 The sp^3 hybridisation in $[Cu(H_2O)_4]^{2+}$

Cu^{2+} has the outermost electronic configuration of $3d^94s^04p^0$. As ligands (water molecules) approach the central metal atom, the 4*s* mixes with three 4*p*-orbitals forming four sp^3 hybrid orbitals with their lobes at 109.5° apart, forming the corners of the tetrahedron as shown in Figure 4.10.

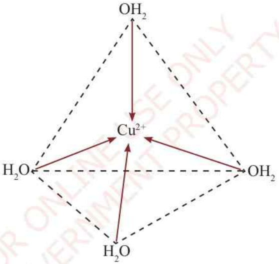


Figure 4.10 Tetrahedral complex ion of $[Cu(H_2O)_4]^{2+}$

An octahedral geometry has a central metal atom or ion coordinated to six ligands. The four of the ligands are in one plane with the fifth one above the plane and the sixth below the plane. An example of an octahedral complex is $[Fe(CN)_6]^{4-}$ (Figure 4.11).

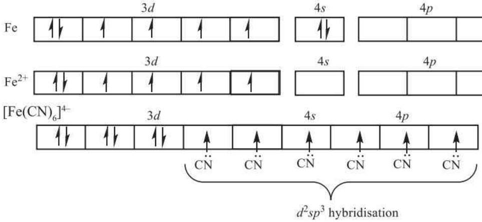


Figure 4.11 The d^2sp^3 hybridisaton in $[Fe(CN)_6]^{4-}$

Fe^{2+} has the ground state outermost configuration of $3d^6 4s^0 4p^0$. As CN^- ligand (strong field ligand) approaches Fe^{2+}, the six electrons in the 3*d* orbitals pair off leaving two vacant *d*-orbitals which hybridise with the 4*s*-orbital and three 4*p*-orbitals forming six d^2sp^3 hybrid orbitals with octahedral geometry (Figure 4.12).

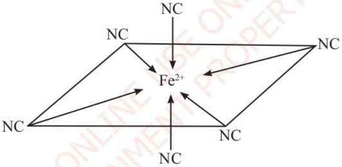


Figure 4.12 Octahedral complex ion of $[Fe(CN)_6]^{4-}$

Formation of a geometry depends on type of hybridisation of central metal ions or atoms. When the central metal ion or atom is *sp* hybridised, the bond angle is 180° and the shape of the complex is linear. Table 4.8 summarises the structures of the complexes by giving the mode of hybridisation of the atomic orbitals of the central metal atom, shapes of the complex ions, coordination numbers, bond angles of the complex crystals, and examples of the complexes encountered.

Table 4.8 Hybridisation of a central metal ion and geometries of complexes

Hybridisation of a central metal	**Coordination number**	**Bond angles of the complex**	**Shape of the complex**	**Example(s)**
sp	2	180°	Linear	$[CuCl_2]^-$
sp^2	3	120°	Trigonal planar	$[Cu(CN)_3]^{2-}$
sp^3	4	90°	Square planar	$[Pt(NH_3)_4]^{2+}$, $[Cu(NH_3)_4]^{2+}$ and $[Ni(CN)_2Br_2]^{2-}$
sp^3	4	109.5°	Tetrahedral	$[Zn(NH_3)_4]^{2+}$ and $[MnCl_4]^{2-}$
dsp^3	5	120° and 90°	Trigonal bipyramidal	$[Fe(CO)_5]$
sp^3d^2 or d^2sp^3	6	90°	Octahedral	$[V(CN)_6]^{4-}$, $[Cr(NH_3)_4Cl_2]^+$, $[Mn(H_2O)_6]^{2+}$ and $[FeCl_6]^{3-}$

Example 4.5

Draw one possible structure of $[Co(NH_3)_4(NO_2)_2]^+$.

Solution

The possible structure of $[Co(NH_3)_4(NO_2)_2]^+$ is as shown in Figure 4.13:

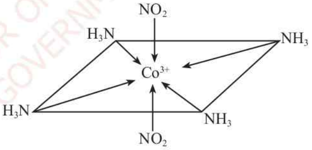


Figure 4.13 Structure of $[Co(NH_3)_4(NO_2)_2]^+$

Naming complexes using the IUPAC system

In order to have common names of the complexes, a universal system of naming them was adopted. Complexes are named by using the International Union of Pure and Applied Chemistry (IUPAC) system. The following are the rules used for naming complexes:

1. The cations are always named before the anions. The oxidation state of the central metal atom or ion is shown in Roman numeral in brackets immediately after its name. For example, the complex $[Fe(H_2O)_6]Cl_3$ is named as hexaaquairon(III) chloride and $[Cu(NH_3)_4]SO_4$ is named as tetraamminecopper(II) sulphate.

2. Within a complex, the ligands are named first followed by the central metal ion. Within each category, if there are more than one types of ligands, they are named in an alphabetical order. For example, the complex $[Co(NH_3)_4Cl_2]^+$ is named tetraamminedichlorocobalt(III) ion, $[Pt(NH_3)_2C1_4]$ is named diamminetetrachloroplatinum(IV) and $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is named tetraamminediaquacopper(II) ion.

3. The number of the same ligands present must be specified by using the following prefixes: *di* = 2 ligands, *tri* = 3 ligands, *tetra* = 4 ligands, *penta* = 5 ligands, *hexa* = 6 ligands, and so on.

4. The names of the negative ligands end up with the suffix *-o*, as in CN^- (cyano) and Cl^- (chloro). Neutral ligands usually retain their normal names except for such special cases as H_2O (aqua), NH_3 (ammine), CO (carbonyl), and NO (nitrosyl).

5. Anionic complexes are those which have an overall negative charge outside the square brackets. These end up in the suffix *-ate* often appended to the Latin or English name of the metal. For example, $[Co(CN)_6]^{3-}$ is named hexacyanocobaltate(III) ion, $[CuC1_4]^{2-}$ is named tetrachlorocuprate(II) ion, $[Fe(CN)_6]^{3-}$ is named hexacyanoferrate(III) ion, and $[Fe(CN)_6]^{4-}$ is named hexacyanoferrate(II) ion. Table 4.9 gives some Latin names used for some metal ions.

6. Cationic complexes are those which have an overall positive charge outside the brackets. These use the English names unchanged for the central metal ion. For example, $[Cr(NH_3)_4Cl_2)]^+$ is named tetraamminedichlorochromium(III) ion and $[Co(NH_3)_4Cl_2]^+$ is named tetraamminedichlorocobalt(III) ion.

7. If a ligand contains a Greek prefix as in ethylenediamine, the prefixes *bis*, *tris,* and *tetrakis* are used to indicate two, three, and four ligands present,

respectively. For example, the ligand $H_2NCH_2CH_2NH_2$ (ethylenediamine) already contains *di* therefore, if two such ligands are present as in $[Pt(en)_2Cl_2]^{2+}$, the name of $(en)_2$ is bis(ethylenediamine).

Table 4.9 Names used for some metal ions in anionic complexes

Common name	Symbol	Latin name for metal ions
Iron	Fe	Ferrate
Copper	Cu	Cuprate
Lead	Pb	Plumbate
Silver	Ag	Argentate
Gold	Au	Aurate
Tin	Sn	Stannate

Example 4.6

1. Give the IUPAC names of the following compounds:

   (a) $K_2[Fe(CN)_2Cl_2(NH_3)_2]$

   (b) $[Co(NH_3)_4(NO_2)_2]Cl$

2. To which class of the complexes do the compounds in (1) belong?

Solution

1 (a) The compound, $K_2[Fe(CN)_2Cl_2(NH_3)_2]$ consists of a non-complex cation and a complex anion. The name starts by first naming the cation (potassium) followed by the name of the complex anion which is obtained by first giving the names of the ligands in alphabetical order. Then, the name of the central atom is followed with the indication of its oxidation state. Thus, its name is potassium diamminedichlorodicyanoferrate(II).

(b) The compound, $[Co(NH_3)_4(NO_2)_2]Cl$ consists of a complex cation and a non-complex anion. The cation is named first followed by the anion. The complex cation is named by first naming the ligands in alphabetical order followed by the name of the central atom with its oxidation state. Lastly, the name of the non-complex anion follows. Thus, the name of the compound is tetraamminedinitrocobalt(II) chloride.

2. (a) Anionic complex (b) Cationic complex

Effects of complexes formation on the solubility of some compounds

Slightly soluble compounds of metals are found to dissolve when excess ammonia, chloride ion or hydroxide ion is added to their solutions. The following observations serve as illustrative examples:

(a) When sodium hydroxide solution is added to a solution of zinc nitrate, a white precipitate of zinc hydroxide is formed. An addition of excess sodium hydroxide solution results into dissolution of the precipitate. To account for this observation, consider the equilibrium established between the solid zinc hydroxide and its ions (Zn^{2+} and OH^-) which is illustrated in the following chemical reaction:

$$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq)$$

According to the Le Châtelier's principle, dissolution of $Zn(OH)_2$ is facilitated by the consumption of Zn^{2+} or OH^- from the equilibrium system. When excess OH^- is added from an extra solution of NaOH, the following chemical reaction takes place:

$$Zn^{2+}(aq) + 4OH^-(aq) \rightleftharpoons \left[Zn(OH)_4\right]^{2-}(aq)$$

This drives the equilibrium to the right, hence facilitates dissolution of $Zn(OH)_2$.

(b) Similarly, when sodium hydroxide solution is added to a solution of copper(II) nitrate, a blue precipitate is formed as represented by the following chemical equation:

$$Cu(NO_3)_2(aq) + 2NaOH(aq) \longrightarrow Cu(OH)_2(s) + 2NaNO_3(aq)$$

The precipitates of copper(II) hydroxide dissolve to form a deep blue solution when ammonia solution is added. To account for this observation, consider the equilibrium which exists between the solid copper(II) hydroxide and its ions, Cu^{2+} and OH^-.

$$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$$

To dissolve $Cu(OH)_2$, Cu^{2+} ions or OH^- ions have to be consumed from the equilibrium system. This can be done by adding ammonia solution which furnishes NH_3 molecules which react with Cu^{2+} ions.

$$Cu^{2+}(aq) + 4NH_3(aq) \longrightarrow [Cu(NH_3)_4]^{2+}(aq)$$

To offset the effect produced by this reaction, more copper hydroxide dissolves to replace the consumed Cu^{2+} ions from the equilibrium system. Aqueous solutions containing Ag^+, Pb^{2+}, Cr^{2+}, and Ni^{2+} also show the same behaviours.

It can therefore be concluded that, complex formation affects the solubility of slightly soluble compounds of the transition elements.

Example 4.7

With the use of a chemical equation, show the effect of complex formation on the solubility of a slightly soluble hydroxide of a transition element.

Solution

Nickel(II) hydroxide is a slightly soluble hydroxide which dissolves in ammonia solution.

$$Ni(OH)_2(s) + 4NH_3(aq) \longrightarrow [Ni(NH_3)_4]^{2+}(aq) + 2OH^-(aq)$$

The formation of the complex $[Ni(NH_3)_4]^{2+}$ causes more $Ni(OH)_2$ to dissolve. It can therefore, be concluded that, complex formation facilitates the dissolution of slightly soluble hydroxides like $Ni(OH)_2$.

Exercise 4.2

1. A complex ion, $[Ni(CN)_2Br_2]^{2-}$ has a square planar geometry. Draw the possible structure of this complex.
2. (a) Define the following terms:
    - (i) Neutral complex
    - (ii) Cationic complex
    - (iii) Anionic complex

   (b) Classify the following complexes as neutral, cationic, and anionic:
    - (i) $[Co(NH_3)_2Cl_4]^-$
    - (ii) $[Co(NH_3)_3Cl_3]$
    - (iii) $[Co(NH_3)_4Cl_2]^+$
    - (iv) $[Cu_3(OH)_2(CO_3)_2]$
    - (v) $[Co(NO_2)_6]^{3-}$
    - (vi) $[Pt(en)_2Cl_2]^{2+}$

3. (a) What features make the transition elements to have the ability to form complexes?

   (b) With the aid of an example, show the effects of complex formation on the solubility of chromium(II) hydroxide in water.

4. Give the IUPAC names of the following compounds:

   (a) $[Co(NH_3)_4Cl_2]SO_4$

   (b) $[Cr(en)_2Cl_2]_3[Co(C_2O_4)_3]$

   (c) $[Cr(H_2O)_4Cl_2]Cl$

   (d) $[Co(en)_3]_2[Ni(CN)_2Br_2]_3$

   (e) $[Co(NH_3)_2Cl_4]^-$

5. Write the structures of the following compounds:

   (a) Dichlorobis(ethylenediamine)platinum(II) chloride
   (b) Sodium tetrachloronickelate(II)
   (c) Ammonium diaquabis(oxalato)nickelate(II)
   (d) Hexaammineiron(III) hexacyanochromate(III)
   (e) Aquabis(ethylenediamine)cyanocobalt(III)

Revision exercise 4

1. Define the term transition elements and describe the characteristic features of transition elements giving example(s) in each case.

2. Write the electronic configurations of the ions: Mg^{2+}, Cr^{3+}, Cu^{+}, S^{2-} and Na^{+}, and compare their outer electronic configurations. Comment on the differences.

3. Define the following and give examples in each case:

   (a) Complex compound
   (b) Coordination number
   (c) Ambidentate ligand
   (d) Coordination sphere
   (e) Octahedral complex

4. Justify the classification of either chromium or iron as transition element, illustrating your answer with reference to:

(a) the formation of coloured ions.

(b) the possession of magnetic properties.

(c) the catalytic activity.

(d) the partially filled 3*d*-orbitals.

5. The colours of the transition metal compounds are characteristic of their hydrated ions and not their simple ions. Explain by giving examples.

6. The complex compounds of cobalt have different colours. For example, $[Co(CN)_6]^{3-}$ is yellow, $[Co(NH_3)_6]^{3+}$ is orange and $[Co(H_2O)_6]^{3+}$ is blue. Account for these observations.

7. Give the name and the formula of each of the following:
   (a) A neutral complex compound
   (b) A complex compound with mixed ligands
   (c) Two complexes of cobalt
   (d) Two complex anions of chromium

8. Calculate the oxidation number of the metals in the following compounds:
   (a) $MnCO_3$ (b) $[Fe(H_2O)_6]Cl_3$
   (c) $[Cr(H_2O)_4(NH_3)_2]Cl_3$ (d) $K_2Cr_2O_7$

9. Name the following complex compounds:
   (a) $[Pt(NH_3)_3Cl_3]Cl$ (b) $[Cr(NH_3)_4Cl_2]Cl$ (c) $K_4[Fe(CN)_6]$

10. Silver nitrate may react with the compound $[Pt(NH_3)_3Cl_3]Cl$ but not with the compound $[Pt(NH_3)_2Cl_4]$. Explain.

11. Write the structures of the following complexes:
    (a) Hexaamminenickel(II) chloride
    (b) Tetraammineplatinum(II) tetrachloroplatinate(II)
    (c) Pentaaquathiocyanoferrate(II)
    (d) Dichlorobis(ethylenediamine)platinum(IV) nitrate.

12. (a) Explain why water molecules readily coordinate with cations of the transition metals but hydroxonium ions (H_3O^+) do not.
    (b) The addition of excess silver nitrate to an aqueous solution containing 0.01 mol of $CoCl_3{\cdot}6NH_3$ leads to an immediate

precipitation of 0.03 mol of silver chloride. However, similar addition to an aqueous solution containing 0.01 mol of $CoCl_3 \cdot 5NH_3$ leads to immediate precipitation of only 0.02 mol of silver chloride. Use this observation to suggest the correct structure of the compounds.

13. (a) A metal ion of an atom of a transition element is described by using d^2sp^3 set of orbitals when forming complexes. What is the coordination number of the metal ion and the shape of the complex formed?

    (b) Explain why $[Ni(NH_3)_6]^{2+}$ is paramagnetic whereas $[Pt(CN)_4]^{2-}$ is diamagnetic even though both the central metal ions are d^8 species. Show the crystal field splitting diagram for the two complexes.

14. (a) Manganese is fused with iron to make steel alloy. What properties does manganese confer to steel?

    (b) What electronic features must a donor atom of any ligand possess?

    (c) What is the difference between coordination number and oxidation number?

    (d) Explain why a white gelatinous precipitate of zinc hydroxide dissolves when excess potassium hydroxide solution is added.

Glossary

Acid	Any species that produces H^+ ions when dissolved in water
Acidity	The quantitative capacity of aqueous solutions to react with hydroxyl ions. It is measured by titration with a standard solution of base to a specified end point.
Alloying	Mixing of a metal with one or more other metals in specified proportions
Alum	Technically, a double sulfate of ammonium or a univalent or trivalent metal but commonly used to denote aluminum sulfate $(Al_2(SO_4)_3$
Alumina	A term used for one of the solid forms of aluminium oxide
Amphoteric substances	Are substances which show both acidic and basic properties
Anionic complexes	Are complexes that have a net negative charge outside the coordination sphere
Anode	An electrode to which oxidation reaction occurs
Anion	A negatively charged ion; or an atom with extra electrons
Anhydrous	A term meaning without water
Atom	The smallest particle of an element that retains the chemical nature of the element
Atomic mass (weight)	The average of the masses of the naturally occurring isotopes of an element weighted according to their abundances
Atomic number (Z)	The unique number of protons in the nucleus of each atom of an element (equal to the number of electrons in the neutral atom)
Atomic size	A term referring to the atomic radius, one half the distance nuclei of identical bonded atom

Aqueous solution	A solution in which water is a solvent
Base	Any substance which contains hydroxyl (OH) groups and furnishes hydroxide ions in solution; a molecular or ionic substance capable of combining with a proton to form a new substance.
Bidentate ligand	A type of ligand that attaches itself to the central atom of a complex at two points in the coordination sphere
Boiling point	The temperature at which the vapour pressure of a substance is equal to the atmospheric pressure
Calcination	The removal of the moisture, water of hydration, and volatile substances during the concentration or dressing of the metal ore through strong heating
Catalyst	A chemical substance that alters the rate of a chemical reaction but remains chemically unchanged at the end of the reaction
Cation	A positively charged ion
Cathode	An electrode to which a reduction reaction takes place
Cationic complexes	Complexes that carry a net positive charge outside the coordination sphere
Caustic	Capable of destroying or eating away by chemical action; a hydroxide of a light metal.
Caustic soda	Sodium hydroxide, NaOH
Central atom	An atom that is bonded to two or more other atoms
Chemical formula	Any of various means of concisely displaying information about the chemical composition of a compound or molecule using letters, numbers, and/or typographical symbols
Chemical equation	A symbolic representation of a chemical reaction
Chemical reaction	A process in which one set of substances (reactants) is transformed into a new set of substances (products)

Compound	Two of more elements combined; a substance having different properties than of the elements used
Complex compound	A molecule or ion composed of a central metal atom which is surrounded by ligands
Concentration	In solutions, the mass, volume, or number of moles of solute present in proportion to the amount of solvent or total solution. Common measures are: molarity, normality, percent, molality, and by specific gravity scales.
Confirmatory tests	Experimental procedures performed after the preliminary tests on a chemical substance so as to approve the chemical species present
Coordination compound	A complex compound or ion in which a central metal atom or ion is combined by coordinate bonds with a definite number of ligands
Coordination number	The number of ligand atoms bonded to the central metal ion
Coordination sphere	The region around a central atom or ion where linkage to ligands can occur to produce a complex
Crystal field theory	A model that explains the colour and magnetism of coordination compounds based on the effects of the ligands on metal ion which result from splitting of *d*-orbital
***d*-block elements**	A group of elements whose valence shells comprise electrons in *d*-orbitals as the highest energy sub – levels
***d*-orbital**	An atomic orbital with $l = 2$
Diamagnetic material	A material which will not respond to magnetism, the atoms of this material contain no unpaired electrons
Dilute	To thin out, or having been thinned out; less than full strength

Diagonal relationship	The resemblance in properties whereby the first element in a particular group has similar properties diagonally with the second element in the next group
Disproportionation	A reaction in which a substance is simultaneously oxidised and reduced giving two different products
Dow's process	Process of extracting bromine from brine
Electronic configuration	A designation on how electrons are distributed or arranged among various orbitals in an atom
Electron pair	Two electrons which occupy the same molecular orbital but have opposite spins
Electron shell	An orbital around the nucleus of an atom which contains a fixed number of electrons (usually two or eight)
Element	A substance composed of a single type of atom
e_g set	A set of orbitals that are formed when the energies of metal ion in *d*-orbitals are split by ligand field
Extraction of metals	A process of obtaining pure metals from their ores
Froth-floatation	A process through which hydrophobic materials are selectively separated from hydrophilic ones using water during ore concentration process
Ferromagnetic material	A material that contains unpaired electron which is more strongly attracted by a magnet
Gangue	In an ore, a material such as rock, clay, sand attached to the mineral
Group in a periodic table	A set of elements which have the same numbers of electrons in their outermost shells and hence have similar properties
Halogen	Any of the five non-metallic elements of group 17 of the periodic table: fluorine, chlorine, bromine, iodine, and astatine.
Hybridisation	The process of mixing orbitals to form stable bonds of molecular orbitals

Hydrolysis	The cleavage of a chemical bond by the addition of water
Inorganic compound	Any chemical compound that does not contain carbon, though there are exceptions
Ionic radius	The distance from the nucleus of an ion to a point where it has an influence on its electron cloud
Ion	An isolated electron or positron; an atom or molecule which by loss or gain of one or more electrons has acquired a net electric charge
Ionisation energy	The minimum energy required to remove one mole of electrons from a gaseous atom to form a cation
Ligand	An ion or molecule that bonds to a central metal atom to form a complex compound
Lime	Any of a family of chemicals consisting essentially of calcium hydroxide made from limestone (calcite) which is composed mostly of calcium carbonate or a mixture of calcium carbonate and magnesium carbonate
Mass number (A)	Total number of protons and neutrons in the nucleus of an atom
Melting point	The temperature required to break bonds and change the physical state of a substance from solid to liquid
Metallic bonds	Are the electrostatic forces of attraction between positive metal ions and the negative delocalised electrons (sea of electrons)
Metal	A substance which is relatively shiny and malleable and is a good conductor of heat and electricity
Metallic character	Referred to as a set of chemical properties that are associated with the elements classified as metals in the periodic table
Metallurgy	The process involved in the extraction and refining of metals

Monodentate ligand	A ligand that is able to attach to a central metal atom in complex at only one position
Neutral complexes	Complexes whose coordination spheres have no net charge
Neutralization	Chemical addition of either acid or base to a solution such that the pH is adjusted to 7.
Neutron	An uncharged sub-atomic particle, with a mass nearly equal to that of a proton. Present in the nucleus of all atoms except hydrogen.
Noble gas	Any of the six non-metallic elements of group 18 of the periodic table: helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn). All of the noble gases have outer electron shells that are completely filled in their naturally occurring states, giving them very low chemical reactivity.
Nomenclature	A systematic way of writing chemical names and formulas
Non-metal	Any chemical element which is not a metal
Nuclear charge	The attractive force that pulls all the electrons closer to the nucleus
Ore	A rock containing substantial amounts of metals and from which metals can be extracted
Ore concentration	The process of removing unwanted materials from the ore during metal extraction
Oxidation state	The number of electrons gained, shared or lost by an atom during combination with other atoms
Oxidation	An electron loss by a substance or increase in oxidation state of a substance or addition of oxygen to a substance or removal of hydrogen from a substance
Oxidising agent	A species that causes oxidation but itself becomes reduced

p-block elements	A group of elements whose valence shells comprise electrons in p-orbitals as the highest energy sub-levels
Passivation	A process of making the surface of iron or any other metal inactive, normally by coating it with an oxide layer through oxidation reaction
Period	A horizontal row of the elements in the periodic table
Periodic table	A table of elements arranged in order of increasing atomic numbers
Periodic trend	A regular variation in the properties of the elements with increasing atomic numbers caused by regular variations in the atomic structures of the elements
Periodicity	A tendency of a particular property of an element to appear every after a certain specific interval in a given arrangement
Polarising power	The ability of a cation to deform a negatively charged radical in a compound
Photon	A particle of light where by the energy of beam of light is concentrated into it
Plaster of Paris	Is material that obtained by heating gypsum. It is used to join broken bones
Polydentate ligand	A ligand that has ability to denote more than a single electron pair in central metal atom of a complex, from different atoms in ligand and different sites in the geometric structure
Reducing agent	A species that causes reduction but itself becomes oxidised in the reaction
s-block elements	A group of elements whose valence shells comprise electrons in s-orbital as the highest energy sub-level
Salt	Ionic compound in which hydrogen atoms of acids are replaced with metal ion

Screening effect	The tendency of the inner most electron to protect the outermost electrons from the attractive influence of the nucleus
Soap	The salts of fatty acids
Solution	A special type of homogeneous mixture composed to or more substances. A solution consists of a solute and a solvent
Slag	A molten waste product formed in a blast furnace by the action of acidic silica with basic metal oxide
Temperature	A measure of how hot or cold a substance is relative to another substance
t_{2g} set	A set of orbitals that are formed when the energies of the metal ion in *d*-orbitals are split by a ligand field
Transition elements	A group of elements which have partially filled *d*-orbitals of their atoms or ions
Valence electron	Any of the outermost electrons of an atom, which are located in electron shells
Valence	The combining capacity of the element
Weight	The force exerted by gravitational field on an object

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Appendix

Appendix 1 Table of elements showing atomic numbers and atomic masses

Name of the element	Symbol	Atomic number	Atomic mass	Empirical atomic radius	Calculated atomic radius
Actinium	Ac	89	227	195	-
Aluminium	Al	13	26.9815	125	118
Americium	Am	95	243	175	-
Antimony	Sb	51	121.75	145	133
Argon	Ar	18	39.948	71	71
Arsenic	As	33	74.9216	115	114
Astatine	At	85	210	-	127
Barium	Ba	56	137.34	215	253
Berkelium	Bk	97	247	-	-
Beryllium	Be	4	9.0122	105	112
Bismuth	Bi	83	208.980	160	143
Bohrium	Bh	107	264	-	-
Boron	B	5	10.811	85	87
Bromine	Br	35	79.909	115	94
Cadmium	Cd	48	112.40	155	161
Caesium	Cs	55	132.905	260	298
Calcium	Ca	20	40.08	180	194
Californium	Cf	98	251	-	-
Carbon	C	6	12.01115	70	67
Cerium	Ce	58	140.40	185	158
Chlorine	Cl	17	35.453	100	79
Chromium	Cr	24	51.996	140	166
Cobalt	Co	27	58.9332	135	152
Copernicium	Cn	112	285	-	-
Copper	Cu	29	63.54	135	145
Curium	Cm	96	247	-	-
Darmstadtium	Ds	110	281	-	-
Dubnium	Db	105	262	-	-
Dysprosium	Dy	66	162.50	175	228
Einsteinium	Es	99	252	-	-
Erbium	Er	68	167.26	175	226
Europium	Eu	63	151.96	185	231
Fermium	Fm	100	257	-	-
Flerovium	Fl	114	289	-	-
Fluorine	F	9	18.9984	50	42
Francium	Fr	87	223	-	-
Gadolinium	Gd	64	157.25	180	233

Gallium	Ga	31	69.72	130	136
Germanium	Ge	32	72.64	125	125
Gold	Au	79	196.967	135	174
Hafnium	Hf	72	178.49	155	208
Hassium	Hs	108	277	-	-
Helium	He	2	4.0026	120	31
Holmium	Ho	67	164.930	175	226
Hydrogen	H	1	1.00797	25	53
Indium	In	49	114.82	155	156
Iodine	I	53	126.904	140	115
Iridium	Ir	77	192.2	135	180
Iron	Fe	26	55.847	140	156
Krypton	Kr	36	83.80	-	88
Lanthanum	La	57	138.91	195	195
Lawrencium	Lr	103	262	-	-
Lead	Pb	82	207.19	180	154
Lithium	Li	3	6.939	145	167
Livermorium	Lv	116	292	-	-
Lutetium	Lu	71	174.97	175	217
Magnesium	Mg	12	24.312	150	145
Manganese	Mn	25	54.9380	140	161
Meitnerium	Mt	109	268	-	-
Mendelevium	Md	101	258	-	-
Mercury	Hg	80	200.59	150	171
Molybdenum	Mo	42	95.94	145	190
Moscovium	Mc	115	289	-	-
Neodymium	Nd	60	144	185	206
Neon	Ne	10	20.183	160	38
Neptunium	Np	93	237	175	-
Nickel	Ni	28	58.71	135	149
Nihonium	Nh	113	286	-	-
Niobium	Nb	41	93	145	198
Nitrogen	N	7	14.0467	65	56
Nobelium	No	102	259	-	-
Oganesson	Og	118	294	-	-
Osmium	Os	76	190	130	185
Oxygen	O	8	15.9994	60	48
Palladium	Pd	46	106.4	140	169
Phosphorus	P	15	30.9734	100	98
Platinum	Pt	78	195.09	135	177
Plutonium	Pu	94	244	175	-

Polonium	Po	84	209	190	135
Potassium	K	19	39.102	220	243
Praseodymium	Pr	59	141	185	247
Promethium	Pm	61	145	185	205
Protactinium	Pa	91	231	180	-
Radium	Ra	88	226	215	-
Radon	Rn	86	222	-	120
Rhenium	Re	75	186	135	188
Rhodium	Rh	45	102.905	135	173
Roentgenium	Rg	111	280	-	-
Rubidium	Rb	37	85.47	235	265
Ruthenium	Ru	44	101	130	178
Rutherfordium	Rf	104	261	-	-
Samarium	Sm	62	150	185	238
Scandium	Sc	21	44.946	160	184
Seaborgium	Sg	106	263	-	-
Selenium	Se	34	78.96	115	103
Silicon	Si	14	28.086	110	111
Silver	Ag	47	107.870	160	165
Sodium	Na	11	22.9898	180	190
Strontium	Sr	38	87.62	200	219
Sulphur	S	16	32.064	100	88
Tantalum	Ta	73	181	145	200
Technetium	Tc	43	98	135	183
Tellurium	Te	52	127.604	140	123
Tennessine	Ts	117	294	-	-
Terbium	Tb	65	159	175	225
Thallium	Tl	81	204.4	190	156
Thorium	Th	90	232.038	180	-
Thulium	Tm	69	169	175	222
Tin	Sn	50	118.71	145	145
Titanium	Ti	22	47.87	140	176
Tungsten	W	74	183.85	135	193
Uranium	U	92	238.03	175	-
Vanadium	V	23	50.942	135	171
Xenon	Xe	54	131.30	-	108
Ytterbium	Yb	70	173.04	175	222
Yttrium	Y	39	88.91	180	212
Zinc	Zn	30	65.38	135	142
Zirconium	Zr	40	91.22	155	206

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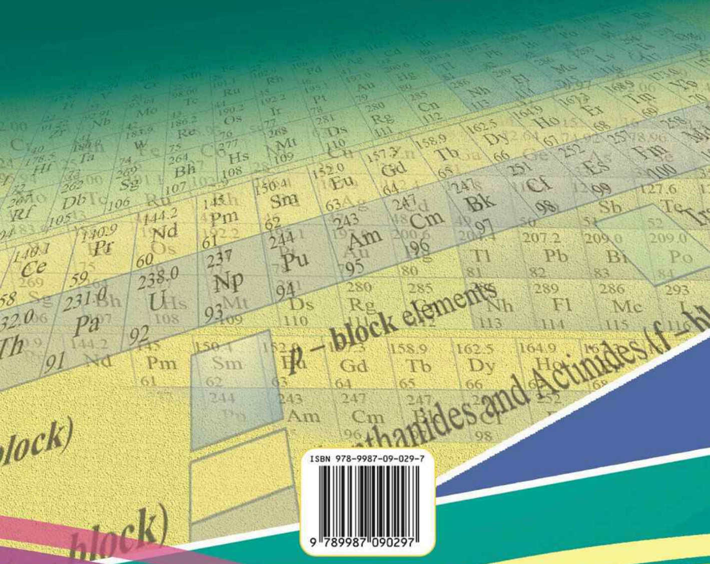

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