

# CHM 112 COURSE CONTENTS

**Periodic Table (description and classification of the elements);**

**Periodic Properties (atomic radius and ionic, ionization energy, electron affinity, metallic character);**

**Electronic configuration and atomic orbitals;**

**Chemical Bonding- bond character, bond theory, hybridization, intermolecular bonds;**

**Structures of solids**

**Chemistry of selected representative elements**

**Qualitative analysis**

## **Recommended Textbooks**

**Basic Concepts in General, Inorganic & Physical Chemistry (3<sup>rd</sup> Edition) by Sontan, A. A.**

**Concise Inorganic Chemistry (5<sup>th</sup> Edition) by J. D. Lee**

**Chemistry by Raymond Chang (6<sup>th</sup> Edition).**

## Table

### Periodic

#### Descriptions and Classification of the Elements

##### Early periodic tables

In 1817: Döbreiner's triads – classified 3 elements based on weight / regularly varying properties: S Se Te

- 1865: Newlands – "law of octaves", about 55 elements
- Early tables were based on mass number (A) or "combining weight"

##### Modern periodic table

- 1869: Mendeleev and Meyer – "properties of the elements are a periodic function of their atomic weights;" 63-element table.
- 1913: Moseley – X-ray emission spectra vary with atomic number (Z).
- Modern periodic law: Periodic properties are a function of atomic number of elements.
- Periods: horizontal rows (seven in all); properties of elements in period show no similarity.

Note that the lanthanides (period six) and the actinides (period seven) are at the bottom of the table

##### We give some groups names

- IA are the Alkali metals
- IIA the Alkali Earth metals
- VIIA the Halogens
- VIIIA the Noble gases
- Btw IIA & IIIA are the Transition elements
- Lanthanides, Actinides and Artificial elements

##### We can classify (arrange) elements in different ways:-

- naturally occurring/made by scientists
- solid/liquid/gas

- metal/non-metal

The Periodic Table lists the chemical elements in increasing atomic number. The Periodic Table arranges elements with similar chemical properties in groups (vertical columns). All the elements in a group have similar chemical properties as they have the same number of outer electrons. The Periodic Table of the elements is a useful way of classifying the elements. A vertical column of elements in the periodic table is called a group. The elements in the same group of the periodic table have similar chemical properties. The noble gases are a group of very unreactive elements.

Every element is made up of very small particles called atoms. Atoms of different elements have a different number called the atomic number. Atoms have a very small, positively charged nucleus, with negatively charged electrons outside the nucleus in energy levels.

The nucleus of every atom (except hydrogen) contains two particles:-

- Protons (+ve charge / mass 1amu)
- Neutrons (no charge / mass 1amu)
- Electrons (-ve charge / mass 1/2000amu)

Atoms are neutral because the positive charge of the nucleus is equal to all of the negative charges of the electrons added together. Atoms are neutral because the numbers of protons and electrons are equal - the opposite charges cancel.

### Metals, Non-Metals and Metalloids

- Metals are shiny, good conductors of heat and electricity, malleable, ductile, and form cations (positive ions, loss of electrons) during chemical change.
- Non-metals are not shiny. They are poor conductors, brittle. They frequently form anions (negative, gain of electrons) in chemical changes.
- Metalloids have some characteristics of both metals and nonmetals. They are B, Si, Ge, As, Sb, Te, Po, At.

### Solid, Liquid and Gaseous Elements at Room Temperature

- Some elements are gases at room temperature : hydrogen, nitrogen, oxygen, fluorine, chlorine, VIIA's;
- two are liquids: bromine and mercury ;

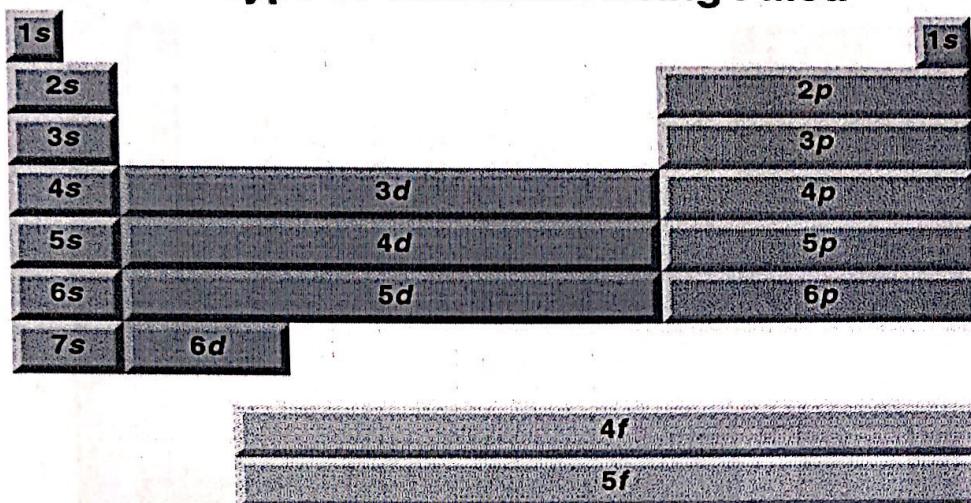
- the rest are solids.

## The Periodic Law

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## Classification of Elements According to the Type of Subshells Being Filled



Groups I – II: s-block elements

Groups III – VIII/0: p-block

Transition elements: d-block

Lanthanides & Actinides: f-block

Modern periodic law states that the periodic properties of elements are a function of their atomic number. Atomic number determines the trend in periodic properties across groups (left to right within the periods).

The following properties, including atomic radius, decrease from left to right:

- Atomic & ionic size
- Ionization energy
- Electron affinity
- Electronegativity
- Metallic character
- Melting & Boiling points
- Electrical & Thermal Conductivities

## The Periodic Table

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA 1A	IIA 2A	IIIB 3B	IVB 4B	VB 5B	VIIB 6B	VIIIB 7B	VIII			IB 1B	IIB 2B	IIIA 3A	IVA 4A	VA 5A	VIa 6A	VIIA 7A	VIIIA 8A
1	<b>H</b> 1.008																<b>He</b> 4.003	
2	<b>Li</b> 6.941	<b>B</b> 9.012											<b>B</b> 10.81	<b>C</b> 12.01	<b>N</b> 14.01	<b>O</b> 16.00	<b>F</b> 19.00	<b>Ne</b> 20.18
3	<b>Na</b> 22.99	<b>Mg</b> 24.31	<b>Al</b> 26.98	<b>Si</b> 28.09	<b>P</b> 30.97	<b>S</b> 32.07	<b>Cl</b> 35.45	<b>Ar</b> 39.95										
4	<b>K</b> 39.10	<b>Ca</b> 40.08	<b>Sc</b> 44.96	<b>Ti</b> 47.88	<b>V</b> 50.94	<b>Cr</b> 52.00	<b>Mn</b> 54.94	<b>Tc</b> 55.85	<b>Fe</b> 58.47	<b>Co</b> 58.69	<b>Ni</b> 63.55	<b>Zn</b> 65.39	<b>Ga</b> 69.72	<b>Ge</b> 72.59	<b>As</b> 74.92	<b>Se</b> 78.96	<b>Br</b> 79.90	<b>Kr</b> 83.80
5	<b>Rb</b> 85.47	<b>Sr</b> 87.62	<b>Zr</b> 88.91	<b>Ta</b> 91.22	<b>W</b> 92.91	<b>Tc</b> 95.94	<b>Ru</b> (98)	<b>Rh</b> 101.1	<b>Pt</b> 102.9	<b>Pd</b> 106.4	<b>Os</b> 107.9	<b>Ir</b> 112.4	<b>In</b> 114.8	<b>Tl</b> 118.7	<b>Sb</b> 121.8	<b>Te</b> 127.6	<b>I</b> 126.9	<b>Xe</b> 131.3
6	<b>Cs</b> 132.9	<b>Ba</b> 137.3	<b>Lr</b> 138.9	<b>Hf</b> 178.5	<b>Ta</b> 180.9	<b>W</b> 183.9	<b>Ru</b> 186.2	<b>Rh</b> 190.2	<b>Pt</b> 192.0	<b>Pd</b> 195.1	<b>Os</b> 197.0	<b>Ir</b> 200.5	<b>Hg</b> 204.4	<b>Pb</b> 207.2	<b>Po</b> 209.0	<b>At</b> (210)	<b>Rn</b> (222)	
7	<b>Fr</b> (223)	<b>Ra</b> (226)	<b>Ac</b> (227)	<b>Rf</b> (237)	<b>Db</b> (260)	<b>Sg</b> (263)	<b>Bh</b> (262)	<b>Hs</b> (265)	<b>Mt</b> (266)	<b>O</b> 0								

Lanthanide Series*	<b>Ce</b> 140.1	<b>Pr</b> 140.9	<b>Nd</b> 141.2	<b>Pm</b> (147)	<b>Sm</b> 150.4	<b>Eu</b> 152.0	<b>Gd</b> 157.3	<b>Tb</b> 160.9	<b>Dy</b> 162.5	<b>Ho</b> 164.9	<b>Er</b> 167.3	<b>Tm</b> 168.9	<b>Yb</b> 173.0	<b>Lu</b> 174.9
Actinide Series~	<b>Th</b> 223.0	<b>Pa</b> (231)	<b>U</b> (238)	<b>Np</b> (237)	<b>Pu</b> (242)	<b>Am</b> (243)	<b>Cm</b> (247)	<b>Bk</b> (247)	<b>Cf</b> (249)	<b>Es</b> (248)	<b>Fm</b> (253)	<b>Md</b> (256)	<b>No</b> (254)	<b>Lr</b> (257)

## Periodic Properties

Modern law of Periodic Table states that the periodic properties of elements are a function of their atomic numbers. Thus, atomic number determines the trend in periodic properties down the groups and from left to right across the periods.

The periodic properties include:

- Atomic & Ionic size
- Ionization energy
- Electron affinity
- Electronegativity
- Metallic character
- Melting & Boiling points
- Electrical & Thermal Conductivities

1. **Atomic size (Atomic radius):** The number of electron in the outermost shell of an atom and the number of shell an atom possess determines its atomic size. Electrostatic force of attraction that exists between the negatively charged electron(s) on the shell and the positively charged nucleus of an atom, makes an atom shrinks as the number of outermost electron increases.

Think of atom as sphere whose radius is determined by the location of the electrons furthest from the nucleus. So atomic radius (size) is determined by:

- Larger value of  $n$  for atom in a group, the larger the atom size. Size increases from top to bottom in group.
- Across a period ( $n$  stays the same), the number of protons in the nucleus increases. The electrons are very spread out and each electron feels the pull of the increasing +charge of the nucleus uninfluenced by the other electrons and size decreases as go from left to right across a period.

Generally, atomic size decreases across the periods due to increase in valence electron and increases down the group due to increase in electron shell.

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## Atomic Radii

Increasing atomic radius

1A	2A	3A	4A	5A	6A	7A	8A
H	Ba	B	C	N	O	F	He
32	152	112	98	91	92	73	72
	Li	Mg	Al	Si	P	S	Cl
	152	160	143	132	128	127	99
	Na	Ca	Ga	Ge	As	Se	Br
	186	197	135	137	139	140	114
	Rb	Sr	In	Sn	Sb	Te	I
	248	215	166	162	159	160	133
	Cs	Ba	Tl	Pb	Bi	Po	At
	265	222	171	175	170	164	142
							140

Increasing atomic radius

Q.4 Arrange each of the lists according to increasing atomic size:

- Al, S, P, Cl, Si
- In, Ga, Al, B, Ti
- Sr, Ca, Ba, Mg, Be
- P, N, Sb, Bi, As
- Na, K, Mg

## Ionic Radii

### Ionic size

Ionic size(radius) increases down the group due to increase in number of shell while it varies according to the ionic charges across the period. The ionic radius of a cation is usually smaller (lower) than its atomic radius of the same atom

For non metallic anion the size of the ion is always greater than the size of the corresponding atom because electron is added into the same shell.

**Q. 5 Which is smaller?** (The one having less number of electrons)

- Cl or  $\text{Cl}^-$
- Na or  $\text{Na}^+$
- $\text{O}^{2-}$  or  $\text{S}^{2-}$
- $\text{Mg}^{2+}$  or  $\text{Al}^{3+}$
- $\text{Au}^+$  or  $\text{Au}^{3+}$

The cation with higher positive charge is smaller, and anion with lower negative charge is larger.

The more positive the charge, the more energy is required to remove an electron from an atom in ground state.

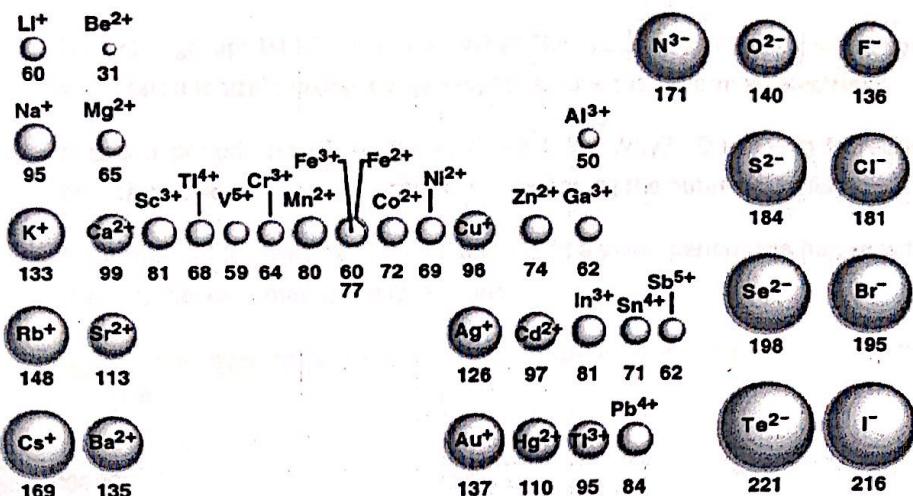
Electrostatic potential energy

- It measures how tightly the electrons are held in atom

Ionization energy is physical state of an atom that influences their chemical properties. Atoms of elements with the same ionic charge, temperature and size of nucleus have similar ionization energies. E.g.



## Ionic Radii



Note for isoelectronic series: i.e. ions of different atoms having the same number of electrons hence the same electronic configuration.

- $\text{Na}^+, \text{Mg}^{2+}, \text{Al}^{3+}, \text{N}^{3-}, \text{O}^{2-}, \text{F}^-$
- $\text{N}^{3-} > \text{O}^{2-} > \text{F}^- > \text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$

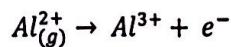
The most positive ion will have the smallest ionic radius, most negative the largest

### 2. Ionization energy

- Minimum energy required to remove an electron from an atom in ground-state, (gaseous atom) to become positively charged
- Energy always positive (requires energy)
- Measures how tightly the electron is held in atom

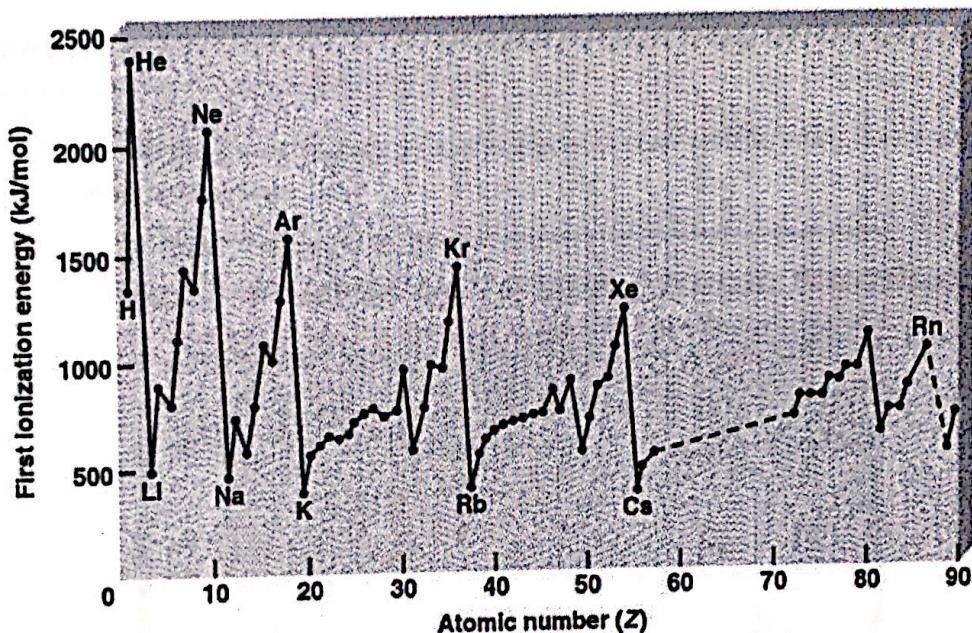
Ionization energy is physical state of atoms that influences their chemical characteristics. Atoms of elements can have several ionization energies, therefore we say first or second or third ionization energies. E.g Al





### Trends in ionization energy

- Down the group: 1st I.E. decreases. Why? This is due to an increase in the number of shells (atomic size) making it very easy to remove the outermost electrons
- Across a period, 1st I.E. increases (irregularly) Why? Due to an increase in the effective nuclear charge i.e difficulties in removing the outermost shell
- Note that noble gases have the largest I.E. in a given period; the halogens the next highest; the alkali metals the lowest, etc.



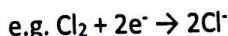
In a group (column),  $I_1$  decreases with increasing  $Z$ . Valence electrons with larger  $n$  are further from the nucleus, less tightly held.

Q.6 Arrange in order of increasing I.E.

- N, O, F
- Li, K, Cs
- Cl, Br, I

### 3. Electron affinity

- Electron affinity is the energy change or energy released when a gaseous atom in its ground state receives an electron to form a univalent negative ion.



- Positive EA means that energy is released, electron addition is favourable and anion is stable!
- First EA's mostly positive, a few negative

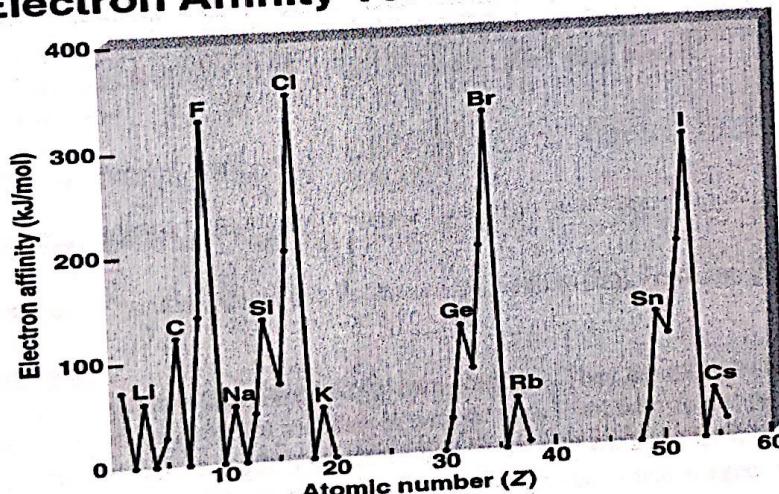
Trends in electron affinities

Electron affinity increases from left to right across the period (except for noble gases whose are positives) and decreases down a group.

- Nonmetals are more likely to accept electrons than metals. VIIA's like to accept electrons the most.

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### Electron Affinity Versus Atomic Number



### 4. Melting and boiling point

Melting point is the temperature at which the smallest part of a substance begins to melt while the boiling point is the temperature at which the atmospheric pressure equals the vapour pressure of a substance and its smallest part begins to boil.

Thus, melting and boiling points of metallic elements increase from left to right across the period and those of non-metallic elements decrease. While melting and boiling points of metallic elements decrease down the group, and those of non-metallic elements increase.

5. Electrical and thermal conductivity: these decreases across the period and increase down the group. Thus, metals are good conductors of heat and electricity.

6. **Electronegativity:** The ability of an atom of an element to attract electron to itself. Electronegativities of elements increase across the period but decrease down the group.

## Families of Main Group Elements

Group I – Alkali metals

Group II - Alkali earth metals

Group VII – The halogens

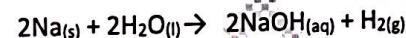
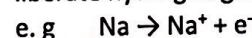
Group VIII/0 – The noble gases

The Transition elements

The Lanthanides and Actinides

### **Group I Elements**

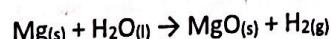
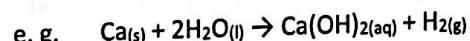
Elements in group I have only one valence electron—they are univalent. They ionize readily to form positive ions by donating an electron to form an electrovalent compound. They are reducing agents and good conductors of electricity. They react with cold water vigorously to liberate hydrogen gas and form alkalis as such they are called alkali metals.



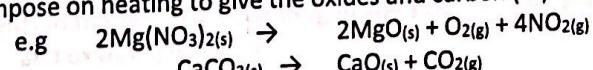
Elements in group I include Lithium (Li), Potassium (K), Sodium (Na), Francium (Fr)

### **Group II elements**

They are divalent because they have two valence electrons. They are electron donors, form electrovalent compounds and are reducing in nature. They react with cold water and steam to liberate hydrogen gas, but calcium reacts slowly with cold water to form hydroxide and magnesium forms oxide. Calcium hydroxide is a weak alkali, while magnesium oxide is practically insoluble in water. They are generally called the alkali earth-metals



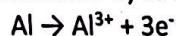
Their trioxonitrate (V) salts decompose on heating to give oxides, oxygen and brown nitrogen (IV) oxide gas. Their trioxocarbonates (IV) salts are insoluble in water, but decompose on heating to give the oxides and carbon (IV) oxide.



Group II elements include beryllium, magnesium, calcium etc

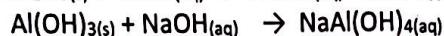
### Group III elements

These are trivalent elements-they have three valence electrons. They are reducing in nature and form electrovalent compounds. The most popular among them is Aluminium, it reacts with steam (above 600°C) to liberate hydrogen.



Aluminium oxide is insoluble in water. Aluminium hydroxide is prepared by precipitation.

Both oxide and hydroxide have both acidic and basic properties (i.e. amphoteric in nature). Aluminium trioxonitrate (V) decomposes to give the oxide, oxygen and nitrogen (IV) oxide gas. Aluminium trioxocarbonate (IV) does not exist.



Other elements in group III include boron and gallium

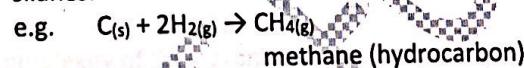
### Group IV elements

The elements in group IV include carbon, silicon, germanium, tin and lead. They are tetravalent (i.e. they have four valence electrons). They tend to form covalent compounds by sharing electrons instead of donating or receiving. They become more metallic from non-metallic down the group. Their compounds exhibit +2 and +4 oxidation states.

+2 oxidation states: CO, SiO, GeO, PbO, SnO

+4 oxidation states: CO<sub>2</sub>, SiO<sub>2</sub>, GeO<sub>2</sub>, PbO<sub>2</sub>, SnO<sub>2</sub>

Carbon and silicon react with hydrogen to form covalent compounds; hydrocarbons and silanes.



Carbon does not react with water in any form, but silicon and tin react with steam at high temperature to form +4 state oxide and hydrogen.



### Group V elements

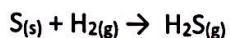
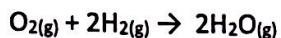
They are non-metals mainly with valencies of 3 and 5. They are electron acceptors and tend to form stable oxides. Most important elements are nitrogen and phosphorus. Their compounds include nitrogen (III) oxide, N<sub>2</sub>O<sub>3</sub>, nitrogen (IV) oxide, NO<sub>2</sub>, Phosphorus (III) oxide, P<sub>4</sub>O<sub>6</sub> etc. All these are acid anhydrides. Nitrogen and phosphorus also form similar hydrides like NH<sub>3</sub>, PH<sub>3</sub> and halides like NCl<sub>3</sub> and PCl<sub>3</sub>.

### Group VI elements

Elements in this group include oxygen and sulphur- they are non-metals, electron acceptors and oxidizing in nature.



Oxygen is slightly soluble in water, but sulphur is insoluble. They both combine with hydrogen gas to form water and hydrogen sulphide gas respectively.



### Group VII Elements

Elements in group VII are known as the halogens. The word halogen means salt former. They are the most reactive non-metals and are even reactive than other elements. Halogens show great similarities in their properties such as:

- they are all non-metals
- they exist as diatomic molecules.
- they are coloured.
- they ionize to form univalent ions which react with metallic ions to form electrovalent (ionic) compounds.
- their hydrides are covalent negative gases at room temperature and dissolve readily in water to form acids.

The halogens show gradation in their properties from fluorine to iodine due to a progressive increase in

- their atomic number, and
- the complexity of their atomic structure.

### Structural properties of the halogens

Halogen	$\text{F}_2$	$\text{Cl}_2$	$\text{Br}_2$	$\text{I}_2$
Atomic number	9	17	35	53
Electron shells	K,L	K,L,M	K,L,M,N	K,L,M,N,O
Electrons in the outermost shell	7	7	7	7

### Group 0 (VIII)

The elements in group 0 are known as rare gases or noble gases. They have no bonding electrons in the outermost shell, hence the group is named zero. The elements include Helium, neon, argon, krypton, xenon and radon. Because of their unreactivity, they form few compounds and exist freely (i.e. uncombined) as monoatomic molecules in the atmosphere. They constitute about 1% of the composition of air. Their unreactive nature can readily be understood from their electronic configuration which satisfies the octet rule for stability. Their melting and boiling points increase while their energies decrease down the group from helium to radon.

### Group trends exhibited by the noble gases

Element	symbol	M.P.(°C)	B.P.(°C)	I.E (kJmol⁻¹)
Helium	He	-270	-269	2378
Neon	Ne	-249	-246	2087
Argon	Ar	-189	-186	1526
Krypton	Kr	-157	-152	1357
Xenon	Xe	-112	-108	1176
Radon	Rn	-71	-62	1044

### Transition Elements

Transition elements are positioned between Group 2 and 3 elements in the periodic table.

They are all metals with typical metallic properties such as high tensile strength and high melting points.

#### Characteristics of transition metals

1) Variable oxidation states: transition elements exist in more than 1 oxidation state.

E.g	Compound	metal	oxidation states
	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	Cr	+6
	Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	Cr	+3
	KMnO <sub>4</sub>	Mn	+7
	K <sub>2</sub> MnO <sub>4</sub>	Mn	+6
	MnO <sub>2</sub>	Mn	+4

2) Formation of complex ions: A complex ion consists of a central atom to which atoms, ions or groups are attached. These atoms, ions or groups are commonly referred to as Ligands.

e.g. [Co(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> - hexaaquacobalt (II) ion

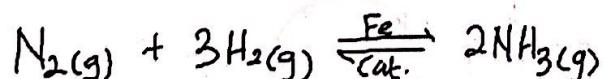
[CoCl<sub>4</sub>]<sup>2-</sup> - tetrachlorocobalt (II) ion

3) Formation of coloured compounds.

e.g	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	orange
	Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	green
	KMnO <sub>4</sub>	purple
	K <sub>2</sub> MnO <sub>4</sub>	green
	MnO <sub>2</sub>	brown
	MnSO <sub>4</sub>	pink
	FeCl <sub>3</sub>	yellow
	CuSO <sub>4</sub>	blue

4) They act as catalysts: Because they can change their oxidation state, they can be used to speed up the rate of reactions.

- E.g.
  - i) In the preparation of oxygen
  - ii) In the manufacture of ammonia



5) They are magnetic. E.g. Iron, cobalt and nickel etc can be attracted/repelled by a magnetic force.

#### Uses of transition metals

- 1) As electrical conductors
- 2) In alloys manufacturing e.g. bronze, brass, steel.
- 3) As catalysts to speed up chemical reactions in industries.
- 4) To make cooking utensils
- 5) To make coins, medals, aircrafts, ships, rail coaches etc
- 6) In welding and plumbing.

#### Lanthanides (Rare-earth elements)

These are sets of fifteen rare elements in the 6th period of the periodic table, beginning with lanthanum (La), and ending with Lutetium (Lu). They show a great resemblance and are generally called the Lanthanides or rare-earth elements.

#### Actinides and the Artificial elements

The Actinides are in the 7th period of the periodic table. They are similar in many ways to the Lanthanides. It starts with Actinium (Ac) and includes the well known element- uranium (U) which is used in nuclear reaction, and ending with Lawrencium (Lw). They do not occur naturally but from the reaction of other natural elements, as such they are called the artificial elements. They are unstable and disintegrate in short time. e.g. plutonium (Pu), curium (Cm), thorium (Th). Etc

## **ATOMIC ORBITAL**

Bohr model describes a simple physical picture of electrons moving round the nucleus of an atom in circular orbits, while Shrodinger developed a mathematical model for the distribution of electrons in an atom that is, the probability that an electron can be found in a region of space at a given time. Therefore;

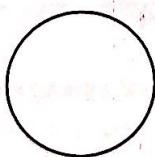
**Atomic ORBITALS** are volumes of space where the probability of finding an electron is high.

#### **Orbital Representation**

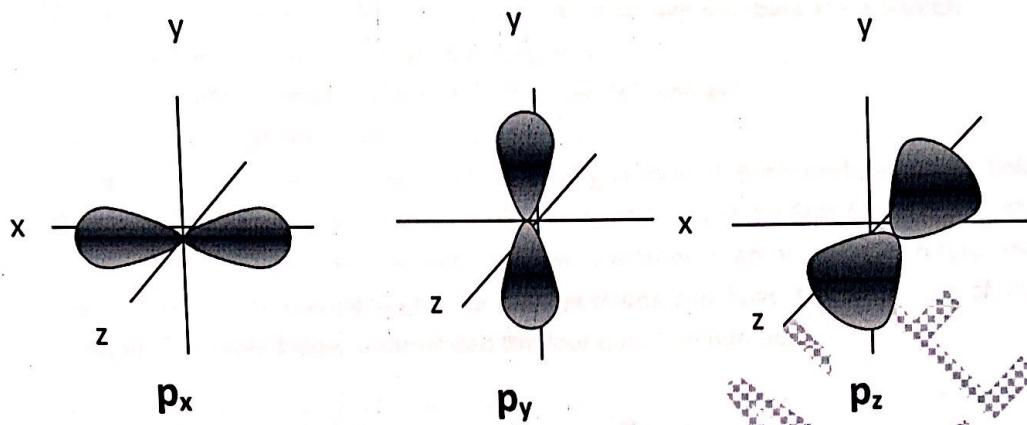
There are four (4) types of orbital electron can occupy, namely; s, p, d and f orbital. They can be represented by three dimensional surface boundaries.

##### **s – orbital**

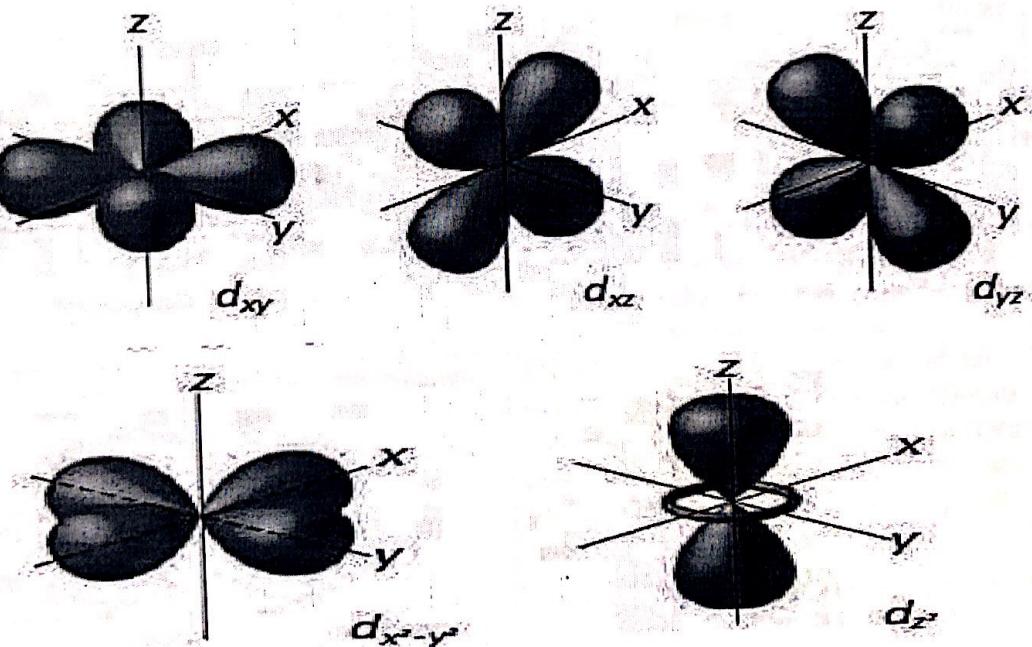
s – orbital is spherical in shape



P – orbitals have a dumbbell shape and there are three sub p-orbitals viz;  $p_x$ ,  $p_y$  and  $p_z$ .



d – orbitals have a double dumbbell shape and there are three sub d-orbitals namely;  $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$ ,  $d_x^2$ ,  $d_z^2$ .



There is one s orbital in each energy level and can holds a maximum number of 2 electrons.  
There are three p orbitals in each energy level and can holds a maximum number of 6 electrons.

There are five d orbitals in each energy level and hold a maximum number of 10 electrons.  
There are seven f orbitals in each energy level and holds a maximum number of 14 electrons.

## QUANTUM NUMBER

Quantum number describes the energy levels of electrons in an atom i.e it is used to describe electronic configuration in atoms.

According to Schrödinger wave equations, three quantum numbers arises namely;

- i. Principal quantum number denoted as  $n$
- ii. Azimuthal (subsidiary) quantum number denoted as  $\ell$
- iii. Magnetic quantum number denoted as  $m_\ell$

All the aforementioned are required in defining an orbital. But an orbital cannot hold more than two (2) electrons, so a fourth quantum number called the Spin Quantum number ( $m_s$ ) is required to differentiate between the two electrons in an orbital. Therefore, there are four (4) quantum numbers and no two electrons can have the same set of quantum number. The table below summarized the four quantum numbers:

Quantum Number	Called	Describes
$n$	Principle quantum number	the energy level of an electron as well as size of a shell. It can have any positive integer greater than zero i.e 1, 2, 3, 4.....n. When $n = 1$ , the energy is at lowest allowed value which is the ground state of hydrogen atom.
$\ell$	Angular momentum (Azimuthal) quantum number	Shape of an orbital or a sub shell and type of orbital. It can assume values of 0, 1, 2, 3.....(n-1)
$m_\ell$	Magnetic quantum number	Orientation of an orbital and electron position in the orbital. It governs the number of orbital of each value of $\ell$ and can assume values ranging from $-\ell$ to $+\ell$ .
$m_s$	Electron spin quantum number	The spin state of an electron in an orbital. It has a value of $+1/2$ for an electron spinning upward and $-1/2$ for an electron spinning downward. A sub shell can accommodate only two electrons and must be of opposite spin

TABLE OF ATOMIC ORBITAL DESIGNATION

Energy Level (n)	Subshell ( $\ell = n-1$ )	Number of Sublevel	Name of Sublevel / Type of Orbital	Maximum number of electrons allowed per energy level = $2n^2$
1	1s	1	1s	2
2	2s	1	2s	2
2	2p	3	2p <sub>0</sub> , 2p <sub>1</sub> , 2p <sub>2</sub>	6
3	3s	1	3s	2
3	3p	3	3p <sub>0</sub> , 3p <sub>1</sub> , 3p <sub>2</sub>	6
3	3d	5	3d <sub>0</sub> , 3d <sub>1</sub> , 3d <sub>2</sub> , 3d <sub>3</sub> , 3d <sub>4</sub>	10
4	4s	1	4s	2
4	4p	3	4p <sub>0</sub> , 4p <sub>1</sub> , 4p <sub>2</sub>	6
4	4d	5	4d <sub>0</sub> , 4d <sub>1</sub> , 4d <sub>2</sub> , 4d <sub>3</sub> , 4d <sub>4</sub>	10
4	4f	7	4f <sub>0</sub> , 4f <sub>1</sub> , 4f <sub>2</sub> , 4f <sub>3</sub> , 4f <sub>4</sub> , 4f <sub>5</sub> , 4f <sub>6</sub>	14

1	0	1	1s	2
2	0, 1	2	2s, 2p	8
3	0, 1, 2	3	3s, 3p, 3d	18
4	0, 1, 2, 3	4	4s, 4p, 4d, 4f	32

Principal quantum number

### Energy Level Diagram for an electron

s-orbital has the lowest energy. The relative energy of the sub shell within a shell is given by;

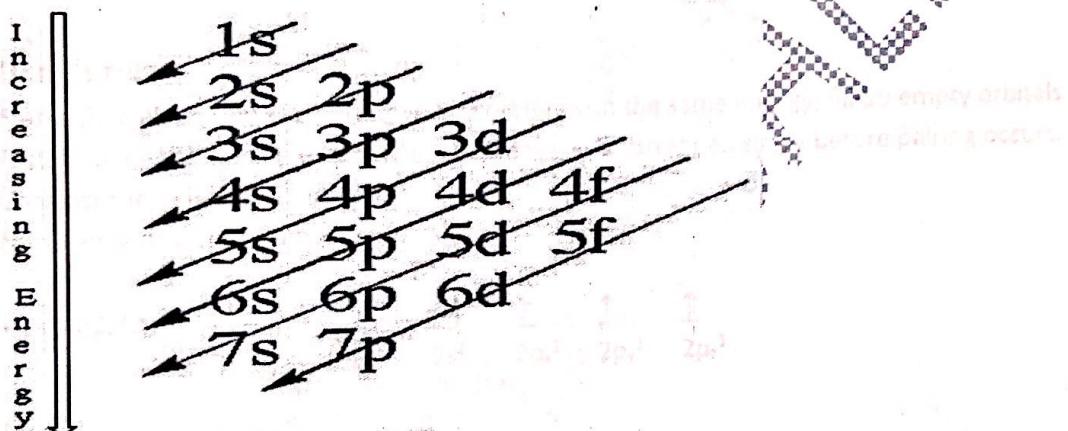
s p d f

Diagram showing the relative energy levels of atomic orbitals

Diagram showing the relative energy levels of atomic orbitals with electron filling pattern

Diagram showing the relative energy levels of atomic orbitals with electron filling pattern

### Order of filling electrons in energy level in an atom



## ELECTRONIC CONFIGURATION

This is the arrangement of electrons in the various orbital around the nucleus of an atom. It is normally applied to atoms in their ground state which is governed by three rules namely;

1. Aufbau's principle
2. Pauli's exclusion principle
3. Hund's rule

### Aufbau's principle

"Aufbau" means building up in German. This states that electrons in their ground states are added to an atom, one at a time, starting with the lowest energy orbital until all the orbitals are filled, that is, principle of electrons filling up the orbitals in order of increasing energy. That is, Electrons go into the lowest energy orbital first.

E.g hydrogen  
Atomic number of hydrogen is 1 (one single electron). It has one electron located in the first shell i.e atomic orbital of lowest energy, the electronic configuration is indicated by;

$1s^1$

Where, 1 indicate the shell, s represent the sub shell and the superscript "1" represent the number of electrons.

### Pauli's Exclusion Principle

States that the maximum number of electrons in an orbital is TWO (2) and must be of opposite spin. That is, if there are two (2) electrons in the same orbital they must have an opposite spin. This means that no two electrons in the same orbital can have the same set of quantum numbers (n, m, l and s)

E.g the atomic number of helium is 2 with electronic configuration of  $1s^2$ . The two electrons must have opposite spin  $\uparrow\downarrow$ .

Two electrons occupying the same orbital with parallel spins ( $\uparrow\uparrow$  or  $\downarrow\downarrow$ ) are not allowed because they will have the same set of quantum numbers.

### Hund's rule

States that When there is more than one orbital with the same energy, fill up empty orbitals first, keeping the spins the same, i.e electrons will be arranged singly before pairing occurs.

Consider the following examples;

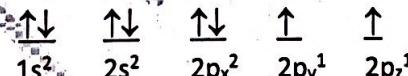
Nitrogen with atomic number seven (7);

$${}_7N = 1s^2 2s^2 2p^3$$



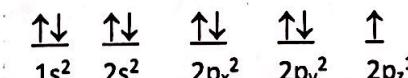
Oxygen with atomic number eight (8);

$${}_8O = 1s^2 2s^2 2p^4$$



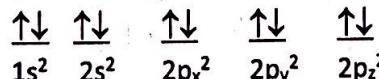
Flourine with atomic number nine (9);

$${}_9F = 1s^2 2s^2 2p^5$$

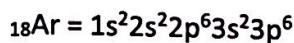
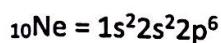
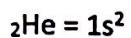


Neon with atomic number ten (10);

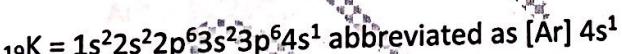
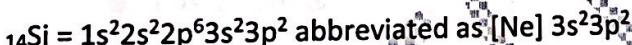
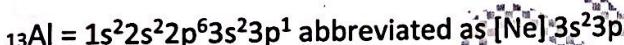
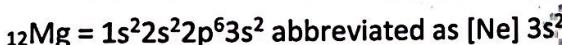
$${}_{10}Ne = 1s^2 2s^2 2p^6$$



In addition, it has been observed experimentally that atom with completely filled sub shells such as



That is noble gases are usually stable. Therefore, by convention electronic configuration of the noble gases and atoms beyond noble gases may be abbreviated as follows;



### Electronic Configuration and the Periodic Table

All the elements in the periodic table can be classified into four (4) as follows;

Group 1 and 2: s-orbitals are completely filled therefore they are called s-block element

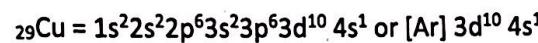
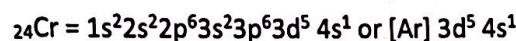
Group 3 -8 corresponds to the filling of the three orbital in p-subshell i.e 2p to 6p, hence, they are referred to as p-block elements

d-block elements are called the transition metals because they serve as transition (bridge) between the s-block and p-block elements.

The f-block elements are the lanthanides and actinides owing to the filling of the seven orbitals in the f-subshell.

### Electronic Configuration of Transition Metal

The valence configuration for first transition metals series is usually  $3d^n 4s^2$ , except for the electronic configurations for chromium and copper;

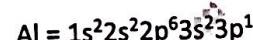
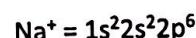
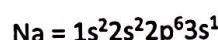


This is because 3d and 4s orbitals are very close in energy, and the energy of 3d orbitals drops going across the row. For both chromium and copper the configuration having more electrons in 3d orbitals is of lower energy and these configurations has the maximum number of unpaired electrons for a d-subshell and are energetically more stable than the expected arrangements.

### Electronic Configuration of Ions:

In general, electrons will be removed from orbitals (ionization) in the reverse order that the orbitals were filled except transition metal ions. In other words, electrons vacate higher energy orbitals first.

E.g



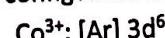
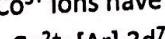
$\text{Na}^+$  and  $\text{Al}^{3+}$  are isoelectronic (i.e. they have the same electronic configuration)

### Electronic Configuration of Transition Metal Ions

When these ions are formed, electrons are removed from the valence shell s-orbitals before they are removed from valence d-orbitals. Examples;

Cobalt has the configuration  $[\text{Ar}] 4s^2 3d^7$

The  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  ions have the following electron configurations.



Exercise:

1. Si \_\_\_\_\_

2.  $\text{S}^{2-}$  \_\_\_\_\_

### Ques 3. $\text{Rb}^+$ bonding

### Ques 4. Se

### Ques 5. Cl

### Ques 6. Nb

### Ques 7. $\text{Zn}^{2+}$

### Ques 8. Cd

### Ques 9. Sb

### Ques 10. $\text{Ca}^{2+}$

The above questions are related to ionic bonding. When atoms that react for the formation of ionic compounds are far apart, the distance between them is large, the magnitude of the electrostatic force of attraction between them is smaller than the total charge of the ions. Therefore, a ionic bond is formed by the electrostatic linkage between two ions. The ionic bonding is able to form a stable molecule. However, atoms with noble electronic configurations are highly stable and do not form a chemical bond because of their complete filled shells. They have no desire to attain a stable electronic config. and hence no tendency to gain or lose electrons.

Therefore, elements may be classified as electropositive if they tend to gain one or more electrons. Electronegative elements will have a strong tendency to attract electrons and thus acquire negative charges.

Valence electron is the outermost electron in an atom. Valence electrons can be used to predict the nature of chemical reactions. For example, the Lewis dot structure of helium and neon are as follows:

He:



Question: Give the Lewis dot structure of the following elements in the 3rd Group of the Periodic Table.

Argon

Type of bond formed between the elements of the same group is called homopolar bond.

The bond formed between the elements of different groups is called heteropolar bond.

Example:  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{F}_2$  are homopolar bonds.

$\text{LiCl}$ ,  $\text{NaCl}$ ,  $\text{MgCl}_2$ ,  $\text{AlCl}_3$  are heteropolar bonds.

Electrostatic attraction between the nuclei of two atoms is called electrostatic force of attraction.

Electrostatic repulsion between the nuclei of two atoms is called electrostatic force of repulsion.

Electrostatic force of attraction is greater than electrostatic force of repulsion.

## Chemical bonding

Chemical bonding is defined as any interaction between atoms that account for the redistribution of their outer electrons to form stable substances. In chemical bonding, the nuclei and electrons of the participating atoms interact and redistribute themselves such that the sum of the energies of the component atoms is higher than the total energy of the group. Therefore, a **chemical bond** is defined as an electrostatic linkage between two or more atoms that allows the formation of chemical substance. A **bond** consists of two electrons originating from either sharing or transfer of electrons between the participating atoms. Chemical bonding enables atoms to attain a stable electronic configuration. However, atom with stable electronic configuration (e.g noble gases) does not involve in chemical bonding because of their completely filled outer electron shell. Atom may attain a stable electronic configuration either by transfer (lost or gain) or by sharing of electrons.

Therefore, element may be divided into electropositive (i.e whose atom give up one or more electrons), electronegative (i.e which will accept electron) and element with little tendency to lose or gain electrons.

**Valence electron** is the outermost electron(s) of an atom. Lewis dot symbol can be used to represent the outer shell electron as dots around the symbol for the element. For example, the Lewis structure of helium and nitrogen are given below.

**He:**



Question: Give the Lewis dot symbol of the following elements (i) Silicon (ii) Oxygen (c) Argon

### Types of Chemical Bond

The various types of chemical bond resulted from different behaviors of the outermost or valence electron of atoms. These include:

- (i) Ionic bond (ii) Covalent bond (iii) Metallic bond

Electropositive Element + Electronegative Element → Ionic bond

Electronegative Element + Electronegative Element → Covalent bond

Electropositive Element + Electropositive Element → Metallic bond

Few bonds are purely ionic, covalent or metallic. Most are intermediate between the three main types of bonds, and show some properties of at least two of the three types.

## Ionic Bond

An ionic bond occurs when electrons are transferred from the valence shell of one atom to the valence shell of another. The atom that loses electrons becomes a cation (a positive ion), while the atom that gains electron(s) becomes an anion (a negative ion). The ionic bond is constituted by the attraction between the ions. Ionic bonds exist between the metals in group I and II and the non-metals in group VIA and VIIA. Also, the anions of certain acids, especially the oxygen acids, can form ionic compounds with group I and II metals.

### Formation of Ionic bonds

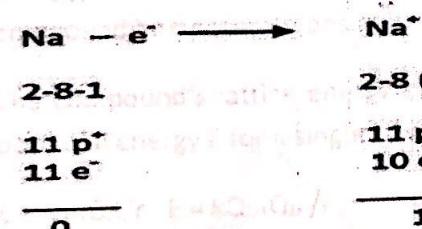
Metals lose electrons to match the number of valence electrons of their nearest noble gas. Cations are formed when the number of electrons is lower than the number of protons. However, non-metals gain electron(s) from anions. The gained electron(s) enable non-metal to achieve a stable electronic configuration (octet arrangement).

**Group 1 metals:**  $M - e^- \rightarrow M^+$

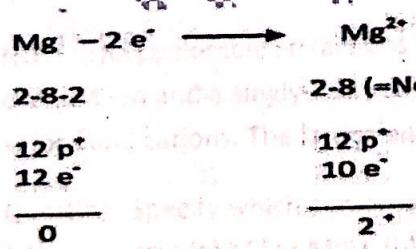
**Group 2 metals:**  $M - 2e^- \rightarrow M^{2+}$

**Group 17 non-metal:**  $X + e^- \rightarrow X^-$

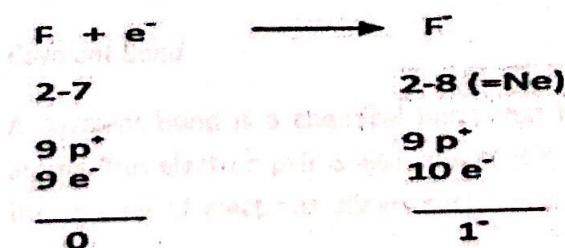
**Sodium atom to sodium ion**

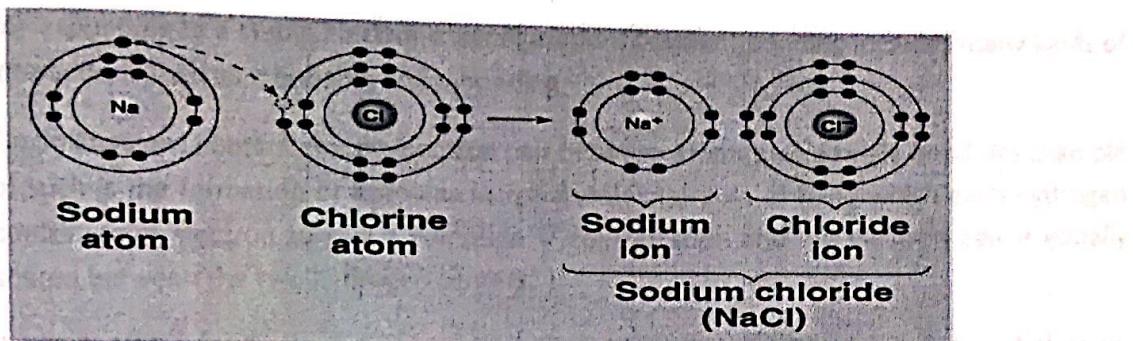


Electron loss by the sodium atom creates a positive charge on the sodium ion. This positive charge is balanced by the negative charge of the extra electron added to the valence shell of the sodium atom. The resulting ionic bond is called an ionic bond.



Electron loss by the magnesium atom creates a positive charge on the Mg<sup>2+</sup> ion. This positive charge is balanced by the negative charge of the extra electron added to the valence shell of the magnesium atom. The resulting ionic bond is called an ionic bond.





**Typical Ionic bonding** – electron from Na is transferred to Cl, this causes a charge imbalance in each atom. The Na becomes ( $\text{Na}^+$ ) and the Cl becomes ( $\text{Cl}^-$ ), charged ions.

### Lattice Energy of Ionic Compounds

In ionic bond formation, the metal releases electron by accepting energy equal to its ionization energy while the non-metal accepts the released electron, and the energy required is equal to the electron affinity. Ionization energy and electron affinity are defined for gaseous phase processes, but at room temperature all ionic compounds are solids. In solid state environment, each cation is surrounded by a specific number of anions, and vice versa. Therefore, the overall stability of a solid ionic compound depends on the interactions of all these ions. A quantitative measure of the stability of any ionic solid is its **lattice energy**, defined as the energy required to completely separate one mole of a solid ionic compound into gaseous ions.

The compound's lattice energy can be calculated using Coulomb's law. For example, the potential energy E for a single  $\text{Li}^+$  and  $\text{F}^-$  ions is given as

$$E \propto Q_{\text{Li}^+}Q_{\text{F}^-}/r; E = kQ_{\text{Li}^+}Q_{\text{F}^-}/r$$

Where  $Q_{\text{Li}^+}$  and  $Q_{\text{F}^-}$  are the charges on the  $\text{Li}^+$  and  $\text{F}^-$  ions respectively. E is a negative quantity, and the formation of Li-F bond is an exothermic process.

**NOTE:** The coulombic attractions between two doubly charged species, or between a doubly charged ion and a singly charged ion, are much stronger than those between singly charged anions and cations. The lattice energy (in KJ/mol) of  $\text{MgO}$  (3890)> $\text{Na}_2\text{O}$  (2570)> $\text{LiF}$  (1017)

**Question:** Specify which compound in the following pairs of ionic compounds has the higher lattice energy: (a)  $\text{KCl}$  or  $\text{MgO}$ , (b)  $\text{LiF}$  or  $\text{LiBr}$ , (c)  $\text{Mg}_3\text{N}_2$  or  $\text{NaCl}$ .

### Covalent Bond

A covalent bond is a chemical bond that involves the sharing of electron pair between atoms. This electron pair is also known as bonding pair or shared pair. For many molecules, the sharing of electrons allows each atom to attain the equivalent of a full outer shell;

corresponding to a stable electronic configuration. Covalent bonding includes many kinds of interactions such as  $\sigma$  bonding and  $\pi$  bonding.

**Single Covalent bond:** A shared electron pair between atoms give a single bond. An example of such is the formation of homonuclear diatomic molecule of  $H_2$  in which each hydrogen contribute  $s^1$  electron to give a complete  $s^2$  configuration and the electron pair is equally shared between the two hydrogen centers.

A comparable covalent bond can be formed in  $F_2$ :  $F + F \rightarrow F_2$ . This type of shared electron pair bond is referred to as single covalent bond. As the covalent bond is between the same types of atom, the sharing is equal and the bond is represented by single stick. Homonuclear diatomic molecules (e.g  $H_2$  and  $F_2$ ) have no dipole moment.

**Polyatomic Covalent Molecules:** Methane, ammonia and water molecules are among simple covalent polyatomic molecules, in which their central atom is surrounded by single bonds.

**Methane ( $CH_4$ ):** The valence electron of carbon in methane is given as  
 $CH_4 \equiv C - 2s^2 2p^2 + 4H - 1S^1$

Total valence electrons of C is  $4 + (4 \times 1) \equiv 8$

Electrons  $\equiv s^2 p^6$

**Lewis Structure of methane**

Each of the four H atoms involves a shared  $s^2$ [He], inert gas configuration and the one carbon atom involves a shared  $s^2 p^6$  configuration of four electron pairs shared with four separates H atoms.

**Multiple Bond:** Sometimes, atoms share more than one electron. Occasionally, they can share 2 or even 3 electrons. Multiple bond arises when atom share two or three electrons with another atom. If two or three electrons are shared, it gives double or triple bonds respectively. A double bond contains one  $\sigma$  bond and  $\pi$  bond while a triple bond contains one  $\sigma$  bond and two  $\pi$  bonds. Multiple bonds have shorter bond length than single covalent bonds i.e for a given pair of atoms, such as carbon and nitrogen, triple bonds are shorter than double bonds, which, in turn, are shorter than single bonds.

Single bond	Double bond	Triple bond
H-H	O=O	N≡N
H : H	• O : : O •	• N : : N •

**Coordinate Covalent bond:** A coordinate covalent bond also known as *dative bond* is one in which both bonding electrons are from one of the atoms involved in the bonding. In this form of covalent bonding, an atom will donate lone pair of electrons for sharing. This bond gives rise to the formation of some Lewis acids and bases. Such bonding occurs in molecules such as the  $\text{NH}_4^+$ ,  $\text{H}_3\text{O}^+$  and  $\text{H}_3\text{BNH}_3$ .

Ammonia is a polyatomic molecule which is formed via ordinary covalent bond. However, ammonium ion is formed from ammonia through dative bonding with hydrogen ion. The hydrogen ion bonds to the lone pair of electrons on the ammonia molecule to form ammonium ion.

**Polar Covalent bond:** A polar covalent bond is a covalent bond with a significant ionic character. It occurs when electrons are shared unequally between atoms. This implies that the electrons are closer to one of the atoms than the other, creating an imbalance of charge. The electronegativity of these bonds is between 0.4 to 1.7. Water is a polar molecule because oxygen is more electronegative than hydrogen, and therefore electrons are pulled closer to oxygen.

**Non-polar Covalent bond:** This occurs when electrons are shared almost equally or equally between atoms. Examples include  $\text{H}_2$ ,  $\text{Cl}_2$ ,  $\text{NH}_4^+$  etc. All homonuclear diatomic molecules form non-polar covalent bond. The electronegativity of these bonds ranges from 0 to 0.4.

**Bond Character:** Bond character is determined by the difference in electronegativity (EN) between the atoms that form the bond. For example Li-F bond has a EN of 3.0 and is an ionic bond that is ionic in character. A notable exemption to this rule is the H-F bond in hydrogen fluoride. H-F bond is a polar covalent bond (because it involves two non-metals) despite that its EN is 1.9.

EN	Bond Character
0-0.4	Non polar covalent bond
0.4-1.7	Polar covalent bond
>1.7	Ionic bond

Question: Predict the nature of the bond between the following pairs of atoms as predominantly non-polar covalent, polar covalent or ionic (a) S-O (b) C-O (c) Al-F

**Question:** Which of the following bonds is covalent, which is polar covalent, and which is ionic? (a) the bond in CsCl, (b) the bond in H<sub>2</sub>S, (c) the N-N bond in H<sub>2</sub>NNH<sub>2</sub>

### Metallic bond

Metallic bonding is the force of attraction between valence electrons and the metal ions. It involves sharing of many detached electrons between many positive ions, where the electrons act as a "glue" giving the substance a definite structure. Most atoms that form metallic bond are good conductors at all state, lustrous with high melting point. Examples are Fe, Al, Au, Co etc.

### Bond Theory

#### Lewis bonding Theory

It is one of the simplest bonding theories that emphasize on valence electron to explain bonding. It is described through Lewis structure models. The theory explains that electrons are transferred or shared such that each atom attains octet arrangement. Lewis bonding theory predicts many properties of molecules such as molecular stability, formal charge, shape and polarity.

**Question:** Draw the Lewis structure of CO<sub>2</sub>, H<sub>2</sub>S, BCl<sub>3</sub>, PH<sub>3</sub>, N<sub>2</sub>H<sub>4</sub> and P<sub>4</sub>

**Formal Charge:** It is the charge assigned to an atom in a molecule, assuming that electrons in all chemical bonds are shared equally between atoms regardless of relative electronegativity. When determining the best Lewis structure for a molecule, the structure is chosen such that the formal charge on each atom is as close to zero as possible.

$$\text{Formal charge (FC)} = V - N - B/2$$

V is the number of valence electrons of the neutral atom in isolation

N is the number of non-bonding valence electrons on this atom in the molecule

B is the total number of electrons shared in bonds with other atoms in the molecule.

For example CO<sub>2</sub>, the formal charge of C and oxygens in CO<sub>2</sub> is calculated as;

$$\text{FC of C} = 4 - 0 - 8/2 = 0$$

$$\text{FC of O} = 6 - 4 - 4/2 = 0$$

**Question:** Draw the Lewis structure including formal charge for SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup> and NO<sub>2</sub>.

#### Valence Shell electron pair repulsion (VSEPR) Theory

It predicts the molecular shapes and geometry. It involves the arrangement of electron in space to minimize electron-electron repulsion.

### **How to predict shape and geometry using VSEPR theory**

1. Draw the Lewis structure for the molecule
2. Count the total number of bonds and lone pair around the central atom
3. Arrange the bond and lone pair in a standard geometry to minimize electron-electron repulsion. Lone pair electrons stay closer to the nucleus and spread over a larger space than the bonding pair. Hence large angles are found between lone pairs

**LP-LP > LP-BP > BP-BP (repulsion tendency)**

**Steric Number = Number of atoms bonded to the central atom + Number of lone pairs on the central atom**

Molecules	Steric No.	Geometry	Example
MA <sub>2</sub>	2	Linear	BeCl <sub>2</sub>
MA <sub>3</sub>	3	Trigonal planar	BF <sub>3</sub>
MA <sub>4</sub>	4	Tetrahedral	SiF <sub>4</sub>
MA <sub>5</sub>	5	Trigonal bipyramidal	PF <sub>5</sub>
MA <sub>6</sub>	6	Octahedral	SF <sub>6</sub>

When considering the shape of molecules using VSEPR-theory, multiple bonds are count as single bond region.

**Bent rule:** It describes the variation in geometry that could be experienced in molecules with the same steric number. This is due to the difference in electron-electron repulsion ability between the bonding and non-bonding electrons, and the fact that more electronegative substituent "prefer" hybrid orbital having less s-character, and more electropositive substituent prefer having more s-character.

For example, CH<sub>4</sub>, NH<sub>3</sub> and H<sub>2</sub>O are MA<sub>4</sub> molecules with steric number of 4. They are all expected to have tetrahedral shape (109.5°) but only methane is tetrahedral among them. NH<sub>3</sub> is pyramidal (107.3°) while H<sub>2</sub>O is bent (104.5°).

**Question:** Use VSEPR-theory to predict the shape of the following molecules: H<sub>2</sub>O, NH<sub>4</sub><sup>+</sup>, BCl<sub>3</sub>, CO<sub>2</sub>, ClF<sub>3</sub>, SO<sub>2</sub>, O<sub>3</sub>, BrF<sub>5</sub>

### **Limitation of VSEPR-Theory**

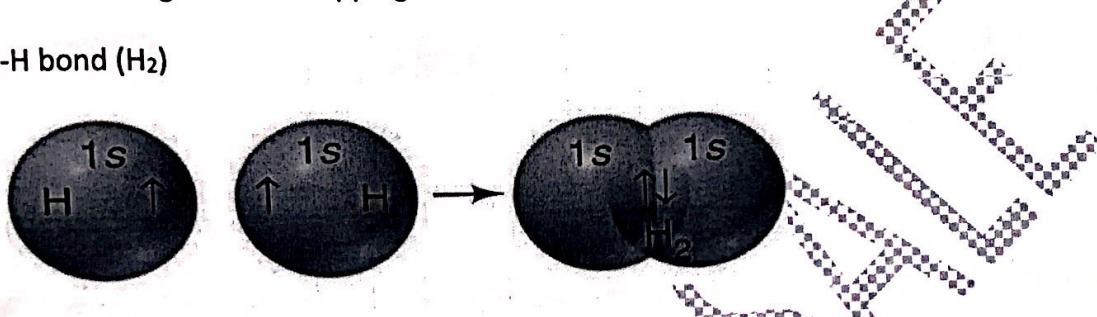
1. Its fails to predict the shapes of isoelectronic species and transition metal compounds
2. It does not take relative sizes of substituent and stereochemically inactive lone pairs into account

3. It cannot be applied to heavy d-block species that experience stereochemical inert pair effect

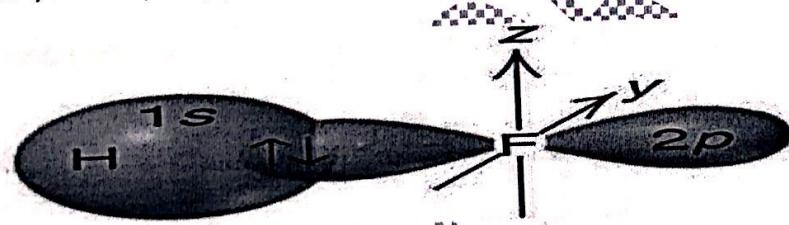
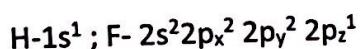
### Valence Bond Theory

Valence bond (VB) theory assumes that all bonds are localized bond which is formed between atoms by donation of electron from each atom. It also assumes that the sharing of electrons between atoms is viewed as an overlapping of atomic orbitals of the bonding atoms. VB-theory uses valence electron to describe bonding. For example, H-H bond is formed through the overlapping of two half-filled s-orbitals.

H-H bond ( $H_2$ )



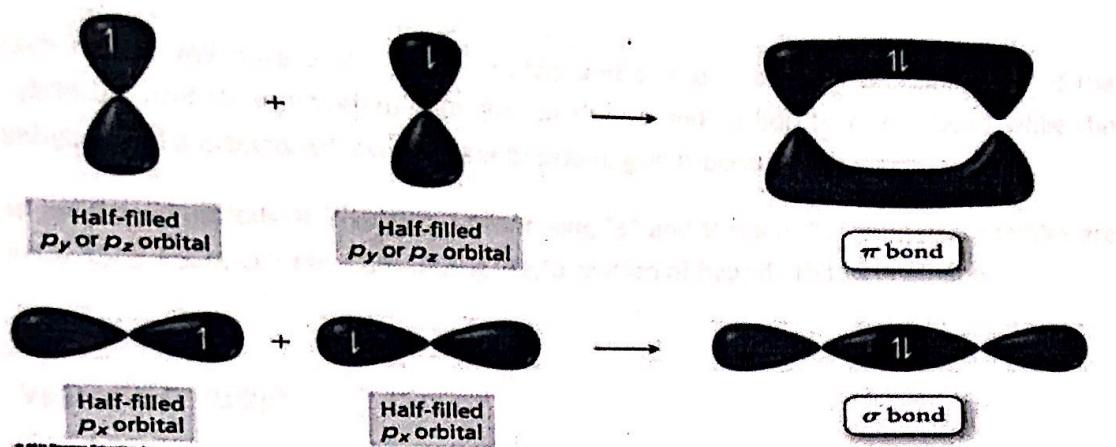
H-F bond



Question: Describe the formation of  $SF_6$  and  $SF_4$  using valence bond theory

Hybridization: It is the mixing of atomic orbitals to form new hybrid orbitals. The hybrid orbitals are useful in explaining molecular geometry and atomic bonding properties. The various types of hybridized orbitals include: sp (form from mixing a "s" and a "p" orbital to give two sp-hybrid orbitals),  $sp^2$ ,  $sp^2d$ ,  $sp^3$ ,  $sp^3d$ ,  $sp^3d^2$ . These hybridized orbitals have the assigned geometry; sp-linear,  $sp^2$ -planar,  $sp^2d$ -square planar,  $sp^3$ -tetrahedral,  $sp^3d^2$ -octahedral.

$\sigma$  bond and  $\pi$ -bond: Sigma ( $\sigma$ ) bond is symmetric about its axis. It is formed through head-on overlapping between atomic orbitals. However,  $\pi$ -bond electrons distribute above and below the axis of the nodal plane.  $\pi$ -bonds are formed through side to side overlapping of two "p-orbitals" and can only be formed from p-orbitals.  $\pi$ -bonds are weaker than  $\sigma$ -bonds. The diagram below shows overlapping of p-orbitals to give  $\sigma$  bond and  $\pi$ -bond.



### Formation of hybridized orbitals

**sp<sup>3</sup> hybridized orbitals:** It is formed from mixing a "s" and three "p" orbitals. Examples are CH<sub>4</sub>, CF<sub>4</sub>, NH<sub>3</sub> etc. Considering the hybridization in methane;

Valence of C – 2s<sup>2</sup>2p<sup>2</sup>

Ground state		
	2s	2p
Excited state		

1s<sup>1</sup> electron of each H will pair with the four sp<sup>3</sup> hybrid orbitals resulting to the formation of CH<sub>4</sub>

**sp<sup>2</sup> hybridized orbitals:** It is formed from mixing a "s" and two of "p" orbitals. Examples are BF<sub>3</sub>, H<sub>2</sub>CO, H<sub>2</sub>C=CH<sub>2</sub> etc. Considering the formation of hybrid orbitals in ethane;

Valence of C – 2s<sup>2</sup>2p<sup>2</sup>

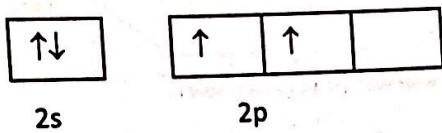
Ground state		
	2s	2p
Excited state		

Each carbon will have 3  $sp^2$  hybrid orbitals and one unhybridized p-orbital. One of the hybridized orbitals will overlap with that of the second carbon to give  $\sigma$  bond while the unhybridized p-orbitals will overlap side to side to give  $\pi$ -bond.

**sp hybridized orbitals:** It is formed from mixing "s" and three of "p" orbitals. Examples are  $BeCl_2$ ,  $C_2H_2$ ,  $H_2CN$ ,  $CO_2$  etc. Considering the formation of hybrid orbitals in ethene;

Valence of C –  $2s^22p^2$

Ground state



Excited state

Each carbon will have 2  $sp$  hybrid orbitals and two unhybridized p-orbital. One of the hybridized orbitals will overlap with that of the second carbon to give  $\sigma$  bond while the unhybridized p-orbitals will overlap side to side to give two  $\pi$ -bonds.

#### Limitation of VB-theory

1. It can't explain colour and spectra
2. It can't explain the relative stability of structural isomers
3. It does not discuss about energies of electron

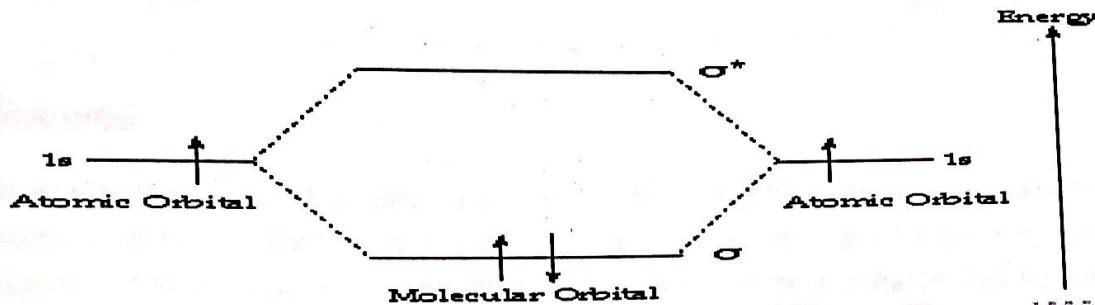
#### Molecular Orbital Theory

The theory predicts that molecular orbitals are obtained by combining the atomic orbitals. The common approximation that allows the generation of molecular orbital diagram for small diatomic molecules is called the "linear combination of atomic orbitals" (LCAO) approach. The following assumptions lie in the core of this model

1. Molecular orbitals are formed from the overlap of atomic orbitals
2. Only atomic orbitals of about the same energy interact to a significant degree

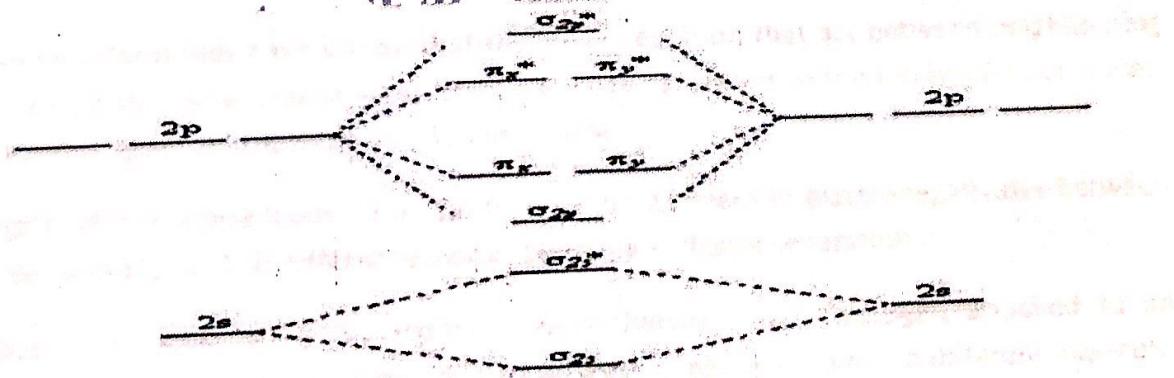
3. when two atomic orbitals overlap, they interact in two extreme ways to form two molecular orbitals, a bonding molecular orbital and antibonding molecular orbital.

Considering the H<sub>2</sub> molecule, one of the molecular orbitals in this molecule is constructed by adding mathematical function for the two 1s atomic orbitals that come together to form this molecule. Another orbital is formed by subtracting one of these functions from the other.

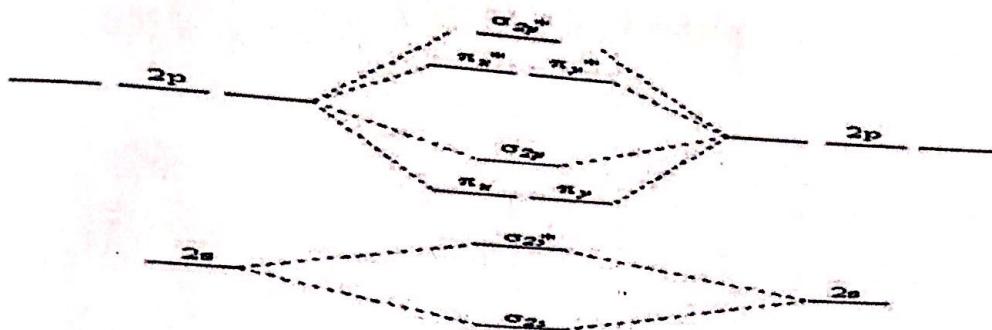


One of these molecular orbitals is called the bonding molecular orbital,  $\sigma$  while the other is called antibonding molecular orbital  $\sigma^*$ . The electrons are in the region between the two nuclei in bonding molecular orbital but away from the region in antibonding molecular orbital.

The order of filling electrons in molecular orbital theory is as follows:  $\sigma_{1s}, \sigma_{1s}^*, \sigma_{2s}, \sigma_{2s}^*, \sigma_{2p}, \pi_{2px}, \pi_{2py}, \pi_{2px}^*, \pi_{2py}^*, \sigma_{2p}^*, \sigma_{3s}, \dots$  It should be noted that  $\pi_{2px}$  and  $\pi_{2py}$  have the same energy, therefore, each of the molecular orbitals have to be singly filled before being paired up. Similar situation is found in  $\pi_{2px}^*$  and  $\pi_{2py}^*$ .



Experiments have shown that the diagram above best described the model of O<sub>2</sub> and F<sub>2</sub>. However, B<sub>2</sub>, C<sub>2</sub> and N<sub>2</sub> are described by a model that include hybridization with the arrangement given as,  $\sigma_{1s}, \sigma_{1s}^*, \sigma_{2s}, \sigma_{2s}^*, \pi_{2px}, \pi_{2py}, \sigma_{2p}, \pi_{2px}^*, \pi_{2py}^*, \sigma_{2p}^*, \sigma_{3s}$



### Bond order

**Bond Order** =  $\frac{1}{2}$  (bonding electrons – antibonding electrons). Bond order determines the number of bond between two atoms. The bond order can also be used to predict the stability of molecules. If the bond order is zero, the molecule is unstable. Bond order greater than zero suggest a stable molecule. The higher the bond order is, the more stable the bond.

Molecular orbital diagram can be used to predict whether a molecule is paramagnetic or diamagnetic. If all the electrons are paired up, the molecule is diamagnetic. If one or more electrons are unpaired, the molecule is paramagnetic.

Question: Write out the molecular orbital configuration of  $F_2$ ,  $Ne_2$ ,  $CO$  and  $NO$ . Calculate the bond order of these molecules and determine whether these molecules are paramagnetic.

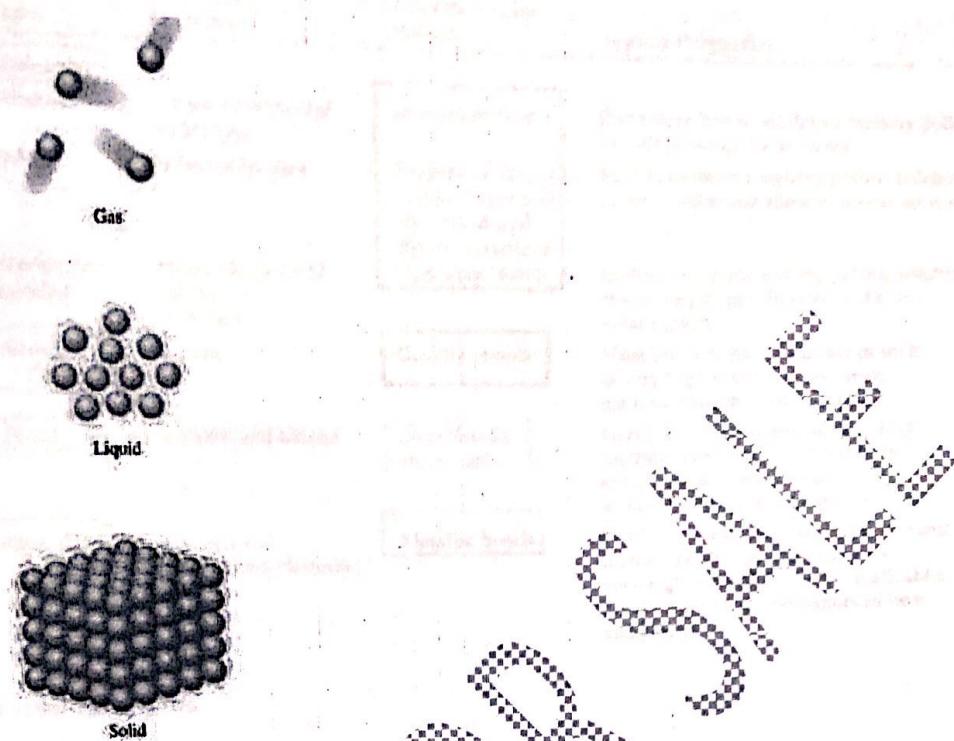
### Intermolecular Bonding

Intermolecular bonds have forces of attraction or repulsion that act between neighbouring particles (atom, molecules or ions). They are weak compared to the intramolecular forces. The various types of intermolecular forces include:

1. Dipole-dipole interactions: This results from the different in electronegativities between two bonded atoms. This difference causes permanent charge separation.
2. Hydrogen bond: It is the attractive force between the hydrogen attached to an electronegative atom of one molecule and an electronegative atom of a different molecule. It occurs in molecule such as  $HF$ ,  $H_2O$ ,  $NH_3$ . Hydrogen bonding is responsible for high boiling point of water and ammonia.
3. London dispersion forces (also known as Van der waal's forces): This arises due to instantaneous dipoles in neighbouring atoms. As the negative charge of the electron is not uniform around the whole atom, there is always a charge imbalance. This small charge will induce a corresponding dipole in a nearby molecule e.g condensation of bromine gas.
4. Cation –π interaction: This occurs between a π-bond and a cation. This type of interaction could be found between benzene and sodium ion.

## States of Matter Compared

## STRUCTURES OF SOLIDS



### Types of Solids

**Crystalline material:** atoms self-organize in a periodic array

**Single crystal:** atoms are in a repeating or periodic array over the entire extent of the material

**Polycrystalline material:** comprised of many small crystals or grains

**Amorphous:** disordered – lack of a systematic atomic arrangement.

### Crystalline Solid State

Single crystals comprise an infinite array of ions, atoms, or molecules, known as a crystal lattice. The strength of the interactions between the species comprising the crystal is known as the lattice energy, and is dependent on the nature and degree of interactions between adjacent species. For example, the extremely high melting points of salts are directly associated with the strength of the ionic bonds between adjacent ions. For molecular species, it is the degree of intermolecular interactions such as van der Waal and hydrogen bonding forces that controls the lattice energy.

Solid-state chemistry uses the same general principles for bonding as those employed for molecules. The physical and chemical properties of a macroscopic crystal can be interpreted by envisioning the crystal as consisting of molecular orbitals extending throughout. There are two major classifications of Crystalline solids: crystals and amorphous materials.

## **Some Characteristics of Crystalline Solids**

Type	Structural Particles	Intermolecular Forces	Typical Properties	Examples
<b>Molecular Nonpolar</b>	Atoms or nonpolar molecules	Dispersion forces	Extremely low to moderate melting points; soluble in nonpolar solvents	Ar, H <sub>2</sub> , I <sub>2</sub> , CCl <sub>4</sub> , CH <sub>4</sub> , CO <sub>2</sub>
<b>Polar</b>	Polar molecules	Dispersion forces, dipole-dipole and dipole-induced dipole attractions Hydrogen bonds	Low to moderate melting points; soluble in some polar and some nonpolar solvents	HCl, H <sub>2</sub> S, CHCl <sub>3</sub> , (CH <sub>3</sub> ) <sub>2</sub> O, (CH <sub>3</sub> ) <sub>2</sub> CO
<b>Hydrogen- bonded</b>	Molecules with H bonded to N, O, or F	Covalent bonds	Low to moderate melting points; soluble in some hydrogen-bonded and some polar liquids	H <sub>2</sub> O, HF, NH <sub>3</sub> , CH <sub>3</sub> OH, CH <sub>3</sub> COOH
<b>Network Covalent</b>	Atoms	Electrostatic attractions	Most are very hard; sublime or melt at very high temperatures; most are nonconductors of electricity	C(diamond), C(graphite) SiC, SiO <sub>2</sub> , BN
<b>Ionic</b>	Cations and anions	Metallic bonds	Hard; brittle; moderate to very high melting points; nonconductors as solids, but electrical conductors as liquids; many are soluble in water	NaCl, CaF <sub>2</sub> , K <sub>2</sub> S, MgO
<b>Metallic</b>	Cations and delocalized electrons		Hardness varies from soft to very hard; melting points vary from low to very high; lustrous; ductile; malleable; good to excellent conductors of heat and electricity	Na, Mg, Al, Fe, Cu, Zn, Mo, Ag, Cd, W, Pt, Hg, Pb

# Crystal Structures

A crystal is comprised of an infinite 3-D lattice of repeating units, of which the smallest building block is known as the asymmetric unit. When acted upon by crystal symmetry operations such as rotation axes or mirror planes, the asymmetric unit is duplicated to produce the contents of a unit cell. For any crystal lattice, it is possible to define an infinite number of possible unit cells. However, by convention, this unit is chosen to be a repeatable unit that possesses the same symmetry elements of the bulk crystal, and will generate the entire extended crystal lattice via translations along the unit cell axes. The structure that

exhibits these properties while having the smallest possible volume is referred to as the primitive unit cell.

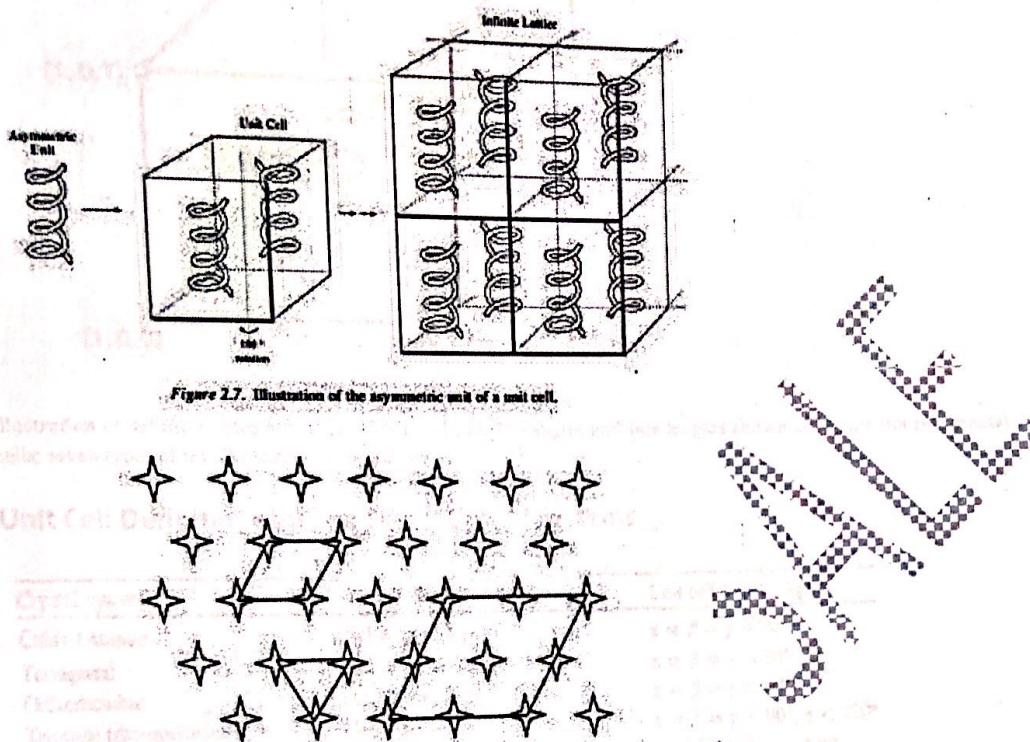


Figure 2.7. Illustration of the asymmetric unit of a unit cell.

Representation of some unit cell selections from a two-dimensional array. The triangle and smaller rhombus selections are known as "primitive" unit cells, as each contains one object per unit cell ( $3 \times 1/3$  for the triangle,  $4 \times 1/4$  for the rhombus). By contrast, there are four objects per unit cell for the larger rhombus ( $4 \times 1/4$  for corner objects;  $4 \times 1/2$  for those on the edges; one in the center). When each of these selections is translated along the two-dimensional axes, they reproduce the positions of all objects in the lattice.

The diagram below provides a schematic of the defining vectors and angles for a unit cell. It is convenient to describe these units as having three vectors (a, b, and c) that may or may not be aligned along the Cartesian axes, based on the values of unit cell angles. Depending on the geometry and volume of the unit cell, there are seven crystal systems that may be generated in the table shown below.

For simplicity, fractional coordinates are used to describe the lattice positions in terms of crystallographic axes, a, b, and c. For instance, the fractional coordinates are  $(1/2, 1/2, 1/2)$  for an object perfectly in the middle of a unit cell, midway between all three crystallographic axes. To characterize crystallographic planes, integers known as Miller indices are used. These numbers are in the format  $(hkl)$ , and correspond to the interception of unit cell vectors at  $(a/h, b/k, c/l)$ .

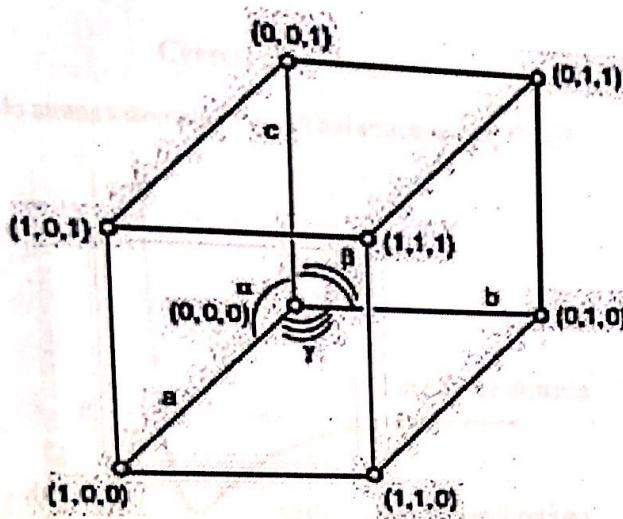


Illustration of definitive axes and angles for a unit cell. The angles and side lengths shown above are not representative of all unit cells; seven types of cell dimensions are possible.

### Unit Cell Definitions for the Seven Crystal Systems

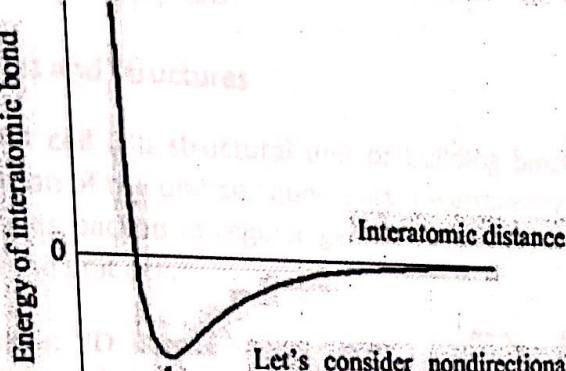
Crystal system	Unit cell vector lengths	Unit cell vector angles
Cubic (isometric)	$ a  =  b  =  c $	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$ a  =  b  \neq  c $	$\alpha = \beta = \gamma = 90^\circ$
Orthorhombic	$ a  \neq  b  \neq  c $	$\alpha = \beta = \gamma = 90^\circ$
Trigonal (rhombohedral)	$ a  =  b  =  c $	$\alpha = \beta = \gamma \neq 90^\circ, \gamma < 120^\circ$
Hexagonal	$ a  =  b  \neq  c $	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$
Monoclinic	$ a  \neq  b  \neq  c $	$\alpha = 90^\circ, \beta \neq 90^\circ$
Triclinic	$ a  \neq  b  \neq  c $	$\alpha \neq 90^\circ, \beta \neq 90^\circ, \gamma \neq 90^\circ$

## Crystal structures

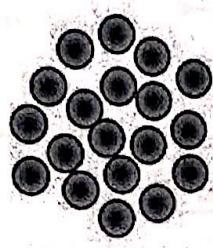
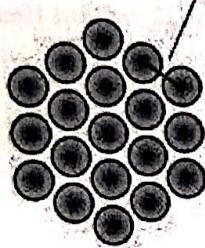
Why do atoms assemble into ordered structures (crystals)?

Forces and structures

The smallest structural unit of a solid body that can determine the crystal structure. Repeating unit of atoms in a crystal lattice. Crystalline solids have alternating layers called planes.



Let's consider nondirectional bonding (like in metals)



Energy of the crystal < Energy of the amorphous solid



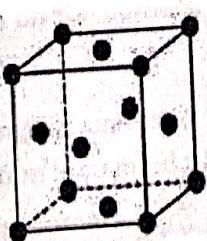
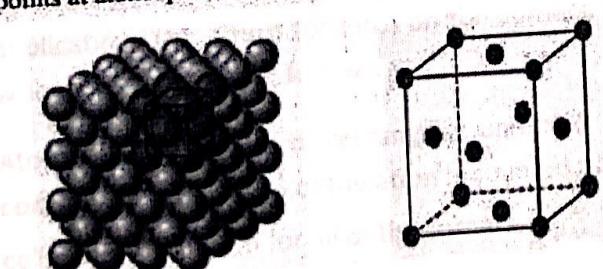
## Crystal structure

To discuss crystalline structures it is useful to consider atoms as being hard spheres with well-defined radii. In this hard-sphere model, the shortest distance between two like atoms is one diameter of the hard sphere.



- hard-sphere model

We can also consider crystalline structure as a lattice of points at atom/sphere centers.



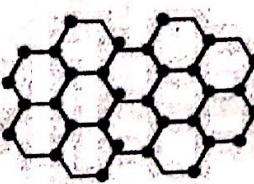
## Types of crystal Structures:

- Ionic crystals
- Covalent crystals
- Molecular crystals
- Metallic crystals

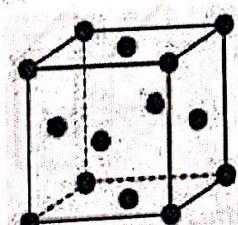
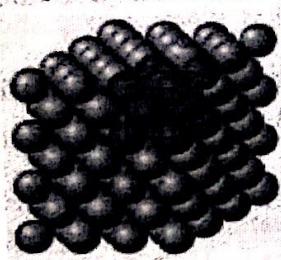
## Formulas and Structures

The unit cell is a structural unit or building block that can describe the crystal structure. Repetition of the unit cell generates the entire crystal. Crystalline solids have atoms, ions, or molecules packed in regular geometric arrays, with the simplest repeating structural unit called the unit cell.

**Example:** 2D honeycomb net can be represented by translation of two adjacent atoms that form a unit cell for this 2D crystalline structure



**Example of 3D crystalline structure:**



### Simple Structure

The crystal structures of metals are relatively simple. Those of some minerals can be complex, but minerals usually have simpler structures that can be recognized within the more complex structure. The unit cell is a structural component that, when repeated in all directions, results in a macroscopic crystal. Structures of the 14 possible crystal structures (Bravais lattices) are shown in below. Several different unit cells are possible for some structures; the one used may be chosen for convenience, depending on the particular application. The atoms (or ions) on the corners, edges, or faces of the unit cell are shared with other unit cells as follows:

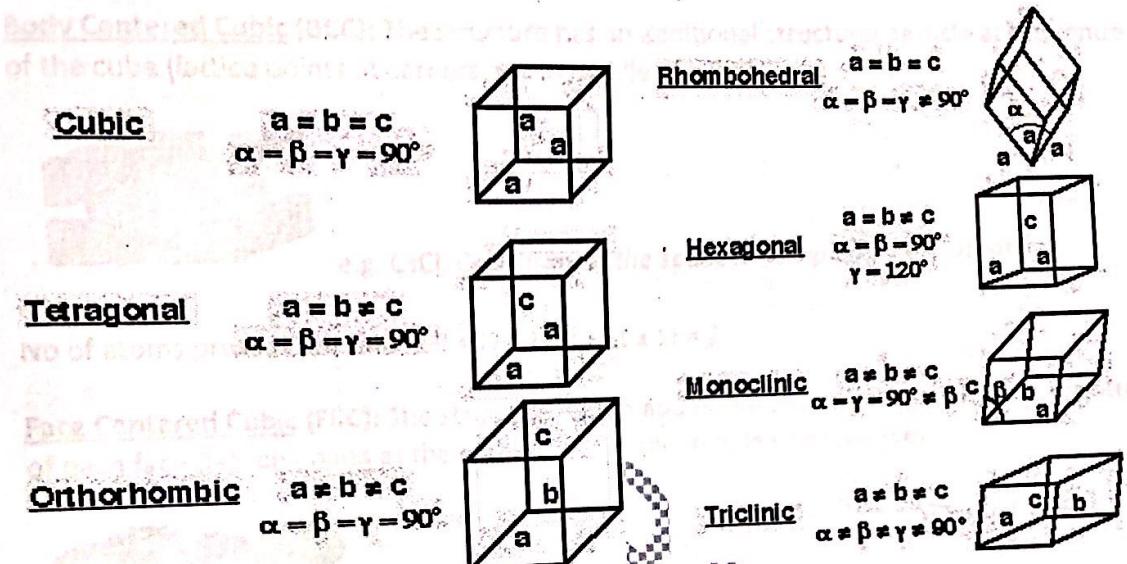
Atoms at the corners of rectangular unit cells are shared equally by eight-unit cells and contribute  $\frac{1}{8}$  to each ( $\frac{1}{8}$  of the atom is counted as part of each cell). The total for a single unit cell is  $8 \times \frac{1}{8} = 1$  atom for all of the corners.

Atoms at the corners of non-rectangular unit cells also contribute one atom total to the unit cell; small fractions on one corner are matched by larger fractions on another.

Atoms on edges of unit cells are shared by four-unit cells—two in one layer, two in the adjacent layer—and contribute  $\frac{1}{4}$  to each.

Atoms on faces of unit cells are shared between two-unit cells and contribute  $\frac{1}{2}$  to each.

We define the size of the unit cell using **lattice parameters** (sometimes called lattice constants, or cell parameters). These are 3 vectors,  $a$ ,  $b$ ,  $c$ . The angles between these vectors are given by  $\alpha$  (angle between  $b$  and  $c$ ),  $\beta$  (angle between  $a$  and  $c$ ), and  $\gamma$  (angle between  $a$  and  $b$ ).



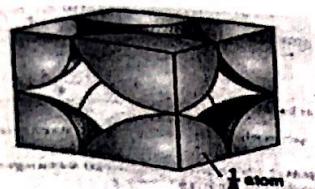
**The Seven Crystal Classes and Fourteen Bravais Lattices.** The points shown are not necessarily individual atoms but are included to show the necessary symmetry.

Although there are only 7 crystal systems or shapes, there are 14 different crystal lattices, called **Bravais Lattices**. (3 different cubic types, 2 different tetragonal types, 4 different orthorhombic types, 2 different monoclinic types, 1 rhombohedral, 1 hexagonal, 1 triclinic). See below.

Real crystals always possess one of these lattice types, but different crystalline compounds that have the same lattice can have different motifs and different lattice parameters (these depend upon the chemical formula and the sizes of the atoms in the unit cell). We will only concern ourselves with the cubic lattices, though we will refer to the hexagonal lattice in passing.

#### Types of Cubic Lattices.

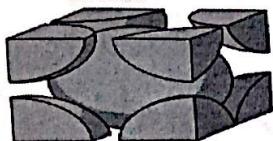
**Simple cubic (also called primitive cubic):** is the simplest unit cell and has structural particles centered only at its corners (lattice points only at corners).



e.g. Polonium (52% of the space is occupied by the atoms)

$$\text{No of atoms per unit cell} = 8 \times 1/8 = 1$$

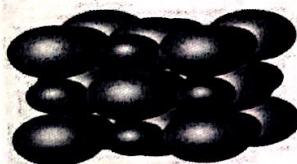
**Body Centered Cubic (BCC):** The structure has an additional structural particle at the centre of the cube (lattice points at corners and in middle of cube).



e.g. CsCl, CsBr (68% of the space is occupied by the atoms)

$$\text{No of atoms present per unit cell} = (8 \times 1/8) + (1 \times 1) = 2$$

**Face Centered Cubic (FCC):** The structure has an additional structural particle at the centre of each face (lattice points at the corners and in the middle of each face).

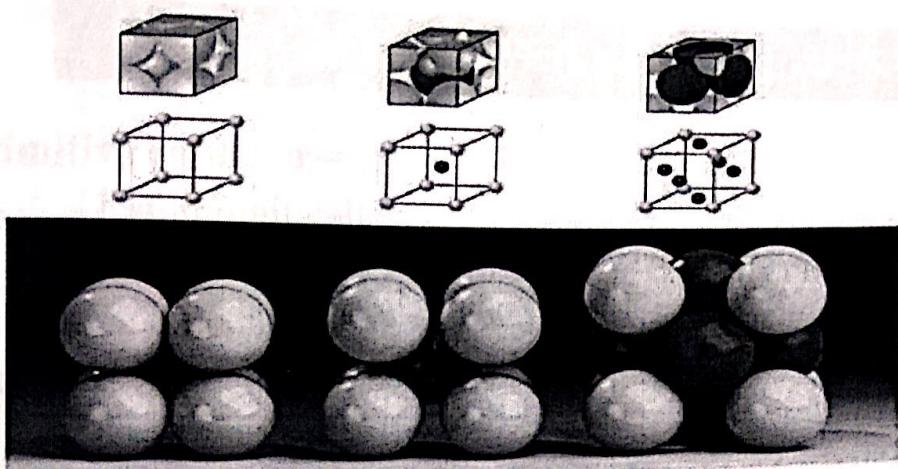


e.g. NaCl, NaF, KBr, MgO (74% of the space is occupied by the atoms)

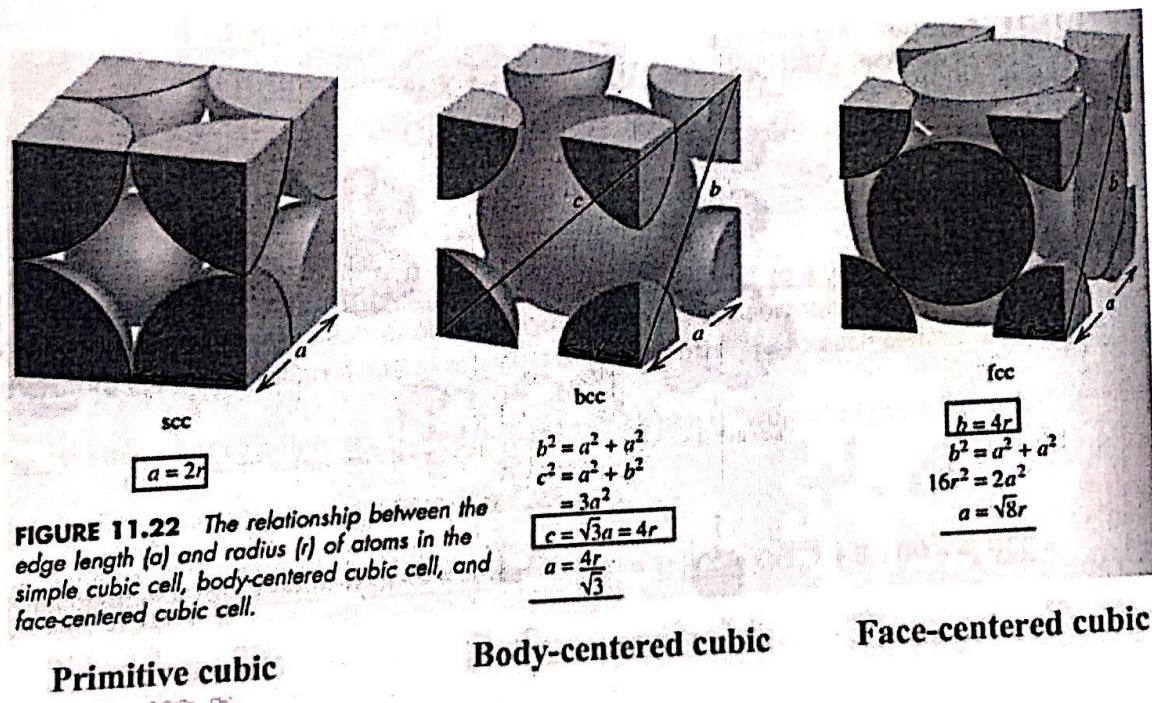
**End-Face Centered Cubic (EFCC):** lattice points at the corners and in the middle of each face.

Question: Draw the structure of EFCC indicating the face points.

$$\text{No of atoms present per unit cell} = (8 \times 1/8) + (2 \times 1/2) = 2$$



(a) simple cubic  
(b) bcc  
(c) fcc



Primitive cubic

Body-centered cubic

Face-centered cubic

# Occupancies per Unit Cells

**Primitive cubic:**  $a = 2r$

1 atom/unit cell

$$\text{occupancy} = \frac{4/3(\pi r^3)}{a^3} = \frac{4/3(\pi r^3)}{(2r)^3}$$
$$= 0.52 = 52\%$$

**Body-centered cubic:**  $a = 4r/(3)^{1/2}$

2 atom/unit cell

$$\text{occupancy} = 2 \times \frac{4/3(\pi r^3)}{a^3} = 2 \times \frac{4/3(\pi r^3)}{[4r/(3)^{1/2}]^3}$$
$$= 0.68 = 68\%$$

**Face-centered cubic:**  $a = (8)^{1/2} r$

4 atom/unit cell

$$\text{occupancy} = 4 \times \frac{4/3(\pi r^3)}{a^3} = 4 \times \frac{4/3(\pi r^3)}{[(8)^{1/2} r]^3}$$
$$= 0.74 = 74\%$$

**Closest packed**

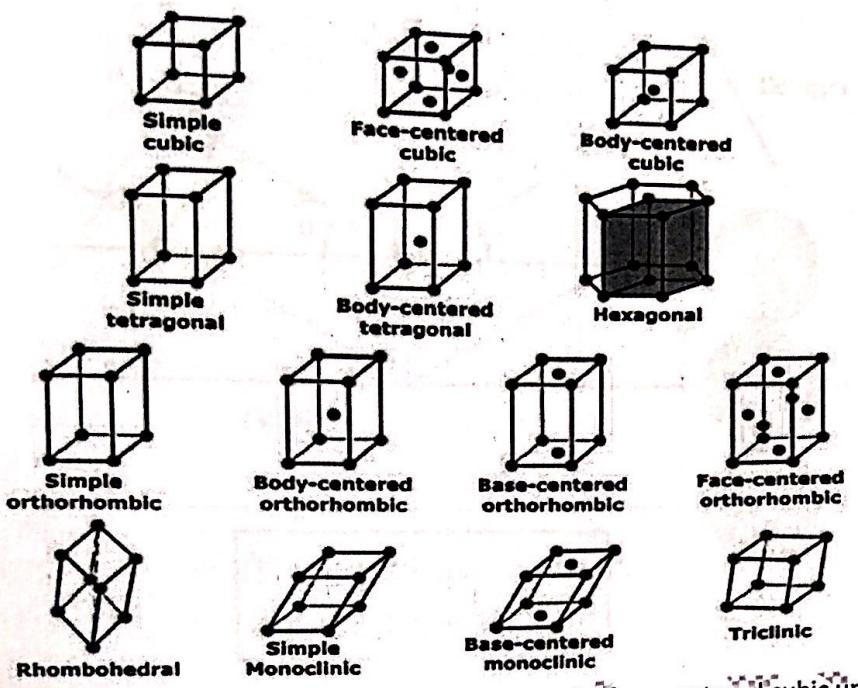
How many lattice points and/or atoms "belong" to a unit cell?

Corners: The points at the corner of the cell are shared by the surrounding unit cells, therefore each one is shared by 8 in total and is only "worth"  $\frac{1}{8}$  to each cell.

Faces: - these lattice points are shared by 2 cells, each one is "worth"  $\frac{1}{2}$  to each cell.

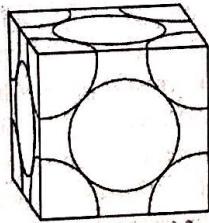
Bod: - this is the sole possession of that cell, worth 1.

Total number lattice points: primitive cubic =  $8(1/8) = 1$ ; FCC =  $6 \times 1/2 + 8(1/8) = 4$ ; BCC =  $8(1/8) + 1 = 2$



The diagram below shows a space-filling diagram of a face-centered cubic unit cell cut to show only the part of each atom that is inside the unit cell boundaries. The corner atoms are each shared among eight-unit cells, so  $\frac{1}{8}$  of the atom is in the unit cell shown.

The face-centered atoms are shared between two-unit cells, so  $\frac{1}{2}$  of the atom is in the unit cell shown. The eight corners of the unit cell then total  $8 \times \frac{1}{8} = 1$  atom, and the six faces total  $6 \times \frac{1}{2} = 3$  atoms; a total of four atoms are in the unit cell.

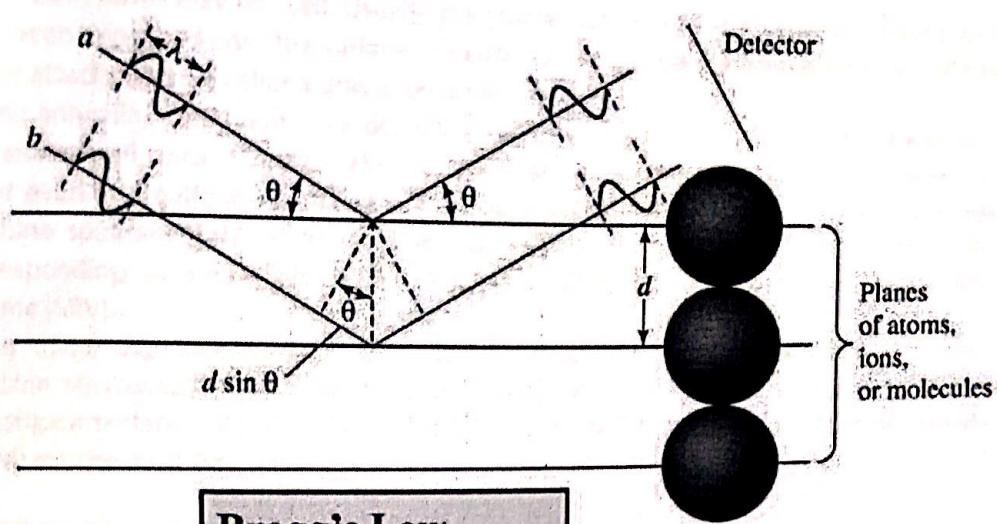


**EXERCISE:** Calculate the number of atoms in each unit cell (from above) of

- a. A body-centered cubic structure
  - b. A hexagonal structure

**b. A hexagonal structure**  
 The positions of atoms are frequently described in **lattice points**, expressed as fractions of the unit cell dimensions. For example, the body-centered cube has atoms at the origin {the corner at which  $x = 0, y = 0, z = 0$ , or  $(0, 0, 0)$ } and at the center of the cube [ $x = \frac{1}{2}, y = \frac{1}{2}, z = \frac{1}{2}$ ] ( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ). The other atoms can be generated by moving these two atoms in each direction in increments of one cell length.

## Experimental Determination of Crystal Structures



### Bragg's Law

$$2d \sin\theta = n\lambda$$

### CRYSTAL DEFECTS

Crystalline solids have a strict ordering of their constituents. At its most fundamental level, the crystal order reduces to the *lattice*, which is a regular pattern of atoms, ions or molecules. A crystal can be regarded as produced by repeated translations of the *unit cell* of the lattice. Examples of latter include the simple cubic (sc), body-centered cubic (bcc), face-centered cubic (fcc), and hexagonal closed packed (hcp) lattices.

However, real crystals in comparison to ideal ones, suffer from residual defects. These may exist in the solid even after a relatively long period of *annealing*. Annealing is a treatment which induces recovery of the solid and hence destroys defects therein. Often an annealing treatment takes the form of long term heating at elevated temperatures.

The defects can be classified according to their dimensionality. *Point defects* are point-like and can be isolated or clustered. The most common types are *vacancies* and *interstitial atoms*. A vacancy is an empty lattice site, whereas an interstitial atom is an atom located outside the perfect crystal ordering, e.g. between some lattice sites. If the solid consists of ions of different kind, there is the additional possibility of *substitutional impurities*. Such a defect is made up of an atom located at a site that belongs to an atom of the other species. When there is an equal number of vacancies and interstitial atoms, one of each kind is taken together and called a *Frenkel pair*. If the interstitial atom that is associated with a vacancy has migrated to the surface and therefore has left the bulk, the vacancy is often called a *Schottky defect*. Vacancies and interstitial atoms may also form clusters, thereby producing three-dimensional defects in the solid.

Two examples of one-dimensional defects are the so-called *edge* and *screw dislocations*. These appear during *slip* of atom planes, occurring when the shear stress exceeds some critical value. The presence of dislocations weakens the shear strength of a crystal. These damage types listed above occur in bulk. At surfaces there are additional ones, like *adatoms* and *craters*. An adatom is simply an atom that has taken residence on top of the surface, whereas a crater is a void that intersects the surface. The conceptual difference between a large multiple vacancy (*i.e.* a vacancy cluster) and a small crater is somewhat

vague, both terms may be used. Usually, the atoms that have been excavated from the solid have been deposited onto the surface or *sputtered*, i.e. ejected out from the surface and no longer attached to the other atoms in the solid.

During annealing treatments, the defects become mobile. As a consequence, Frenkel pairs are annihilated, local stresses relieved, etc. However, some spontaneous annealing may occur even at a quite low temperature. For example, the members of a Frenkel pair may combine spontaneously, if the interstitial is inside a critical region concentrated on the corresponding vacancy. This region is usually called the *spontaneous recombination volume* (SRV).

Many major experimental techniques exist to investigate damage, namely Transmission Electron Microscopy (TEM) to study defect clusters and Scanning Probe Methods (SPM) to investigate surfaces. Scanning Tunnelling Microscopy (STM) and Atomic Force Microscopy (AFM) are the most common examples of scanning probe methods.

## IMPERFECTIONS IN SOLIDS

In practice, all crystals have imperfections. If a substance crystallizes rapidly, it is likely to have many more imperfections, because crystal growth starts at many sites almost simultaneously. Each small crystallite grows until it runs into its neighbours; the boundaries between these small crystallites are called grain boundaries, which can be seen on microscopic examination of a polished surface. Slow crystal growth reduces the number of grain boundaries, because crystal growth starts from a smaller number of sites. However, even if a crystal appears to be perfect, it will likely have imperfections on an atomic level caused by impurities in the material or by dislocations within the lattice.

### Vacancies and Self-Interstitials

Vacancies are missing atoms and are the simplest defects. Because higher temperatures increase vibrational motion and expand a crystal, more vacancies are formed at higher temperatures. However, even near the melting point, the number of vacancies is small relative to the total number of atoms—on the order of 1 in 10,000. The effect of a vacancy on the rest of the lattice is small, because it is a localized defect, and the rest of the lattice remains unaffected. Self-interstitials are atoms displaced from their normal location that appear in one of the interstices in the lattice. Here, the distortion spreads at least a few layers in the crystal, because the atoms are much larger than the available space. In most cases, the number of these defects is much smaller than the number of vacancies.

### Substitutions

Substitution of one atom for another is a common phenomenon. Such mixtures are also called solid solution. For example, nickel and copper atoms have similar sizes and electronegativities and form the same FCC crystal structures. Mixtures of the two are stable in any proportion, with random arrangement of the atoms in the alloys. Other combinations that can work well have a very small atom in a lattice of larger atoms. In this case, the small atom occupies one of the interstices in the larger lattice, with small effects on the rest of the lattice but potentially large effects on the behaviour of the mixture. If the impurity atoms are larger than the holes, lattice strains result, and a new solid phase may be formed.

## Dislocations

Edge dislocations result when atoms in one layer do not match up precisely with those of the next. As a result, the distances between the dislocated atoms and atoms in adjacent rows are larger than usual, and the angles between atoms are distorted for a number of rows on either side of the dislocation.

A screw dislocation is one that has part of one layer shifted a fraction of a cell dimension. This kind of dislocation frequently causes a rapidly growing site during crystal growth, and it forms a helical path, hence the name. Because they provide sites that allow atoms from the solution or melt to fit into a corner where attractions from three directions can hold them in place, screw dislocations are frequently growth sites for crystals.

In general, dislocations are undesirable in crystals. Mechanically, they can lead to weakness that can cause fracture. Electrically, they interfere with conduction of electrons and reduce reliability, reproducibility, and efficiency in semiconductor devices. For example, one of the challenges of photocell manufacture is to raise the efficiency of cells made of polycrystalline silicon to levels that are reached by single crystals.

## QUALITATIVE ANALYSIS OF CATIONS AND ANIONS

### Introduction:

The experiments which analyze known and unknown solutions for the presence of specific cations and anions is known as qualitative analysis. The general approach to finding out what ions are in a solution is to test for the presence of each possible component by adding a reagent that will cause that component, if present, to react in a certain way. This method involves a series of tests, one for each component, carried out on separate samples of solution. Difficulty sometimes arises, particularly in complex mixtures, because one of the species may interfere with the analytical test for another. Although interferences are common, many ions in mixtures can usually be identified by simple tests.

**Common Cations:**  $\text{Ag}^+$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$

**Common Anions:**  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{S}^{2-}$ ,  $\text{NO}_3^-$

Ions are usually identified by the characteristic reaction they show on the addition of a certain reagent. This reaction may result in the formation of a precipitate or a coloured solution. If each ion in the above list had a specific reagent with which it, and it alone, would react to form a precipitate or coloured solution then all that would be required for quantitative analysis would be a complete set of these reagents. Each one would be added in turn to samples of the solution and it would be noted for which reagents a positive reaction was observed.

**Definition:** Qualitative analysis is a chemical method to determine the substances present in a compound but not their quantities, the ions present in salt are needed to be identified in during qualitative analysis.

### Qualitative Analysis Steps:

- (i) Observation physical properties of salts
- (ii) Action of heat on salt
- (iii) Make aqueous solution of the salt to test for anions and cations present

(iv) Carry out confirmatory tests  
**How to identify cation and anion in salt???**

- (i) Colour and solubility of the salt
- (ii) Gas test
- (iii) Effect of heat on salt
- (iv) Confirmatory test for anions
- (v) Confirmatory test for cations

### Colour and solubility of the salt

SALT	COLOUR	
	SOLID	AQUEOUS SOLUTION
$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Al}^{3+}$ , $\text{Pb}^{2+}$ , $\text{NH}_4^+$	white	colourless
$\text{CuSO}_4$ , $\text{Cu}(\text{NO}_3)_2$	Blue	Blue
$\text{CuCl}_2$	Green	Blue
$\text{FeSO}_4$ , $\text{Fe}(\text{NO}_3)_2$ , $\text{FeCl}_2$	Green	Green
$\text{Fe}(\text{SO}_4)_3$ , $\text{Fe}(\text{NO}_3)_3$ , $\text{FeCl}_3$	Brown	Yellow/Brownish
$\text{CuCO}_3$	Green	(Insoluble)
$\text{PbO}$	Brown when Hot & Yellow when cooled	Insoluble
$\text{CuO}$	black	Insoluble
$\text{ZnO}$	Yellow when Hot & White when cooled	Insoluble
$\text{PbCl}_2$	white	Insoluble in cold water but soluble in hot water
$\text{PbI}_2$	Yellow	Insoluble in cold water but soluble in hot water

### Gas Test

Gas	Colour	Smell	Confirmatory Test
$\text{O}_2$	colourless	Odourless	Light up a glowing wooden splinter
$\text{H}_2$	colourless	Odourless	Produces a 'pop' sound with lighted wooden
$\text{CO}_2$	colourless	Odourless	Turn lime water cloudy

NH <sub>3</sub>	colourless	Pungent smell	Turn moist red litmus paper blue
Cl <sub>2</sub>	Grenish Yellow	Pungent smell	Bleaches moist red litmus paper Turn moist blue LP to red and bleaches it.
HCl	colourless	Pungent smell	Form dense white fumes with ammonia gas
NO <sub>2</sub>	Brown	Pungent smell	Turn moist blue litmus paper to red
SO <sub>2</sub>	colourless	Pungent smell	Turn moist blue litmus paper to red

### Action of Heat on Salts:

when salts are heated, three things happen, they are: colour change, release of a certain gas and release of water vapour.

#### Heating CO<sub>3</sub> salt:

- All carbonates are decomposed by heat to release CO<sub>2</sub> except K<sub>2</sub>CO<sub>3</sub> and NaCO<sub>3</sub>.
- MCO<sub>3</sub> → MO + CO<sub>2</sub>
- CO<sub>2</sub> will turn lime water, Ca(OH)<sub>2</sub> milky (CaCO<sub>3</sub> + H<sub>2</sub>O)

#### Heating NO<sub>3</sub> salt:

- Most metal nitrate decompose to produce a metal oxide, nitrogen oxide and oxygen.
- KNO<sub>3</sub> & NaNO<sub>3</sub> produced Oxygen gas and nitrites when heated
- NO<sub>2</sub> (brown gas: acidic), turn moist blue litmus paper red.
- O<sub>2</sub> relight glowing wooden splinter.

#### Heating SO<sub>4</sub> salt:

- All sulphate salt are not decomposed by heat.
- Some (Fe, Zn, Cu) will decomposed during strong heating producing sulphur trioxide gas.
- Ex: ZnSO<sub>4</sub> → ZnO + SO<sub>3</sub>

#### Heating Chloride salt:

- All chloride salts are not decomposed by heat except ammonium chloride.
- NH<sub>4</sub>Cl produced white fumes.

- Ex:  $\text{NH}_4 \rightarrow \text{NH}_3 + \text{HCl}$

### Deduction Of Types Of Ion Present From Gas Produced:

Gas produced	Types of ion
$\text{CO}_2$	$\text{CO}_3^{2-}$ (except $\text{Na}_2\text{CO}_3, \text{K}_2\text{CO}_3$ )
$\text{NO}_2$	$\text{NO}_3^-$
$\text{NO}_2$ and $\text{O}_2$	$\text{NO}_3^-$ (excepts $\text{NaNO}_3, \text{KNO}_3$ )
$\text{SO}_2$	$\text{SO}_4^{2-}$
$\text{NH}_3$	$\text{NH}_4^+$

### Test for Anion:

Anion	Confirmatory Test
$\text{CO}_3^{2-}$	<ul style="list-style-type: none"> <li>Bubbles with dilute acid and the gas produced will cause limewater milky</li> </ul>
$\text{SO}_4^{2-}$	<ul style="list-style-type: none"> <li>Mixed with dilute sulphuric acid and barium chloride and a white precipitate is formed.</li> </ul>
$\text{Cl}^-$	<ul style="list-style-type: none"> <li>Mixed with dilute nitric acid followed by silver nitrate solution and a white precipitate is formed</li> </ul>
$\text{NO}_3^-$	<ul style="list-style-type: none"> <li>Brown ring test and a brown ring will be formed.</li> </ul>

### Test for Cation:

Cation	NaOH Solution	NH <sub>3</sub> Solution
$\text{Ca}^{2+}$	<ul style="list-style-type: none"> <li>White precipitate formed.</li> <li>Not soluble in excess</li> </ul>	<ul style="list-style-type: none"> <li>No reaction</li> </ul>

$Mg^{2+}$	<ul style="list-style-type: none"> <li>White precipitate formed.</li> <li>Not soluble in excess</li> </ul>	<ul style="list-style-type: none"> <li>White precipitate formed.</li> <li>Not soluble in excess</li> </ul>
$Al^{3+}$	<ul style="list-style-type: none"> <li>White precipitate formed.</li> <li>Soluble in excess</li> </ul>	<ul style="list-style-type: none"> <li>White precipitate formed.</li> <li>Not soluble in excess</li> </ul>
$Zn^{2+}$	<ul style="list-style-type: none"> <li>White precipitate formed.</li> <li>Soluble in excess</li> </ul>	<ul style="list-style-type: none"> <li>White precipitate formed.</li> <li>Soluble in excess</li> </ul>
$Pb^{2+}$	<ul style="list-style-type: none"> <li>White precipitate formed.</li> <li>Soluble in excess</li> </ul>	<ul style="list-style-type: none"> <li>White precipitate formed.</li> <li>Not soluble in excess</li> </ul>
$Fe^{2+}$	<ul style="list-style-type: none"> <li>Green precipitate formed.</li> <li>Not soluble in excess</li> </ul>	<ul style="list-style-type: none"> <li>Green precipitate formed.</li> <li>Not soluble in excess</li> </ul>
$Fe^{3+}$	<ul style="list-style-type: none"> <li>Brown precipitate formed.</li> <li>Not Soluble in excess</li> </ul>	<ul style="list-style-type: none"> <li>Brown precipitate formed.</li> <li>Not soluble in excess</li> </ul>
$Cu^{2+}$	<ul style="list-style-type: none"> <li>Blue precipitate formed.</li> <li>Not soluble in excess</li> </ul>	<ul style="list-style-type: none"> <li>Blue precipitate formed.</li> <li>Not Soluble in excess and a dark blue solution is produced</li> </ul>
$NH_4^+$	<ul style="list-style-type: none"> <li>White precipitate formed.</li> <li>Soluble in excess</li> </ul>	<ul style="list-style-type: none"> <li>No reaction</li> </ul>

### Confirmatory Tests for $Fe^{2+}$ , $Fe^{3+}$ , $Pb^{2+}$ , $NH_4^+$

Cation	Specific reagent	Observation
$Pb^{2+}$	• KI, NaI	<ul style="list-style-type: none"> <li>Yellow precipitate, soluble in hot water and recrystallises when cooled</li> </ul>
	• KCl, NaCl, HCl	<ul style="list-style-type: none"> <li>White precipitate, soluble in hot water and recrystallises when cooled</li> </ul>
	• $K_2SO_4$ , $Na_2SO_4$ , $H_2SO_4$	<ul style="list-style-type: none"> <li>White precipitate, insoluble in hot water</li> </ul>

$\text{Fe}^{2+}$	• Potassium hexacyanoferreta (II) $\text{K}_4\text{Fe}(\text{CN})_6$	• Light blue precipitate
	• Potassium hexacyanoferreta (III) $\text{K}_3\text{Fe}(\text{CN})_6$	• Dark blue precipitate
	• Acidified $\text{KMnO}_4$	• Purple colour decolourises
Cation	Specific reagent	Observation
$\text{Fe}^{3+}$	• Potassium thiocyanate, $\text{KSCN}$	• Brown precipitate formed. • Not soluble in excess
	• Potassium hexacyanoferrate (II), $\text{K}_4\text{Fe}(\text{CN})_6$	• Dark blue precipitate
	• Potassium hexacyanoferrate (III), $\text{K}_4\text{Fe}(\text{CN})_6$	• Greenish-brown solution
$\text{NH}_4^+$	• Nessler reagent	• Brown precipitate