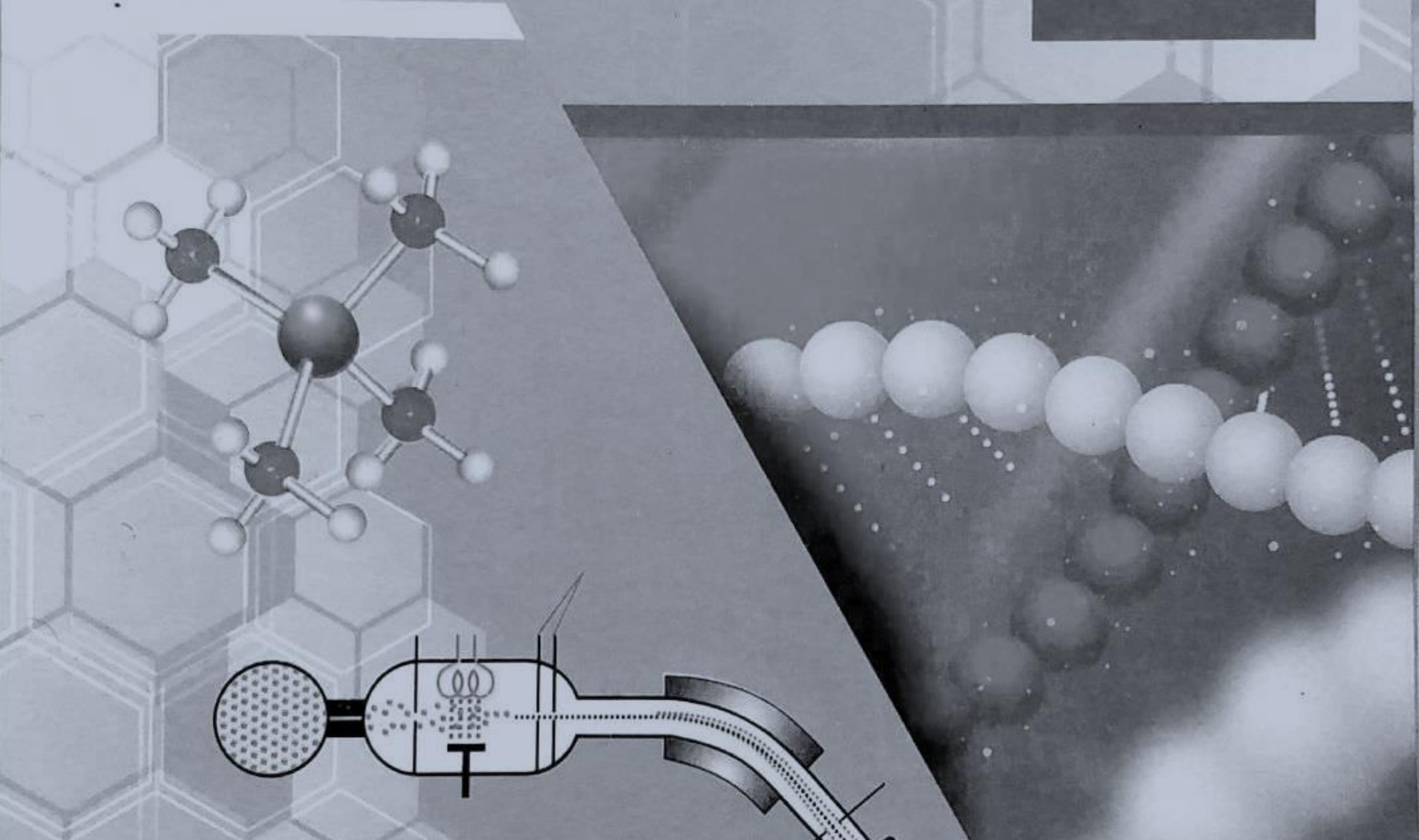
A Textbook of
CHEMISTRY XII



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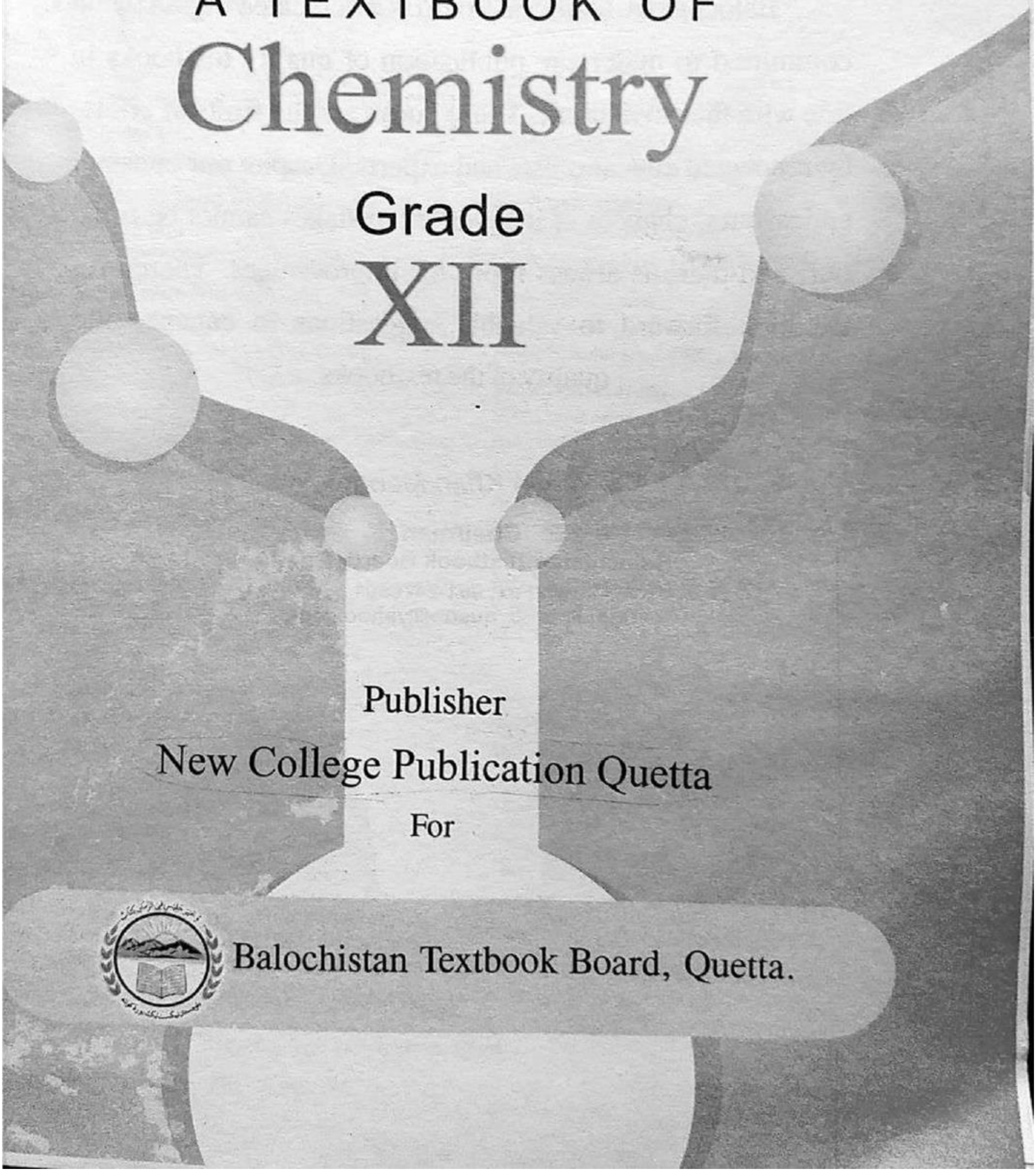
بسم الله الرحمن الرحيم

(In the name of ALLAH the most beneficent and the most merciful)



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Chapter 13

s- and p-Block Elements

Major Concepts

13.1 Period 3 (Na to Ar)
13.2 Group 1
13.3 Group 2
13.4 Group 14
13.5 Group 17 (Halogens)

Learning Outcomes:

Students will be able to:

- Recognize the demarcation of the Periodic Table into s-block, p-block, d-block, and f-block. **(Understanding)**
- Describe how physical properties like atomic radius, ionization energy, electronegativity, electrical conductivity, melting and boiling point of elements change within a group and with in a period in the Periodic Table. **(Analyzing)**
- Describe reactions of period 3 elements with water, oxygen and chlorine. **(Applying)**
- Describe physical properties and acid-base behaviour of oxides, chlorides and hydroxides of period 3 elements. **(Applying)**
- Describe reactions of oxides and chlorides of period 3 elements with water. **(Applying)**
- Explain the trends in physical properties and oxidation states in groups I, II, IV and VII of the Periodic Table. **(Analyzing)**
- Describe reactions of Group I elements with water, oxygen and chlorine. **(Applying)**
- Explain effect of heat on nitrates, carbonates and hydrogen carbonates of Group-I elements. **(Applying)**
- Describe reactions of Group II elements with water, oxygen and nitrogen. **(Applying)**
- Discuss the trend in solubility of the hydroxides, sulphates and carbonates of Group-II elements. **(Analyzing)**
- Discuss the trends in thermal stability of the nitrates and carbonates of Group-II elements. **(Analyzing)**
- Differentiate beryllium from other members of its group. **(Analyzing)**
- Describe reactions of Group IV elements with water. **(Applying)**
- Discuss the chlorides and oxides of group IV elements. **(Applying)**
- Explain the relative behaviour of halogens as oxidizing agents and reducing agents. **(Applying)**
- Compare the acidity of hydrogen halides. **(Analyzing)**
- Distinguish between an oxide and a peroxide. **(Understanding)**
- Write representative equations for the formation of oxides and sulphides. **(Applying)**
- Compare the outer most s and p-orbital system of an element with its chemical properties. **(Analyzing)**

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Introduction

The periodic table can be divided into four blocks. These are *s*, *p*, *d* and *f*-blocks. The classification of elements into blocks is based upon the valence orbital of the element involved in bond formation.

i) The elements of group 1, group 2 and period 1 are *s*-block elements. In these elements the last electron enters into *s*-subshell. There are two *s*-block elements in each period because *s*-subshell can accommodate maximum of two electrons. Their general electronic configuration is ns^{1-2} where 'n' represents the valence shell.

ii) The elements of group 13 to 18 except helium are *p*-block elements. In these elements the last electron enters into *p*-subshell. There are six elements of *p*-block in each period because *p*-subshell can hold up at the most six electrons. Their general electronic configuration is $ns^2\ np^{1-6}$.

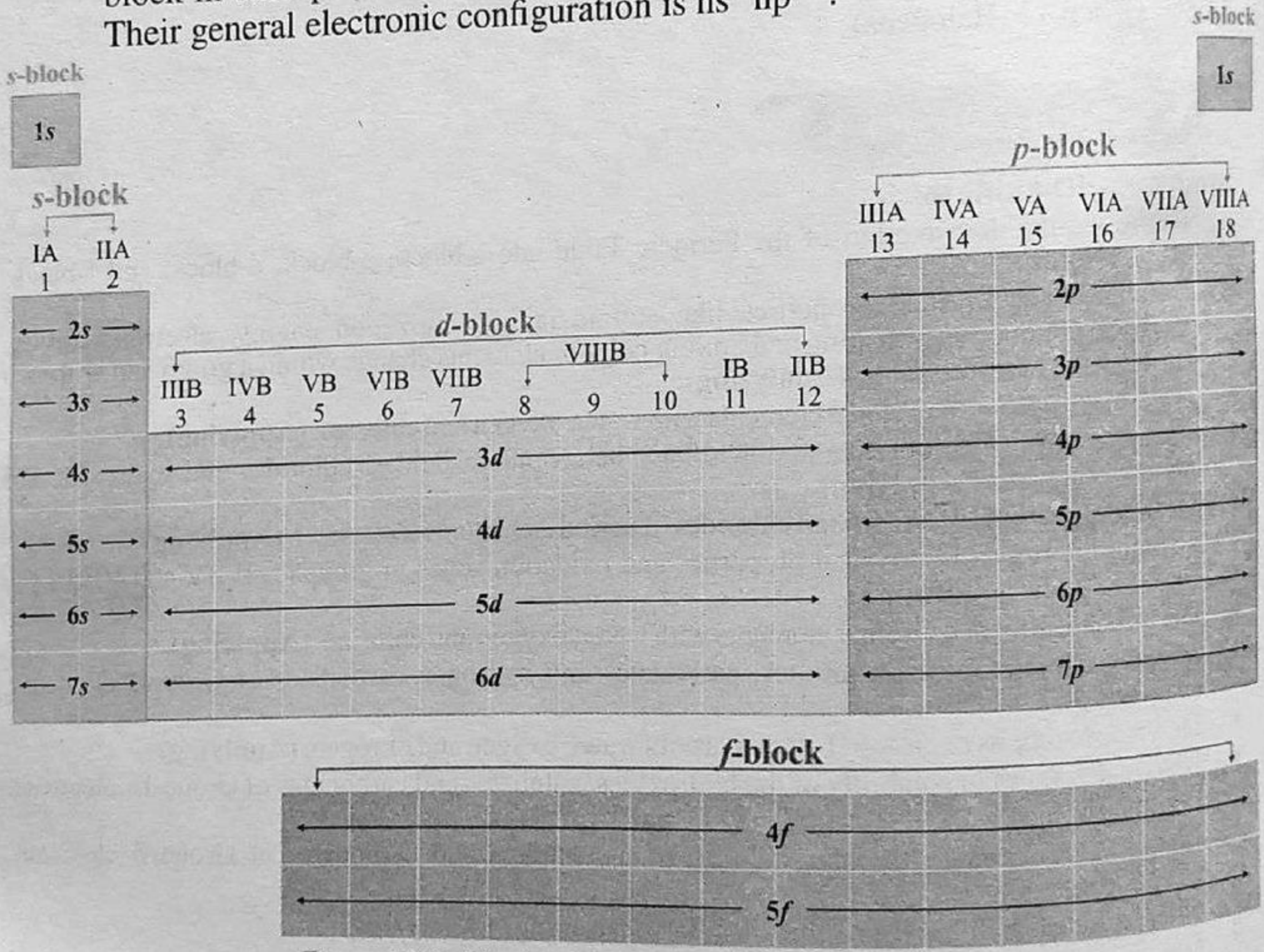

Figure 13.1: Blocks of Elements in the Periodic Table

iii) The elements of group 3 to 12 are *d*-block elements. In these elements the last electron enters into *d*-subshell. There are ten elements of *d*-block in each period because *d*-subshell can accommodate maximum of ten electrons. Their general electronic configuration is $(n-1)d^{1-10}\ ns^{1-2}$. The specific *d*-subshell is one less (n–1) than the period number. The *d*-block elements are also known as transition elements.

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iv) Lanthanides and actinides are *f*-block elements. In these elements the last electron enters into *f*-subshell. There are fourteen *f*-block elements in each period because *f*-subshell can hold up at the most fourteen electrons. Their general electronic configuration is $(n-2)f^{1-14}\ (n-1)d^{0\ \text{or}\ 1}\ ns^2$. The specific *f*-subshell is two less (n−2) than the period number. In most of the periodic tables, the *f*-block elements are placed below the periodic table to save the space.

Groups and Periods of Elements in the Periodic Table

The vertical columns of elements in the periodic table are called groups or families. There are two systems for numbering the groups: the older system and the newer IUPAC system. According to latest IUPAC system, the modern periodic table has 18 groups of the elements. Elements in the same group of periodic table show similar properties because they have same number of valence electrons.

The horizontal rows of elements in the periodic table are called periods. The modern periodic table has seven periods. The first period is the shortest period and has only two elements: the hydrogen and helium. The second and third periods contain 8 elements each and are called short periods. The fourth and fifth periods contain 18 elements each and are called long periods. The sixth and seventh periods contain 32 elements each and are called the longest periods.

13.1 Period 3 Elements (Na to Ar)

Period 3 consists of eight elements *viz.* sodium (Na), magnesium (Mg), aluminium (Al), silicon (Si), phosphorus (P), sulphur (S), chlorine (Cl) and argon (Ar).

13.1.1 Physical and Atomic Properties of the Elements

The properties of elements tend to change from left to right across a period or from top to bottom down a group. The properties that change across a period or down the group with the rise of atomic number are called periodic properties. These properties are also known as atomic properties. These properties are based upon the electronic configurations (valence shell electronic configurations) of atoms of the elements. Some of the atomic properties are atomic radius, ionization energy, electronegativity, electrical conductivity, melting and boiling points.

13.1.1.1 Electronic Structure

Across the period 3 of the periodic table, from Na to Ar, each element has one more proton and one more electron than the one preceding it.

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Table 13.1: Electronic Configuration of Atoms of the Period 3 Elements

Element	Symbol	Atomic Number	Complete Electronic Configuration	Valence Shell Electronic Configuration
Sodium	Na	11	$1s^2 2s^2 2p^6 3s^1$	$3s^1$
Magnesium	Mg	12	$1s^2 2s^2 2p^6 3s^2$	$3s^2$
Aluminium	Al	13	$1s^2 2s^2 2p^6 3s^2 3p^1$	$3s^2 3p^1$
Silicon	Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$	$3s^2 3p^2$
Phosphorus	P	15	$1s^2 2s^2 2p^6 3s^2 3p^3$	$3s^2 3p^3$
Sulphur	S	16	$1s^2 2s^2 2p^6 3s^2 3p^4$	$3s^2 3p^4$
Chlorine	Cl	17	$1s^2 2s^2 2p^6 3s^2 3p^5$	$3s^2 3p^5$
Argon	Ar	18	$1s^2 2s^2 2p^6 3s^2 3p^6$	$3s^2 3p^6$

Electronic configurations of atoms play an important role in knowing the physical and chemical properties of the elements and their compounds.

13.1.1.2 Trends in Atomic Radius

The average distance between the centre of nucleus and the outermost electronic shell of an atom is called atomic radius. The units used to measure atomic radius are nanometre (1nm = 10^{-9} m), angstrom (1A° = 10^{-10} m), and picometre (1pm = 10^{-12} m).

Table 13.2: The Atomic Radius of Atoms of the Period 3 Elements

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Atomic Radius (pm)	190	145	118	111	98	88	79	71

The atomic radius generally decreases from Na to Ar across the period. This is due to increase in the nuclear charge that pulls the electrons closer to the nucleus. The number of core electrons remains the same across the period. Because of this, the shielding effect remains almost constant for the elements.

13.1.1.3 Trends in Ionization Energy

Ionization energy is the minimum amount of energy required to remove an electron from the isolated gaseous atom or ion in its ground state. The value of ionization energy shows how tightly the electron is bound to the nucleus of an atom. The higher the value of ionization energy, the more difficult it is to remove the electron. For example, 496 kJ/mol energy is required to remove an electron from a gaseous sodium atom.

$$\text{Na} \xrightarrow{\quad} \text{Na}^+ + 1e^- \qquad \text{IE} = 496\ \text{kJ/mol}$$

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Table 13.3: First Ionization Energy of Atoms of the Period 3 Elements

Element	Na	Mg	Al	Si	P	S	Cl	Ar
IE (kJ/mol)	496	738	578	786	1012	1000	1251	1520

The minimum amount of energy needed to remove the first electron from an isolated gaseous atom is called first ionization energy. For example, the first ionization energy of magnesium is:

$$Mg \longrightarrow Mg^{+} + 1e^{-} \qquad IE_1 = 738\ kJ/mol$$

The minimum amount of energy needed to remove the second most loosely bound electron is called second ionization energy. For example, the second ionization energy of magnesium is:

$$Mg^{+} \longrightarrow Mg^{++} + 1e^{-} \qquad IE_2 = 1451\ kJ/mol$$

The amount of energy needed to remove the third electron is the third ionization energy and so on. For example, the third ionization energy of magnesium is:

$$Mg^{++} \longrightarrow Mg^{+++} + 1e^{-} \qquad IE_3 = 7730\ kJ/mol$$

Ionization energy values increase with the removal of each electron because the repulsion among the remaining electrons decreases. As a result of this, the force of attraction between nucleus and valence electron increases.

Ionization energy values increase in the following order:

$1^{st}\ IE < 2^{nd}\ IE < 3^{rd}\ IE < \dots$

Ionization energy depends upon:

i) Atomic radius
ii) Nuclear charge
iii) Shielding effect
iv) Electronic configuration of Elements

The ionization energy generally increases from sodium (Na) to argon (Ar) across the period. This is either due to increase in the nuclear charge or decrease in the atomic radius along the period. The metals (Na, Mg and Al) have small values of ionization energies while non-metals (P, S, Cl and Ar) have high values of ionization energies. The high values of ionization energies of non-metals are due to their smaller size. The high ionization energy of argon is due to its stable electronic configuration.

13.1.1.4 Trends in Electronegativity

Electronegativity is the relative tendency (ability or power) of an atom in a molecule to attract a shared pair (bond pair) of electrons towards itself. Electronegativity has no unit. Elements with low electronegativity values are metals and have tendency to lose electrons. Elements with high electronegativity values are non-metals and have tendency to gain electrons.

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Table 13.4: The Electronegativity of Atoms of the Period 3 Elements

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Electronegativity	0.93	1.31	1.81	2.02	2.19	2.58	3.16	–

The electronegativity of argon is not included in the table because the compounds of argon are rare.

Electronegativity increases from sodium to chlorine due to increase in nuclear charge. The shielding effect remains constant along the period.

13.1.1.5 Trends in Electrical Conductivity

Electrical Conductivity is the ability of a material to carry an electric current. The electrical conductivity is due to loose electrons in a material. Sodium, magnesium and aluminium are good conductors, silicon is semiconductor while the rest of the elements of period 3 are non-conductors.

Table 13.5: Electrical Conductivity of the Period 3 Elements

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Electrical Conductivity	Good	Good	Good	Poor	None	None	None	None

Electrical conductivity increases from sodium to aluminium. This rise is due to the increasing number of delocalized electrons in the metallic solid. Silicon has giant covalent structure similar to that of diamond and has few delocalized electrons. Because of this, it is a semiconductor. The elements from phosphorus to argon are non-conductors because their electrons are tightly bound to the nucleus and are not free to move.

13.1.1.6 Trends in Melting and Boiling Points

The melting and boiling points of period 3 elements increase from left to right up to the silicon and then gradually decrease.

Table 13.6: Melting and Boiling Points of the Period 3 Elements

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Melting Point (°C)	98	650	660	1420	600	119	−102	−189
Boiling Point (°C)	883	1100	2400	2480	1000	444	−34	−186

Melting and boiling points of elements depend upon the number of valence electrons or bond strength. The sodium, magnesium and aluminium have strong metallic bonds while silicon has strong covalent bonds. The sodium, magnesium and aluminium contain one, two and three valence electrons respectively. Hence, sodium provides one, magnesium two and aluminium three electrons for metallic bonds. Silicon, a semimetal, has four valence electrons and forms four covalent bonds with other silicon atoms.

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The other elements of period 3 (P, S, Cl and Ar) are non-metals and have low melting and boiling points. This is because, they form simple molecules and their molecules are held together by London dispersion forces which are very weak attractive forces. The small amount of energy is required to overcome these attractive forces.

The melting and boiling points of sulphur are higher than other three non-metals (P, Cl and Ar). This is because; the size of sulphur (S_8) molecule is larger than other three non-metals (P_4, Cl_2 and Ar). The strength of London forces depend upon the size of molecules. The larger the size of molecules, the stronger is the London forces. Consequently, the melting and boiling points decrease in the following order:

$$S_8 > P_4 > Cl_2 > Ar$$

13.1.2 Reactions of Period 3 Elements with Water, Oxygen, and Chlorine

13.1.2.1 Reactions of Period 3 Elements with Water

Reaction of Sodium with Water

Sodium reacts with cold water violently to produce hydrogen gas and a colourless solution of sodium hydroxide. The reaction is exothermic.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

Reaction of Magnesium with Water

Magnesium reacts with cold water gently to produce magnesium hydroxide.

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$$

Magnesium burns in steam with white flame to produce magnesium oxide and hydrogen gas.

$$Mg + H_2O \longrightarrow MgO + H_2$$

Reaction of Aluminium with Water

Finely divided aluminium reacts with steam to give aluminium oxide and hydrogen gas. This reaction is relatively slow due to the formation of aluminium oxide layer on the surface of metal.

$$2Al + 3H_2O \longrightarrow Al_2O_3 + 3H_2$$

Reaction of Silicon with Water

Silicon does not react with water in its elemental form at room temperature. It reacts with water at extremely high temperature producing silicon dioxide and hydrogen gas. The inertness of silicon is due to a protective layer of silicon dioxide on its surface.

$$Si + 2H_2O \longrightarrow SiO_2 + 2H_2$$

Reactions of Phosphorus, Sulphur and Argon with Water

Phosphorus, sulphur and argon do not react with water.

$$P_4 + H_2O \longrightarrow \text{No Reaction}$$

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$$S + H_2O \longrightarrow \text{No Reaction}$$

$$Ar + H_2O \longrightarrow \text{No Reaction}$$

Reaction of Chlorine with Water

Chlorine reacts with water to produce mixture of hydrochloric acid and hypochlorous acid. This reaction is reversible.

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$

The HOCl, in the presence of sunlight, is slowly decomposed into hydrochloric acid and oxygen gas.

$$2HOCl \longrightarrow 2HCl + O_2$$

The equation that shows the overall change is as:

$$2Cl_2 + 2H_2O \rightleftharpoons 4HCl + O_2$$

13.1.2.2 Reactions of Period 3 Elements with Oxygen

Reaction of Sodium with Oxygen

Sodium burns with a yellow flame to give a mixture of sodium oxide and sodium peroxide.

$$4Na + O_2 \longrightarrow 2Na_2O$$

$$2Na + O_2 \longrightarrow Na_2O_2$$

Reaction of Magnesium with Oxygen

Magnesium burns in oxygen with a brilliant white flame to form magnesium oxide.

$$2Mg + O_2 \longrightarrow 2MgO$$

Reaction of Aluminium with Oxygen

Finely divided aluminium burns in oxygen with a brilliant white flame to produce white alumina (aluminium oxide).

$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$

Reaction of Silicon with Oxygen

Silicon burns in oxygen with a bright yellow flame at high temperature and produces silicon dioxide .

$$Si + O_2 \xrightarrow{400\text{–}1000^\circ C} SiO_2$$

Reaction of Phosphorus with Oxygen

Phosphorus burns in oxygen with a white flame and produces white smoke. The smoke contains phosphorus (III) oxide and phosphorus (V) oxide.

$$P_4 + 3O_2 \longrightarrow P_4O_6$$

$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

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Reaction of Sulphur with Oxygen

Sulphur burns in oxygen with a brilliant blue flame and gives sulphur dioxide gas.

$$S + O_2 \longrightarrow SO_2$$

Reaction of Chlorine with Oxygen

Chlorine does not react with oxygen directly.

$$Cl_2 + O_2 \longrightarrow \text{No Reaction}$$

Reaction of Argon with Oxygen

Argon does not react with oxygen.

$$Ar + O_2 \longrightarrow \text{No Reaction}$$

13.1.2.3 Reactions of Period 3 Elements with Chlorine

Reaction of Sodium with Chlorine

Sodium burns in the presence of chlorine with bright yellow or orange flame and forms sodium chloride.

$$2Na + Cl_2 \longrightarrow 2NaCl$$

Reaction of Magnesium with Chlorine

Magnesium burns in chlorine with intense white flame and forms magnesium chloride.

$$Mg + Cl_2 \longrightarrow MgCl_2$$

Reaction of Aluminium with Chlorine

Aluminium readily combines with chlorine on heating to form aluminium chloride.

$$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$

Reaction of Silicon with Chlorine

Silicon reacts with chlorine on heating to form liquid silicon tetrachloride.

$$Si + 2Cl_2 \longrightarrow SiCl_4$$

Reaction of Phosphorus with Chlorine

When dry chlorine gas is passed over molten white phosphorus, a mixture of two chlorides (phosphorus trichloride and phosphorus pentachloride) is obtained. The phosphorus gives phosphorus trichloride with limited supply of chlorine and phosphorus pentachloride with excess chlorine.

$$P_4 + \underset{\text{Limited}}{6Cl_2} \longrightarrow 4PCl_3$$

$$P_4 + \underset{\text{Excess}}{10Cl_2} \longrightarrow 4PCl_5$$

Reaction of Sulphur with Chlorine

Sulphur reacts with chlorine on heating to form disulphur dichloride liquid.

$$2S + Cl_2 \longrightarrow S_2Cl_2$$

Reaction of Argon with Chlorine

Argon does not react with chlorine.

$$Ar + Cl_2 \longrightarrow \text{No Reaction}$$

13.1.3 Physical Properties of the Oxides of Period 3 Elements

Oxides are the binary compounds (compounds composed of only two elements) of oxygen with other elements. There may be oxides of all the elements except fluorine.

The relationship between the physical properties of oxides of period 3 elements and their structures is discussed here in this topic. Argon does not form an oxide because it has complete outermost shell.

13.1.3.1 Structure of Oxides

The oxides of sodium, magnesium and aluminium consist of giant structure of metal ions and oxide ions. Silicon dioxide has giant covalent structure. The oxides of phosphorus, sulphur and chlorine consist of molecules.

Table 13.7: The Structure of Oxides of Period 3 Elements

Na_2O	MgO	Al_2O_3	SiO_2	P_4O_6	SO_3	Cl_2O
				P_4O_{10}	SO_2	Cl_2O_7
Giant ionic	Giant ionic	Giant ionic with covalent character	Giant covalent	Molecular Covalent	Molecular Covalent	Molecular Covalent

Na_2O, MgO, Al_2O_3 and SiO_2 have strong attractive forces (Intra molecular forces) in all directions. Hence, they have regular arrangement of particles (atoms or ions) and have giant structures because the arrangement is repeated many times with large number of particles throughout the substance. The oxides of non-metals (phosphorus, sulphur and chlorine) consist of molecules and have weak intermolecular forces (London Forces). Hence, they have simple structures and the arrangement of their atoms is not repeated.

13.1.3.2 Nature of Oxides

Sodium and magnesium oxides are ionic. The aluminium oxide is mostly ionic and has a significant covalent character. Silicon dioxide has a covalent character. The oxides of silicon phosphorus, sulphur and chlorine have covalent characters.

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Table 13.8: The Ionic Character of Oxides of Period 3 Elements

Oxides	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_6	SO_3	Cl_2O
					P_4O_{10}	SO_2	Cl_2O_7
Character	Ionic	Ionic	Mostly Ionic	Covalent	Covalent	Covalent	Covalent
ΔEN	2.51	2.13	1.83	1.54	1.25	0.86	0.44

The ionic character of period 3 elements decreases while covalent character increases along the period due to decrease in the electronegativity difference. The elements form ionic bonds when the electronegativity difference between two elements is large. The elements form covalent bonds when the electronegativity difference between two elements is small.

13.1.3.3 Melting and Boiling Points of Oxides

The oxides of sodium, magnesium and aluminium have high melting and boiling points because they are ionic and a lot of energy is required to break the strong attractive forces between the ions (cations and anions).

The melting and boiling points of silicon dioxide are also high because a large amount of energy is required to break very strong silicon-oxygen covalent bond. It is concluded that the oxides of metals (Na_2O, MgO and Al_2O_3) and silicon (SiO_2) have giant ionic and covalent structures, hence they have high melting and boiling points.

Table 13.9: Melting and Boiling Points of Oxides of Period 3 Elements

Oxides	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	P_4O_6	SO_3	SO_2	Cl_2O_7	Cl_2O
Melting Point (°C)	1275	2852	2040	1610	340	24	17	-72	-92	-120.6
Boiling Point (°C)	1950	3600	2977	2230	360	173	45	-10	82	2.2

The oxides of phosphorus (P_4O_6 and P_4O_{10}), sulphur (SO_2 and SO_3) and chlorine (Cl_2O and Cl_2O_7) are simple molecular covalent. The melting and boiling points of these oxides are much lower than those of metal oxides or silicon dioxide. Because they consist of molecules and have intermolecular forces (dipole-dipole forces or London dispersion forces). The strength of these forces depends either on the polarity of molecules or on the size of molecules.

13.1.3.4 Electrical conductivity

The oxides of metals (Na_2O, MgO and Al_2O_3) do not conduct electricity in the solid state due to absence of mobile electrons or free ions. They conduct electricity in the molten state because of the movement of ions.

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Silicon dioxide does not conduct electricity either as a liquid or solid. This is due to absence of mobile electrons or ions in the SiO_2.

Table 13.10: The Electrical Conductivity of Oxides of Period 3 Elements

Oxides	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_6	SO_3	Cl_2O
					P_4O_{10}	SO_2	Cl_2O_7
In the Solid State	None	None	None	None	None	None	None
In the Molten State	High	High	High	Very Low	None	None	None

The oxides of non-metals (P_4O_6, P_4O_{10}, SO_2, SO_3, Cl_2O and Cl_2O_7) do not conduct electricity either as a gas, liquid or solid. Because they consist of molecules and none of them have free electrons or ions.

13.1.4 Acid-Base Behaviour of the Oxides of Period 3 Elements

The ionic character of period 3 elements decreases while covalent character increases along the period due to decrease in the electronegativity difference. The elements form ionic bonds when the electronegativity difference between two elements is large, while they form covalent bonds when the electronegativity difference between two elements is small.

Sodium and magnesium oxides are ionic and contain O^{2-} ion. Oxide ion is a strongly basic ion that reacts with water to form hydroxide ions.

$$\mathbf{O^{2-} + H_2O \longrightarrow 2OH^-}$$

Al_2O_3 has both ionic and covalent characters and is amphoteric. It reacts with both acids and bases to form salts.

SiO_2 has a covalent character. It does not contain oxide ion. It is weakly acidic. It reacts with strong bases to form salts.

Oxides of non-metals have covalent characters and are acidic in nature. They form acidic solutions when dissolved in water.

Table 13.11: The Acid-Base Behaviour of Oxides of Period 3 Elements

Oxides	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
Character	Strongly Basic	Weakly Basic	Amphoteric	Weakly Acidic	Acidic	Strongly Acidic	Very Strongly Acidic
ΔEN	2.51	2.13	1.83	1.54	1.25	0.86	0.44

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13.1.4.1 Trends in Acid-Base Behaviour

The basic character of oxides of period 3 elements decreases while acidic character increases along the period due to decrease in the electronegativity difference (ΔEN).

13.1.4.2 Reactions of Oxides with Water, Acids and Bases

Reactions of Oxides with Water

Sodium oxide reacts readily with water to form basic solution. The pH of solution is around 14.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

Magnesium oxide reacts with water to form basic solution. The reaction is slow and some magnesium hydroxide is formed in the reaction. The pH of solution is around 9.

$$MgO + H_2O \longrightarrow Mg(OH)_2$$

Aluminium oxide is insoluble in water and does not react with water.

$$Al_2O_3 + H_2O \longrightarrow \text{No Reaction}$$

Silicon dioxide does not react with water because it has a giant covalent structure and is completely insoluble in water.

$$SiO_2 + H_2O \longrightarrow \text{No Reaction}$$

The oxides of non-metals (phosphorus, sulphur, and chlorine) react with water to form acidic solutions.

$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$ **(Phosphorous acid)**

$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$ **(Phosphoric acid)**

$SO_2 + H_2O \longrightarrow H_2SO_3$ **(Sulphurous acid)**

$SO_3 + H_2O \longrightarrow H_2SO_4$ **(Sulphuric acid)**

$Cl_2O + H_2O \longrightarrow 2HClO$ **(Hypochlorous acid)**

$Cl_2O_7 + H_2O \longrightarrow 2HClO_4$ **(Perchloric acid)**

Reactions of Oxides with Acids

Sodium oxide reacts with dilute hydrochloric acid to form aqueous solution of sodium chloride.

$$Na_2O + 2HCl \longrightarrow 2NaCl + H_2O$$

Magnesium oxide reacts with warm dilute hydrochloric acid to form aqueous solution of magnesium chloride.

$$MgO + 2HCl \longrightarrow MgCl_2 + H_2O$$

Aluminium oxide reacts with hot dilute hydrochloric acid to form aqueous solution of aluminium chloride.

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$

In this reaction aluminium oxide acts as a base.

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Silicon dioxide is a stable compound and does not react with most of the acid at normal conditions. It reacts only with hydrofluoric acid (HF).

$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$

Tetrafluorosilane (SiF_4) reacts further with HF to produce hexafluorosilici acid.

$SiF_4 + 2HF \longrightarrow H_2[SiF_6]$

Reactions of Oxides with Bases

Aluminium oxide reacts with hot concentrated sodium hydroxide to form colourless solution of sodium tetrahydroxoaluminate.

$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2Na[Al(OH)_4]$

In this reaction aluminium oxide acts as an acid.

Silicon dioxide slowly reacts with hot concentrated sodium hydroxide to form colourless solution of sodium silicate and water.

$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$

Phosphorus trioxide reacts directly with sodium hydroxide to produce two series of salts (sodium dihydrogenphosphite and sodium hydrogenphosphite).

$4NaOH + P_4O_6 + 2H_2O \longrightarrow 4NaH_2PO_3$

$8NaOH + P_4O_6 \longrightarrow 4Na_2HPO_3 + 2H_2O$

Phosphorus pentaoxide reacts directly with sodium hydroxide to produce three series of salts (sodium dihydrogen phosphate, sodium hydrogen phosphate and sodium phosphate).

$4NaOH + P_4O_{10} + 2H_2O \longrightarrow 4NaH_2PO_4$

$8NaOH + P_4O_{10} \longrightarrow 4Na_2HPO_4 + 2H_2O$

$12NaOH + P_4O_{10} \longrightarrow 4Na_3PO_4 + 6H_2O$

Sulphur dioxide reacts directly with sodium hydroxide solution to produce sodium sulphite.

$SO_2 + 2NaOH \longrightarrow Na_2SO_3 + H_2O$

When SO_2 is in excess then sodium bisulphite is formed.

$SO_2 + NaOH \longrightarrow NaHSO_3$

Sulphur trioxide reacts directly with sodium hydroxide solution to produce sodium sulphate.

$SO_3 + 2NaOH \longrightarrow Na_2SO_4 + H_2O$

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Dichlorine monoxide reacts with solution of sodium hydroxide to produce sodium hypochlorite.

$$Cl_2O + 2NaOH \longrightarrow 2NaClO + H_2O$$

Dichlorine heptoxide reacts with solution of sodium hydroxide to produce sodium perchlorate.

$$Cl_2O_7 + 2NaOH \longrightarrow 2NaClO_4 + H_2O$$

13.1.5 Chlorides of the Period 3 Elements

The binary compounds of chlorine with period 3 elements are called chlorides of the period 3 elements. The formulae of the chlorides of period 3 elements are given in the table.

Table 13.12: Chlorides of Period 3 Elements

Formula of Chloride	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3 PCl_5	SCl_2
Oxidation Number	+1	+2	+3	+4	+3 +5	+2

The oxidation number of the element in its chloride is equal to the number of chlorine atoms attached to the element.

13.1.5.1 Nature and Structure of Chlorides

NaCl and $MgCl_2$ are white ionic compounds and consist of giant structures. They composed of oppositely charged ions that held together by strong electrostatic forces.

$AlCl_3$ is white covalent compound. It has a layered lattice at room temperature. It turns to dimeric gas (Al_2Cl_6) on heating to about 180°C and then has a simple molecular structure.

Table 13.13: Chlorides of Period 3 Elements

Formula of Chloride	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3 PCl_5	SCl_2
Structure	Ionic	Ionic	Covalent	Molecular covalent	Molecular covalent	Molecular covalent

$SiCl_4$ and PCl_3 are colourless covalent compounds. They are found in the liquid states. They have simple molecular structures. Their molecules are held together by weak van der Waal's forces.

PCl_5 is a white ionic compound in the solid state and has an ionic lattice of $[PCl_6]^-[PCl_4]^+$. However, it has a simple molecular structure in the gaseous state.

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SCl_2 is a cherry red liquid. It is a covalent compound and has a simple molecular structure.

13.1.5.2 Melting and Boiling Points of Chlorides

Sodium chloride and magnesium chloride have high melting and boiling points because they need a large amount of energy to break the strong electrostatic attractions between their ions.

Aluminium chloride and silicon tetrachloride have low melting and boiling points because they need small amount of energy to break weak van der Waal's forces between their molecules.

Table 13.14: Melting and Boiling Points of Chlorides

Formula of Chloride	$NaCl$	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	PCl_5	SCl_2
Melting Point (°C)	801	714	192.6	−68.74	−93.6	160.5	−121
Boiling Point (°C)	1413	1412	180	57.65	76.1	166.8	59

Phosphorus trichloride (PCl_3) has low melting and boiling points due to presence of weak intermolecular forces between their molecules.

Phosphorus pentachloride (PCl_5) has higher melting and boiling points than phosphorus trichloride because they have different structures. The forces of attractions that hold solid lattice of PCl_3 together are weak van der Waal's forces and that hold solid lattice of PCl_5 together are strong ionic bonds.

SCl_2 has low melting and boiling points because their molecules are held together by weak intermolecular forces.

13.1.5.3 Electrical Conductivity of Chlorides

The chlorides of the period 3 elements on the left such as $NaCl$ and $MgCl_2$ are ionic. They do not conduct electricity in the solid because their ions are locked in place and not able to move. They can only conduct electricity when they are either melted or dissolved in polar solvents such as water because in molten state or in solution form their ions are free to move.

Note that aluminium chloride is covalent not ionic as would normally be expected from a metal and a non-metal binary compound. It does not conduct electricity either in solid state or in liquid state.

The chlorides of the elements on the right of the period such as $SiCl_4$, PCl_3, PCl_5, and SCl_2 are covalent in nature. They do not conduct electricity either in solid or molten state because they do not have any ions or any mobile electrons.

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13.1.5.4 Solubility of Chlorides in Water

NaCl does not react with water. It dissolves in water to form a neutral solution (pH ≈7) of metal cations and chloride ions.

$$NaCl \xrightarrow{Water} Na^+ + Cl^-$$

$MgCl_2$ also does not react with water. It dissolves in water to form slightly acidic solution (pH ≈ 6.5) of metal cations and chloride ions.

$$MgCl_2 \xrightarrow{Water} Mg^{++} + 2Cl^-$$

The covalent chlorides (Al_2Cl_6, $SiCl_4$, PCl_3 and PCl_5) are hydrolysed by water to form acidic solutions.

$$Al_2Cl_6 + 6H_2O \xrightarrow{Water} 2Al(OH)_3 + 6HCl \quad (pH \approx 3)$$

$$SiCl_4 + 2H_2O \xrightarrow{Water} SiO_2 + 4HCl \quad (pH \approx 2)$$

$$PCl_3 + 3H_2O \xrightarrow{Water} H_3PO_3 + 3HCl \quad (pH \approx 2)$$

$$PCl_5 + 4H_2O \xrightarrow{Water} H_3PO_4 + 5HCl \quad (pH \approx 2)$$

Keep in Mind

Ionic chlorides generally give neutral solutions and covalent chlorides generally give acidic solutions in water.

13.1.6 Hydroxides of Period 3 Elements

The hydroxides of sodium and magnesium viz. NaOH and $Mg(OH)_2$ are basic. They are white hygroscopic crystalline solids. Sodium hydroxide is highly soluble in water and magnesium hydroxide is slightly soluble in water. Sodium hydroxide reacts with dil. HCl to produce colourless solution of sodium chloride.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

Magnesium hydroxide reacts with dil. HCl to produce colourless solution of magnesium chloride.

$$Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O$$

The hydroxide of aluminium viz. $Al(OH)_3$ is amphoteric. It can react both as an acid and as a base. Aluminium hydroxide reacts with dil. HCl to produce colourless solution of aluminium chloride.

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

Aluminium hydroxide reacts with the solution of sodium hydroxide to produce colourless solution of sodium tetrahydroxoaluminate (III).

$$Al(OH)_3 + NaOH \longrightarrow Na[Al(OH)_4]$$

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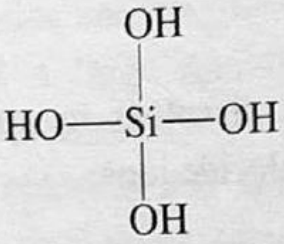
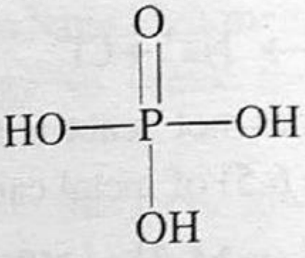
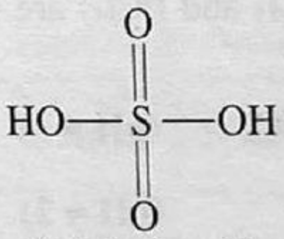
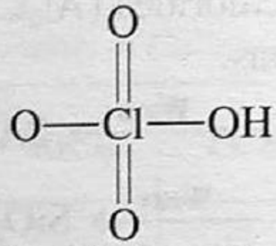
The hydroxides of Si, P, S and Cl are $Si(OH)_4$, H_3PO_4, H_2SO_4, and $HClO_4$. They are all acidic. Their acidity ranges from the very weak silicic acid to the very strong perchloric acid.


Orthosilicic acid


Phosphoric acid


Sulphuric acid


Perchloric acid

The —OH groups of these hydroxides are covalently bonded to the atoms of period 3 elements.

13.2 Group 1 Elements

The elements of group 1 (IA) include lithium, sodium, potassium, rubidium, cesium and francium, and are known as alkali metals. The word alkali has been taken from an Arabic word meaning "ashes". Because many compounds of alkali metals particularly sodium and potassium were isolated from the ashes of wood by early chemists. These are the most active metals in the periodic table. They have to be stored in oil (kerosene) to prevent their reaction with oxygen and water in the air. They are not found in the elemental state; they found only in combined states. Alkali metals are soft enough to be cut with a knife. They have silvery appearance. This can only be seen when they are freshly cut. They are good conductors of electricity.

Table 13.15: Electronic Configuration of Alkali Metals

Name	Symbol	Atomic number	Electronic configuration	Valence shell electronic configuration
Lithium	Li	3	$1s^2 2s^1$	$2s^1$
Sodium	Na	11	$1s^2 2s^2 2p^6 3s^1$	$3s^1$
Potassium	K	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	$4s^1$
Rubidium	Rb	37	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$	$5s^1$
Cesium	Cs	55	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^1$	$6s^1$
Francium	Fr	87	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^1$	$7s^1$

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Their valence shell electronic configuration is "ns^1". They are excellent reducing agents. They form monovalent positive ions (M^+) by losing one valence electron and attain the stable electronic configuration of noble gases. They show oxidation state of +1.

13.2.1 Atomic and Physical Properties of the Group 1 Elements

The trends in some atomic and physical properties of the group 1 elements are discussed below:

13.2.1.1 Trends in Atomic Radius

The atomic radius of alkali metals increases as we move down the group. This is due to increase in number of shells and shielding effect.

Table 13.16: Atomic Radius of Group 1 Elements

Element	Li	Na	K	Rb	Cs	Fr
Atomic Radius (pm)	152	186	227	248	265	348 By (van der Waal's)

Francium has the largest atomic radius of any other neutral element but it is an extremely unstable element and little is known about its properties. The credit is, therefore, goes to cesium.

13.2.1.2 Trends in First Ionization Energy

Alkali metals have one electron in the valence shell (ns^1). This ns^1 electron is loosely bound to the nucleus and this electron can be detached easily. They have, therefore, the lowest first ionization energies of all the elements in the periodic table. Thus, they are the powerful reducing agents.

Table 13.17: Ionization Energies of Group 1 Elements

Element	Li	Na	K	Rb	Cs
Ionization Energy (kJ/mol)	520.3	495.8	418.9	403.0	375.7

The ionization energy of alkali metals decreases down the group. This is due to increase in atomic size.

13.2.1.3 Trends in Electronegativity

Alkali metals have greater tendency to lose their valence electrons and are highly electropositive. Because of this, they have very low electronegativity values.

Table 13.18: Electronegativity Values of Group 1 Elements

Element	Li	Na	K	Rb	Cs
Electronegativity Values	0.98	0.93	0.82	0.82	0.79

The values of electronegativity decrease down the group due to increase in atomic size.

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13.2.1.4 Trends in Melting and Boiling Points

They have very low melting and boiling points. This is due to the presence of weak metallic bonds of the alkali metals in the solid state.

Table 13.19: Melting and Boiling Points of Group 1 Elements

Element	Li	Na	K	Rb	Cs
Melting Point (°C)	180.5	97.8	63.7	38.9	28.7
Boiling Point (°C)	1330	892	760	688	670

The melting and boiling points of alkali metals decrease as we go down the group. This is due to increase in atomic size. As the size of atoms get larger, the attraction between the metal cations and the negatively charged electronic cloud becomes weaker and thus the melting and boiling points decrease.

13.2.1.5 Trends in Density

Mass per unit volume (m/V) is called density. It means how much mass a substance has in a unit volume. Alkali metals have low densities due to large atomic volumes.

Table 13.20: The Densities and Atomic Volumes of Group 1 Elements

Element	Li	Na	K	Rb	Cs
Atomic Volumes (cm^3/mol)	12.97	23.68	45.36	55.80	69.95
Density (g/cm^3)	0.54	0.97	0.86	1.53	1.90

Lithium, sodium and potassium are the only metals, which are less dense than water ($1 g/cm^3$). When they are added to water, they float on the surface of water. Density of group 1 elements generally increases down the group. This is due to increase in atomic masses. The potassium, however, is less dense than sodium. This is due to an abnormal increase in the atomic volume of potassium.

13.2.2 Trends in Reactivity with Water

Alkali metals react with water to produce hydroxide and liberate hydrogen gas. The hydroxides of group 1 elements are water soluble, thus they dissolve in water and form an alkaline solution of metal hydroxide.

Metal (M) + Water (H_2O) ⟶ Metal hydroxide (MOH) + Hydrogen (H_2)

The reactivity of group 1 elements increases down the group. Lithium is the least reactive and caesium is the most reactive.

The equations for the reactions of alkali metals with water are:

$$2Li + 2H_2O \longrightarrow 2LiOH + H_2$$

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

$$2K + 2H_2O \longrightarrow 2KOH + H_2$$

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13.2.3 Reactions of Alkali Metals with Oxygen

Alkali metals react with oxygen or air quickly and thus becomes tarnished (dull) due to the formation of a film of oxides on their surfaces. The alkali metals are, therefore, stored in kerosene or paraffin oil to ensure safety and purity.

13.2.3.1 Formation of Oxides

Lithium reacts with oxygen to form mainly normal oxide, Li_2O (and some peroxide).

$4Li + O_2 \longrightarrow 2Li_2O$ **(Lithium monoxide)**

$2Li + O_2 \longrightarrow Li_2O_2$ **(Lithium peroxide)**

Sodium reacts with oxygen to give mainly peroxide, Na_2O_2 (and some normal oxide).

$4Na + O_2 \longrightarrow 2Na_2O$ **(Sodium monoxide)**

$2Na + O_2 \longrightarrow Na_2O_2$ **(Sodium peroxide)**

Potassium, rubidium and cesium react with oxygen to give KO_2, RbO_2 and CsO_2 respectively.

$K + O_2 \longrightarrow KO_2$ **(Potassium super oxide)**

$Rb + O_2 \longrightarrow RbO_2$ **(Rubidium super oxide)**

$Cs + O_2 \longrightarrow CsO_2$ **(Cesium super oxide)**

Keep in Mind

The binary compounds of oxygen are called oxides. They are mainly of three types: normal oxides, peroxides and superoxides. The main difference between normal oxide, peroxide and superoxide is that the oxidation state of oxygen of normal oxide is -2, peroxide is -1 and that of superoxide is $-\frac{1}{2}$. Examples of normal oxides are Na_2O and CO_2, peroxides are Na_2O_2 and K_2O_2 while those of superoxides are KO_2 and RbO_2.

13.2.3.2 Reactions of Oxides with Water

The normal oxides of alkali metals react with water to produce metal hydroxides.

$Li_2O + H_2O \longrightarrow 2LiOH$

$Na_2O + H_2O \longrightarrow 2NaOH$

The peroxides of alkali metals react with water to produce metal hydroxides and hydrogen peroxides.

$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$

The super oxides of alkali metals react with water to produce metal hydroxides and hydrogen peroxides with the liberation of oxygen gas.

$2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$

$2RbO_2 + 2H_2O \longrightarrow 2RbOH + H_2O_2 + O_2$

13.2.3.3 Reactions of Oxides with Dilute Acids

The normal oxides react with dilute acids to produce salt and water.

$Li_2O + 2HCl \longrightarrow 2LiCl + H_2O$

$Na_2O + 2HCl \longrightarrow 2NaCl + H_2O$

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The peroxides are strong oxidizing agents. They combine with dilute acids to produce salt and hydrogen peroxide.

$$Na_2O_2 + 2HCl \longrightarrow 2NaCl + H_2O_2$$

The super oxides are also strong oxidizing agents. They combine with dilute acids to produce salt, hydrogen peroxides and oxygen gas.

$$2KO_2 + 2HCl \longrightarrow 2KCl + H_2O_2 + O_2$$

13.2.4 Reactions of Alkali Metals with Halogens

Alkali metals react directly with halogens to produce their respective metal halides.

$$2M + X_2 \longrightarrow 2MX$$

Where,

'M' represents Li, Na, K, Rb or Cs and 'X_2' represents F_2, Cl_2, Br_2 or I_2.

For example; when sodium reacts with chlorine, then sodium chloride is formed.

$$2Na + Cl_2 \longrightarrow 2NaCl$$

The halides of alkali metals are white crystalline solids and are readily soluble in water. They are good conductors of electricity in the molten state or in solution form.

13.2.5 Effect of Heat on Nitrates, Carbonates and Bicarbonates

13.2.5.1 Effect of Heat on Nitrates

The nitrates of alkali metals are highly stable toward heat. They decompose into nitrites and oxygen gas on strong heating except lithium nitrate. Lithium nitrate decomposes more readily into oxide, nitrogen peroxide and oxygen gas.

$$4LiNO_3 \xrightarrow{\text{Heat}} 2Li_2O + 4NO_2 + O_2$$

$$2NaNO_3 \xrightarrow{\text{Heat}} 2NaNO_2 + O_2$$

The thermal stability of nitrates increases down the group due to increase in the polarizing power of positive ions.

13.2.5.2 Effect of Heat on Carbonates

The carbonates of alkali metals are highly stable toward heat. The lithium carbonate is significantly less stable towards heat and decomposes more readily. The carbonates of other alkali metals do not decompose even at higher temperature.

$$2Li_2CO_3 \xrightarrow{\text{Heat}} 2Li_2O + 2CO_2$$

The thermal stability of carbonates increases down the group due to increase in he polarizing power of positive ions.

13.2.5.3 Effect of Heat on Bicarbonates

The bicarbonates of alkali metals are stable toward heat but are not much stable. However, they decompose on heating to produce carbonates, carbon dioxide and water vapours.

$$2NaHCO_3 \xrightarrow{Heat} Na_2CO_3 + CO_2 + H_2O$$

The thermal stability of bicarbonates increases down the group due to increase in the polarizing power of positive ions.

13.2.6 Flame Tests: Origin of the Flames

Various metals give very attractive coloured flames when burnt in air. The colours of flames are the result of electrons moving from higher energy levels to lower energy levels in metal atoms. The alkali metals give characteristic coloured flames when a sample of an alkali metal or its salt is heated in the Bunsen burner. The colour of the emitted light (flames) can be used to identify the alkali metals. This process is known as flame test. Since the amount of energy released during the returning of electron to the ground state is different in different atoms, hence, different colours are imparted by the atoms to the flame.

Table 13.21: Alkali metals and their Flame Colours

Elements	Lithium	Sodium	Potassium	Rubidium	Cesium
Flame Colour	**Crimson** 	**Yellow** 	**Lilac** 	**Red-violet** 	**Blue** 

13.3 Group 2 Elements

The elements of group 2 (IIA) are beryllium, magnesium, calcium, strontium, and barium. They are all metals and are known as alkaline earth metals. They are harder, denser and have high melting and boiling points than alkali metals. Alkaline earth metals are always found in combined states with other elements. These are the second most active metals in the periodic table. They must be stored in oil (kerosene) to prevent their reaction with oxygen and water vapours in the air. They are not found as pure elements because of their high chemical reactivity. They are white or silvery except beryllium which is grey in colour.

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Table 13.22: Electronic Configuration of Alkaline Earth Metals

Name	Symbol	Atomic number	Electronic configuration	Valence shell electronic configuration
Beryllium	Be	4	$1s^2 2s^2$	$2s^2$
Magnesium	Mg	12	$1s^2 2s^2 2p^6 3s^2$	$3s^2$
Calcium	Ca	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	$4s^2$
Strontium	Sr	38	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2$	$5s^2$
Barium	Ba	56	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$ $5s^2 4d^{10} 5p^6 6s^2$	$6s^2$
Radium	Ra	88	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$ $5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2$	$7s^2$

They have two electrons in the valence shell. They form dipositive ions by losing two valence electrons and attain the stable electronic configuration of noble gases. They show oxidation state of +2. Alkaline earth metals are less reactive than alkali metals.

13.3.1 Atomic and Physical Properties of the Group 2 Elements

The trends in some atomic and physical properties of the group 2 elements are discussed as:

13.3.1.1 Trends in Atomic Radius

The atomic radius of alkaline earth metals increases down the group. This is due to increase in number of shells and shielding effect.

Table 13.23: Atomic Radius of Group 2 Elements

Element	Be	Mg	Ca	Sr	Ba	Ra
Atomic Radius (pm)	112	160	197	215	222	283 (van der Waal's)

Atomic radii of alkaline earth metals are smaller than those of alkali metals in the same period. This is due to high charge density of alkaline earth metals.

13.3.1.2 Trends in Ionization Energies

Alkaline earth metals have two electrons in their valence shell (ns^2). Their valence electrons are more tightly bound to the nucleus than those of alkali metals. They have, therefore, higher first ionization energies than alkali metals.

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Table 13.24: Ionization Energies of Group 2 Elements

Element	Be	Mg	Ca	Sr	Ba	Ra
First Ionization Energy (kJ/mol)	899	737	590	549	503	509
Second Ionization Energy (kJ/mol)	1757	1450	1145	1064	965	979

Their first and second ionization energies decrease down the group due to increase in atomic radii. The ionization energy of radium is, however, higher than barium.

Keep in Mind

The ionization energy of radium is higher than barium. This is because the radium has a filled 4f subshell; the 4f electrons shield very poorly so that nuclear charge for radium is 32 units higher than barium. The higher nuclear charge available for the radium valence electrons causes a contraction of the 7s orbital and an increase of the ionization energy.

13.3.1.3 Trends in Electronegativity Values

The electronegativity values of alkaline earth metals are small, but are higher than values for the alkali metals.

Table 13.25: Electronegativity Values of Group 2 Elements

Element	Be	Mg	Ca	Sr	Ba	Ra
Electronegativity	1.57	1.31	1.00	0.95	0.89	0.89

The values of electronegativity decrease down the group due to increase in atomic size.

13.3.1.4 Trends in Melting and Boiling Points

The melting and boiling points of these elements are higher than alkali metals.

Table 13.26: Melting and Boiling Points of Group 2 Elements

Element	Be	Mg	Ca	Sr	Ba	Ra
Melting Point (°C)	1287	649	839	768	727	700
Boiling Point (°C)	2500	1105	1494	1381	1850	1700

Melting and boiling points of these metals do not show any regular trend because they adopt different crystal structures.

13.3.2 Trends in Reactivity with Water

Although alkaline earth metals are less reactive than alkali metals, but they are still more reactive than the majority of other metals. Alkaline earth metals (except beryllium) react with water to produce hydroxides with the liberation of hydrogen gas.

$$\mathbf{Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2}$$

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The reactivity of alkaline earth metals increases down the group due to increase in atomic size. Beryllium does not react with water even at high temperature. Magnesium does not react with water at room temperature (25°C), but it will react with steam to form magnesium hydroxide and hydrogen gas. Whereas calcium, strontium and barium react with water at room temperature to produce hydroxides and hydrogen gas.

13.3.3 Reactions with Oxygen and Nitrogen

13.3.3.1 Formation of Simple Oxides and Peroxides

Alkaline earth metals react with oxygen to form normal oxides except barium and radium. Barium and radium, however, produce peroxides. The tendency of alkaline earth metals to form peroxides increases from top to bottom in a group.

The reactivity of alkaline earth metals with oxygen increases going from the top of the group to the bottom. Beryllium is relatively inert because it has a strong thin layer of oxide on its surface. It reacts with oxygen at 600°C. It is much reactive in the powder form.

Formation of normal oxides:

$$2Be + O_2 \longrightarrow 2BeO$$

$$2Mg + O_2 \longrightarrow 2MgO$$

$$2Ca + O_2 \longrightarrow 2CaO$$

Formation of peroxides:

$$Ba + O_2 \longrightarrow BaO_2$$

$$Sr + O_2 \longrightarrow SrO_2$$

13.3.3.2 Formation of Nitrides on Heating in Air

All the alkaline earth metals react with nitrogen to produce nitrides of the general formula, M_3N_2.

$$3Be + N_2 \longrightarrow Be_3N_2$$

$$3Mg + N_2 \longrightarrow Mg_3N_2$$

$$3Ca + N_2 \longrightarrow Ca_3N_2$$

Keep in Mind

Beryllium nitride is a covalent compound due to small size, high charge density and low ionization energy of beryllium. It has weak intermolecular force of attractions, which leads to its volatile nature. On the other hand the nitrides of other alkaline earth metals are ionic or electrovalent and are non-volatile.

13.3.4 Trends in Solubility of the Hydroxides, Sulphates and Carbonates

13.3.4.1 Solubility of Hydroxides

The solubility of hydroxides in water increases gradually on going down the group. $Be(OH)_2$ and $Mg(OH)_2$ are almost insoluble in water whereas the hydroxides of other alkaline earth metals are slightly soluble in water.

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13.3.4.2 Solubility of the Sulphates

The solubility of sulphates in water gradually decrease down the group. Thus $BeSO_4$ and $MgSO_4$ are fairly soluble, however $CaSO_4$ is slightly soluble in water, while the sulphates of strontium, barium and radium are almost water insoluble.

13.3.4.3 Solubility of Carbonates

The carbonates of alkaline earth metals are very slightly soluble in water. The solubility decreases down the group.

13.3.5 Trends in Thermal Stability of Nitrates and Carbonates

13.3.5.1 Trends in Thermal Stability of Carbonates

The carbonates of alkaline earth metals decompose on heating to form metal oxide and give off carbon dioxide gas.

$$CaCO_3 \xrightarrow{\text{Heat}} CaO + CO_2$$

Thermal stabilities of carbonates of alkaline earth metals increase down the group due to increase in ionic radii of cation moving down the group. This increase in atomic radii of metal cations reduces their polarizing power, which results in less polarization of the anion (CO_3^{-2}) by the larger metal cations. Because of this the decomposition of carbonates becomes more difficult.

13.3.5.2 Trends in Thermal Stability of Nitrates

The nitrates of alkaline earth metals decompose on heating to produce metal oxide, nitrogen peroxide and oxygen gas.

$$2Ca(NO_3)_2 \xrightarrow{\text{Heat}} 2CaO + 4NO_2 + O_2$$

The temperature at which thermal decomposition occurs increases moving down the group.

13.3.6 Peculiar behaviour of Beryllium

Beryllium differs in many of its properties from other alkaline earth metals due to its small atomic size and comparatively high electronegativity. The main points of difference of beryllium from other family members are:

i) Beryllium is much harder than other family members.

ii) The melting and boiling points of beryllium are much higher than other alkaline earth metals.

iii) The compounds of beryllium are more covalent than other members of its family. This is due to high charge density of beryllium than the rest. The high charge density of beryllium makes the removal of electron difficult.

iv) Beryllium does not react with either cold water or steam. Other alkaline earth metals react with water to form hydroxides and hydrogen gas.

$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$$

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v) Beryllium reacts with alkalis to produce hydrogen gas while other elements of its group do not react with alkalis.

$$Be + 2NaOH \longrightarrow \underset{\text{Sodium beryllate}}{Na_2BeO_2} + H_2$$

vi) The oxides and hydroxides of beryllium are amphoteric. They behave as acids towards strong bases and act as bases towards strong acids.

$$Be(OH)_2 + 2NaOH \longrightarrow Na_2Be(OH)_4$$

Sodium tetrahydroxoberyllate (II)

$$Be(OH)_2 + H_2SO_4 \longrightarrow BeSO_4 + 2H_2O$$

The oxides and hydroxides of other elements of group 2 are basic.

vii) Beryllium carbide forms methane gas while other alkaline earth metals form acetylene gas on hydrolysis.

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

viii) The nitride of beryllium, Be_3N_2 is volatile while the nitrides of other alkaline earth metals are non-volatile.

ix) Beryllium forms a large number of stable complex compounds whereas the other alkaline earth metals form very few complex compounds.

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Mining and Extraction of Elements/Metals

Mining of Elements/Metals

The earth crust is made up of various compounds and native elements such as gold, silver, copper and sulphur. The main elements in the earth crust are oxygen (46%) and silicon (28%). The rest of the earth crust is predominantly made up of aluminium (8%), iron (5%), calcium (4%), sodium (3%), magnesium (2%), and potassium (2%). Metals are important to society and support our modern standard of living. The naturally occurring rocks that contain metals or metal compounds in sufficient amounts to make it profitable to extract them are called ores. The extraction of ores from the earth is called mining. Ores are natural resources that human beings have been mining for thousands of years. The ores are mined from the ground, either by surface or underground methods.

Extraction of Elements/Metals from Their Ores

The method of extraction of a metal from its ore depends on the reactivity of metals. The most reactive metals are extracted hardly while the less reactive metals are extracted easily from their ores. The unreactive metals such as gold are not found in ores and are found in un-combined states.

The reactive metals such as potassium, sodium, calcium, magnesium and aluminium are extracted by electrolysis while the less reactive metals such as zinc, iron, tin and lead are extracted by reaction with carbon or carbon monoxide.

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Metal oxide + Carbon ⟶ Metal + Carbon dioxide

The carbon removes the oxygen from the metal oxide and forms carbon dioxide, leaving the pure metal behind. Reactions which involve the removal of oxygen in this way are called reduction reactions.

The native metals such as copper, silver, gold and platinum do not need to be chemically extracted from their ores, but chemical reactions may be required to remove other elements that might contaminate the metals.

13.4 Group 14 Elements

The group 14 (IVA) consists of carbon, silicon, germanium, tin and lead. They have four electrons in the valence shell and can form four covalent bonds. Carbon is an essential constituent of life. It is found in proteins, carbohydrates, fats, etc. Silicon is the second most abundant element in the earth's crust. It is a semiconductor and is commonly used in solar cells, transistors and computer chips. Germanium, a semiconductor, is used in computer industry. Lead, a metal, has been used for plumbing and to block radiation. Nowadays it is mainly used in the manufacture of car batteries, protective shielding around nuclear reactors and containers used for storing and transporting radioactive materials. Tin, a metal, is used to coat other metals to prevent corrosion. It can also be used in alloy formation such as solder, bronze and pewter.

The elements of group IVA show intermediate properties. These elements are present between strongly electropositive elements (Group IA, IIA and IIIA) and strongly electronegative elements (Group VA, VIA and VIIA).

Table 13.27: Electronic Configurations of Group 14 Elements

Name	Symbol	Atomic number	Electronic configuration	Valence shell electronic configuration
Carbon	C	6	$1s^2 2s^2 2p^2$	$2s^2 2P^2$
Silicon	Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$	$3s^2 3P^2$
Germanium	Ge	32	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$	$4s^2 4P^2$
Tin	Sn	50	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^2$	$5s^2 5P^2$
Lead	Pb	82	$1s^2 2s^2 2p^6$ $3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^2$	$6s^2 6P^2$

Their valence shell electronic configuration is $ns^2 np^2$.

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13.4.1 Physical Properties of Group 14 (IVA) Elements

The trends in physical properties of group 14 elements are discussed below:

13.4.1.1 Trends in Melting and Boiling Points

The melting and boiling points of group 14 elements decrease down the group. This is due to increase in atomic size and decrease in inter-atomic forces.

Table 13.28: Melting and Boiling Points of Group 14 Elements

Element	C	Si	Ge	Sn	Pb
Melting Point (°C)	3550	1420	945	232	327
Boiling Point (°C)	4830	2480	2850	2623	1751

The melting and boiling points of carbon and silicon are very high because they have tendencies to form macromolecules.

13.4.1.2 Trends from Non-metal to Metal

Metallic character increases down the group. Carbon and silicon are non-metals, germanium is semimetal, and tin and lead are metals. The electrical properties of silicon are similar to that of a semimetal.

13.4.1.3 Oxidation State

The elements of group IVA have four electrons in their valence shells and they have an oxidation state of +4. The first three elements may also have an oxidation state of –4 when they are bonded to more electropositive elements. Tin (Sn) and lead (Pb) also show an oxidation state of +2 that is the only oxidation state in which they produce ionic compounds.

The stability of +4 oxidation state decreases and that of +2 oxidation state increases on moving down the group. For example, the compounds of Ge^{2+} are less stable than Ge^{4+}. The compounds of Ge^{2+} act as strong reducing agents while those of Ge^{4+} act as oxidizing agents.

On the other hand, the compounds of Pb^{2+} ($PbCl_2$) are more stable than Pb^{4+}($PbCl_4$). Therefore, the compounds of Pb^{2+} are ionic and more common than Pb^{4+}. The compounds of Pb^{2+} act as reducing agents while those of Pb^{4+} act as oxidizing agents.

Inert Pair Effect and the Nature of Bond

The tendency of ns^2 electrons of the valence shell of metallic elements to remain unshared or unionized is called inert pair effect. The ability of an electron to get closer to the nucleus is called penetration. The penetration power of *s*-orbital is the maximum and it experiences stronger attraction to the nucleus. As a result of which the *s*-electrons fail to participate in bond formation. So the ns^2 electrons need more energy to remove. Hence, the oxidation states of heavier elements (esp. the last two elements of group IIIA, IVA, VA and VIA) are two less than what would be expected.

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The nature of bond is also affected by oxidation state. The metal compounds in their lower oxidation states are ionic in character while in their higher oxidation states they are covalent. For example, stannous chloride ($SnCl_2$) and plumbous chloride ($PbCl_2$) have +2 oxidation states and they are mainly ionic. Conversely the stannic chloride ($SnCl_4$) and plumbic chloride ($PbCl_4$) have +4 oxidation states and they are fairly covalent. This is because the size of Sn^{4+} and Pb^{4+} ions is smaller than Sn^{2+} and Pb^{2+} ions. The smaller the size of cation, the greater its tendency to form covalent bond. The tendency of cations to form ionic bonds increases down the group.

13.4.2 Chlorides of Carbon, Silicon and Lead

The chlorides of carbon, silicon and lead have general formula MCl_4. They are simple covalent molecules that are held together by weak van der Waal's forces. Since, they have low melting and boiling points and are frequently volatile liquids. Their melting points generally increase with increase in molecular mass. They have tetrahedral geometries.

13.4.2.1 Preparation of Tetrachlorides

The tetrachlorides may be prepared either by heating the element with appropriate halogen or by passing dry halogen over a highly heated mixture of dioxide and carbon.

$$M + 2Cl_2 \longrightarrow MCl_4$$

$$MO_2 + 2C + 2Cl_2 \longrightarrow MCl_4 + 2CO$$

Where, M represents C, Si and Pb.

13.4.2.2 Thermal Stability

The chlorides of carbon and silicon (CCl_4 and $SiCl_4$) are stable at high temperature and does not decompose easily. Conversely, the chloride of lead decomposes on heating. The thermal stability of tetrachlorides decreases from CCl_4 to $PbCl_4$. Thus: $CCl_4 > SiCl_4 > PbCl_4$

13.4.2.3 Reactions with Water (Hydrolysis)

Carbon tetrachloride does not react with water.

$$CCl_4 + H_2O \longrightarrow \text{No reaction}$$

Silicon tetrachloride (or tetrachlorosilane) and plumbic chloride react with water readily.

$$SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$$

$$PbCl_4 + 2H_2O \longrightarrow PbO_2 + 4HCl$$

Some of the $PbCl_4$ decomposes into $PbCl_2$ due to the instability of $PbCl_4$.

$$PbCl_4 \longrightarrow PbCl_2 + Cl_2$$

$PbCl_2$ is ionic in nature and slightly soluble in cold water and more soluble in hot water.

$$PbCl_2 \xrightarrow{\text{Water}} Pb^{2+} + 2Cl^{1-}$$

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13.4.3 Oxides of Group 14 (IVA) Elements

There are two main types of group IVA oxides and they are:

Monoxides: They have general formula MO. Examples are: CO, SnO and PbO.

Dioxides: They have general formula MO_2. Examples are: CO_2, SiO_2, SnO_2 and PbO_2.

13.4.3.1 Structure of Carbon Dioxide and Silicon Dioxide

The physical properties of carbon dioxide are different from silicon dioxide. Carbon dioxide is a colourless and odourless gas. It is commercially used in fire extinguishers and to carbonate beverages. The silicon dioxide is a high melting solid at ordinary temperature. The oxides of the rest of the group are also exist as solid. Because of this the structure of carbon dioxide is different from the rest of the oxides of group IVA.

Structure of Carbon Dioxide

Carbon dioxide consists of simple molecules. The molecule of carbon dioxide is triatomic. The bond strengths and bond lengths show that there are two carbon-oxygen double bonds in the carbon dioxide molecule.

$$\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}=C=\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}$$

The molecule of carbon dioxide has two dipoles. They are equal and have opposite directions. So they cancel the effect of each other. Therefore, the dipole moment of carbon dioxide is zero. Thus the only intermolecular forces in pure carbon dioxide are London dispersion forces. Hence, CO_2 is a gas. The solid CO_2 is called dry ice and has a face centred cubic structure. It is used in carbonated drinks, freeze meat, frozen foods and ice cream.

Structure of Silicon Dioxide

Silicon dioxide is commonly called silica. Most sands contain particle of silica and some impurities like iron oxide. Silicon dioxide is very stable. The structure of silicon dioxide is very different from carbon dioxide. It has no discrete molecules. It has three dimensional polymeric structure. In the crystal structure of silicon dioxide, each silicon atom is bonded to four oxygen atoms and every oxygen atom is bonded to two silicon atoms.

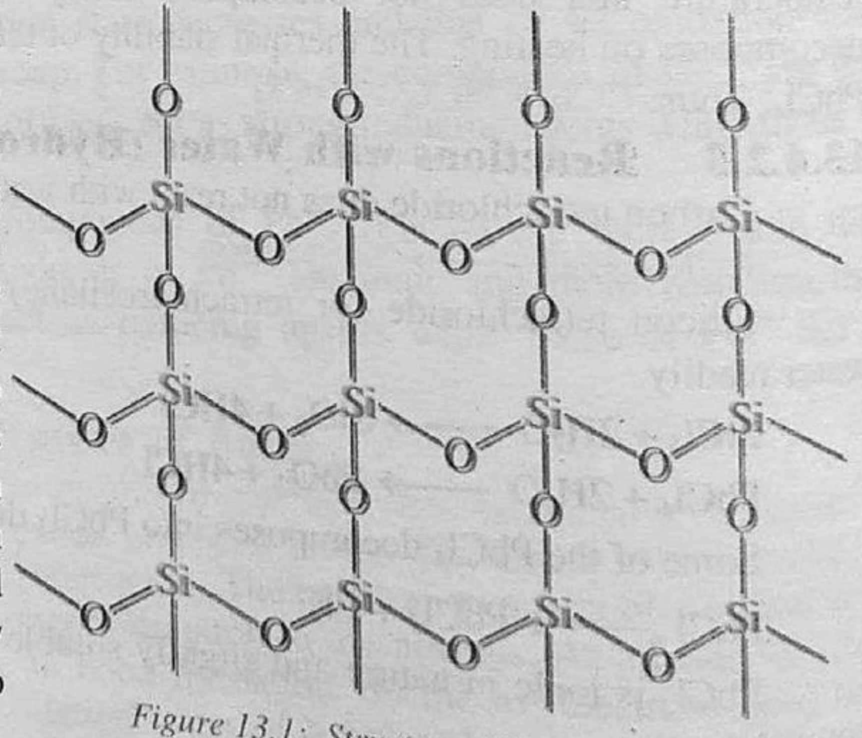

Figure 13.1: Structure of Silicon Dioxide

There is a regular tetrahedral arrangement of four oxygen atoms around each silicon atom. This arrangement gives a giant structure of silicon and oxygen atoms.

All the bond angles around silicon atom are 109.5°, consequently it has tetrahedral geometry. Silicon atom in silicon dioxide has no free electrons. Thus it does not conduct electricity under normal conditions.

13.4.3.2 Acid-Base Behaviour of Group 14 (IVA) Oxides

The acidity of oxides of group 14 decreases down the group. The dioxides of carbon and silicon are acidic while the dioxides of germanium, tin and lead are amphoteric. The monoxide of carbon (CO) is neutral while those of tin and lead are amphoteric.

Oxides of Carbon and Silicon

Carbon monoxide is often regarded as neutral oxide, but it is very slightly acidic. It does not react with water to produce the expected formic acid, but it can react with hot concentrated sodium hydroxide solution to produce solution of sodium formate.

$$NaOH + CO \longrightarrow HCOONa$$

Carbon dioxide is acidic and reacts slightly (about 0.1%) with water to produce the carbonic acid.

$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$

The carbonic acid then ionizes slightly to form hydrogen ion and bicarbonate ion.

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

The bicarbonate ion can further ionize to give carbonate ion.

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{--}$$

Carbon dioxide reacts with cold sodium hydroxide to produce solutions of either sodium carbonate or sodium bicarbonate, depending on the quantity of reactants.

$$NaOH + CO_2 \longrightarrow NaHCO_3$$
$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

Silicon dioxide does not react with water because it has giant covalent structure. It reacts with hot concentrated sodium hydroxide solution to produce sodium silicate.

$$2NaOH + SiO_2 \longrightarrow Na_2SiO_3 + H_2O$$

The Oxides of Germanium, Tin and Lead

The monoxides of germanium, tin and lead (GeO, SnO and PbO) are amphoteric as they react with both acids as well as bases.

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i) $$GeO + 2HCl \longrightarrow GeCl_2 + H_2O$$
$$GeO + 2NaOH \longrightarrow \underset{\text{Sodium Germinate (II)}}{Na_2GeO_2} + H_2O$$

ii) $$SnO + 2HCl \longrightarrow SnCl_2 + H_2O$$
$$SnO + 2NaOH \longrightarrow \underset{\text{Sodium Stannate (II)}}{Na_2SnO_2} + H_2O$$

iii) $$PbO + 2HCl \longrightarrow PbCl_2 + H_2O$$
$$PbO + 2NaOH \longrightarrow \underset{\text{Sodium Plumbate (II)}}{Na_2PbO_2} + H_2O$$

The dioxides of germanium, tin and lead such as GeO_2, SnO_2 and PbO_2 are amphoteric as they react with both acids and bases to form salts.

i) $$GeO_2 + 4HCl \longrightarrow GeCl_4 + 2H_2O$$
$$GeO_2 + 2NaOH \longrightarrow \underset{\text{Sodium Germanate (IV)}}{Na_2GeO_3} + H_2O$$

ii) $$SnO_2 + 4HCl \longrightarrow SnCl_4 + 2H_2O$$
$$SnO_2 + 2NaOH \longrightarrow \underset{\text{Sodium Stannate (IV)}}{Na_2SnO_3} + H_2O$$

iii) $$PbO_2 + 4HCl \longrightarrow PbCl_4 + 2H_2O$$
$$PbO_2 + 2NaOH \longrightarrow \underset{\text{Sodium Plumbate (IV)}}{Na_2PbO_3} + H_2O$$

Molten NaOH is required for the reaction of PbO_2 to produce sodium plumbate (IV).

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Canning process and the use of Metals

Canning is a method of preserving food from spoilage by storing it in airtight container where the food contents are processed. The concept of canning is to heat a food in a airtight container so that no microbial growth can occur in the food until the package is opened. When the package is opened, the effects of canning will be lost and the food is regarded as perishable. Canning was invented by Nicolas Appert of France in 1809, in response to the need to supply Napoleon's army and navy with good quality food. Appert used glass bottles for preserving foods such as pickles, jams etc. but Durand, an English, used metal and pottery at about the same time. The two ideas together gave us the tin cans. Today, canned foods are stored in steel, tin and aluminum, which keeps the food safe and sealed, and retains the food's nutritional value. Canning is a very effective method of food preservation. Canned food can be stored for a long time.

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13.5 Group 17 Elements

The group 17 (VIIA) elements consist of fluorine, chlorine, bromine, iodine and astatine, and are collectively called halogens. The word 'halogen' comes from the Greek 'halos' and 'genes' meaning 'salt formers'. This is because all of these elements react directly with metals produce salts. They are all poisonous and corrosive. They are the most reactive nonmetals. Fluorine is the most reactive nonmetal known. Because of high chemical reactivity, they cannot exist as free in nature. They are found in combined form as minerals deposits in sea water, salt lakes and in underground salt beds.

Table 13.29: Electronic Configuration of VIIA Group Elements

Name	Symbol	Atomic number	Electronic configuration	Valence shell electronic configuration
Fluorine	F	9	$1s^2 2s^2 2p^5$	$2s^2 2p^5$
Chlorine	Cl	17	$1s^2 2s^2 2p^6 3s^2 3p^5$	$3s^2 3p^5$
Bromine	Br	35	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$	$4s^2 4p^5$
Iodine	I	53	$1s^2 2s^2 2p^6$ $3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^5$	$5s^2 5p^5$
Astatine	At	85	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$ $5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^5$	$6s^2 6p^5$

They have seven electrons in their outermost shells. Two electrons in the *ns* orbital and five electrons in the *np* orbital. The fluorine is the only halogen which shows only –1 oxidation sate while other elements show –1 as well as +1, +3, +5, +6 and +7 oxidation states.

The halogens exist as diatomic molecules and they are all coloured. Their molecules are held together by weak van der Waal's forces.

Table 13.30: Physical States and Colours of Halogens

Elements	F_2	Cl_2	Br_2	I_2
Physical States	Gas	Gas	Liquid	Solid
Colours	Pale yellow ■	Greenish yellow ■	Reddish brown ■	Lustrous violet black ■

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13.5.1 Atomic and Physical Properties of the Group VIIA Elements

The trends in some atomic and physical properties of the group VIIA elements are discussed below:

13.5.1.1 Trends in Atomic Radius

The atomic radii of group VIIA elements go on increasing as we move down the group. This is due to increase in the number of shells.

Table 13.31: Atomic Radius of Halogens

Element	F	Cl	Br	I
Atomic Radii (pm)	72	99	114	133

13.5.1.2 Trends in Electronegativity

Halogens have very high values of electronegativity. These values decrease from fluorine to iodine as the atomic number increases. The fluorine is the most electronegative atom among all of the elements.

Table 13.32: Electronegativity Values of Halogens

Element	F	Cl	Br	I
Electronegativity	3.98	3.00	2.96	2.56

13.5.1.3 Trends in Electron Affinity

Electron affinity values decrease from chlorine to iodine. The electron affinity of fluorine is less than that of chlorine. This is due to smaller size of fluorine. When an extra electron is added to fluorine atom, the high electron density is produced round the fluoride ion. This high electron density increases the repulsion between the electrons already present in the relatively compact 2p orbitals of fluorine and the electron being added. Due to this electron-electron repulsion, the fluorine atom shows lesser tendency to attract an electron towards itself to form fluoride ion and hence the electron affinity of fluorine becomes less than that of chlorine. The order of electron affinity values of halogens is: $Cl < F > Br > I$.

Table 13.33: Electron Affinity of Halogens

Element	F	Cl	Br	I
Electron Affinity (kJ/mol)	−328	−349	−325	−295

13.5.1.4 Trends in Melting and Boiling Points

Halogens have low melting and boiling points. Their melting and boiling points gradually increase down the group. This is because the London dispersion forces become stronger as we move down the group.

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Table 13.34: Melting and Boiling Points of Halogens

Element	F_2	Cl_2	Br_2	I_2
Melting Points (°C)	−220	−101	−7.2	114
Boiling Points (°C)	−188	−35	59	184

13.5.1.5 Bond Enthalpies in Halogens

The amount of energy required to break all bonds in one mole of gaseous substance is called bond enthalpy or bond energy.

Table 13.35: Bond Enthalpies of Halogens

Element	F_2	Cl_2	Br_2	I_2
Bond Enthalpy (kJ/mol)	159	243	193	151

The bond enthalpies of the halogens decrease from chlorine to iodine due to increase in atomic size, but the bond enthalpy of fluorine does not fit the pattern. The expected value of bond enthalpy of F—F bond is about 290 kJ/mol. The actual value of bond enthalpy of fluorine is 159 kJ/mol. The decrease in bond enthalpy of fluorine is due to larger repulsion between the nonbonding electrons of small sized atoms of the molecule.

13.5.1.6 Bond Enthalpies in Hydrogen Halides

The binary compounds of halogens with hydrogen are called hydrogen halides. They are also known as hydrides of halogens or hydrohalic acids.

Table 13.36: Bond Enthalpies of Hydrogen Halides

Hydrogen Halide	HF	HCl	HBr	HI
Bond Enthalpy (kJ/mol)	565	432	366	299

The bond enthalpies of hydrogen halides decrease as we move down the group. This is due to increase in the size of halogen atoms. As the size of halogen atoms increases from fluorine to iodine, the hydrogen and halogen bond length in hydrogen halides (HX) also increase from H—F to H—I. The increase in H—X bond length decreases the bond strength. Because of this the bond enthalpies decrease from H—F to H—I.

13.5.2 Strength of Halogens as Oxidizing Agents

Halogens are strong oxidizing agents because they can easily accept one electron to complete their octet in chemical reactions. The strength of halogens as oxidizing agents decreases as we move down the group. This is due to increase in atomic size and decrease in electronegativity. The oxidizing power of halogens decreases in the following order:

$$F_2 > Cl_2 > Br_2 > I_2$$

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The oxidizing power of fluorine is maximum among the halogens because of its small size and high electronegativity.

The oxidizing properties of halogens can be explained as follows:

The fluorine has ability to oxidize the chloride, bromide and iodide ions to chlorine, bromine and iodine respectively.

$F_2 + 2Cl^- \longrightarrow 2F^- + Cl_2$

$F_2 + 2Br^- \longrightarrow 2F^- + Br_2$

$F_2 + 2I^- \longrightarrow 2F^- + I_2$

The chlorine has ability to oxidize the bromide and iodide ions to bromine and iodine respectively.

$Cl_2 + 2F^- \longrightarrow$ No action

$Cl_2 + 2Br^- \longrightarrow 2Cl^- + Br_2$

$Cl_2 + 2I^- \longrightarrow 2Cl + I_2$

The bromine has ability to oxidize the iodide ions to iodine.

$Br_2 + 2F^- \longrightarrow$ No action

$Br_2 + 2Cl^- \longrightarrow$ No action

$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$

The iodine cannot oxidize any halide ion.

$I_2 + 2F^- \longrightarrow$ No action

$I_2 + 2Cl^- \longrightarrow$ No action

$I_2 + 2Br^- \longrightarrow$ No action

13.5.3 The Acidity of Hydrogen Halides

All the halogens combine with hydrogen to produce hydrogen halides (e.g. HF, HCl ,HBr, HI) and their aqueous solutions are commonly known as hydrohalicacids or simply halogen acids. The general formula of hydrogen halides is HX. All the hydrogen halides are irritant.

$H_2 + X_2 \longrightarrow 2HX$

All the hydrogen halide molecules in the gaseous state are essentially covalent and hence are not able to ionize to give hydrogen ion (proton) but in aqueous solution they ionize to give hydrogen ions. The hydrogen ions combine with water molecules to form hydronium ions, H_3O^+ and hence hydrogen halide molecules act as acids.

$HX + H_2O \longrightarrow H_3O^+ + X^-$

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The acidic strength (proton releasing power) of HX molecules increases from HF to HI. The acidic strength of hydrogen halides is in the following order: HF < HCl < HBr < HI. Thus HF is the weakest and HI is the strongest acid. HF ionizes only slightly and is therefore a weak acid whereas HCl, HBr and HI ionize almost completely and are therefore strong acids.

Table 13.37: Dissociation Energies of Hydrogen Halides

Hydrogen Halide	HF	HCl	HBr	HI
Dissociation Energy (kJ/mol)	565	432	366	299

The weakest acidic nature of HF is due to (i) the high dissociation energy of the H—F bond and (ii) the formation of weakest conjugate base (F^-) during the ionization of HF molecules. Its conjugate base has very little tendency to gain proton from water.

13.5.4 Halide Ions as Reducing Agents and Trends in Reducing Strength of Halide Ions

A substance that loses electrons during a chemical reaction is called reducing agent while a substance that gains electrons during a chemical reaction is called oxidizing agent.

The reducing agent reduces other substances (decrease the oxidation states of other substances) and is oxidized itself (its oxidation state is increased). The halide ions (or hydrogen halides) reduce the oxidizing agents and are oxidized to X_2 molecules. For example,

$$4HX + O_2 \longrightarrow 2H_2O + 2X_2$$

In the above reaction, the halide ion (or hydrogen halide) acts as a reducing agent because it loses electrons.

The trend in the reducing ability of halide ions (or hydrogen halides) is opposite to the trend in the oxidizing power of the halogens. The reducing properties of halide ions (or hydrogen halides) increase from fluoride ion (or HF) to iodide ion (or HI). This is due to increase in the ionic radii of halide ions down the group of periodic table. The reducing properties of halide ions or hydrogen halides are in the following order:

$F^- < Cl^- < Br^- < I^-$ or $HF < HCl < HBr < HI$

The fluoride ion or HF is the weakest reducing agent while the iodide ion or HI is the strongest reducing agent. In reality, the fluoride ion or HF has no considerable reducing properties at all. The fluoride ion or HF is so weak that it does not reduce

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even very strong oxidizing agents such as SO_2, and HI. It is also not able to reduce any of the halogens (Cl_2, Br_2 and I_2) to its corresponding halide ions (or halogen acids). For example:

$$2F^- + Cl_2 \longrightarrow \text{No action}$$

$$2F^- + Br_2 \longrightarrow \text{No action}$$

$$2F^- + I_2 \longrightarrow \text{No action}$$

The chloride ion (Cl^-) or HCl molecule reduces only strong oxidizing agents like F_2 and is itself oxidized to Cl_2. It can neither reduce Br_2 nor I_2.

$$2Cl^- + F_2 \longrightarrow 2F^- + Cl_2$$

$$2Cl^- + Br_2 \longrightarrow \text{No action}$$

$$2Cl^- + I_2 \longrightarrow \text{No action}$$

The bromide ion (Br^-) or HBr molecule reduces $F_2$and Cl_2 but not I_2.

$$2Br^- + F_2 \longrightarrow 2F^- + Br_2$$

$$2Br^- + Cl_2 \longrightarrow 2Cl^- + Br_2$$

$$2Br^- + I_2 \longrightarrow \text{No action}$$

The iodide ion (I^-) or HI molecule, being the strongest reducing agent, can reduce all of the other three halogens to their corresponding halide ions (or halogen acids).

$$2I^- + F_2 \longrightarrow 2F^- + I_2$$

$$2I^- + Cl_2 \longrightarrow 2Cl^- + I_2$$

$$2I^- + Br_2 \longrightarrow 2Br^- + I_2$$

We may say that a given halide ion (or halogen acid) can reduce only that halogen molecule which lies above it in the group 17 (VIIA) of the periodic table. The halide ion (or halogen acid) cannot reduce that halogen molecule which lies below it in the group.

Society, Technology and Science

Properties and Commercial Uses of the Halogens

Properties and Uses of Fluorine

Fluorine is highly toxic colourless gas. It is the most electronegative and reactive element. It reacts directly with all elements except helium (He), neon (Ne) and argon (Ar). It is used in the manufacture of chlorofluorocarbons, commercially known as Freons.

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Freons are used as refrigerant in refrigerators, cooling agent in air conditioners, aerosol propellants and cleaning agents. Fluorine is also used in the manufacture of Teflon. Teflon is a valuable plastic and is used for coating the electrical wiring. It provides a non-stick surface for frying pans and other cooking related products.

Properties and Uses of Chlorine

Chlorine (Cl_2) is a highly toxic gas with a pale yellow-green colour. Chlorine is chemically less active than fluorine but more active than bromine and iodine. Some of the uses of chlorine depend on its toxic effects. For example, chlorine is used as a disinfectant in swimming pools and water treatment plants. Many organic compounds of chlorine are used in the manufacture of antiseptics, insecticides, weed killers and herbicides. Chlorine is a very strong oxidizing agent and is used commercially as a bleaching agent. Large amounts of chlorine are used to make solvents such as carbon tetrachloride (CCl_4), chloroform ($CHCl_3$), dichloroethylene ($C_2H_2Cl_2$), and trichloroethylene (C_2HCl_3).

Properties and Uses of Bromine

Bromine (Br_2) is a reddish-orange liquid with an unpleasant, choking odour. The vapours of bromine are irritating to the eyes and throat. The liquid is highly corrosive and can cause serious burns if spilled on the skin. Bromine is chemically less active than fluorine and chlorine but more active than iodine. Bromine is used to prepare flame retardants, fire-extinguishing agents, sedatives, germicides, pesticides, fungicides and insecticides. Bromine can also be used as a disinfectant like chlorine.

Properties and Uses of Iodine

Iodine is an intensely coloured solid with an almost metallic lustre. Iodine vapours are irritating to the eyes and respiratory system. Iodine is chemically less active than other halogens (not counting astatine). Iodine acts as an antioxidant in our blood. It is also used as a cough expectorant, and is also helpful in treating allergies, dermatitis, bladder infections, and moles. The human body uses iodine to make thyroxine, an important hormone (chemical messenger) produced by the thyroid gland. The thyroid is a gland located in the neck that plays an important role in metabolism. The deficiency of iodine in the human body can lead to 'goiter', a swelling around the neck. Iodine can be used as a water purifying agent. It is also used as a sterilizing agent. Iodine can also be used for the preparation of antiseptics such as iodex and tincture.

Properties and Uses of Bleaching Powder

Bleaching powder is also known as calcium hypochlorite or sometimes calcium oxychloride and its chemical formula is $CaOCl_2$. It is a pale yellow powder and has a strong smell of chlorine. It loses chlorine when it reacts with carbon dioxide as:

$$CaOCl_2 + CO_2 \longrightarrow CaCO_3 + Cl_2$$

It is mainly used to bleach cotton, wool, linen in textile industries, and wood pulp. It is used as an oxidizing agent in many industries to obtain various chemical products. It is used in the sterilization of water and makes water free from germs. It is used in the manufacture of chloroform, which is used as anaesthetics in hospitals by doctors before surgery. It is used as a disinfectant and germicide in sewers and drains. It is used as bathroom cleanser. It makes wool unshrinkable.

Fluoride Toxicity and Deficiency

Fluoride is a trace mineral, which means it is only needed in a small amount. This trace mineral is currently considered essential by some scientists. The main function of fluoride is to harden the bones and teeth. An adult male needs 1.5 to 4.0 mg daily. An adult woman requires less and children require even less depending on how much they weigh. It is found in grape products, dried fruits, dried beans, cocoa powder and walnuts. The good dietary sources of fluoride are fluorinated water, sea food, seaweed and tea.

Fluoride Deficiency

The term fluoride deficiency means a condition where the concentration of fluoride essential to human health is less than required limit. The reduced intake could lead to a fluoride deficiency and result in the development of dental caries (tooth decay). Deficiency of fluoride can cause dental caries, brittle and weak bones, and fractured hips in the elderly. The dental carries in children is more, where the fluoride in drinking water is less than 0.5 mg/L. Normally water containing 0.5 to 1 mg/L is considered to be sufficient in most parts of the world.

Fluoride Toxicity (Overdose)

The term fluoride toxicity means a condition where the concentration of fluoride essential to human health is high than required limit. Excess fluorine can accumulate in teeth and bones, causing fluorosis. Fluorosis is a cosmetic condition, not a disease. Often, it is so mild that only a dental professional can detect it. Teeth affected by mild fluorosis may show no changes or changes visible only to a dental professional. Mild to moderate fluorosis produces white lines, streaks or spots. In more severe fluorosis, the teeth can become pitted and have brown, grey or black spots. The enamel also may have an unusual shape.

The massive doses of fluoride (20 to 80 ppm daily) can give rise to:

- Skeletal fluorosis, which is a hardening of the bones along with arthritic pain, stiffness, nerve damage and finally paralysis.
- Gastrointestinal irritation and haemorrhage

Summary of Facts and Concepts

- There are four blocks of elements in the periodic table, namely s-, p-, d- and f-block.
- The s-block elements are those elements in which last electron enters into s-orbitals.
- The elements of group 1A are called alkali metals except hydrogen. They are soft, silvery-white metals and good conductors of heat and electricity.
- The elements of group IIA are called alkaline earth metals. They are harder and denser and have high melting and boiling points than the alkali metals.
- Alkali metals form 1+ ions by losing their one outer s-electron, while the alkaline earth metal form 2+ ions by losing their two outer s-electrons.
- The elements of second period from multiple (double or/and triple) bonds but are generally unable to form more than four bonds.
- The ionization energy and electronegativity generally increase, while atomic radius and metallic character generally decrease from left to right in a period of periodic table.
- The ionization energy and electronegativity generally decrease, while atomic radius and metallic character generally increase from top to bottom in a group of periodic table.
- The electronic configuration of group IVA show that they contain four electrons in their outer most shells, two electrons of which are in s-orbital and the remaining two are in p-orbitals.
- The elements of group IVA (C, Si, Ge, Sn and Pb) show the usual increase in metallic character down the group. They frequently adopt an oxidation state of +4, but the +2 state becomes increasingly more stable from Ge to Sn to Pb.
- Halogens (F, Cl, Br and I) are very reactive non-metals. Oxidizing power of halogens decreases from F_2 to I_2.
- The acidic strength of hydrogen halides increases from HF to HI.
- The reducing properties of hydrogen halides increase from HF to HI.

Multiple Choice Questions

Select one answer from the given choices for each question:

i) Which of the following give strong alkaline solution in water?

(a) Sodium
(b) Potassium
(c) Beryllium
(d) Magnesium

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ii) The total number of electrons in the valence shell of p-block elements varies from:

(a) 1 to 6 (b) 2 to 7
(c) 3 to 8 (d) 1 to 8

iii) The atomic radii in s-block elements:

(a) Decrease down the group
(b) Increase down the group
(c) Remains same in the group
(d) First decreases and then increases

iv) The general electronic configuration of p-block elements is as:

(a) ns^1, ns^2 (b) ns^1, np^6
(c) ns^2, np^6 (d) ns^2, np^{1-6}

v) Alkali and alkaline earth metals give flame tests when burnt in air. It is due to:

(a) Excitation of electrons
(b) De-excitation of electrons
(c) Smaller ionic radius of these metals
(d) Smaller charge density of these metals

vi) Basic oxides react with acidic oxides to form

(a) Hydrides (b) Halides
(c) Hydrogen halides (d) Salts

vii) The characteristic flame colour of cesium is:

(a) Green (b) Blue
(c) Yellow (d) Violet

viii) Which one of the following oxides is acidic?

(a) CO_2 (b) GeO_2
(c) SnO_2 (d) PbO_2

ix) Which one of the following elements only form dioxide?

(a) Carbon (b) Silicon
(c) Germanium (d) Tin

x) The lowest melting points in carbon family (group IVA) is of:

(a) Silicon (b) Germanium
(c) Tin (d) Lead

xi) Which one of the following reacts with water in elemental form at room temperature?

(a) Argon (b) Sulphur
(c) Chlorine (d) Silicon

xii) Which one of the following is liquid at room temperature?

(a) Fluorine (b) Chlorine
(c) Bromine (d) Iodine

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xiii) Which one of the following is the strongest oxidizing agent?
(a) Fluorine (b) Chlorine
(c) Bromine (d) Iodine

xiv) The bond enthalpy of fluorine is:
(a) Less than chlorine (b) More than chlorine
(c) More than bromine (d) Less than iodine

xv) Which one of the following has giant structure?
(a) SO_2 (b) SiO_2
(c) Cl_2O_7 (d) P_4O_{10}

xvi) Which halogen of the following can oxidize all other halide ions?
(a) Iodine (b) Fluorine
(c) Bromine (d) Chlorine

xvii) The HCl is unable to reduce:
(a) Cl_2 (b) F_2
(c) I_2 (d) HF

xviii) Which halogen acid cannot be stored in glass containers?
(a) HF (b) HCl
(c) HBr (d) HI

Short Answer Questions

Q.1. Why are the alkali metals so reactive?

Q.2. Why are alkali metals stored in oil?

Q.3. Why the reaction of caesium with water is very fast, violent and exothermic?

Q.4. What are the general trends in melting and boiling points going down the alkali metals?

Q.5. What is the effect of atomic radius on the chemical reactivity of the alkali metals?

Q.6. Which are the most and the least reactive alkali metals?

Q.7. What are the products of a reaction between:
(i) An alkali metal and water? (ii) An alkaline earth metal and water?

Q.8. How many electrons do alkaline earth metals have to lose to attain the electronic configuration of noble gases?

Q.9. Why are metals like sodium, potassium and aluminium not available in free state in nature?

Q.10. Why is the ionization energy of radium higher than barium?

Q.11. Why is $BeCl_2$ covalent and not ionic?

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Q.12. $Be(OH)_2$ is amphoteric, how?

Q.13. Can you explain why alkaline earth metals are less reactive than alkali metals?

Q.14. Write an equation to show the thermal decomposition of calcium carbonate.

Q.15. Write an equation to show the reaction of beryllium hydroxide with an acid and base.

Q.16. Why is molten sodium chloride a good conductor of electricity?

Q.17. Why hydrogen and helium belong to s-block elements.

Q.18. Stannous chloride is more stable than stannic chloride, why?

Q.19. SiO_2 is a solid and CO_2 is a gas, why?

Q.20. Why Fluorine is the most reactive element in Group 17?

Q.21. Explain why the electron affinity of fluorine is less than that of chlorine?

Q.22. Why the bond energy of fluorine is less than that of chlorine?

Q.23. Why is HF a weak acid than other hydrohalic acids?

Q.24. Explain why the HCl molecule can reduce only F_2 to HF but neither Br_2 to HBr nor I_2 to HI?

Q.25. Why the reactivity of halogens decreases down the group?

Q.26. Why are iodide ions stronger reducing agents than chloride ions?

Q.27. What makes one atom more electronegative than another?

Long Answer Questions

Q.1. Write a short note on s-block, p-block, d-block and f-block elements?

Q.2. Discuss the atomic and physical properties of period 3 elements.

Q.3. Explain the reactions of period 3 elements with:
(i) water (ii) oxygen (iii) chlorine.

Q.4. Describe physical properties of oxides of period 3 elements.

Q.5. What do you know about acid-base behaviour of the oxides of period 3 elements?

Q.6. Describe reactions of the oxides of period 3 elements with:
(i) water (ii) acids (iii) bases.

Q.7. Write note on structure, electrical conductivity, solubility, melting and boiling points of chlorides of period 3 elements.

Q.8. Write down properties of hydroxides of period 3 elements.

Q.9. What are alkali and alkaline earth metals and draw their electronic configurations?

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Q.10. Describe the atomic and physical properties of alkali metals.

Q.11. Explain the trends in reactivity with water of alkali metals.

Q.12. Explain the reactions of alkali metals with oxygen and halogens.

Q.13. Describe the effect of heat on nitrates, carbonates and hydrogen carbonates of alkali metals.

Q.14. How are the colours produced in the flame tests?·Explain.

Q.15. Explain atomic and physical properties of alkaline earth metals.

Q.16. Discuss the trends in reactivity of alkaline earth metals with water.

Q.17. Describe the reactions of alkaline earth metals with oxygen and nitrogen.

Q.18. Discuss the trends in solubility of hydroxides, sulphates, and carbonates of alkaline earth metals.

Q.19. Explain the trends in thermal stability of the nitrates and carbonates of alkaline earth metals.

Q.20. How beryllium differs from other members of its group?

Q.21. Write short note on group 14 (IVA) elements. What are the atomic and physical properties of group IVA elements?

Q.22. Define the term inert pair effect. Explain inert pair effect in the formation of ionic and covalent bonds.

Q.23. Write down preparation and thermal stability of chlorides of carbon, silicon and lead.

Q.24. Describe the reactions of group IVA elements with water.

Q.25. Discuss the important oxides of group IVA elements.

Q.26. Describe the acid-base behaviour of group IVA oxides.

Q.27. What are halogens and draw their electronic configuration?

Q.28. Explain the atomic and physical properties of halogens.

Q.29. Briefly discuss strength of halogens as oxidizing agents.

Q.30. Write note on acidity of hydrogen halides.

Q.31. Halide ions act as reducing agents. Explain.

Q.32. Give the trends in reducing strength of halide ions.

Q.33. Write a balance chemical equation for the reaction of:

i) Calcium with water
ii) Sodium monoxide with water
iii) Aluminium with water
iv) Sulphur trioxide with water
v) Chlorine(VII) oxide (Dichlorine heptaoxide) with water.

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