CHEMISTRY
CHE23CT101

UNIT-I : Fundamentals of Chemical Bonding, Transition Metal Complexes, and Organic Chemistry

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Introduction

Living things are made up of atoms, but in most cases, those atoms aren't just floating around individually. Instead, they're usually interacting with other atoms (or groups of atoms).

For instance, atoms might be connected by strong bonds and organized into molecules or crystals. Or they might form temporary, weak bonds with other atoms that they bump into or brush up against. Both the strong bonds that hold molecules together and the weaker bonds that create temporary connections are essential to the chemistry of our bodies, and to the existence of life itself.

Why form chemical bonds? The basic answer is that atoms are trying to reach the most stable (lowest-energy) state that they can. Many atoms become stable when their valence shell is filled with electrons or when they satisfy the octet rule (by having eight valence electrons). If atoms don't have this arrangement, they'll "want" to reach it by gaining, losing, or sharing electrons via bonds.

Ions and ionic bonds

Some atoms become more stable by gaining or losing an entire electron (or several electrons). When they do so, atoms form **ions**, or charged particles. Electron gain or loss can give an atom a filled outermost electron shell and make it energetically more stable.

Ions come in two types. **Cations** are positive ions formed by losing electrons. For instance, a sodium atom loses an electron to become a sodium cation, Na+. Negative ions are formed by electron gain and are called **anions**. Anions are named using the ending "-ide": for example, the anion of chlorine Cl- is called chloride.

When one atom loses an electron and another atom gains that electron, the process is called **electron transfer**. Sodium and chlorine atoms provide a good example of electron transfer.

Sodium (Na) only has one electron in its outer electron shell, so it is easier (more energetically favorable) for sodium to donate that one electron than to find seven more electrons to fill the outer shell. Because of this, sodium tends to lose its one electron, forming Na+.

Chlorine (Cl), on the other hand, has seven electrons in its outer shell. In this case, it is easier for chlorine to gain one electron than to lose seven, so it tends to take on an electron and become Cl-.
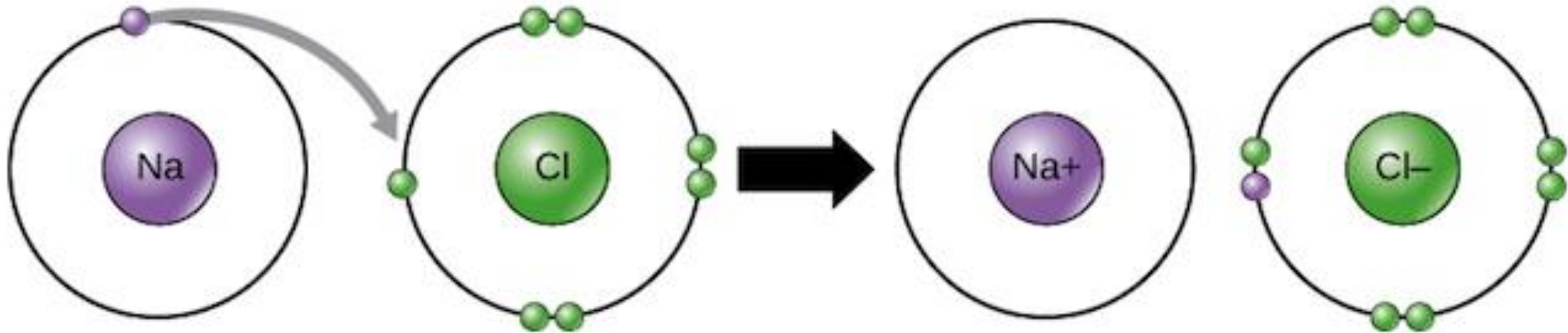
When sodium and chlorine are combined, sodium will donate its one electron to empty its shell, and chlorine will accept that electron to fill its shell. Both ions now satisfy the octet rule and have complete outermost shells. Because the number of electrons is no longer equal to the number of protons, each atom is now an ion and has a +1 (Na+) or –1 (Cl-) charge.

In general, the loss of an electron by one atom and gain of an electron by another atom must happen at the same time.

Making an ionic bond

Ionic bonds are bonds formed between ions with opposite charges. For instance, positively charged sodium ions and negatively charged chloride ions attract each other to make sodium chloride, or table salt. Table salt, like many ionic compounds, doesn't consist of just one sodium and one chloride ion; instead, it contains many ions arranged in a repeating, predictable 3D pattern (a crystal).

Certain ions are referred to in physiology as **electrolytes** (including sodium, potassium, and calcium). These ions are necessary for nerve impulse conduction, muscle contractions and water balance. Many sports drinks and dietary supplements provide these ions to replace those lost from the body via sweating during exercise.

Covalent bonds

Another way atoms can become more stable is by sharing electrons (rather than fully gaining or losing them), thus forming **covalent bonds**. Covalent bonds are more common than ionic bonds in the molecules of living organisms.

For instance, covalent bonds are key to the structure of carbon-based organic molecules like our DNA and proteins. Covalent bonds are also found in smaller inorganic molecules, such as H_2O, CO_2 and O_2. One, two, or three pairs of electrons may be shared between atoms, resulting in single, double, or triple bonds, respectively. The more electrons that are shared between two atoms, the stronger their bond will be.

As an example of covalent bonding, let's look at water. A single water molecule, H_2O, consists of two hydrogen atoms bonded to one oxygen atom. Each hydrogen shares an electron with oxygen, and oxygen shares one of its electrons with each hydrogen:
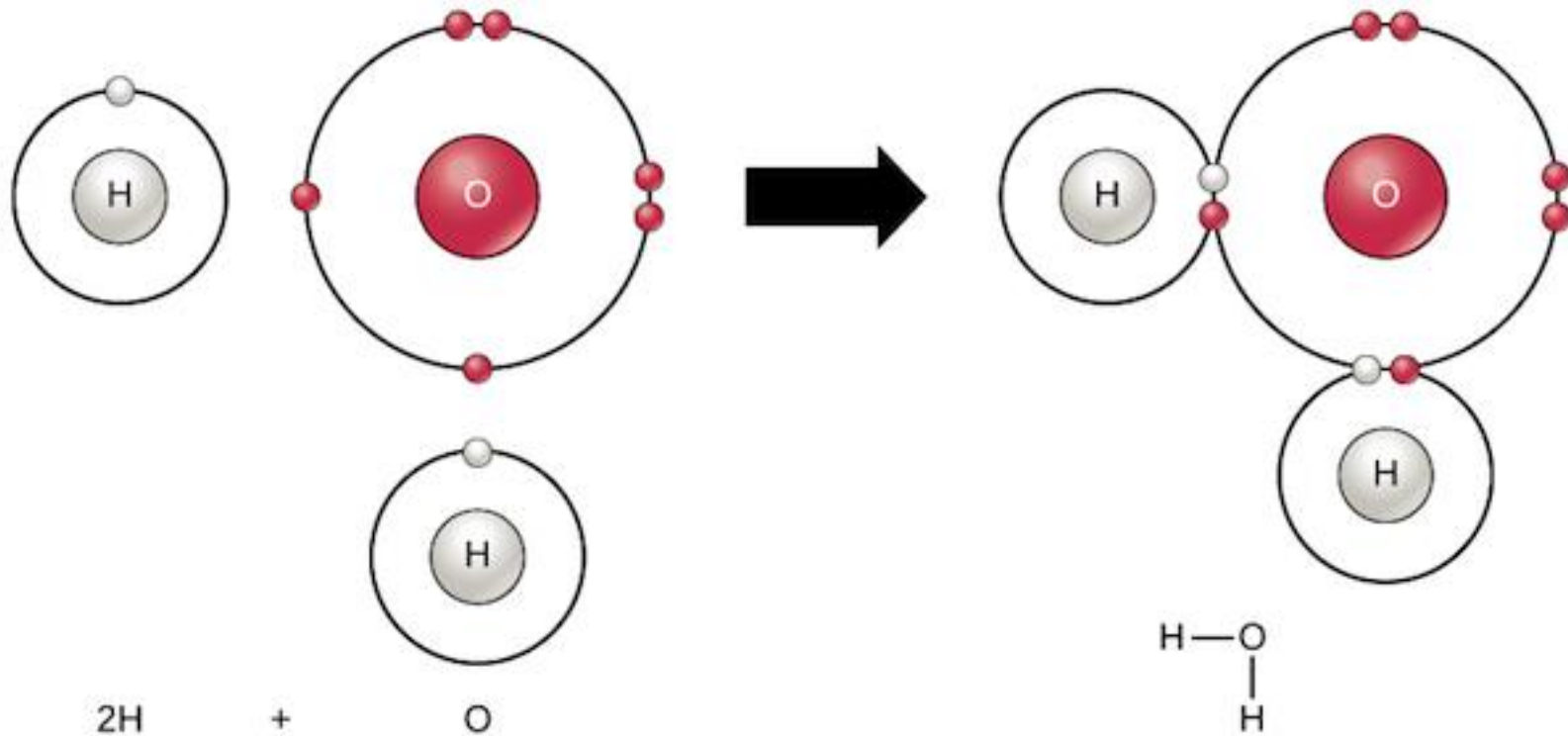
The shared electrons split their time between the valence shells of the hydrogen and oxygen atoms, giving each atom something resembling a complete valence shell (two electrons for H, eight for O). This makes a water molecule much more stable than its component atoms would have been on their own.

Polar covalent bonds

There are two basic types of covalent bonds: polar and nonpolar. In a **polar covalent bond**, the electrons are unequally shared by the atoms and spend more time close to one atom than the other. Because of the *unequal distribution of electrons between the atoms of different elements, slightly positive ($\delta+$) and slightly negative ($\delta-$) charges develop in different parts of the molecule.*
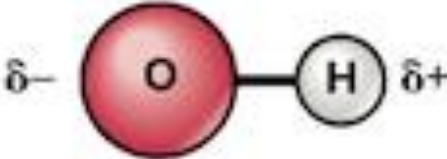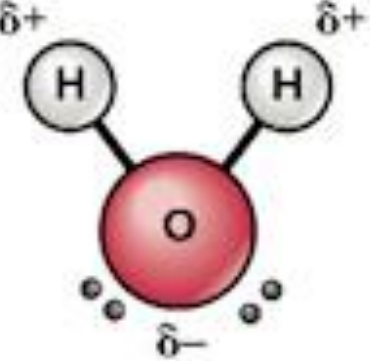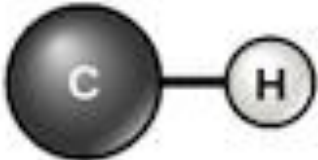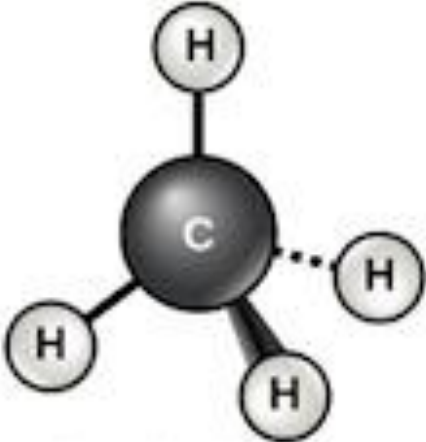
In a water molecule (above), the bond connecting the oxygen to each hydrogen is a polar bond. *Oxygen is a much more electronegative atom than hydrogen, meaning that it attracts shared electrons more strongly*, so the oxygen of water bears a partial negative charge (has high electron density), while the hydrogens bear partial positive charges (have low electron density).

Nonpolar covalent bonds

Nonpolar covalent bonds form between two atoms of the same element, or between atoms of different elements that share electrons more or less equally. For example, molecular oxygen (O_2) is nonpolar because the electrons are equally shared between the two oxygen atoms.

Another example of a nonpolar covalent bond is found in methane (CH4). Carbon has four electrons in its outermost shell and needs four more to achieve a stable octet. It gets these by sharing electrons with four hydrogen atoms, each of which provides a single electron. Reciprocally, the hydrogen atoms each need one additional electron to fill their outermost shell, which they receive in the form of shared electrons from carbon. Although carbon and hydrogen do not have exactly the same electronegativity, they are quite similar, so carbon-hydrogen bonds are considered nonpolar.

|	Bond type	Molecular shape
Water	$\delta-$ O — H $\delta+$ Polar covalent	$\delta+$ H H $\delta+$ O $\delta-$ Bent
Methane	C — H Nonpolar covalent	H C — H H H Tetrahedral

Hydrogen Bonding

A hydrogen bond is a type of attractive (dipole-dipole) interaction between an electronegative atom and a hydrogen atom bonded to another electronegative atom. This bond always involves a hydrogen atom. Hydrogen bonds can occur between molecules or within parts of a single molecule.

A hydrogen bond tends to be stronger than van der Waals forces, but weaker than covalent bonds or ionic bonds.
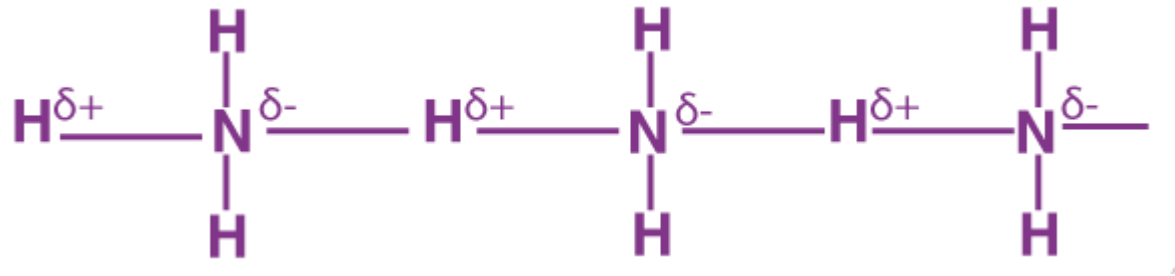
Examples of Hydrogen Bonding

Hydrogen Bonding in Hydrogen Fluoride

Fluorine, having the highest value of electronegativity, forms the strongest hydrogen bond.
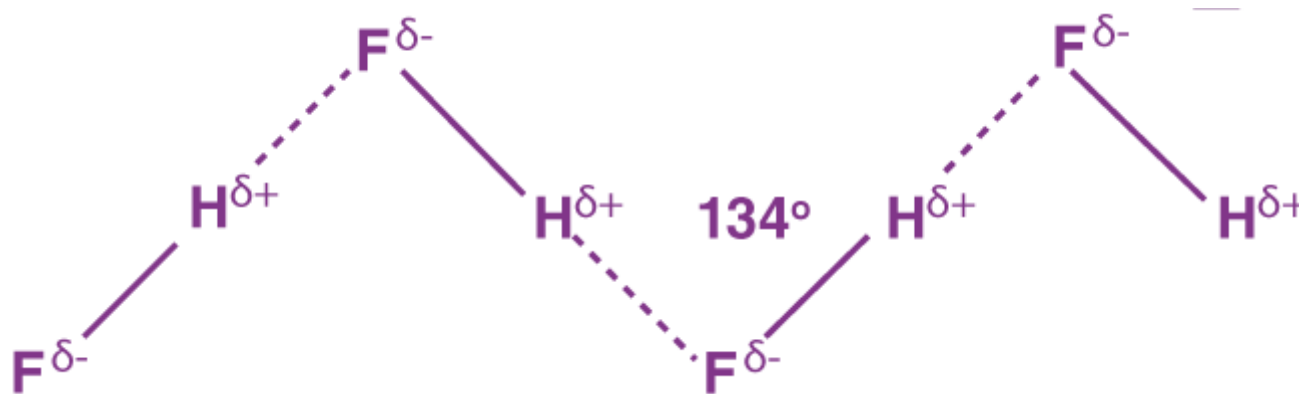
Hydrogen Bonding in Ammonia

It contains highly electronegative atom nitrogen linked to hydrogen atoms.

Types of Hydrogen Bonding

There are two types of H bonds, and it is classified as the following:

•Intermolecular Hydrogen Bonding

•Intramolecular Hydrogen Bonding

Intermolecular Hydrogen Bonding

When hydrogen bonding takes place between different molecules of the same or different compounds, it is called intermolecular hydrogen bonding.

For example, hydrogen bonding in water, alcohol, ammonia etc.

Intramolecular Hydrogen Bonding

The hydrogen bonding which takes place within a molecule itself is called intramolecular hydrogen bonding.

Ortho-Nitrophenol   Salicilaldehyde
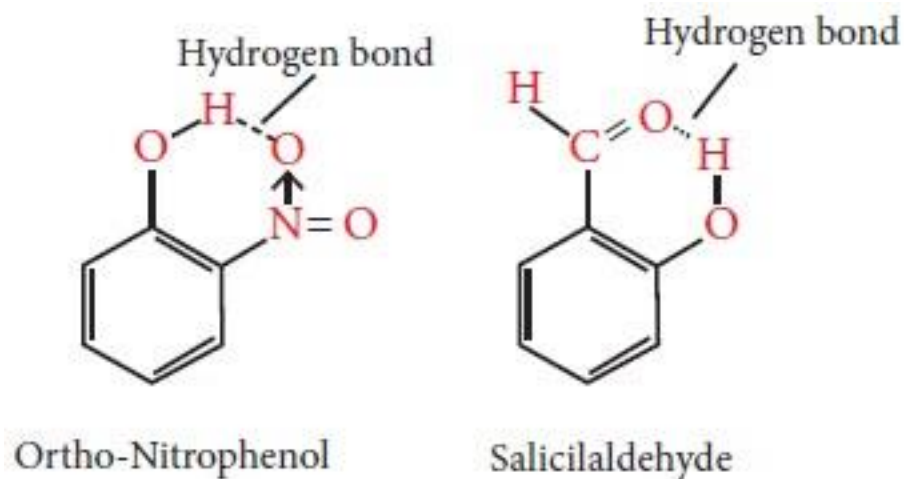
How are hydrogen bonds different from covalent and ionic bonds?

In a covalent bond, two atoms share one or more electrons. Water is a polar molecule. A hydrogen bond is a relatively weak bond between two oppositely partially charged sides of two or more molecules. In an ionic bond, an atom gives away one or more electrons to another atom.

Acids and Bases

An acid is any hydrogen-containing substance that is capable of donating a proton (hydrogen ion) to another substance. A base is a molecule or ion able to accept a hydrogen ion from an acid.

Acidic substances are usually identified by their sour taste. An acid is basically a molecule which can donate an H+ ion and can remain energetically favourable after a loss of H+. *Acids are known to turn blue litmus red.*

Bases, on the other hand, are characterized by a bitter taste and a slippery texture. A base that can be dissolved in water is referred to as an alkali. When these substances chemically react with acids, they yield salts. *Bases are known to turn red litmus blue.*
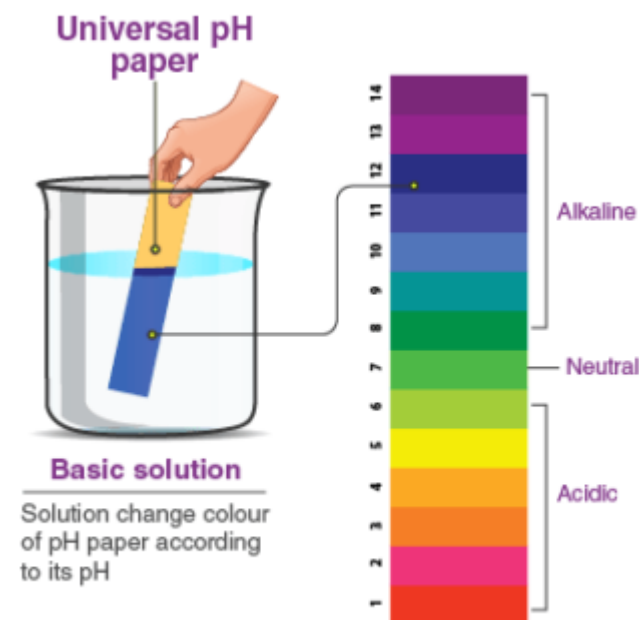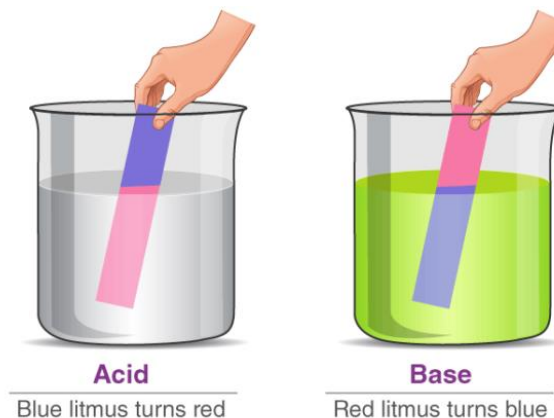
Theories of Acids and Bases

Three different theories have been put forth in order to define acids and bases. These theories include the Arrhenius theory, the Bronsted-Lowry theory, and the Lewis theory of acids and bases. A brief description of each of these theories is provided in this subsection. Acids and bases can be defined via three different theories.

• The *Arrhenius theory* of acids and bases states that "an acid generates H^+ ions in a solution whereas a base produces an OH^- ion in its solution".

• The *Bronsted-Lowry theory* defines "an acid as a proton donor and a base as a proton acceptor".

• Finally, the *Lewis definition* of acids and bases describes "acids as electron-pair acceptors and bases as electron-pair donors".

pH of Acids and Bases

In order to find the numeric value of the level of acidity or basicity of a substance, the pH scale (wherein pH stands for 'potential of hydrogen') can be used. The pH scale is the most common and trusted way to measure how acidic or basic a substance is. A *pH scale measure can vary from 0 to 14*, where 0 is the most acidic and 14 is the most basic a substance can be.

Another way to check if a substance is acidic or basic is to use litmus paper. There are two types of litmus paper available that can be used to identify acids and bases – red litmus paper and blue litmus paper. Blue litmus paper turns red under acidic conditions and red litmus paper turns blue under basic or alkaline conditions.

Acid
Blue litmus turns red

Base
Red litmus turns blue

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Universal pH paper

Basic solution
Solution change colour of pH paper according to its pH

Alkaline

Neutral

Acidic

Properties of Acids and Bases

1. Properties of Acids

•Acids are corrosive in nature.

•They are good conductors of electricity.

•Their pH values are always less than 7.

•When reacted with metals, these substances produce hydrogen gas.

•Acids are sour in taste.

•Examples: Sulfuric acid [H_2SO_4], Hydrochloric acid [HCl], Acetic acid [CH_3COOH].

2. Properties of Bases

•They are found to have a soapy texture when touched.

•These substances release hydroxide ions (OH^- ions) when dissolved in water.

•In their aqueous solutions, bases act as good conductors of electricity.

•The pH values corresponding to bases are always greater than 7.

•Bases are bitter-tasting substances which have the ability to turn red litmus paper blue.

•Examples: Sodium hydroxide [NaOH], calcium hydroxide [$Ca(OH)_2$].

Difference between Acids and Bases

Acids	Bases
Acid gives off hydrogen ions when dissolved in water.	Bases give off hydroxyl ion when dissolved in water.
It turns blue colour litmus paper into red.	It turns red colour litmus paper into blue.
It has a sour taste.	It has bitter taste and soapy to touch.
Its pH value ranges from 1 to 7.	Its pH value ranges from 7 to 14.
Example: HCl, H_2SO_4 etc.	Example: NaOH, KOH etc.

Lewis Concept of Acids and Bases

•The Lewis definition of an acid states that it is a species that has a vacant orbital and therefore, has the ability to accept an electron pair.

•A Lewis base is a species that holds a lone pair of electrons and can, therefore, act as an electron-pair donor.

•This theory does not involve the hydrogen atom in its definition of acids and bases.

•Lewis acids are electrophilic in nature whereas Lewis Bases possess nucleophilic qualities.

•Examples of Lewis acids: Cu^{2+}, BF_3, and Fe^{3+}. Examples of Lewis bases: F^-, NH_3, and C_2H_4 (ethylene).

•A Lewis acid accepts an electron pair from a Lewis base, forming a coordinate covalent bond in the process. The resulting compound is referred to as a Lewis adduct.

•A notable advantage of this concept is that many compounds can be defined as acids or bases by it. However, it offers little insight into the strength of these acids and bases.

•One of the disadvantages of this theory is that it fails to explain the acid-base reactions that do not involve the formation of a coordinate covalent bond.

Electron Configurations

Electron configurations describe where electrons are located around the nucleus of an atom. For example, the electron configuration of lithium, $1s^2 2s^1$, tells us that lithium has two electrons in the 1s subshell and one electron in the 2s subshell.

Type of orbital

$1s^1$

Number of electron in the orbital

Energy level
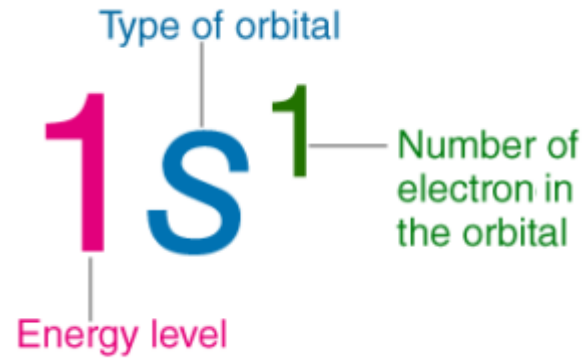
Electron Configurations are useful for:

•Determining the valency of an element.

•Predicting the properties of a group of elements (elements with similar electron configurations tend to exhibit similar properties).

•Interpreting atomic spectra.

Writing Electron Configurations

Shells

The maximum number of electrons that can be accommodated in a shell is based on the *principal quantum number* (n). It is represented by the formula $2n^2$, where 'n' is the shell number.

The shells, values of n, and the total number of electrons that can be accommodated are tabulated below.

Shell and 'n' value	Maximum electrons present in the shell
K shell, n=1	$2*1^2 = 2$
L shell, n=2	$2*2^2 = 8$
M shell, n=3	$2*3^2 = 18$
N shell, n=4	$2*4^2 = 32$
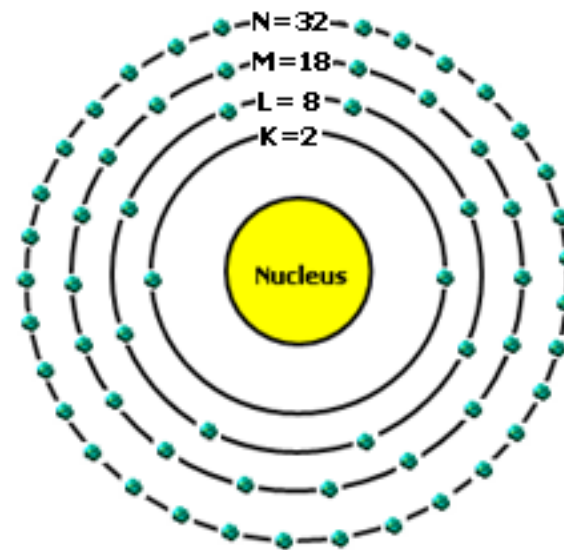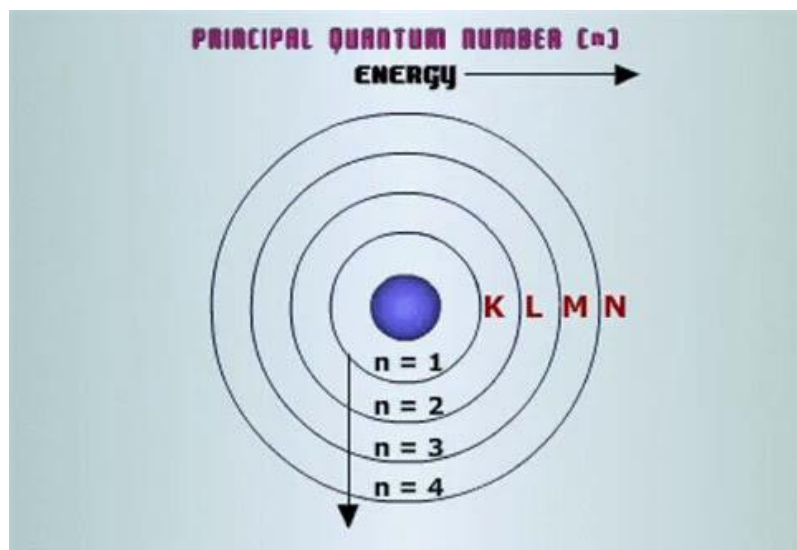
Subshells

- The subshells into which electrons are distributed are based on the [azimuthal quantum number](#) (denoted by 'l').

- This quantum number is dependent on the value of the principal quantum number, n. Therefore, when n has a value of 4, four different subshells are possible.

- When n=4. The subshells correspond to l=0, l=1, l=2, and l=3 and are named the s, p, d, and f subshells, respectively.

- The maximum number of electrons that can be accommodated by a subshell is given by the formula $2*(2l + 1)$.

- Therefore, the s, p, d, and f subshells can accommodate a maximum of 2, 6, 10, and 14 electrons, respectively.

All the possible subshells for values of n up to 4 are tabulated below.

Principle Quantum Number Value	Value of Azimuthal Quantum Number	Resulting Subshell in the Electron Configuration
n=1	l=0	1s
n=2	l=0	2s
	l=1	2p
n=3	l=0	3s
	l=1	3p
	l=2	3d
n=4	l=0	4s
	l=1	4p
	l=2	4d
	l=3	4f

Filling of Atomic Orbitals

Aufbau Principle

• This principle is named after the German word 'Aufbeen' which means 'build up'.

• The Aufbau principle dictates that electrons will occupy the orbitals having lower energies before occupying higher energy orbitals.

• The energy of an orbital is calculated by the sum of the principal and the azimuthal quantum numbers.

• According to this principle, electrons are filled in the following order: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p…

l = 0	l = 1	l = 2	l = 3

n = 1   (1s)

n = 2   (2s)   (2p)

n = 3   (3s)   (3p)   (3d)

n = 4   (4s)   (4p)   (4d)   (4f)

n = 5   (5s)   (5p)   (5d)   (5f)

n = 6   (6s)   (6p)   (6d)

n = 7   (7s)   (7p)

n = 8   (8s)
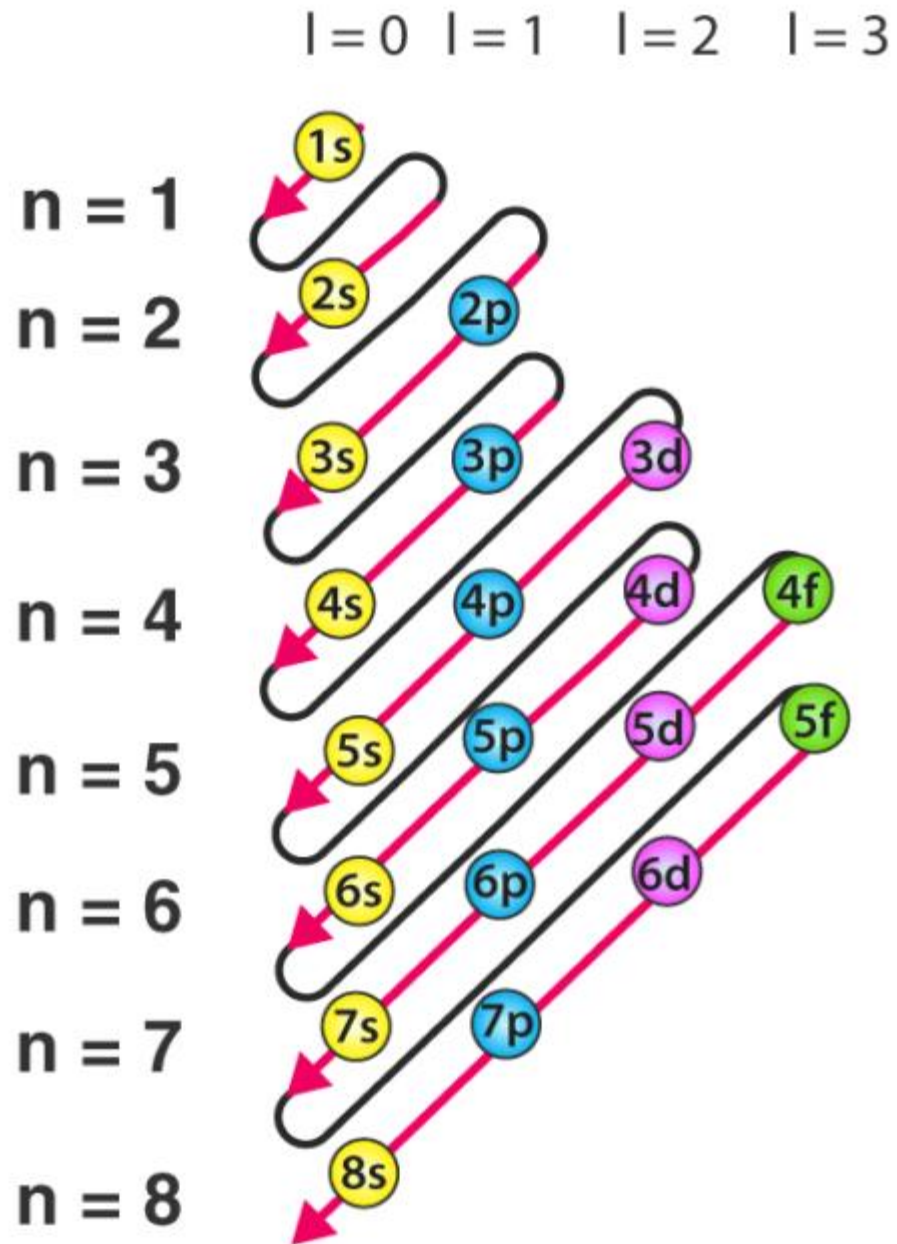
Electron Configuration of Hydrogen

The atomic number of hydrogen is 1. Therefore, a hydrogen atom contains 1 electron, which will be placed in the s subshell of the first shell/orbit. The electron configuration of hydrogen is **$1s^1$**, as illustrated below.
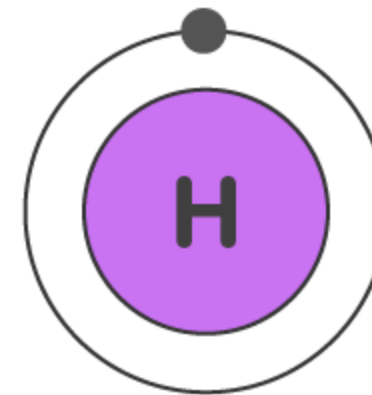
Electron Configuration of Oxygen

The atomic number of oxygen is 8, implying that an oxygen atom holds 8 electrons. Its electrons are filled in the following order:

K shell – 2 electrons

L shell – 6 electrons

Therefore, the electron configuration of oxygen is $1s^2\ 2s^2\ 2p^4$, as shown in the illustration provided below.
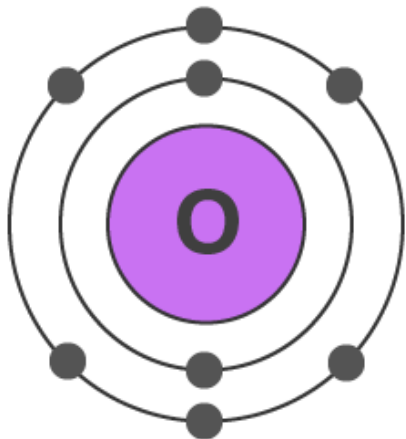
Chlorine Electronic Configuration

Chlorine has an atomic number of 17. Therefore, its 17 electrons are distributed in the following manner:

K shell – 2 electrons

L shell – 8 electrons

M shell – 7 electrons

The electron configuration of chlorine is illustrated below. It can be written as $1s^2 2s^2 2p^6 3s^2 3p^5$ or as $[Ne]3s^2 3p^5$
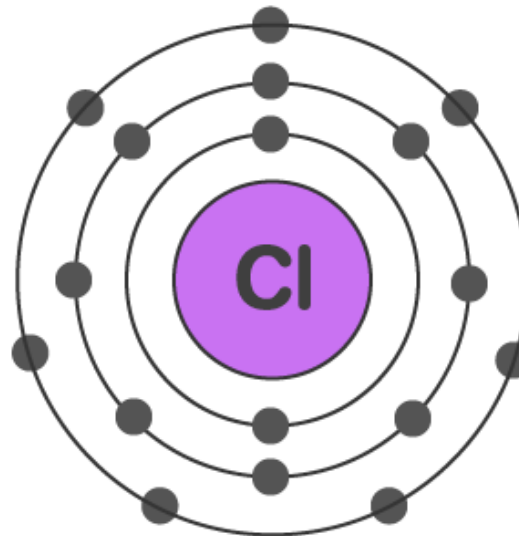
Atomic Radius

Atomic radius is defined as the size of an atom, and it is determined by *measuring the distance between the centre of the nucleus and the outermost electron in an atom*.

Atomic radius *decreases as we move from left to right across a period in the periodic table and increases as we move from top to bottom down a group*.

Factors Affecting Atomic Radii

1.Number of Shells

2.Effective Nuclear Charge (ZEff)

3.Screening Effect

Number of Shells: As the number of shells increases, so do the atomic radii.

Atomic Radius $\propto$ Number of shells

Example:

Cs > Rb > K > Na > Li

Effective Nuclear Charge: As the effective nuclear charge in an atom increases, the atomic radius decreases.

$$\text{Atomic Radius} \propto \frac{1}{\text{Effective nuclear charge}}$$

Screening Effect: More the screening effect of the electrons in the completely filled orbitals on the outer electrons, the more will be the atomic radius.

$$\text{Atomic Radius} \propto \text{Screening effect}$$

Example: Cs > Rb > K > Na > Li

Ionic Radius

Ions are formed either by gaining or losing electrons of an atom. Ionic radius is the distance between the centre of the nucleus and the outermost electron in an ion.

Ionic radius decreases as we move from left to right across a period in the periodic table and increases as we move from top to bottom down a group. Generally, anions have a higher ionic radius than cations.

Cation

- **Smaller** than its parent atom
- **Less** electrons than its parent atom
- $\dfrac{\text{electron}}{\text{proton}} \left(\dfrac{e}{p} \right) < 1$
- **More Z_{eff}**

Anion

Larger than its parent atom

More electrons than its parent atom

$$\frac{electron}{proton}\left(\frac{e}{p}\right) > 1$$

Less Z_{eff}
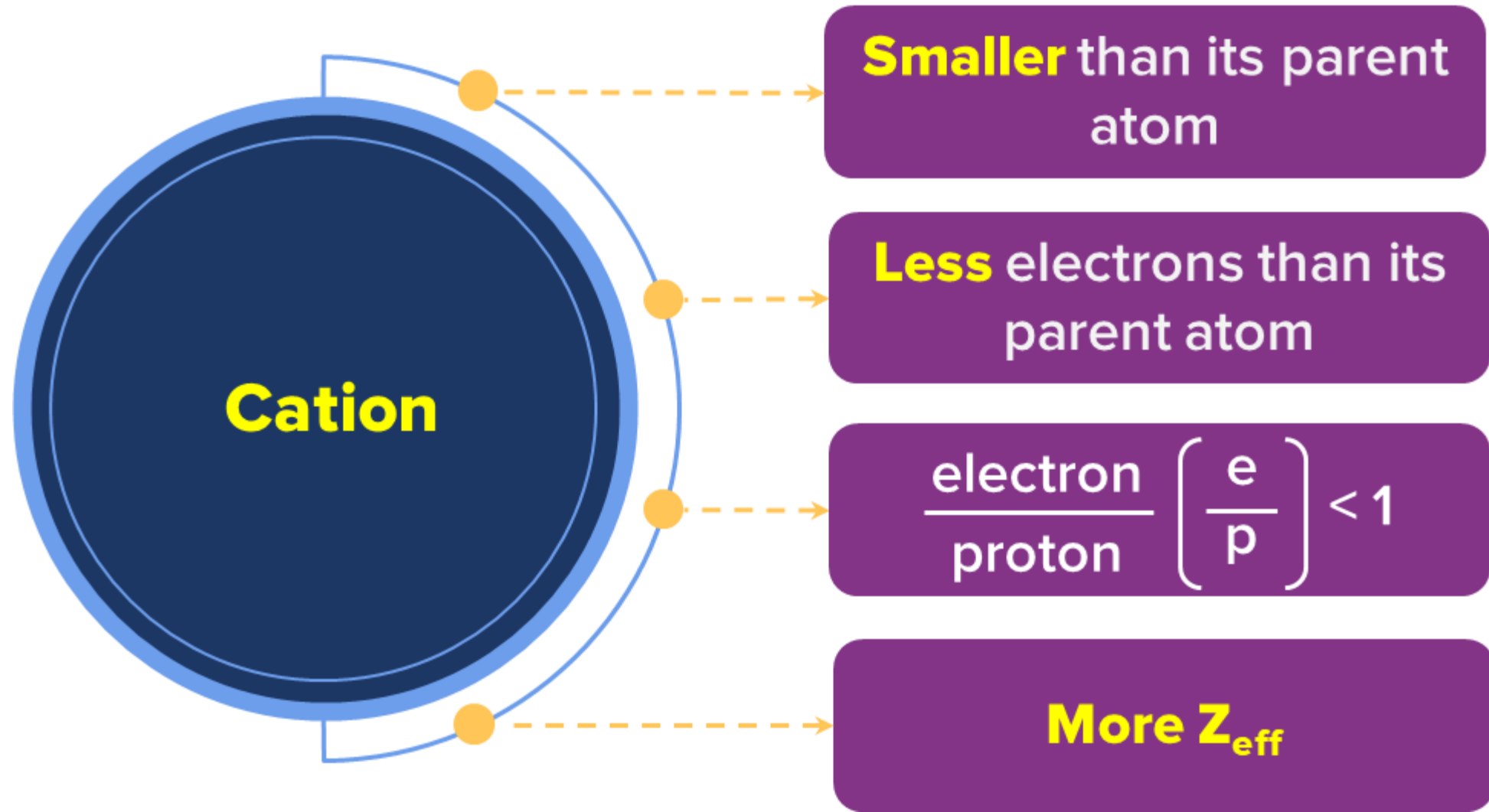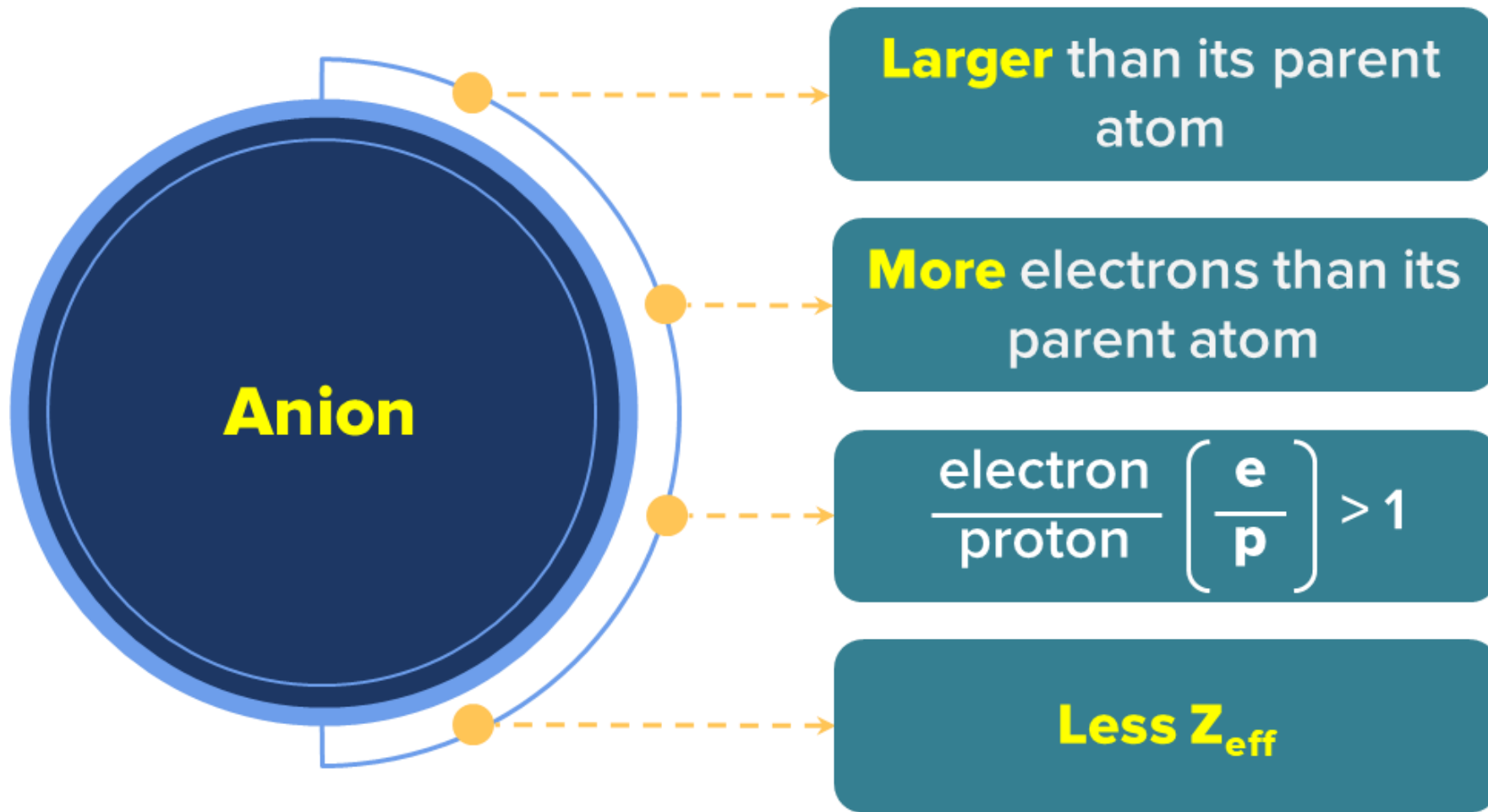
For the same element.

Size of anion > Size of atom > Size of cation

Ionisation Energy

Ionisation energy is the minimum energy required to remove an electron from an isolated gaseous atom in its ground state.

$$M\ (g) \longrightarrow M^+\ (g) + e^-$$

Unit - kJ/mol, kcal/mol, eV

The smaller the ionization energy, easier it is for a neutral atom to change itself into a positive ion.

Factors Affecting Ionisation Energy

1. Size of the Atom

2. Effective Nuclear Charge (ZEff)

3. Screening Effect

4. Electronic Configuration

Size of the Atom: As the size of the atom increases, ionisation energy decreases. This is because as size increases, the distance between the outermost electron and the nucleus increases. Therefore less energy is required to remove the electron from the atom.

$$\text{Ionisation Energy} \propto \frac{1}{\text{Size of the Atom}}$$

Effective Nuclear Charge (ZEff): As the effective nuclear charge increases, the force of attraction between the nucleus and the outermost electron increases. Therefore, more energy is required to remove an electron from the atom.

$$\text{Ionisation Energy} \propto \text{Effective nuclear charge } (Z_{eff})$$

Screening Effect: More the screening effect in an atom, the less the ionisation energy. This is because, as the inner electrons screen the outermost electrons from the nucleus, the force of attraction between the nucleus and the outermost electrons decreases. Therefore, less energy is required to remove an electron from the atom.

$$\text{Ionisation Energy} \propto \frac{1}{\text{Screening Effect}}$$

Electronic Configuration: According to Hund's rule, the stability of half-filled and fully-filled degenerate orbitals is extremely high. Therefore, the removal of electrons from a half-filled or fully-filled orbital required more energy.

The order of IE for fully-filled, half-filled and partially filled orbitals is as follows.

$$\text{Fully filled} > \text{Half filled} > \text{Partially filled}$$

First Ionisation Energy: It is the energy required to remove the outermost electron from a gaseous neutral atom in the ground state.

$$M (g) \longrightarrow M^+ (g) + e^-, IE_1$$

Second Ionisation Energy: The energy required to remove an electron from a mono-positive isolated gaseous ion.

$$M^+ (g) \quad M^{2+} (g) + e^-, IE_2$$

Third ionisation Energy: The energy required to remove the third most loosely bound electron.

$$M^{2+} (g) \longrightarrow M^{3+} (g) + e^-, IE_3$$

For an isolated atom/ion, the removal of an electron from a cation is more difficult than the removal of an electron from a neutral atom.

Therefore,

$$I.E._1 < I.E._2 < I.E._3 ...$$

Periodic property	Across the period	Down the group
Ionization energy	Increases	Decreases

Electronegativity

Electronegativity is the property of an atom in a molecule to attract the shared pair of electrons towards itself. The electronegativity of any atom is not constant, rather it is relative to the element to which it is bonded. Electronegativity helps in predicting the type of bond formed between two atoms.

Numerical scales of EN

Pauling scale

Mulliken-Jaffe scale

Allred-Rochow scale
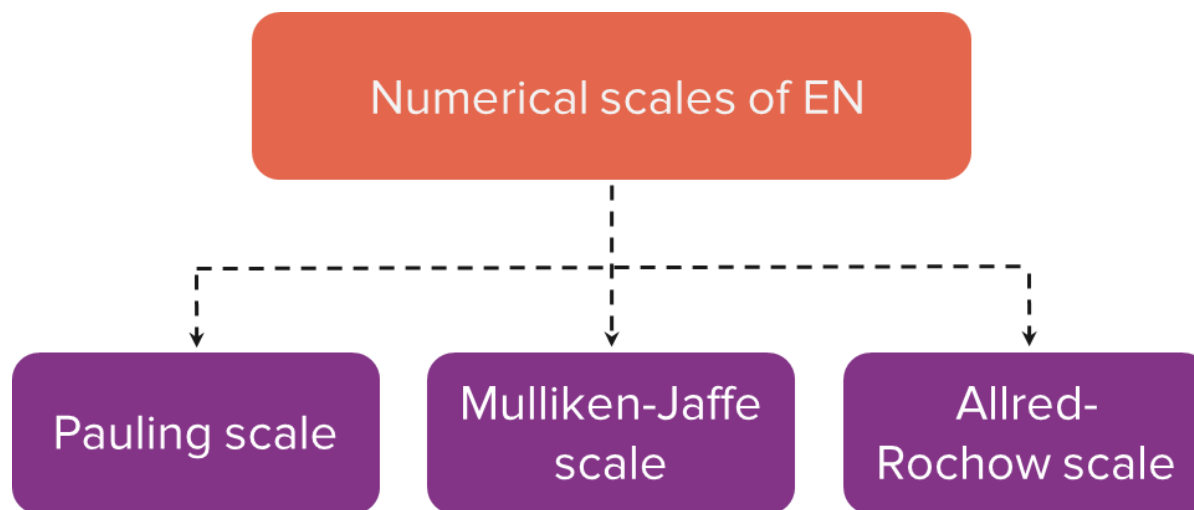
The Pauling scale is the most commonly used scale of electronegativity.

Factors Affecting Electronegativity

1.Atomic Size

2.Effective Nuclear Charge (ZEff)

3.Magnitude of Positive Charge on the Atom

Atomic Size: As the size of the atom increases, the force of attraction between the nucleus and the outermost electron decreases. Therefore, the electronegativity of the atom decreases.

$$\text{Electronegativity} \propto \frac{1}{\text{Atomic Size}}$$

Effective Nuclear Charge (ZEff): As the effective nuclear charge increases, the force of attraction between the nucleus and the outermost electron increases. Therefore, the electronegativity of the atom increases.

$$\text{Electronegativity} \propto \text{Effective Nuclear Charge}$$

Magnitude of Positive Charge on the Atom: As the magnitude of the positive charge on the atom increases, the force of attraction between the nucleus and the outermost electron increases. Therefore, the electronegativity of the atom increases.

Electronegativity $\propto$ **Magnitude of Positive Charge on the Atom**

Electronegativity increases as we move from left to right across a period. This is because, on moving from left to right across a period, more electrons are added to the same shell, which increases the force of attraction between the nucleus and the outermost electrons.

Electronegativity decreases as we move down a group. This is because, as we move down a group, subsequent shells are added and therefore, the distance between the nucleus and the outermost electrons increases. Therefore, the force of attraction between the nucleus and the outermost electrons decreases and subsequently electronegativity decreases.

Electron Affinity

Electron affinity is the energy released when an electron is added to the valence shell of an isolated neutral gaseous atom.

$$X \text{ (g)} + e^- \longrightarrow X^- \text{ (g)}$$
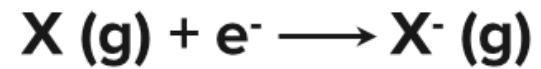
eV/atom, kJ/mol

- ***Electron affinity increases going left to right across a period*** because of increased nuclear attraction.

- ***Going down the group the electron affinity should decrease*** since the electron is being added increasingly further away from the nucleus. Electron becomes less tightly bound and can be easily removed

Factors Affecting Electron Affinity
The general factors that affect electron affinity are listed below.

- $Electron\ affinity = \dfrac{1}{Atomic\ Size}$
- $Electron\ affinity = Effective\ Nuclear\ Charge$
- $Electron\ affinity = \dfrac{1}{Screening\ Effect}$

Atomic size: If the atomic size is small, then there will be greater electron gain enthalpy because the effective nuclear forces will be greater in the smaller atoms and the electrons will be held firmly.

Nuclear charge: The greater the nuclear charge, more will be the value of electron gain enthalpy because increase in nuclear change increase nuclear force on valence electrons.

Coordination Number
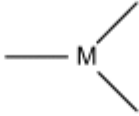
Coordination number, also known as ligancy, is the number of atoms, ions, or molecules that a central atom

or ion carries in a complex or coordination compound or in a crystal as its closest neighbours.
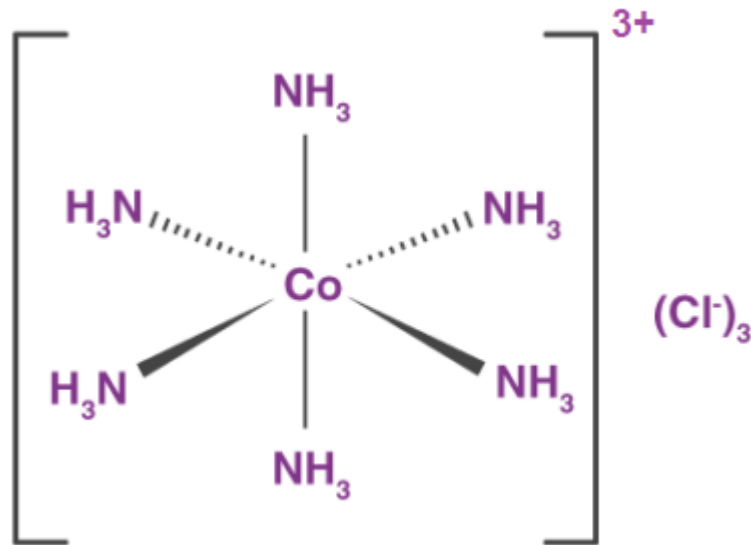
Geometry of Molecules Based on Coordination Number

There exist multiple possible geometric combinations for each value of the coordination number for the central atom. These possible geometric shapes are tabulated below.

Coordination Number	Geometric Structure
2	Linear
3	Trigonal planar, T-shaped, or trigonal pyramidal
4	Square planar or tetrahedral
5	Trigonal bipyramidal or square pyramid structures
6	Trigonal prism structure, hexagonal planar, or octahedral
7	Pentagonal bipyramidal, capped octahedron, or a capped trigonal prism structure.
8	Cubic, hexagonal bipyramidal, square antiprism, or dodecahedron
9	Three-face centered trigonal prism
10	A bicapped square antiprism structure
11	All faced capped trigonal prism structure
12	Cuboctahedron structure

Coordination number	Name	Geometry	Polyhedron	Example
2	Linear	—M—		$AuCl(PPh_3)$
3	Trigonal planar			$Pt(PPh_3)_3$
4	Square planar			$RhCl(PPh_3)_3$
4	Tetrahedral			$Ni(CO)_4$
5	Trigonal bipyramidal			$Fe(CO)_5$
5	Square pyramidal			$[VOCl_4]^{2-}$
6	Octahedral			$Mo(CO)_6$
6	Trigonal prismatic			$W(CH_3)_6$

p_x

p_z

d_{yz}

d_{xy}

d_{z^2}

d_{xz}

$d_{x^2-y^2}$
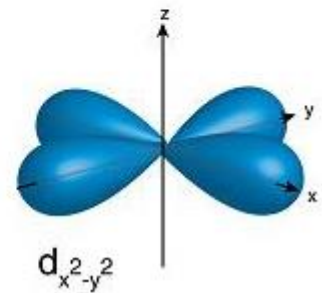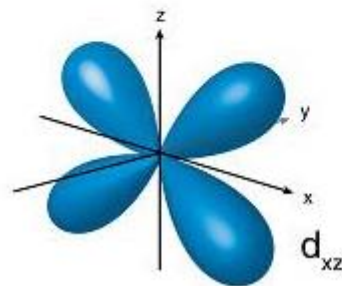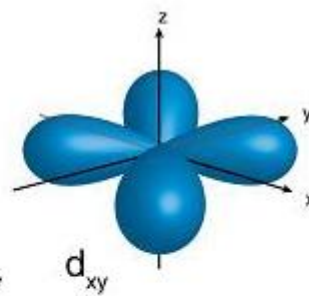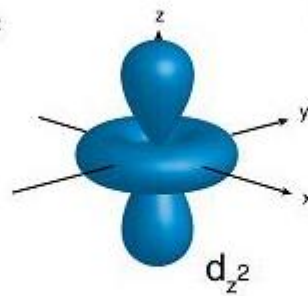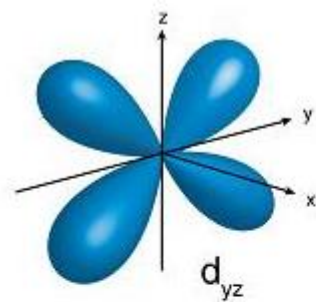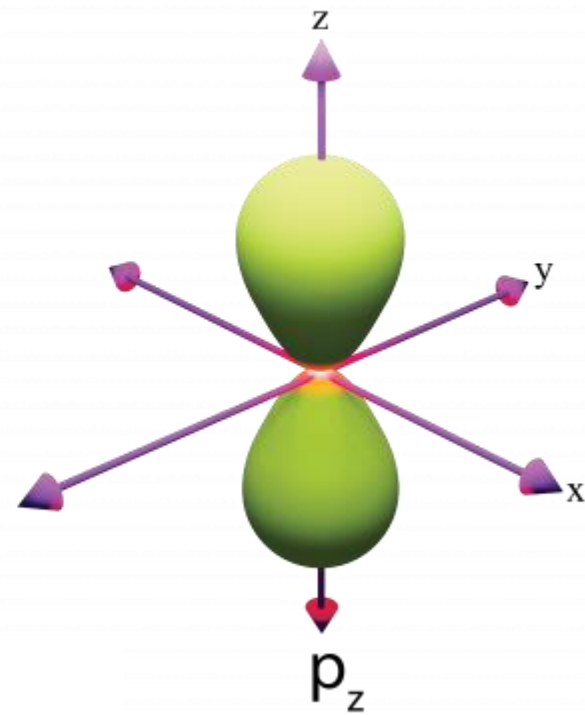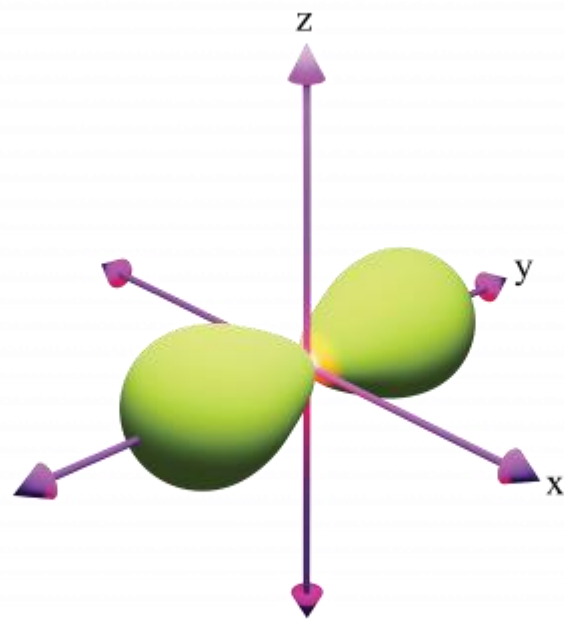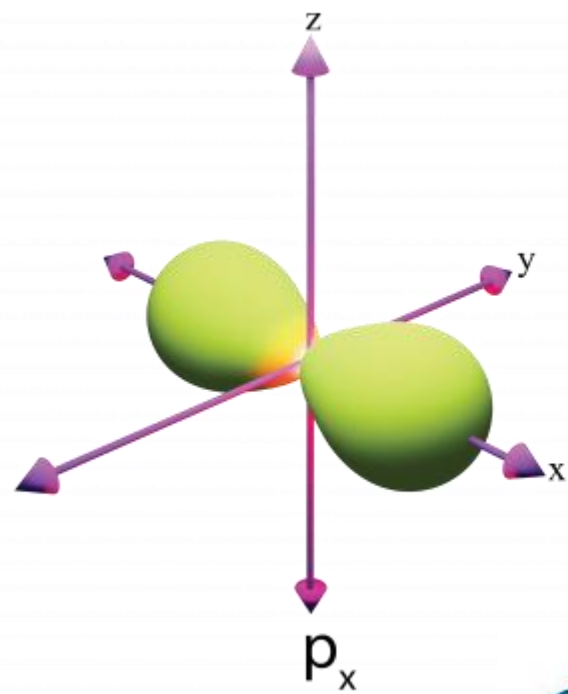
Crystal field theory (CFT)

Crystal field theory (CFT) describes the breaking of orbital degeneracy in transition metal complexes due to the presence of ligands. CFT qualitatively describes the strength of the metal-ligand bonds. Based on the strength of the metal-ligand bonds, the energy of the system is altered. This may lead to a change in magnetic properties as well as color.

Crystal field theory describes the net change in crystal energy resulting from the orientation of d orbitals of a transition metal cation inside a coordinating group of anions also called ligands.

A major feature of transition metals is their tendency to form complexes. A complex may be considered as consisting of a central metal atom or ion surrounded by a number of ligands. The interaction between these ligands with the central metal atom or ion is subject to crystal field theory.

In order to understand clearly the crystal field interactions in transition metal complexes, it is necessary to have knowledge of the geometrical or spatial disposition of d orbitals. The d-orbitals are fivefold degenerate in a free gaseous metal ion. If a spherically symmetric field of negative ligand filed charge is imposed on a central metal ion, the d-orbitals will remain degenerate but followed by some changes in the energy of the free ion.
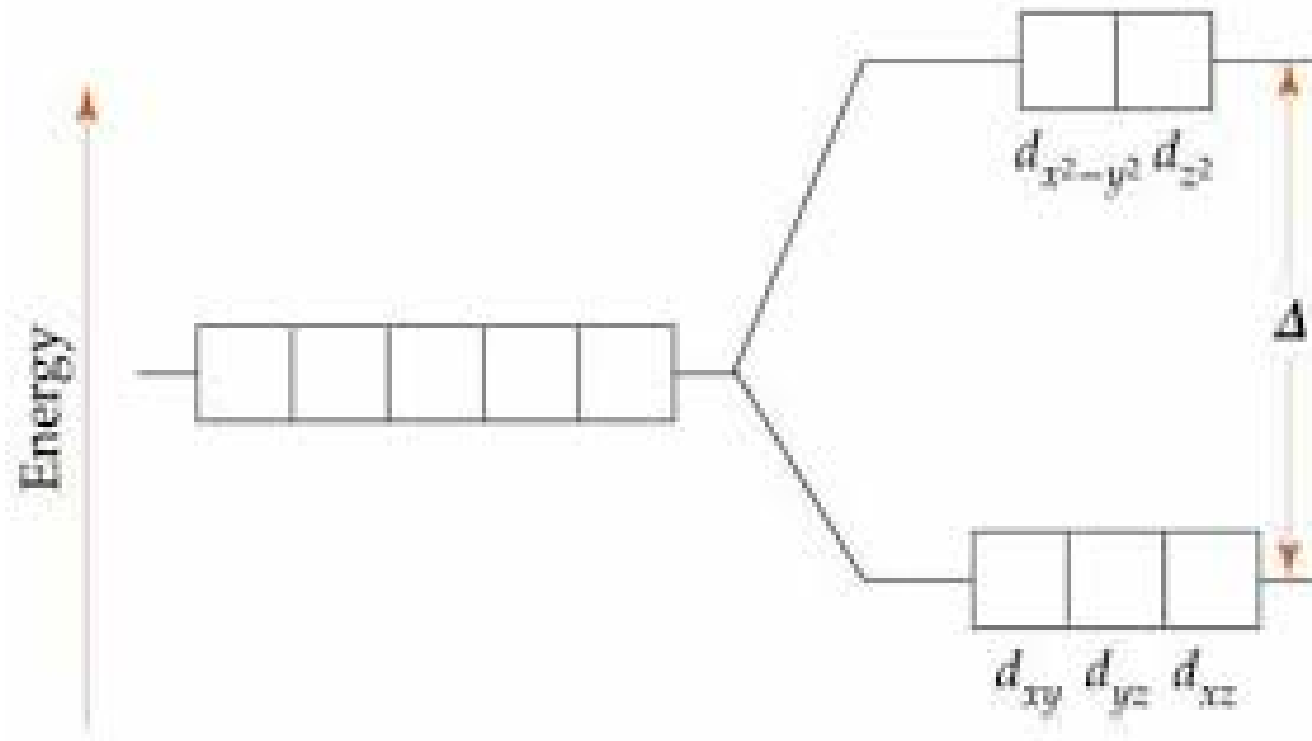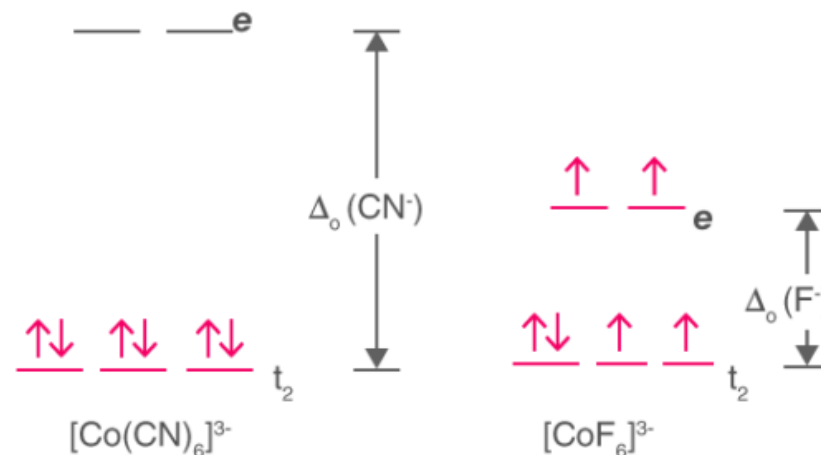
High Spin and Low Spin

The complexion with the greater number of unpaired electrons is known as the high spin complex, the low spin complex contains the lesser number of unpaired electrons. High spin complexes are expected with weak field ligands whereas the crystal field splitting energy is small Δ. The opposite applies to the low spin complexes in which strong field ligands cause maximum pairing of electrons in the set of three t_2 atomic orbitals due to large Δ_o.

High spin – Maximum number of unpaired electrons.

Low spin – Minimum number of unpaired electrons.

Example: $[Co(CN)_6]^{3-}$ & $[CoF_6]^{3-}$

•$[Co(CN)_6]^{3-}$ – Low spin complex
•$[CoF_6]^{3-}$ – High spin complex

$\Delta_o (CN^-)$

$[Co(CN)_6]^{3-}$

$\Delta_o (F^-)$

$[CoF_6]^{3-}$

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Calculate the Number of unpaired electrons in $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$; show the number electrons occupancy in the t_{2g} and e_g orbital

- For example, the hexaaquairon(II) ion, $[Fe(OH_2)_6]^{2+}$, has four unpaired electrons, whereas the hexacyanoferrate(II) ion, $[Fe(CN)_6]^{4-}$, has no unpaired electrons.
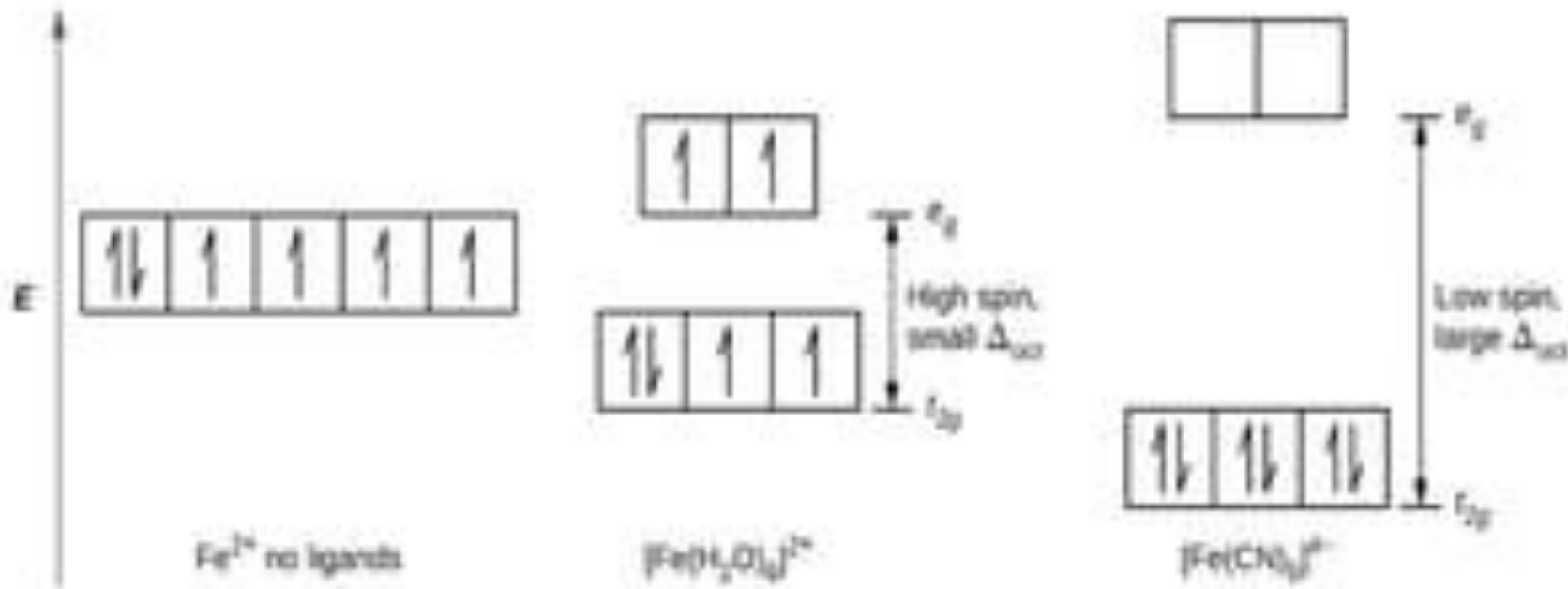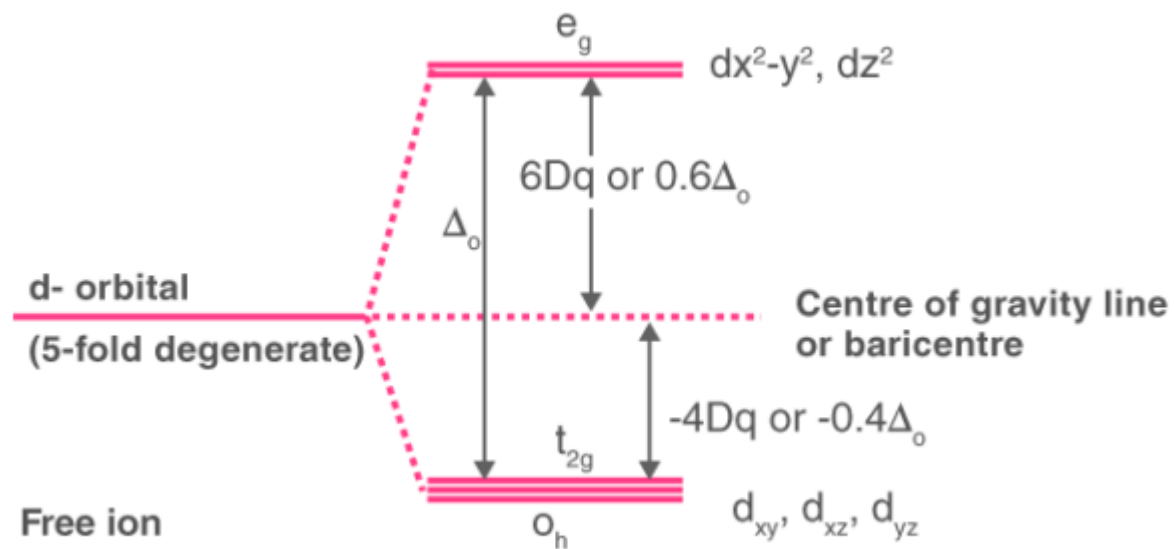
Crystal Field Splitting in Octahedral Complex

•In the case of an octahedral coordination compound having six ligands surrounding the metal atom/ion, we observe repulsion between the electrons in d orbitals and ligand electrons.

•This repulsion is experienced more in the case of $d_{x^2-y^2}$ and d_{z^2} orbitals as they point towards the axes along the direction of the ligand.

•Hence, they have higher energy than average energy in the spherical crystal field.

•On the other hand, d_{xy}, d_{yz}, and d_{xz} orbitals experience lower repulsions as they are directed between the axes.

•Hence, these three orbitals have less energy than the average energy in the spherical crystal field.

Thus, the repulsions in octahedral coordination compound yield two energy levels:

•*t_{2g}– set of three orbitals (d_{xy}, d_{yz} and d_{xz}) with lower energy*

•*e_g – set of two orbitals ($d_{x^2-y^2}$ and d_{z^2}) with higher energy*

This splitting of degenerate level in the presence of ligand is known as *crystal field splitting*. The difference between the energy of t_{2g} *and* e_g *level is denoted by* "Δ_o" (subscript o stands for octahedral). Some ligands tend to produce strong fields thereby causing large crystal field splitting whereas some ligands tend to produce weak fields thereby causing small crystal field splitting.

Crystal Field Splitting in Tetrahedral Complex

The splitting of fivefold degenerate d orbitals of the metal ion into two levels in a tetrahedral crystal field is the representation of two sets of orbitals as T_d. The electrons in $d_{x^2-y^2}$ and d_{z^2} orbitals are less repelled by the ligands than the electrons present in d_{xy}, d_{yz}, and d_{xz} orbitals. As a result, the energy of d_{xy}, d_{yz}, and d_{xz} orbital sets are raised while that of the $d_{x^2-y^2}$ and d_{z^2} orbitals are lowered.

•There are only four ligands in T_d complexes and therefore the total negative charge of four ligands and hence the ligand field is less than that of six ligands.

•The direction of the orbitals does not coincide with the directions of the ligands approach to the metal ion.
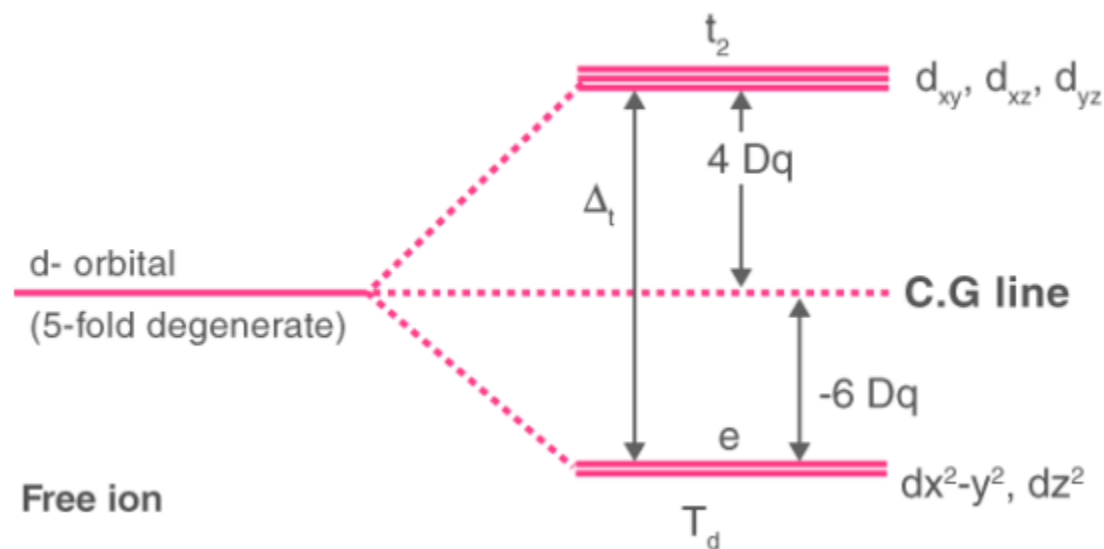
Thus, the repulsions in tetrahedral coordination compound yield two energy levels:

•*t_2– set of three orbitals (d_{xy}, d_{yz} and d_{xz}) with higher energy*

•*e – set of two orbitals ($d_{x^2-y^2}$ and d_{z^2}) with lower energy*

The crystal field splitting in a tetrahedral complex is intrinsically smaller in an octahedral filed because there are only two thirds as many ligands and they have a less direct effect of the d orbitals. The relative stabilizing effect of e set will be -6Dq and the destabilizing effect of t_2 set will be +4Dq

Compounds that have the same chemical formula but different structural arrangements are called isomers. Due to their complicated formulae of many coordination compounds, the variety of bond types and the number of shapes possible, many different types of isomerism occur.

IonizationIsomerism:

This type of isomerism is due to the exchange of groups between the complex ion and the ions outside it. $[Co(NH_3)_5Br]SO_4$ is red – violet. An aqueous solution gives a white precipitate of $BaSO_4$ with $BaCl_2$ solution, thus confirming the presence of free SO_4^{2-} ions. In contrast $[Co(NH_3)_5SO_4]Br$ is red. A solution of this complex does not give a positive sulphate test with $BaCl_2$. It does give a cream – coloured precipitate of AgBr with $AgNO_3$, the confirming the presence of free Br– ions.

HydrateIsomerism:

Three isomers of CrCl3.6H2O are known. From conductivity measurements and quantitative precipitation of the ionized chlorine, they have been given the following formuale:

•[Cr(H2O)6]Cl3 : violet (three ionic chlorines)

•[Cr(H2O)5Cl]Cl2.H2O : green (two ionic chlorines)

•[Cr(H2O)4Cl2].Cl.2H2O : dark green (one ionic chlorine)

Linkage Isomerism:

Certain ligands contain more than one atom which could donate an electron pair. In the NO2- ion, either N or O atoms could act as the electron pair donor. Thus there is the possibility of isomerism. Two different complexes [Co(NH3)5NO2]Cl2have been prepared, each containing the NO2- group in the complex ion.

Geometrical Isomer:

•Isomers refer to the compounds that contain the same empirical formula but differ in the structural arrangement of atoms.

•A geometric isomer describes the orientation of a functional group in a compound.

•Generally in a geometric isomer, the atoms are bonded by a double bond that does not rotate but it can also happen because of the ring structure.

•Based on the position of the functional group the isomers are named cis and trans.

•When a similar group is placed at an adjacent position the compound is named with the prefix *cis*

•When a similar group is placed at the opposite position the compound is named with the prefix *trans*
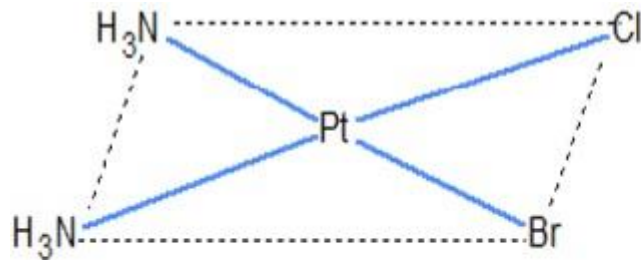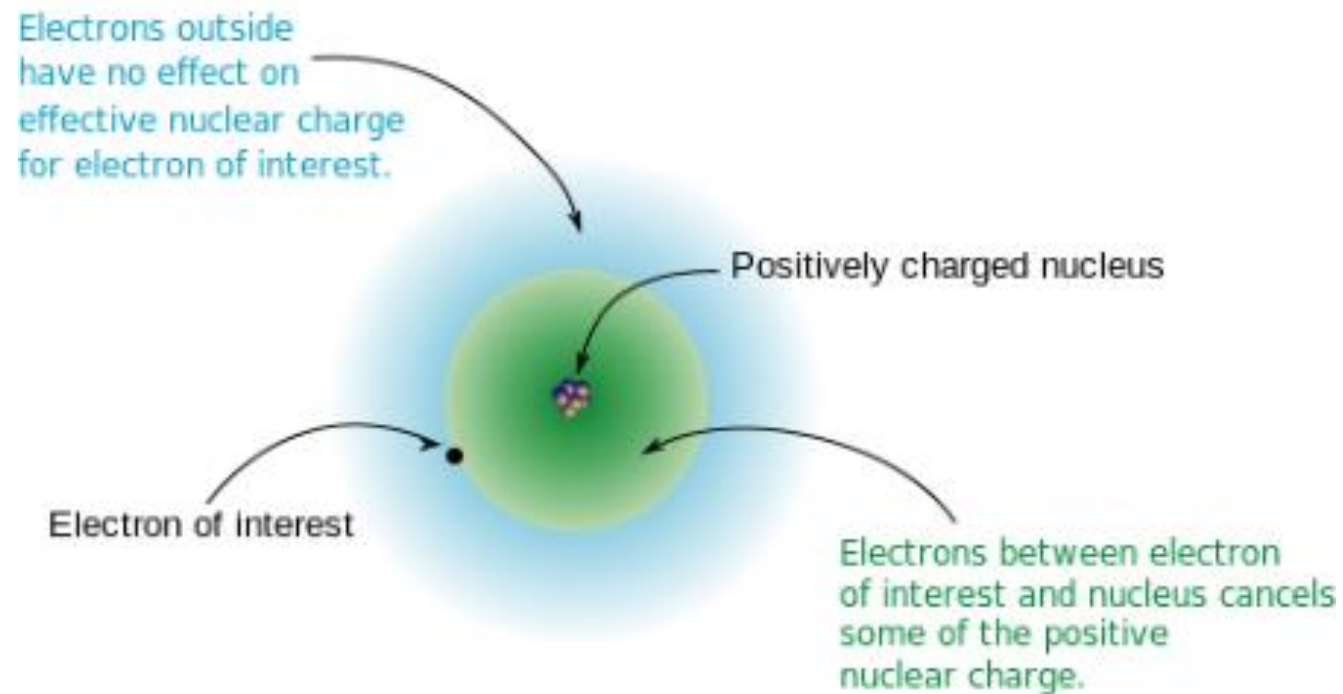
Cis - isomer
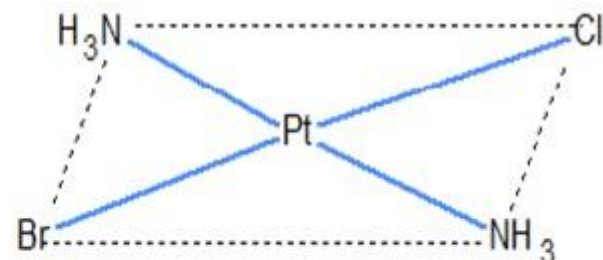
trans - isomer

Effective nuclear charge

What is the effective nuclear charge?

The effective nuclear charge (Z effective or Zeff) is defined as the net positive charge pulling the electrons towards the nucleus. The stronger the pull on the outermost electrons (valence electrons) towards the nucleus, the higher the effective nuclear charge.

Electrons outside have no effect on effective nuclear charge for electron of interest.

Positively charged nucleus

Electron of interest

Electrons between electron of interest and nucleus cancels some of the positive nuclear charge.

The effective nuclear charge may be approximated by the equation:

$$Z_{eff} = Z - S$$

Where Z is the atomic number and S is the number of shielding electrons.

Trends
The periodic table tendency for effective nuclear charge:

Increase across a period (due to increasing nuclear charge with no accompanying increase in shielding effect).
Decrease down a group (although nuclear charge increases down a group, shielding effect more than counters its effect).

Electron in a orbital	Per electron in orbital		
	n	n-1	n-2, n-3…….
S (OR) P orbital	0.35	0.85	1
d (or) f orbital	0.35	1	1

n order: (1s) (2s 2p) (3s 3P) (3d) (4s 4p) (4d) (4f)