MODULE ONE

PREDICTING THE SHAPE OF MOLECULES

In order to know the symmetry of a molecule one must have an idea of the shape it has. To be able to predict the shape of molecule follow the steps below:

1. **Write the Lewis structure of the molecules considering the electron pair around the central atom of the molecule.**
2. **Count the number of electron pairs around the central atom (bonding pairs and lone pairs). Treat double bonds and triple bonds as though they are single bonds.**
3. **Note the number of bond pairs and lone pairs.**
4. **Then from 3 above and using the summary of shapes below determine the shape.**

Writing Lewis Structure

1. Write the skeletal structure of the compound, using chemical symbols and placing bonding atoms next to one another.

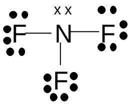
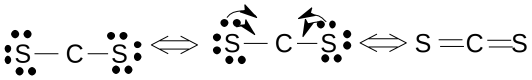
2. Count the total number of valence electrons present

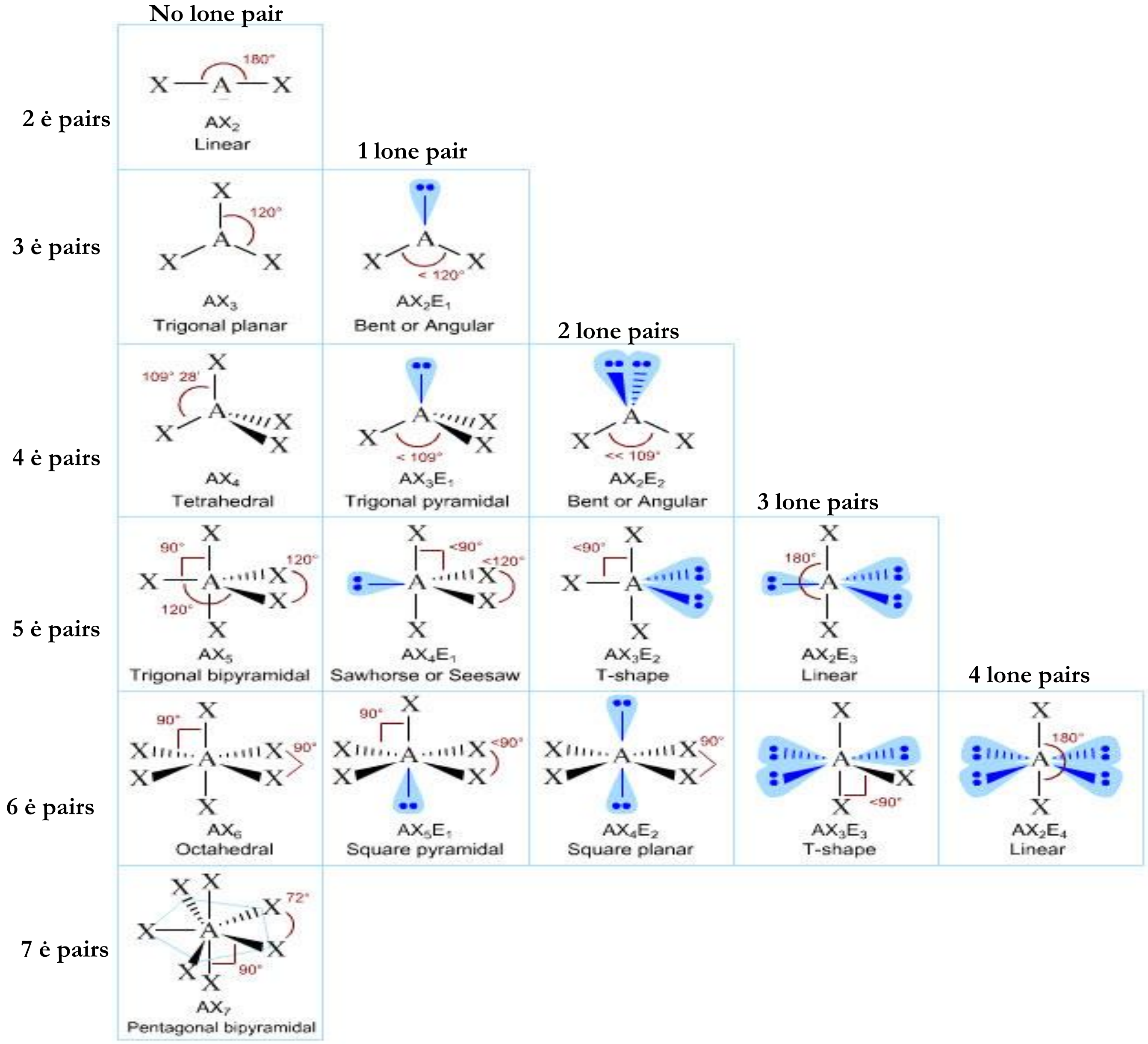
a) For polyatomic anions e.g. CO_3^{2-} add the additional number electrons responsible for the charges.
b) For polyatomic cations e.g. NH_4^+ remove the number of electrons responsible positively charge.

3. Draw a single covalent bond between the central atom and each of the surrounding atoms, show complete octet of the surrounding atoms, and add extra electrons to central atom as lone pair.

4. If after steps 1-3 the central atom has less than *8é,* then add double bonds or triple bonds between the central atom and the surrounding atoms using lone pairs from the surrounding atoms to complete the octet of the central atom.

ii

	Step 1	Step 2	Step 3	Step 4
NF_3	F N F F	N = 5e 3F = 3 X 7e= 21e Total = 26e		
CS_2	S C S	C = 4e 2S = 2 X 6e= 12e Total = 16e		



iii

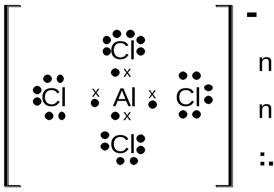
$AlCl_4^-$

Al = 3e

4Cl 4 x 7 = 28e

charge = 1e

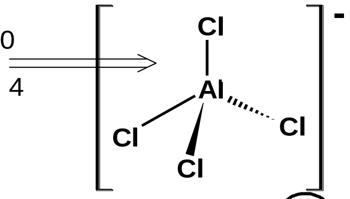
Total = 32e



no of lone pair around Al = 0

no of bond pair around Al = 4

:. shape = tetrahedral

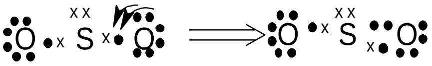


SO_2

S = 6e

2O = 2 x 6 = 12e

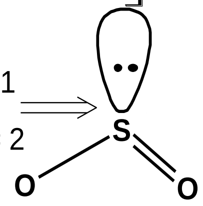
Total = 18



no of lone pair around S = 1

no of bond pair around S = 2

:. Shape = Bent

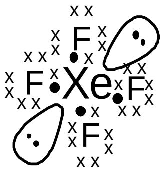


XeF_4

Xe = 8e

4F = 4 x7e = 28e

Total = 36e

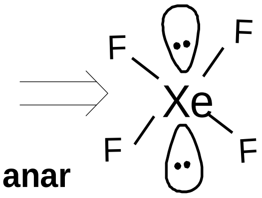


6 e pairs

2 lone pairs

4 bond pairs

:. shape = square planar



MODULE ONE

Predicting the shape of Molecules

- It is very important to be able to predict the shape of a molecule.

- This is because it enables us understand how the molecule interacts and/or reacts with other molecules.

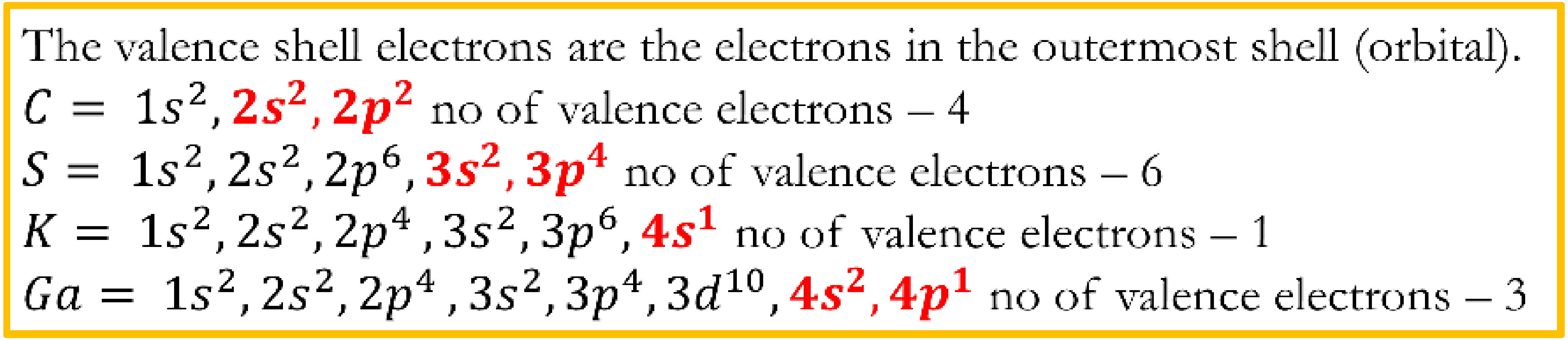
- The physical properties of some materials are influences by the shape of its molecules. For example, if the shape of water was linear, it would not be polar and probably not have its strong hydrogen bonding responsible for it being a liquid with a boiling point of 100˚.

Molecules are have a central atom bonded by one or more other atoms.

The fact that molecules are bonded to the same number of atoms does not mean that they would have the same shape. For example, CH_4, XeF_4 both seem similar yet **CH_4 is tetrahedral in shape** while **XeF_4 is square planar.**

The shape of a molecule is **largely dependent on the number and nature of the valence electrons of the central atom.**

This is based on **Valence Shell Electron Repulsion (VSEPR)** theory.



The valence shell electrons are the electrons in the outermost shell (orbital).

$C = 1s^2, \mathbf{2s^2, 2p^2}$ no of valence electrons – 4

$S = 1s^2, 2s^2, 2p^6, \mathbf{3s^2, 3p^4}$ no of valence electrons – 6

$K = 1s^2, 2s^2, 2p^4, 3s^2, 3p^6, \mathbf{4s^1}$ no of valence electrons – 1

$Ga = 1s^2, 2s^2, 2p^4, 3s^2, 3p^4, 3d^{10}, \mathbf{4s^2, 4p^1}$ no of valence electrons – 3

Valence electrons are the electrons that are used in forming bonds with other atoms.

When atoms are involved in bonding, all their valence electrons are contributing to shape.

These valence electrons are always repelling each other. It is this force of repulsion that is responsible for the shape that is adopted.

Sometimes not all the valence electrons are involved in bonding. These are referred to as **lone pairs (lp).**

Those participating in bonding are called **bond pairs (bp).**

- The order of strength of repulsion is

lp-lp > lp-bp > bp-bp

H_2O has 2lp and 2bp **(O atom is bonded to 2 H atoms, is it linear?)**

NH_3 has 1lp and 3bp **(N atom is bonded to 3 H atoms, is it trigonal planar?)**

CH_4 has no lp and 4bp **(C atom is bonded to 4 H atoms is it tetrahedral or square planar)**

As a result they all have different shapes

Therefore if we know the number of lone pairs and bond pairs we would be able to predict the shape of the molecule.

Step 1: Determining the number of bond pair and lone pair from the Lewis structure.

Step 2: Using the info from the Lewis structure and apply VSEPR theory

Step 3: Draw the shape

Step 1: Determining the number of bond pair and lone pair from the Lewis structure.

NF_3

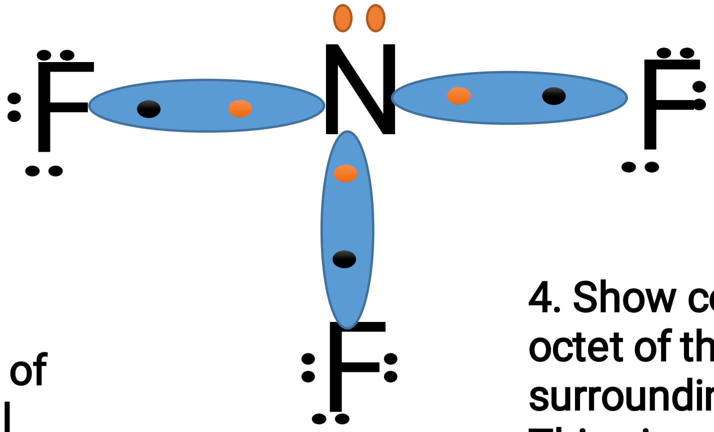
2. Count the total number of valence electrons present.

$N = 5e$

$3F = 7e \times 3 = 21e$

Total = 26e

- Remember that these are covalent bonds – each atom donates an electron and they share, forming the bond
- N is contributing 5e but to complete its octet it is using 3e, one from each F atom.
- Similarly, each F atom has 7e and is using one electron from N to complete its octet.



3. Draw a single covalent bond between the central atom and each of the surrounding atoms.

4. Show complete octet of the surrounding atoms. This gives a total of 24 electrons so far.

1. Write the skeletal structure of the compound, using chemical symbols and placing bonding atoms next to one another.

5. Add extra electrons to central atom as lone pair.

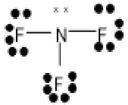
NF_3 has 3bp and 1lp

Step 1 Step 2 Step 3 Step 4

NF_3

F N F
F

N = 5e
3F = 3e X 7e = 21e
Total = 26e



CS_2

S C S

C = 4e
2S = 2 X 6e = 12e
Total = 16e

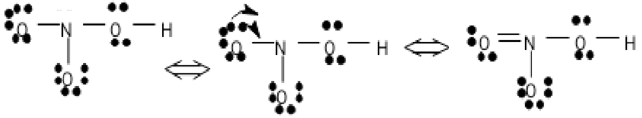
Notice that C has only 4 electrons (2bp)

It completes its octet by using a lp from each of the S atoms forming a double bond.

HNO_3

O N O H
O

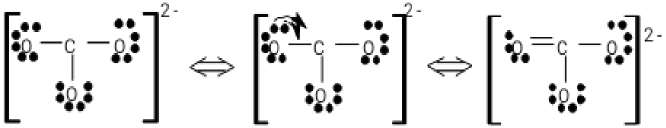
H = 1e
N = 5e
3O = 3 X 6e = 18e
Total = 24e



CO_3^{2-}

O C O
O

C = 4e
3O = 3 X 6e = 18e
charge = 2e
Total = 24e

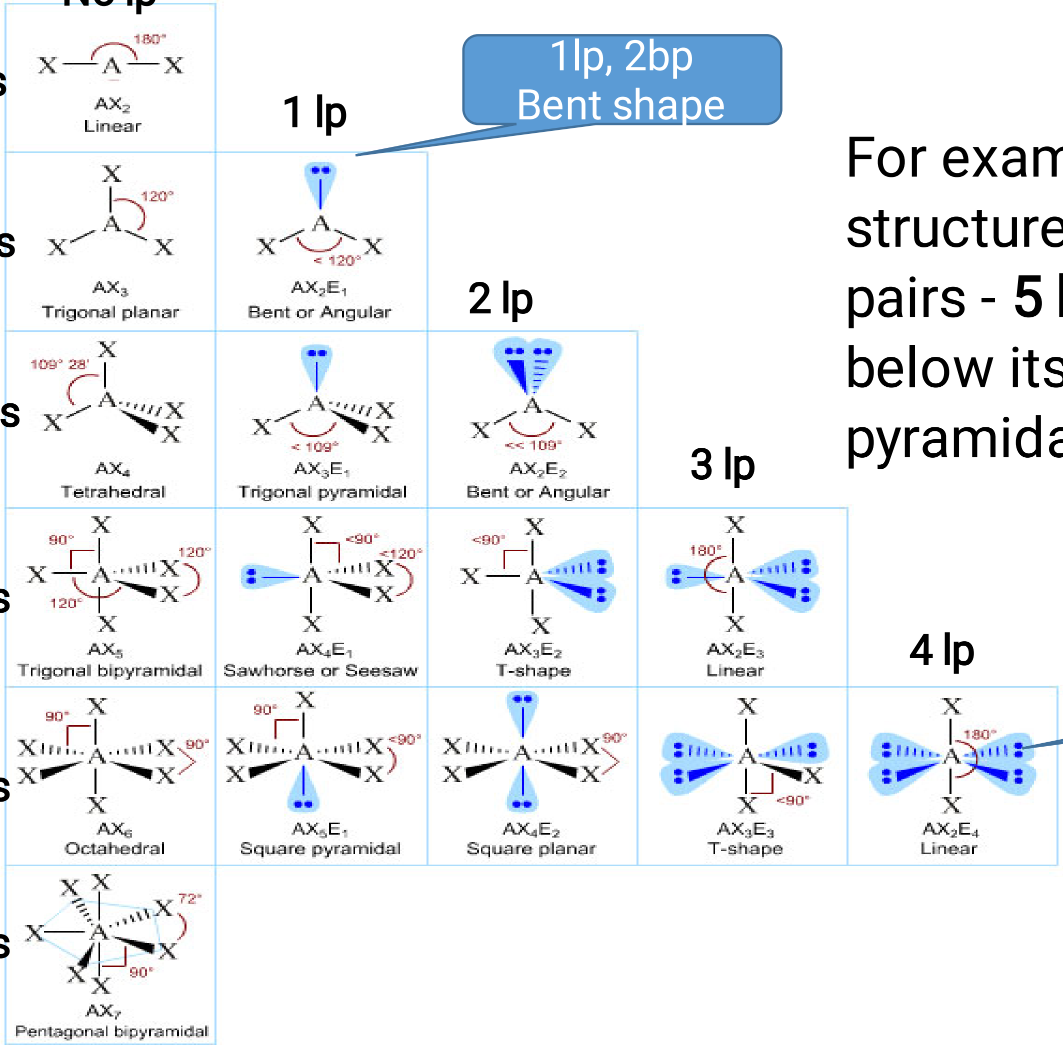


Step 2: Using the info from the Lewis structure and apply VSEPR theory

- Draw the Lewis structure of the molecules considering the electron pair around the central atom of the molecule.

- Count the number of electron pairs around the central atom (bonding pairs and lone pairs). Treat double bonds and triple bonds as though they are single bonds.

- Study and apply the table below.



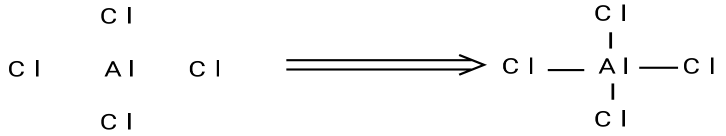
	No lp	1 lp	2 lp	3 lp	4 lp
2 ė pairs	AX_2 Linear				
3 ė pairs	AX_3 Trigonal planar	AX_2E_1 Bent or Angular			
4 ė pairs	AX_4 Tetrahedral	AX_3E_1 Trigonal pyramidal	AX_2E_2 Bent or Angular		
5 ė pairs	AX_5 Trigonal bipyramidal	AX_4E_1 Sawhorse or Seesaw	AX_3E_2 T-shape	AX_2E_3 Linear	
6 ė pairs	AX_6 Octahedral	AX_5E_1 Square pyramidal	AX_4E_2 Square planar	AX_3E_3 T-shape	AX_2E_4 Linear
7 ė pairs	AX_7 Pentagonal bipyramidal				

1lp, 2bp
Bent shape

4lp, 2bp
Linear shape

For example, after drawing the Lewis structure of a molecule that has 6é pairs - **5 bp and 1 lp,** from the table below its shape will be square pyramidal.

$AlCl_4^-$

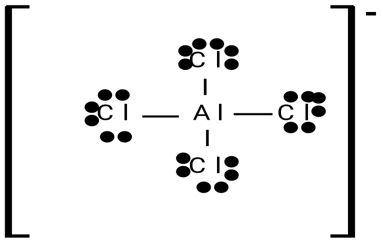


Al = 3e

4Cl 4 x 7 = 28e

charge = 1e

Total = 32e

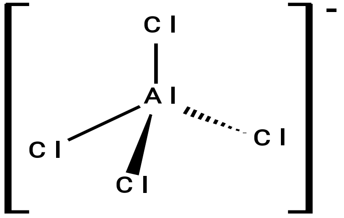


Lewis Structure

no of lone pair around Al = 0

no of bond pair around Al = 4

:. AB_4 **tetrahedral**



SO_2

S = 6e

2O = 2 x 6 = 12e

Total = 18

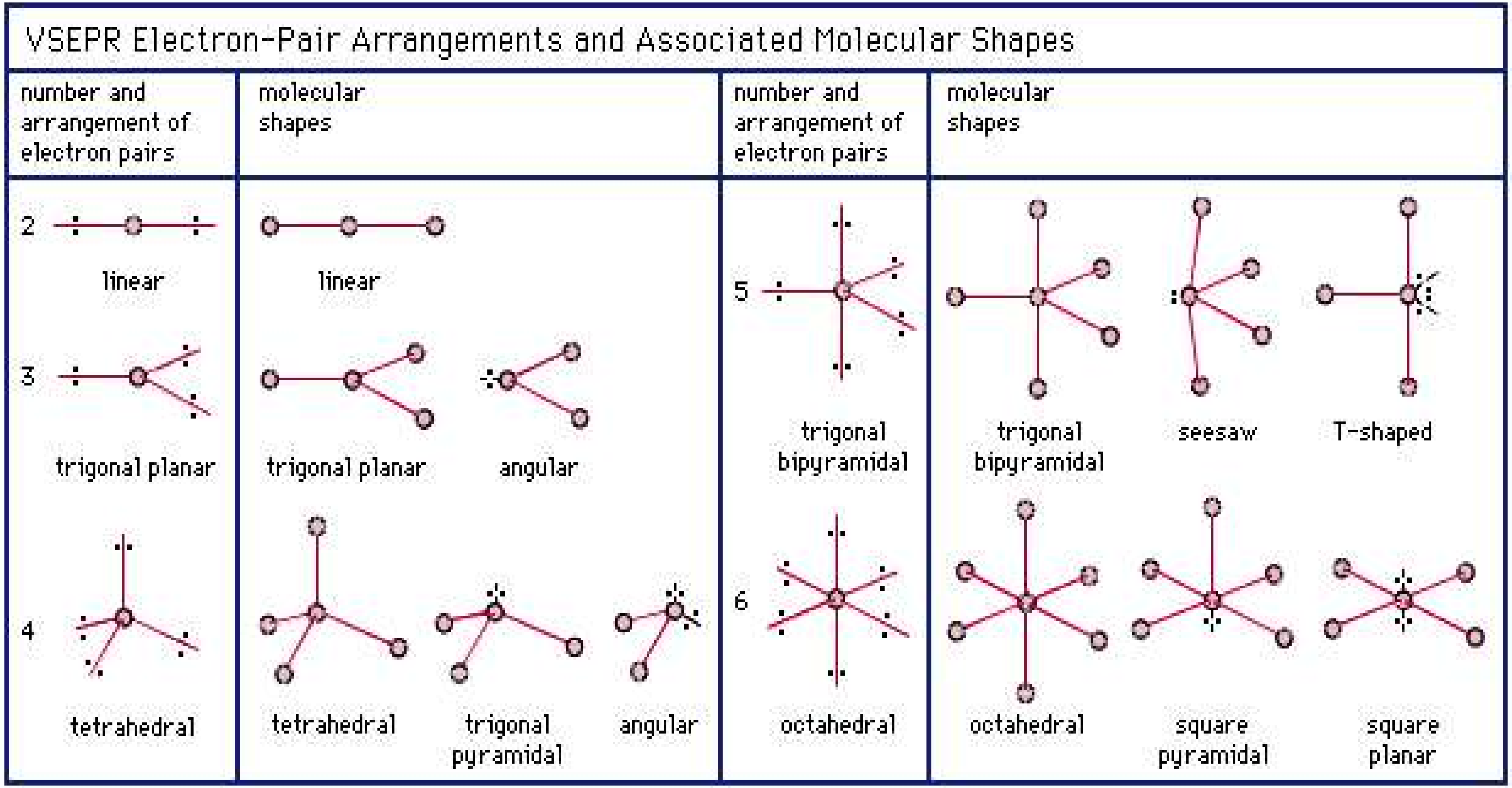
Lewis Structure

no of lone pair around S = 1

no of bond pair around S = 2

:. $\overset{\bullet\bullet}{A}B_2$ Bent

Step 3: Draw the shape



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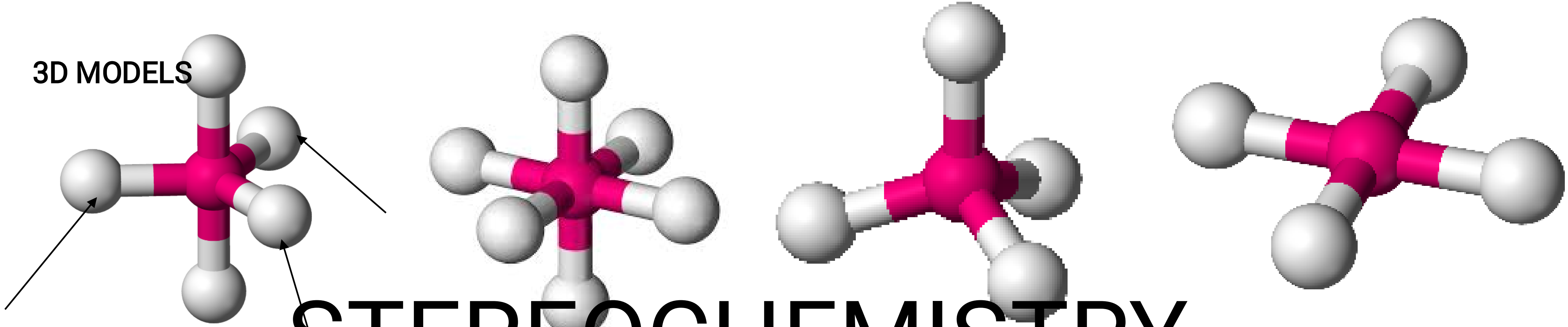
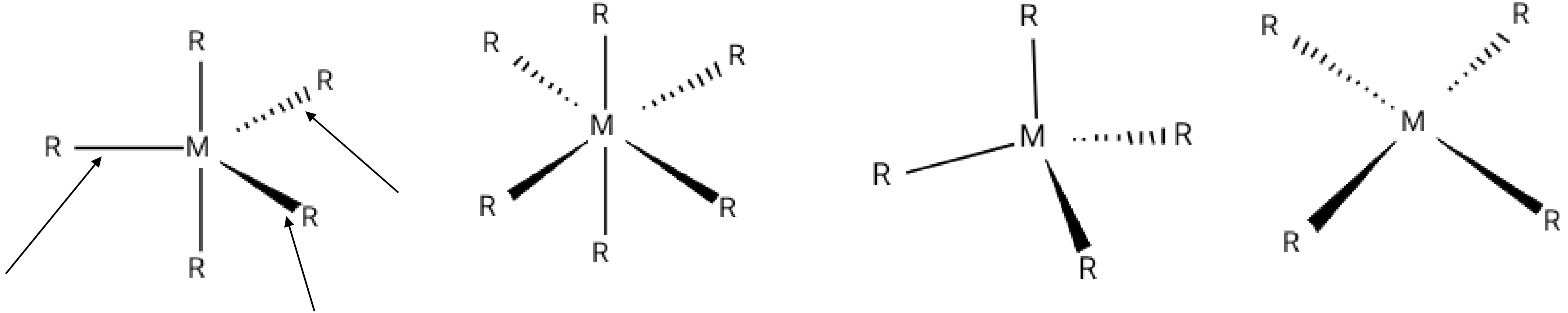
Dots are electrons and circles are atoms

3D MODELS



STEREOCHEMISTRY



Why is all this important?

In the next module we would be talking about symmetry of molecules. You cannot get the symmetry of molecule if you have no idea of its true shape.

XeF_4 and CH_4 look similar but they have different shapes and that means they would have different symmetries.

MODULE TWO

SYMMETRY OPERATIONS

- **Unit One –** Identity and n-fold Rotation
- **Unit Two –** Reflection and inversion
- **Unit Three –** Improper rotation
- **Unit Four –** Point group

UNIT ONE – Identity and n-fold Rotation

A molecule is said to have symmetry if when it is 'turned' there is no change in the placement of the atoms of the molecules. The symmetry of a molecule is determined by the existence of **symmetry operations** performed with respect to **symmetry elements**.

A symmetry element is a line, a plane or a point in or through an object (a molecule), about which the 'turnings' are made and the object has an orientation that indistinguishable from the original.

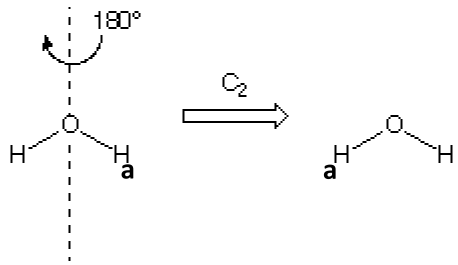
A symmetry operation is the movement of the object (molecule) about a line, plane or point.

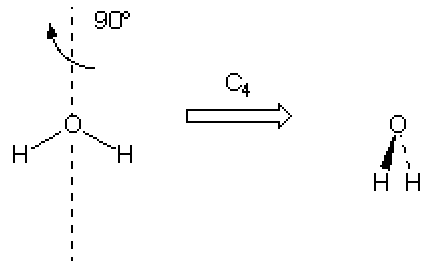
There are 5 kinds of operations
1. Identity
2. n-Fold Rotations
3. Reflection
4. Inversion
5. Improper n-Fold Rotation

1. **Identity E:** For this operation there is no 'turning' is done to the molecule. The molecule does not move and all the atoms of the molecule stay at the same place. All molecules have the identity operation. Identity operation can also be a combination of different operations resulting in the molecule returning to its original position after these operations are performed.

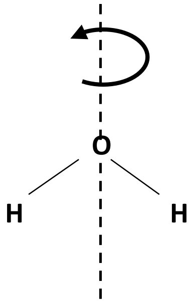
2. **<u>n-Fold Rotations</u> C_n**, (where n is an integer). This a rotation by $\frac{360°}{n}$ about a particular axis defined as the **n-fold rotation axis**. The symmetry element is a line and the operation is a rotation along this line. C_2 = 180° rotation, C_3 = 120° rotation, C_4 = 90° rotation, C_5 = 72° rotation, C_6 = 60° rotation, etc. Clockwise and anticlockwise rotations must yield the same result for it to count.

Rotation of H_2O about the axis shown by 180° (C_2) gives the same molecule back. Therefore, H_2O possess the C_2 symmetry element.



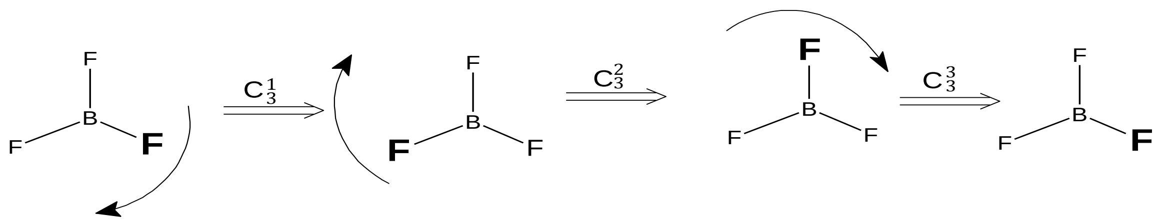


However, rotation by 90° about the same axis does not give back the identical molecule. Therefore, H_2O does NOT possess a C_4 symmetry axis.



Water has 1 C_2; one line passing through oxygen and bisecting the H-O-H bond angle.

BF_3 possesses a C_3 rotation axis of symmetry. This is a line passing through B coming out of the paper. (Both directions of rotation must be considered).

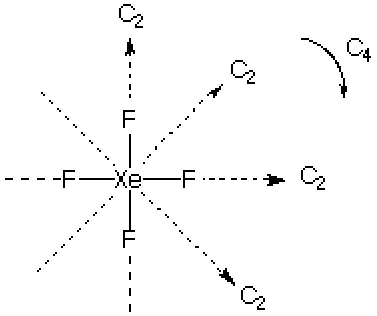


- C_2 means one 180° rotation
- C_3 means a 120°
- C_6^2 means two 60° rotations
- C_6^5 means five 60° rotations
- C_4^2 means two 90° rotations

Note:

The axis with the greatest value of n is the PRINCIPLE AXIS

$\boldsymbol{C_n^n = E}$



XeF$_4$ is square planar. It has four DIFFERENT C_2 axes;

- 2 are in line with the F-Xe-F bonds
- 2 are bisecting the F-Xe-F bond angle.
- It also has a C_4 axis coming out of the page through Xe and it is the principle axis because it has the largest n.

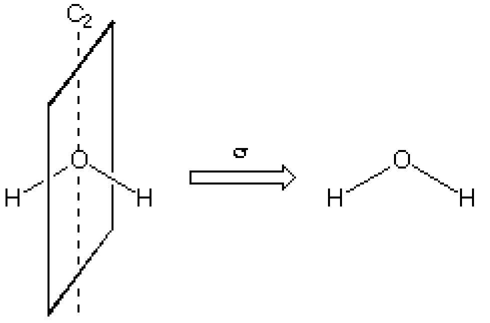
UNIT TWO – Reflection and Inversion

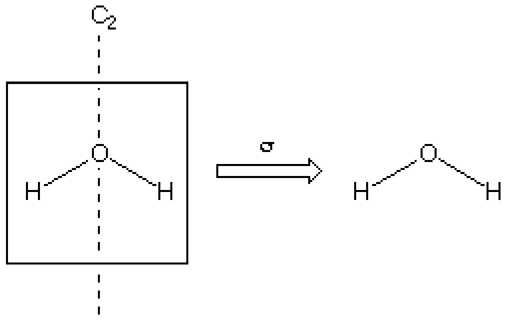
3. **Reflection:** $\mathbf{s}$ or $\boldsymbol{\sigma}$ the symmetry element is called a mirror plane (or plane) of symmetry.

- If reflection about a mirror plane gives the same molecule/object back than there is a plane of symmetry ($\mathbf{s}/\boldsymbol{\sigma}$).
- If plane lies on the principle rotation axis (i.e., parallel), it is a vertical plane ($\mathbf{s}_v$ or $\boldsymbol{\sigma}_v$)
- If plane is perpendicular to the principle rotation axis, it is a horizontal plane ($\mathbf{s}_h$ or $\boldsymbol{\sigma}_h$)
- If plane is parallel to the principle rotation axis, but bisects angle between 2 C_2 axes, it is a diagonal plane ($\mathbf{s}_d$ or $\boldsymbol{\sigma}_d$)
- If the shape of the molecule is **linear, bent or planar** (i.e. trigonal planar, square planar) they would always appear to be "lying" on a plane and can only be labelled as $\boldsymbol{\sigma}_h$ if and only if this plane "they are lying on" is perpendicular to the principle rotation axis.

When mirror plane is operated n times, we have $\sigma^n = \begin{matrix} E\ (when\ n\ is\ even) \\ \sigma\ (when\ n\ is\ odd) \end{matrix}$

H_2O possess 2 σ_v mirror planes of symmetry because they are both parallel to the principle rotation axis (C_2).



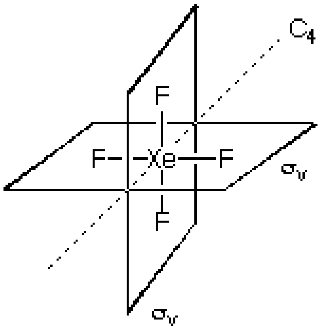


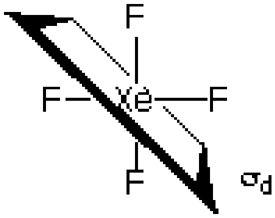
H_2O possesses 2 vertical mirror planes of symmetry because they are both parallel to the principle rotation axis (C_2). The first plane is bisecting the molecule through oxygen such that there is a hydrogen atom on either side of the plane such what is seen on the left side of the plane is seen at the right side as well.

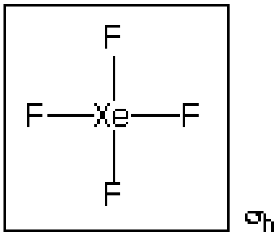
The second plane is also bisecting the molecule but it is doing so through all the 3 atoms such that what is seen in front of the plane is the same as what is seen behind the plane.

Symmetry of operation of H_2O are: E, C_2, $2\sigma_v$

- XeF_4 has two planes of symmetry parallel to the principle rotation axis i.e. along the 2 F-Xe-F bonds: σ_v
- XeF_4 has two planes of symmetry parallel to the principle rotation axis and bisecting the angle between 2 C_2 axes i.e. bisecting the F-Xe-F bond angles: σ_d
- XeF_4 has one plane of symmetry perpendicular to the principle rotation axis. The whole molecule is sort of "lying" on this plane: σ_h



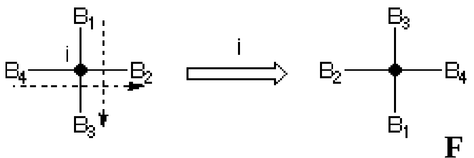




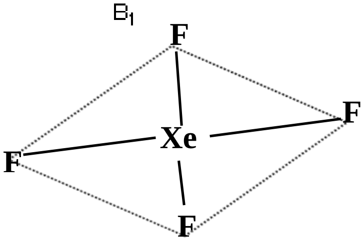
XeF_4 – has E, $4C_2$, C_4, $2\sigma_v$, $2\sigma_d$ and σ_h symmetry operations.

4. Inversion i:

The element of this operation is a point found at the centre of the molecule and it's called the inversion center or center of symmetry. The operation is to move every atom in the molecule in a straight line through the inversion center to the opposite side of the molecule.



XeF_4 possesses an inversion centre at the Xe atom.



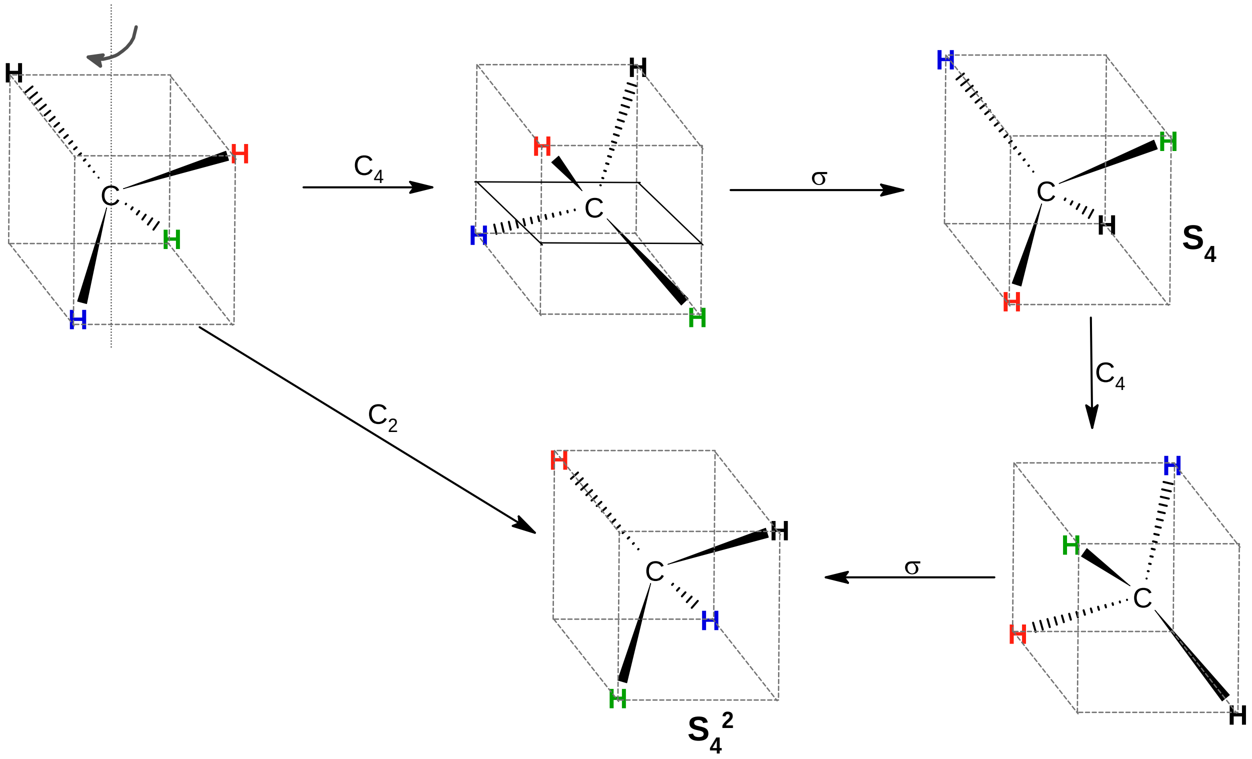
When inversion is operated n times, we have $i^{n} = \begin{matrix} E\ (when\ n\ is\ even) \\ i\ (when\ n\ is\ odd) \end{matrix}$

UNIT THREE – Improper Rotation

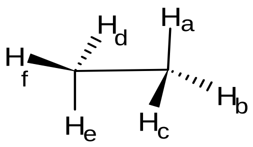
This is an n-fold rotation followed by reflection through mirror plane perpendicular to the axis of rotation. It can also be done in the reverse, first a reflection through the mirror plane then followed by the n-fold rotation. Whichever route is taken be consistent.

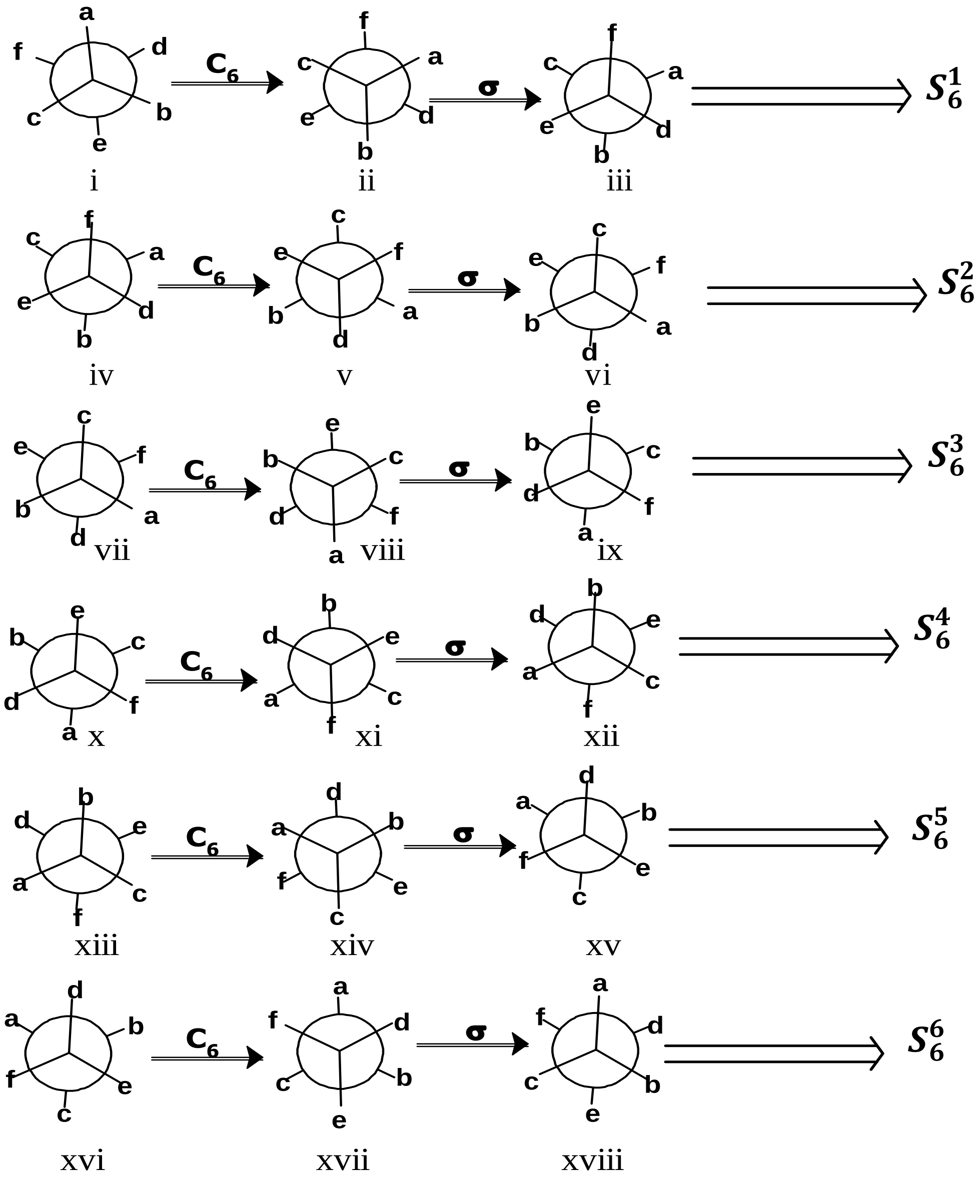
This is the improper rotation of tetrahedral molecule e.g. CH_4, each hydrogen is distinguished from the other with different colours so as to be able to track the movement.

Notice that by just doing a C_2 you to methane you end up with S_4^2



Below is the **staggered conformation** of ethane (CH_3CH_3), several improper rotations were carried out on it.





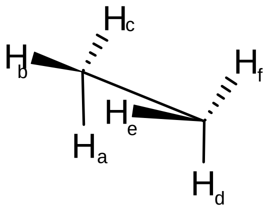
Doing a series of operation will lead to and equivalent operation. An S_6 axis will generate the following operations.

Operation	**Symbol**
$S_6 = \sigma C_6$	S_6
$S_6^2 = C_6^2 = C_3$	C_3
$S_6^3 = S_2 = (\sigma C_6^3 \quad = \sigma C_2 \ ) \quad = i$	i
$S_6^4 = C_6^4 = C_3^2$	C_3^2
$S_6^5 = \sigma C_6^5$	S_6^5
$S_6^6 = E$	E

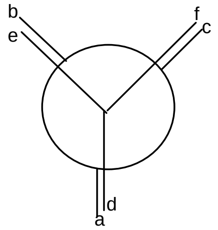
- σC_6 means the reflection is done followed by rotation by 60°
- S_2 means a C_2 (180° rotation) then the reflection
- σC_6^5 means a reflection followed by means five 60° rotations

S_6^5 means a C_6 (60° rotation) then the reflection done five times

For the **eclipse ethane**, it does not undergo C_6 operation but a C_3.



Eclipse ethane



An S_5 axis will generate the following operations.

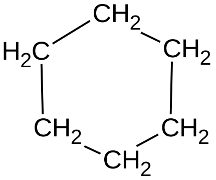
Operation	Symbol
$S_5 = \sigma C_5$	S_5
$S_5^2 = C_5^2$	C_5^2
$S_5^3 = \sigma C_5^3$	S_5^3
$S_5^4 = C_5^4$	C_5^4
$S_5^5 = \sigma$	σ
$S_5^6 = C_5$	C_5
$S_5^7 = \sigma C_5^2$	S_5^7
$S_5^8 = C_5^3$	C_5^3
$S_5^9 = \sigma C_5^2$	S_5^9
$S_5^{10} = E$	E

Generally for improper rotations S_n when **n** is EVEN, there are n operations $\{S_n^1, S_n^2, \ldots \ldots S_n^n\}$, while when **n** is ODD, there are 2n operations $\{S_n^1, S_n^2, \ldots \ldots S_n^{2n}\}$.

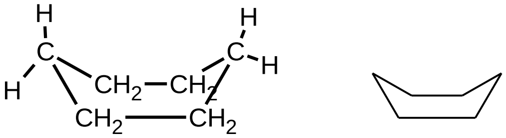
For an improper rotation S_n^m when m is even an alternative route of operation can be found e.g. $S_6^2 = C_3^2$ but when m is odd it the regular improper operation occurs $S_6^5 = \sigma C_6^5$.

UNIT FOUR – Point group

A selected collection of symmetry elements present in a molecule forms a group and is technically called a **Point Group.** It called point group because all the symmetry elements (points, lines and planes) will intersect at a single point. Let's take water for example water has the following symmetry element E, C_2, $2\sigma_v$ and it belongs to C_{2v} point group. Another molecule that belongs to the C_{2v} group is the boat conformation of cyclohexane. Even though they have different shapes they belong to the same point group. Therefore, molecules can be classified according to their point group.



cyclohexane



Boat conformation

Chair conformation

Molecular Point Groups

1. **$C_{\infty v}$:** Signifies the presence of an ∞-fold axis of rotation which is possessed by a **linear molecule**. For molecules that belong to this group
    - will have an infinite number of σ_v planes
    - no σ_h planes or inversion centre.

   The molecules that satisfy these conditions are

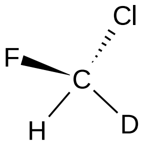
   (a) asymmetrical diatomic molecules HF, CO, CN^- and

   (b) linear polyatomic molecules (having 3 or more atoms) that do not and do not have a centre of symmetry OCS, HCN

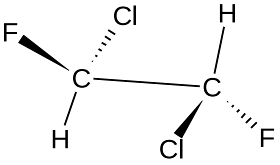
   $$H—F \quad H—C\equiv N \; [(C_\infty), E, \sigma_v]$$

2. **$D_{\infty h}$:** These are symmetrical diatomics (e.g. H_2, $[O_2]^{2-}$) and linear polyatomics (that contain a centre of symmetry (e.g. $[N_3]^-$, CO_2, C_2H_2))
    - They have a σ_h plane
    - in addition to a C_∞ axis and
    - an infinite number of σ_v planes.

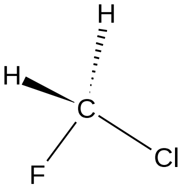
3. **C_1:** this contain only identity ***E*** (i.e. a C_1 rotation is a 360° rotation and it is the same as identity operation ***E*** e.g. CDFHCl



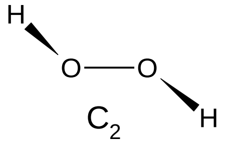
4. **C_i:** This group has only identity ***E*** and a centre of inversion ***i***

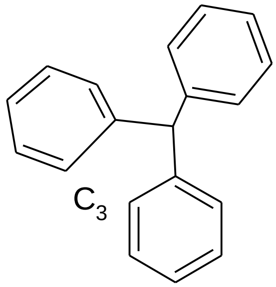


5. **C_s:** This has identity ***E*** and a plane of reflection ***σ***



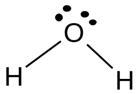
6. **C_n:** In this is identity ***E*** and an n-fold axis of rotation ***C_n***





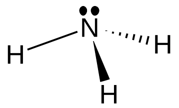
7. **C_{nv}:** here there is the ***E,*** a ***C_n axis***, and might have more than one vertical mirror planes ***σ_v***

C_{2v} ⟹



[C_2, E, 2σ_v]

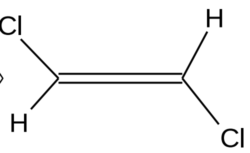
C_{3v} ⟹



[C_3, E, 3σ_v]

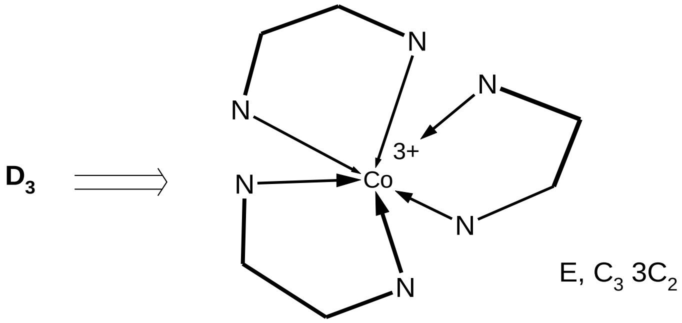
8. **C_{nh}:** contains ***E,*** a ***C_n axis***, and might have more than one horizontal mirror planes ***σ_h***. Note that it might have centre of inversion

C_{2h} ⟹



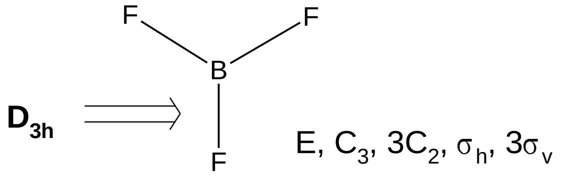
[E, i, C_2, σ_h]

9. **D_n:** In this is identity ***E*** and an n-fold axis of rotation ***C_n*** and might have more than one 2-fold rotational axes which are perpendicular to the principle axis

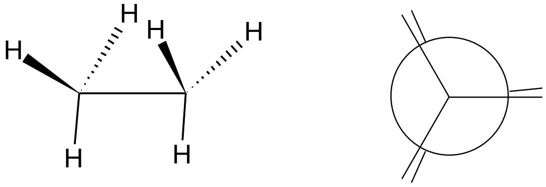


Trisethylenediamnecobalt(III) $[Co(en)_3]^{3+}$

10. **D_{nh}:** contains the same symmetry elements as **D_n** with the addition of one or more horizontal mirror planes ***σ_h***

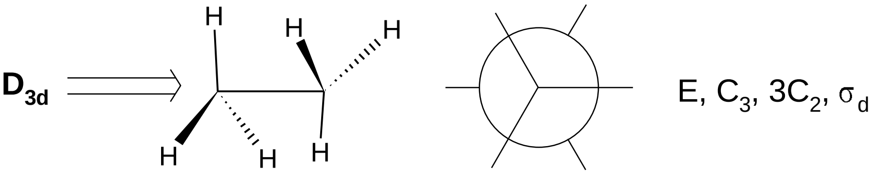


- eclipse ethane D_{3h} = E, C_3, $3C_2$, σ_h, $3\sigma_v$
- benzene D_{6h} = E, C_6, $6C_2$, σ_h, $6\sigma_v$



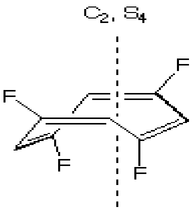
eclispe ethane

11. **D_{nd}:** contains the same symmetry elements and **D_n** with the addition of one or more dihedral mirror planes ***σ_d***



staggered ethane

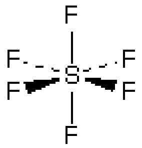
12. **S_n:** In this is identity ***E*** and one ***S_n*** axis



$S_4 = E, C_2, S_4$

The following groups contain more than one principle axis and they all meet at the centre of the molecule. and are referred to as the cubic group. They are high symmetry groups. The more common ones are divided into the Tetrahedral groups (T_d, T_h and T) and the Octahedral groups (O_h and O) and there are other that do not fall under these categories.

13. **T_d:** contains all the symmetry element of a regular tetrahedron – 4C_3 axes, 3C_2 axes, 6 dihedral mirror planes and 4S_4 axes e.g. CH_4
14. **T:** same as T_d but no planes of reflection
15. **T_h:** same T but contains has a centre of inversion *i*
16. **O_h:** group of regular octahedron e.g. $SF_6 = E, 8C_3, 6C_2, 6C_4, i, 6S_4, 8S_6, 3\sigma_h, 6\sigma_d$



17. **O:** same as O_h but with no planes of reflection.
18. **I_h:** $E, 12C_5, 20C_3, 15C_2, i, 12S_{10}, 20S_6$, 15s in Icosahedron e.g. C_{60}, dedocahedrane molecule ($C_{20}H_{20}$).
19. **R_3:** it has an infinity number of **C_n axes** with all the possible values of n and is the symmetry of sphere. Atoms belong to this group.

MODULE TWO

Symmetry Operations

- **Unit One –** Identity and n-fold Rotation
- **Unit Two –** Reflection and inversion
- **Unit Three –** Improper rotation
- **Unit Four –** Point group

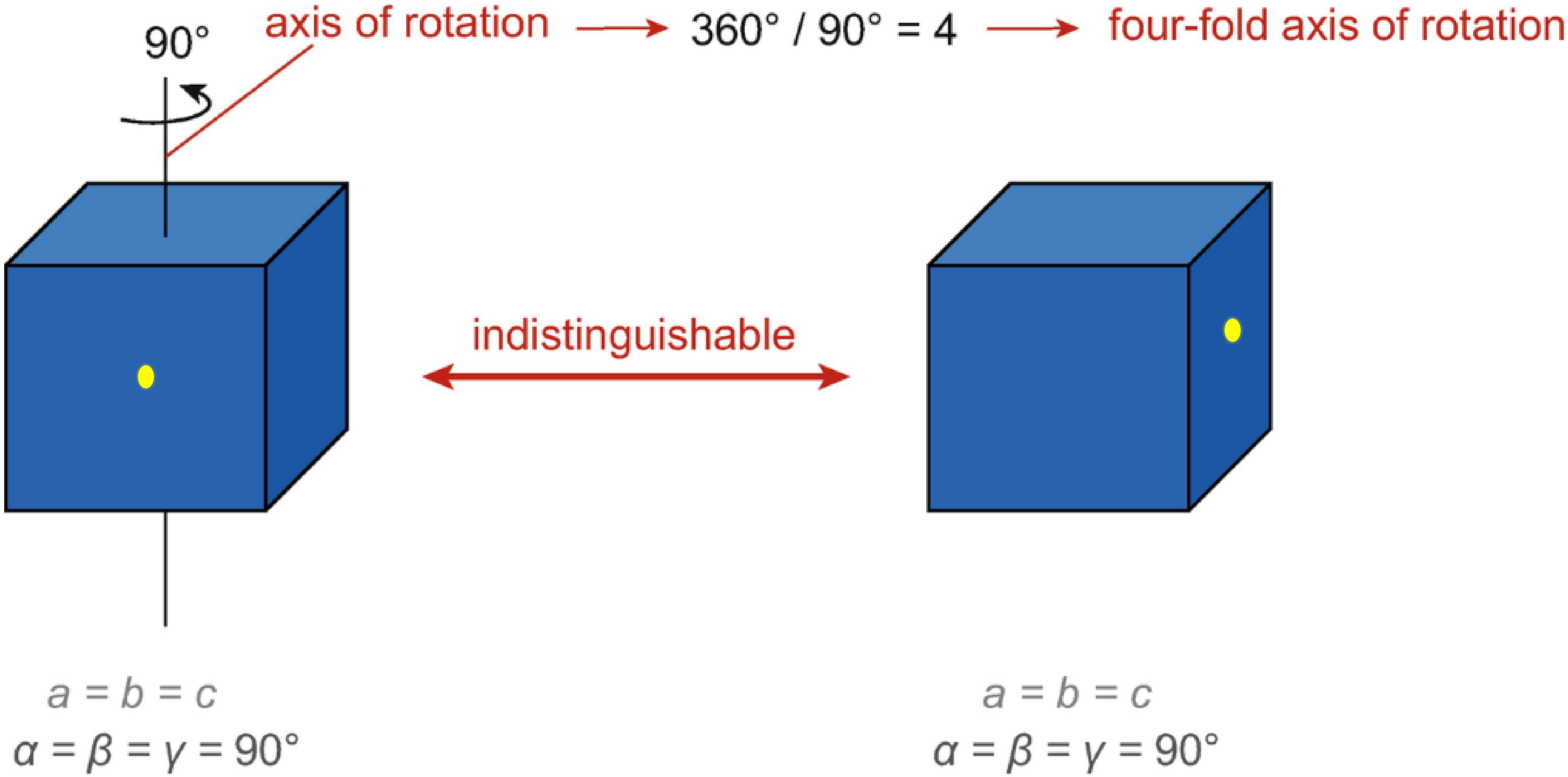
UNIT ONE

Identity and n-fold Rotation

- A molecule is said to have **symmetry** if when it is 'turned' there is no change in the placement of the atoms of the molecules.

- **A symmetry element** is a line, a plane, a point in or through an object (a molecule), about which the 'turnings' are made and the object has an orientation that cannot be differentiated from the original.

- **A symmetry operation** is the movement of the object (molecule) about a line, plane or point.



90°

axis of rotation → 360° / 90° = 4 → four-fold axis of rotation

indistinguishable

$a = b = c$

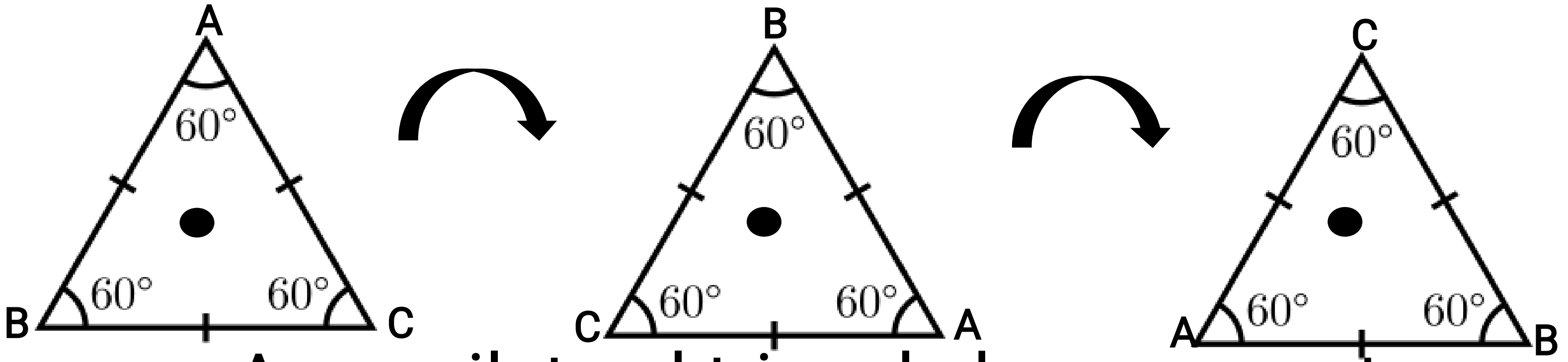
$\alpha = \beta = \gamma = 90°$

$a = b = c$

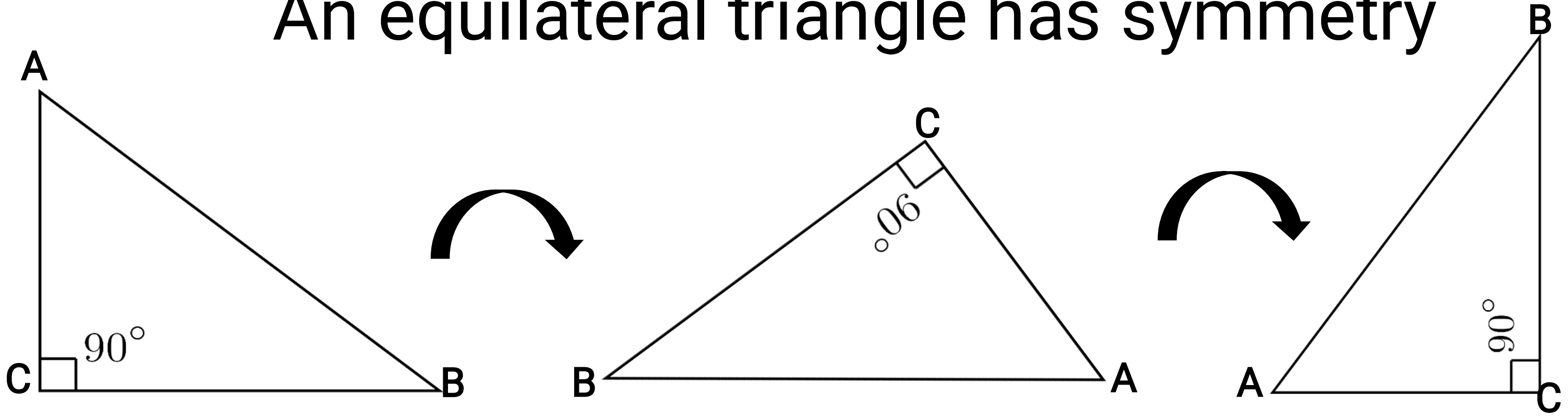
$\alpha = \beta = \gamma = 90°$

Hoffmann F. (2020) Symmetry (Is Everywhere). In: Introduction to Crystallography. Springer, Cham. https://doi.org/10.1007/978-3-030-35110-6_3

‘Turning’



An equilateral triangle has symmetry



A right-angle triangle has no symmetry

Types of Operations

- There are 5 kinds of operations
- 1. Identity
- 2. n-Fold Rotations
- 3. Reflection
- 4. Inversion
- 5. Improper n-Fold Rotation

Identity E: For this operation no 'turning' is done to the molecule. The molecule does not move and all the atoms of the molecule stay at the same place. **EVERY MOLECULE HAS E**

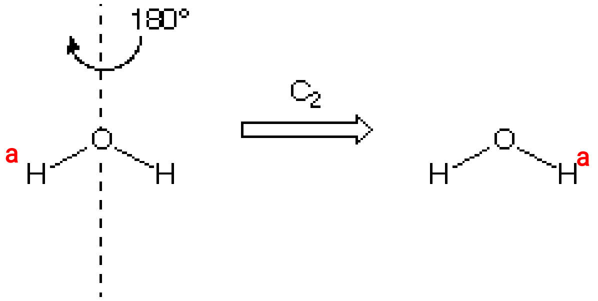
n-fold Rotation (C_n)

This is a rotation by $\frac{360°}{n}$ about a particular axis called the **n-fold rotation axis** which is symmetry element (a line).

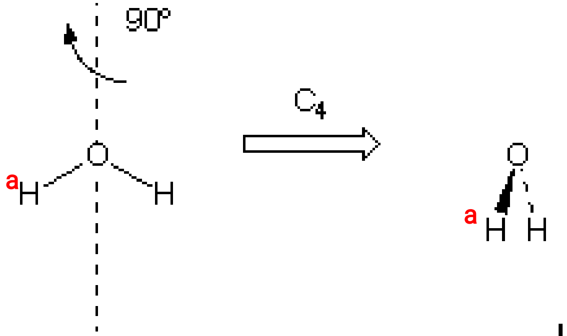
No of Rotating atom	n	Degree of rotation	Symmetry operation	Example
2	2	$\frac{360°}{2} = 180°$	C_2	H_2O
3	3	$\frac{360°}{3} = 120°$	C_3	BF_3
4	4	$\frac{360°}{4} = 90°$	C_4	XeF_4

http://faculty.otterbein.edu/djohnston/sym/tutorial/proper.html

Water has bent shape. The n-fold rotating axis of H_2O a line passing through **O** and bisecting the **H–O–H** bond angle.
This will be a 180° rotation to give the same molecule back.
Therefore, H_2O possesses the C_2 symmetry element. (the letter a is used to distinguish the hydrogen atoms). To see this operation in 3D visit https://www.chemtube3d.com/sym-waterc2v/

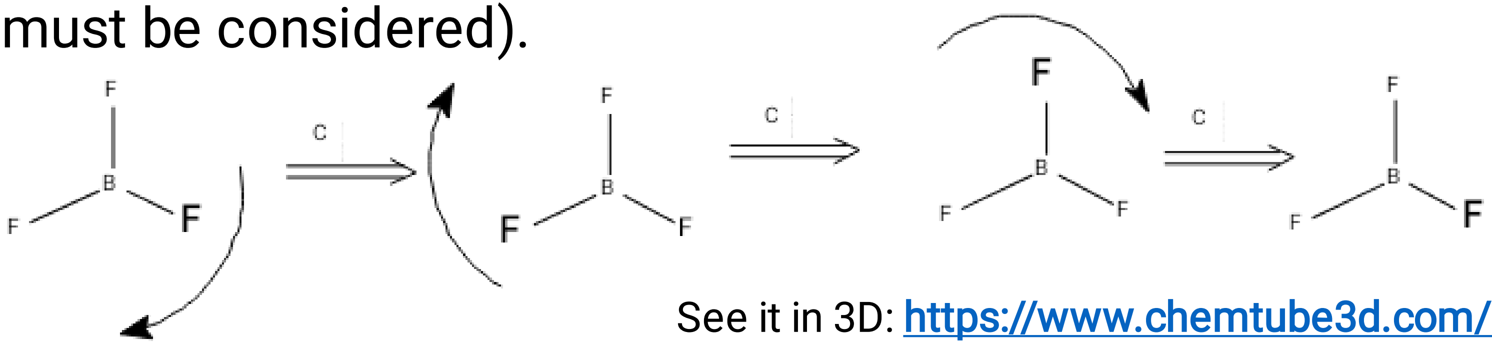


However, rotation by 90° about the same axis does not give back the identical molecule. Here H_a is in front of the other H instead of beside it. Therefore, H_2O does NOT possess a C_4 symmetry axis.



H_2O has E and C_2 – operations (but these are not all)

BF_3 is trigonal planar in shape. It possesses a C_3 rotation axis of symmetry. This is a line passing through **B** coming out of the paper. (Both directions of rotation must be considered).



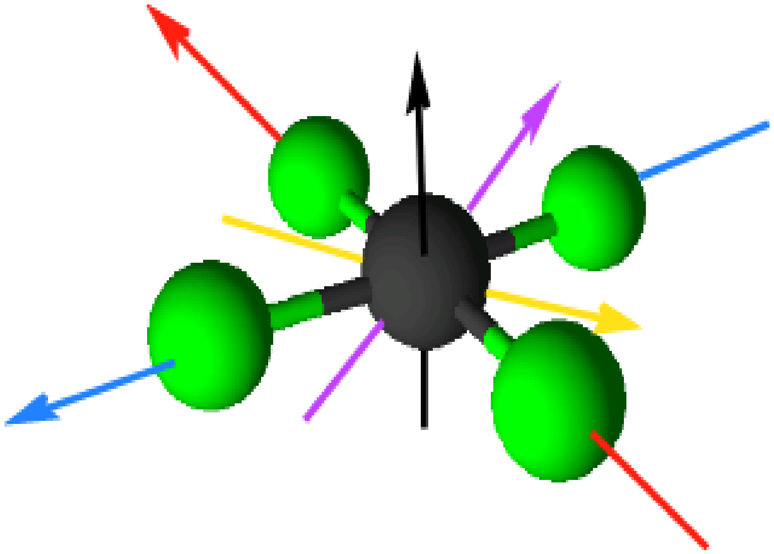
See it in 3D: https://www.chemtube3d.com/sym-d3hbf3new/

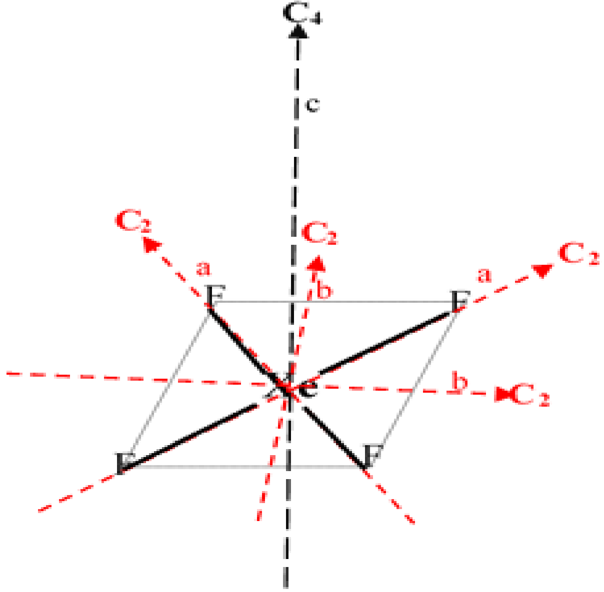
- C_2 means one 180° rotation
- C_3 means a 120°
- C_6^2 means two 60° rotations in the same direction
- C_6^5 means five 60° rotations in the same direction
- C_4^2 means two 90° rotations in the same direction
- $C_n^n = E$

Note: The axis with the greatest value of n is the PRINCIPLE AXIS

This means that BF_3 has E, C_3, C_3^2, C_3^3 (= E) – operations (but these are not all).

See it in 3D https://www.chemtube3d.com/xef4-symmetry-d4h/





XeF_4 is square planar in shape.

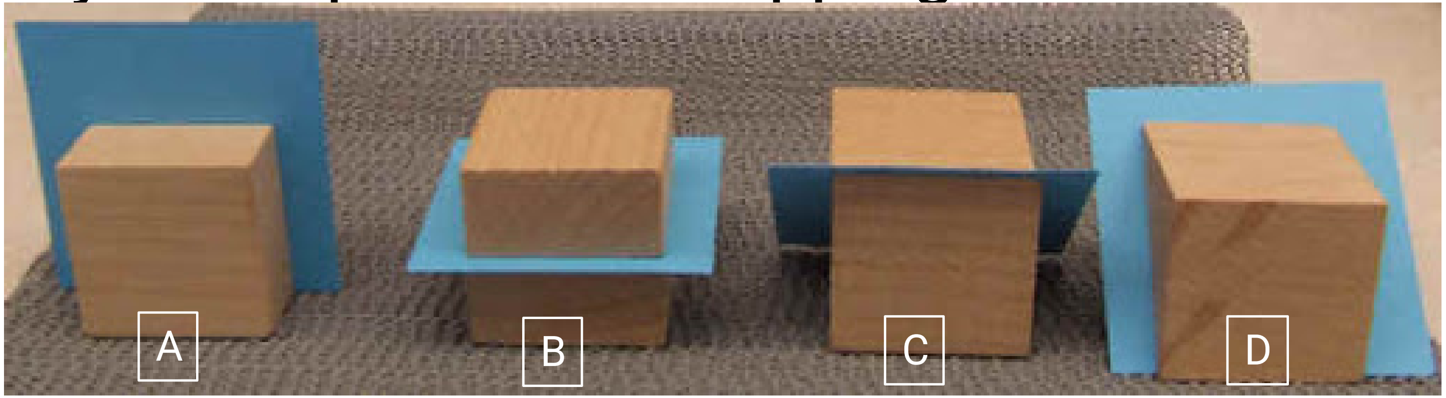
- It has four C_2 axes;
- 2 are *in line* with the F−Xe−F bonds (a) (blue and red)
- 2 are bisecting the F−Xe−F bond angle (b) (yellow and purple)
- It also has a C_4 axis coming out of the page through Xe (c) (black) and it is the principle axis because it has the largest n.

XeF_4 – has E, $4C_2$, C_4, symmetry operations.

END OF UNIT ONE

Reflections (s or σ)

The symmetry element is called a mirror plane (or plane) of symmetry. The operation is ‘flipping the molecule’ to obtain its reflecti



In the image above the blue cardboard represent the mirror plane.

A. The mirror is vertical.
B. It is horizontal.
C. It is diagonal (cutting across a set of angles)
D. It is also diagonal (cutting across the other set of angles)

If you were to move the cube to the opposite side of the mirror, the cube would be exactly the same.

Image was got from the link below.
tcdsbstaff.ednet.ns.ca
Cube Planes of Symmetry

Terms and Conditions

If reflection about a mirror plane gives the same molecule/object back than there is a plane of symmetry (s/σ).

If plane lies on the principle rotation axis (i.e. parallel), it is a vertical plane (s_v or σ_v)

If plane is perpendicular to the principle rotation axis, it is a horizontal plane (s_h or σ_h)

If plane is parallel to the principle rotation axis, but bisects angle between 2 C_2 axes, it is a diagonal plane (s_d or σ_d)

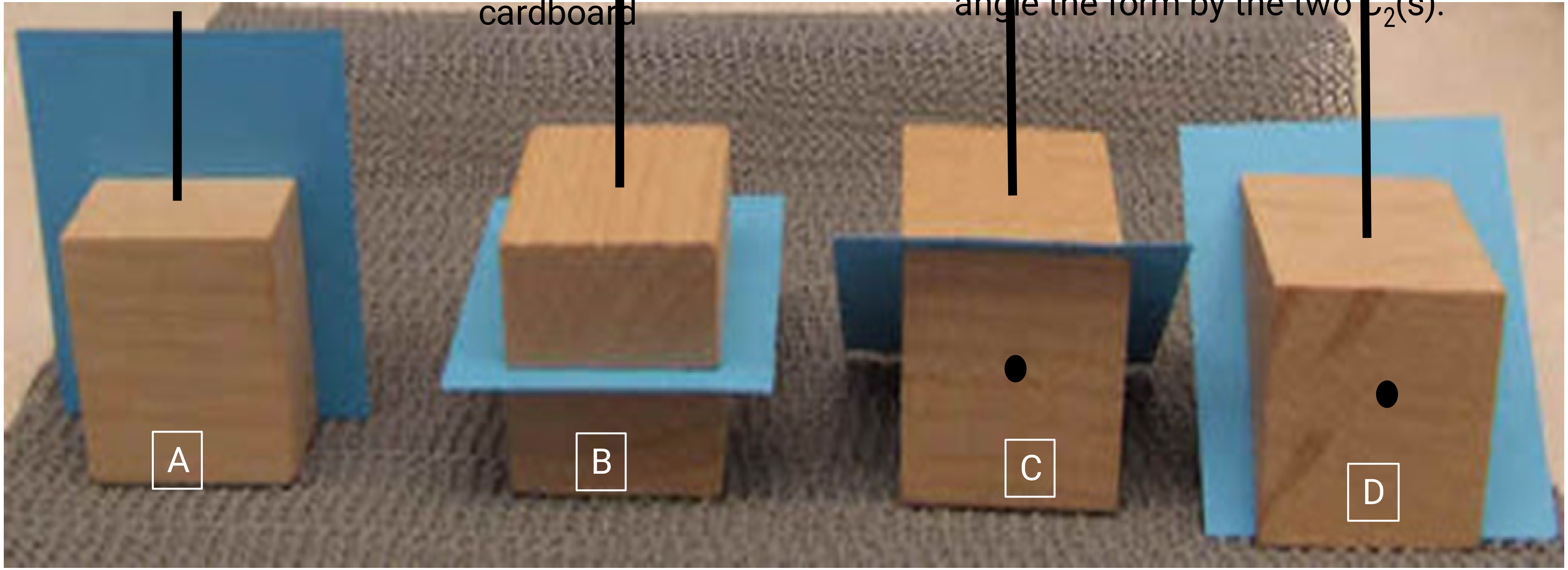
*If the shape of the molecule is linear, bent or planar (i.e. trigonal planar, square planar) they would always have a plane that cuts across ALL its atoms. This also occurs in octahedral and trigonal bipyramid molecules

Assuming the black line is the principle axis of rotation of these cubes (C_4)

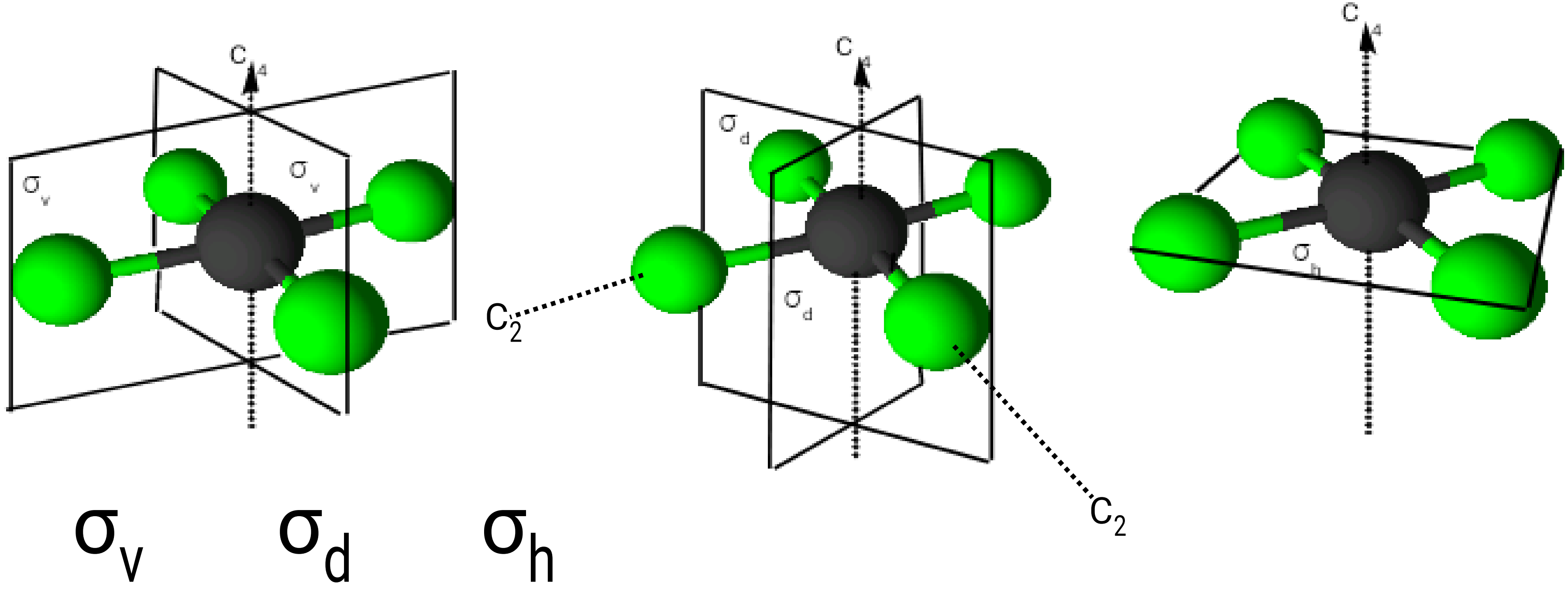
The box has a σ_v . Notice that the black line is in line/parallel to the blue cardboard

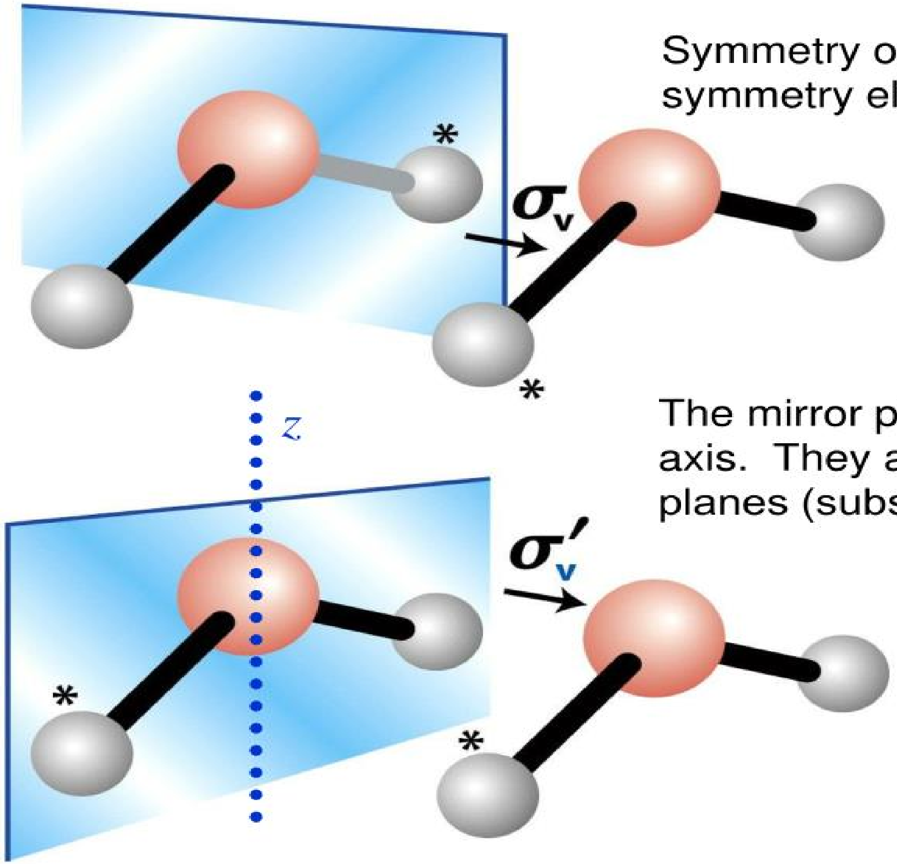
The box has a σ_h . The black line is in perpendicular to the blue cardboard

The box has a σ_d . The black line is also a C_2 and the black dot is another C_2 axis of rotation. The blue cardboard is bisecting the angle the form by the two C_2(s).



Green ball is fluorine
Black ball is xenon



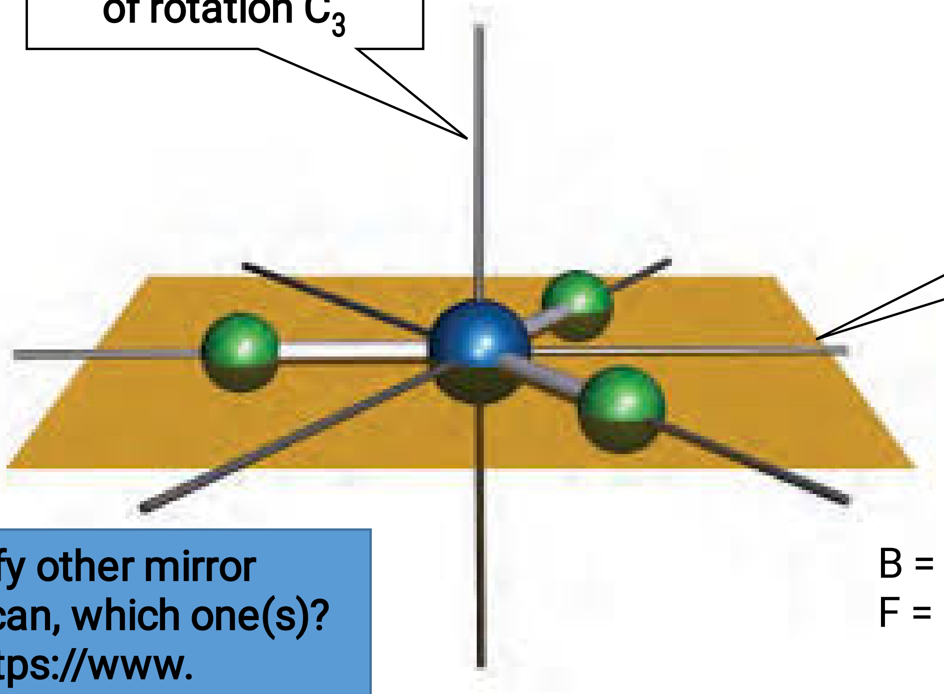


Symmetry operation *reflection* through the symmetry element *mirror plane*, σ

The mirror planes contain the principal C_2 axis. They are therefore *vertical* mirror planes (subscript "v").

Figure 7-4
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Did you notice the asterix. It was used to help differentiate between the atoms. (This is water molecule.



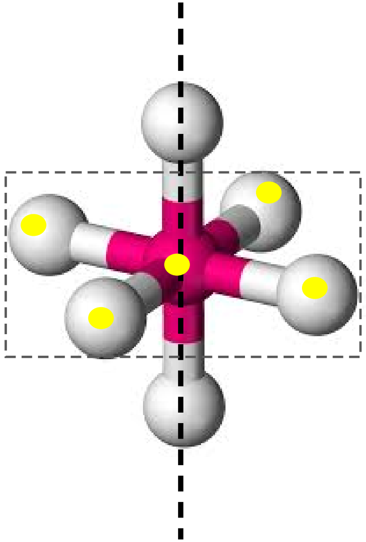
Principle axis of rotation C_3

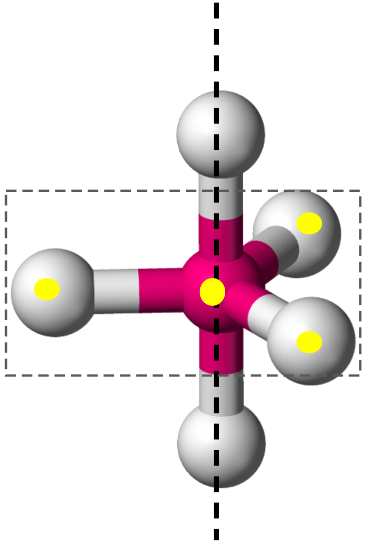
Horizontal plane perpendicular to the principle axis of rotation σ_h

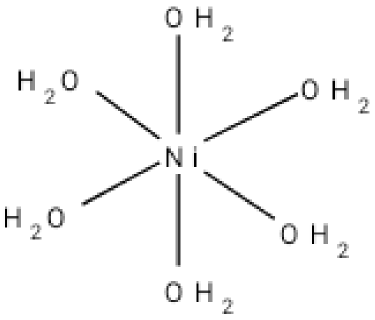
B = blue ball
F = green balls

Can you identify other mirror planes. If you can, which one(s)? See it in 3D. https://www.chemtube3d.com/sym-d3hbf3new/

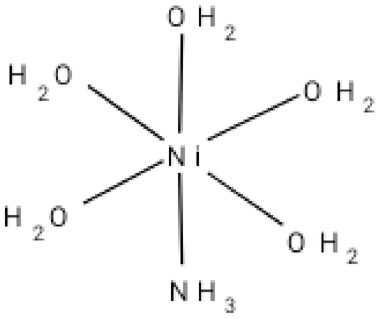
https://www.google.com/url?sa=i&url=https%3A%2F%2Fpeople.unica.it%2Fmariacarlaaragoni%2Ffiles%2F2012%2F04%2FHousecroft_Introd-Mol-Symm.pdf&psig=AOvVaw3toS87SPY2JLiUHRzQTdbz&ust=1613060848837000&source=images&cd=vfe&ved=0CAIQjRxqFwoTCIiOupTe3-4CFQAAAAAdAAAAABAR







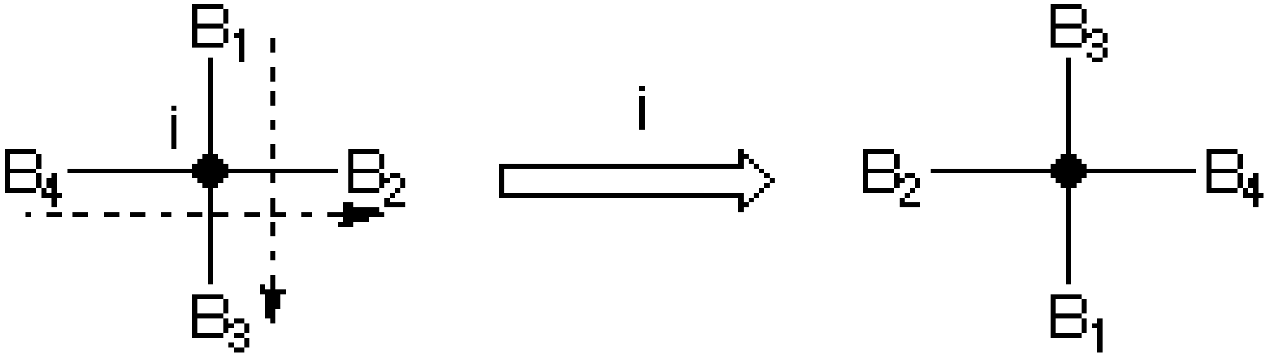
A



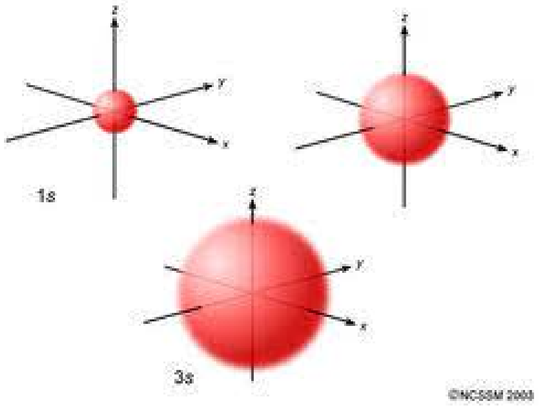
B

Inversion (i)

The element of this operation is **a point** found at the centre of the molecule and it’s called the inversion center or center of symmetry. The operation is to move every atom in the molecule in a straight line through the inversion center to the opposite side of the molecule.

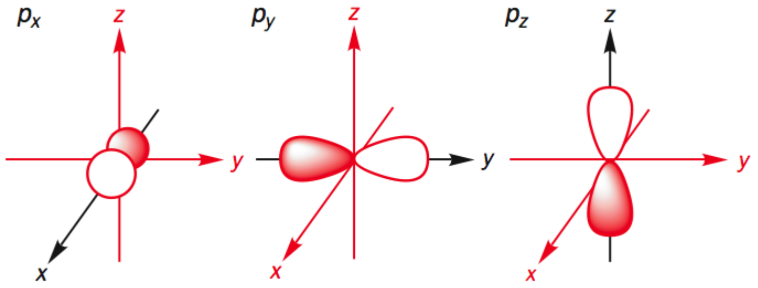


https://www.chemtube3d.com/syminversion/

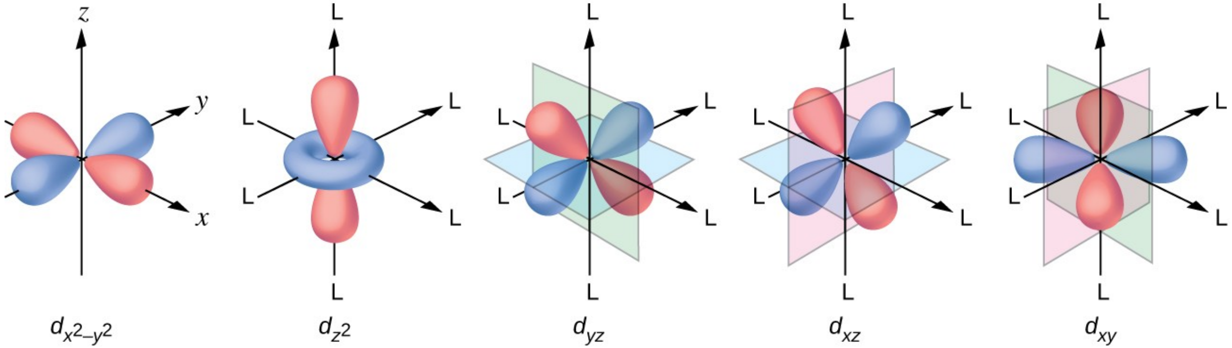


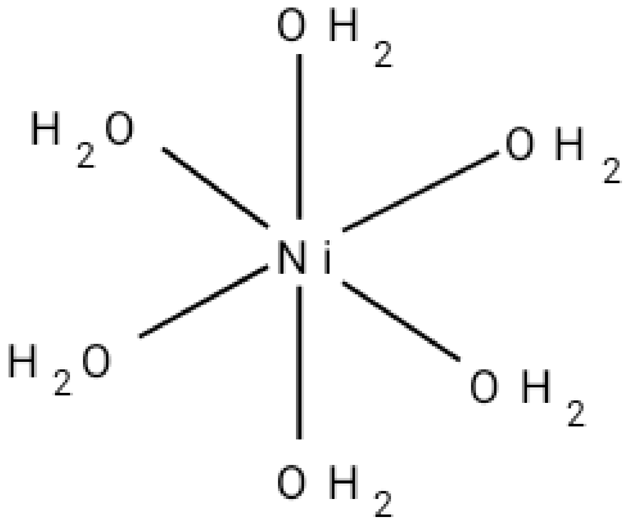
Orbitals *have a center of symmetry* can undergo an inversion operation and are said to be gerade (g).
Orbitals *don't have a centre of symmetry are* ungerade (u) and cannot undergo an inversion operation.

s-orbitals are gerade.
p-orbitals are ungerade
d-orbitals are gerade

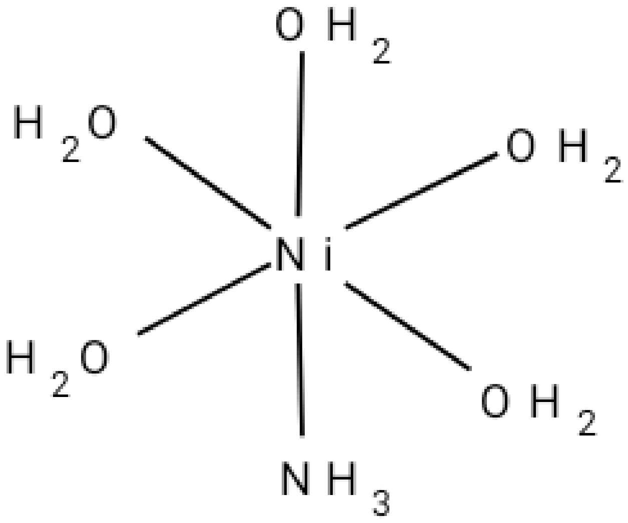


Remember the wave property of the electron.
In an s-orbital are in one phase (+ or -).
While for the p-orbitals each lobe exist in two phases at the same time (+ and -). One lobe is in a +ve phase (let say the red portion) while the second lobe in a -ve phase (white portion) at the same.
In d-orbitals each lobe exist in one phase, which is the opposite of the other lobe.





A

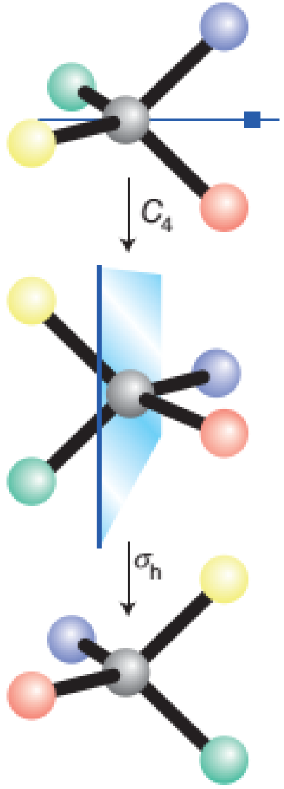


B

END OF UNIT TWO

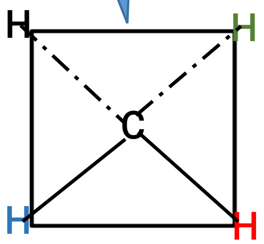
Improper rotation (S_n)

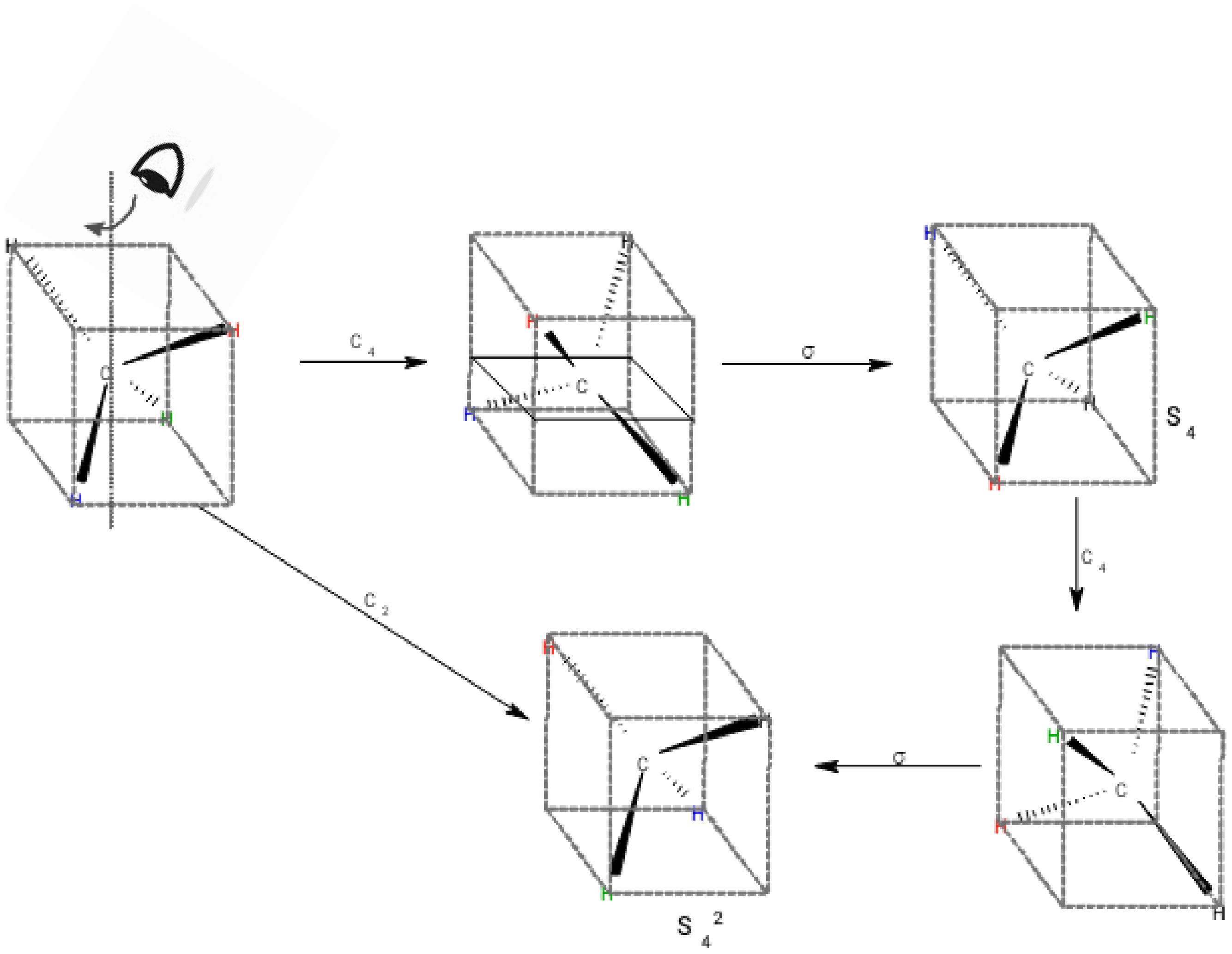
This is an n-fold rotation followed by reflection through mirror plane perpendicular to the axis of rotation. It can also be done in the reverse, first a reflection through the mirror plane then followed by the n-fold rotation. Whichever route is taken be consistent.



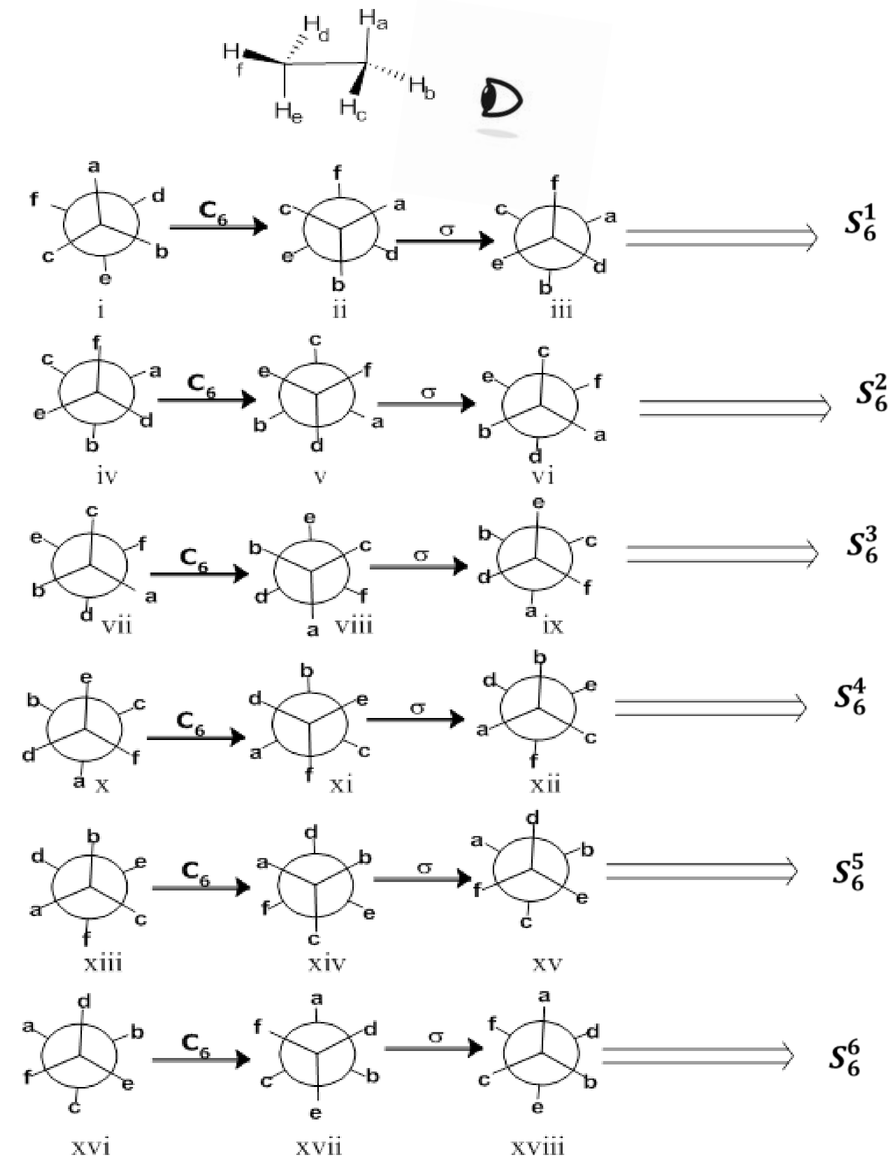
http://openchemistryhelp.blogspot.com/2013/03/guide-to-symmetry.htmlot.com/2013/03/guide-to-symmetry.html

Looking from the top, you see this.





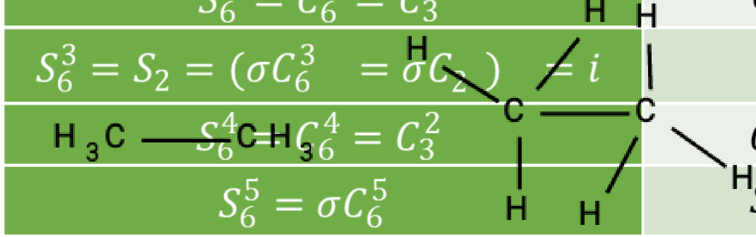
https://www.chemtube3d.com/methane-tetrahedral-symmetry-td/



https://www.chemtube3d.com/sym-ethanestaggered/

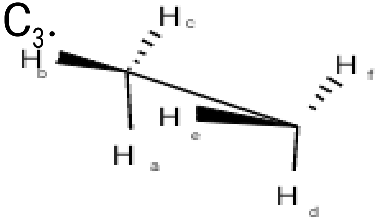
Doing a series of operation will lead to and equivalent operation. An S_6 axis will generate the following operations

Operation	Symbol
$S_6 = \sigma C_6$	S_6
$S_6^2 = C_6^2 = C_3$	C_3
$S_6^3 = S_2 = (\sigma C_6^3 = \sigma C_2) = i$	i
$S_6^4 = C_6^4 = C_3^2$	C_3^2
$S_6^5 = \sigma C_6^5$	S_6^5
$S_6^6 = E$	E

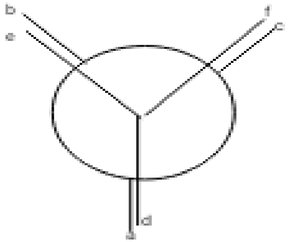


- σC_6 means the reflection is done followed by rotation by 60°
- S_2 means a C_2 (180° rotation) then the reflection
- σC_6^5 means a reflection followed by means five 60° rotations
- S_6^5 means a C_6 (60° rotation) then the reflection done five times

For the **eclipse ethane**, it does not undergo C$_6$ operation but a C$_3$.



Eclipse ethane



An S$_5$ axis will generate the following op

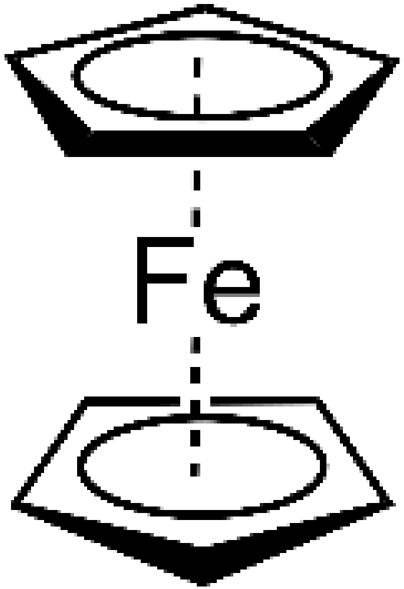
Operation	Symbol
$S_5 = \sigma C_5$	S_5
$S_5^2 = C_5^2$	C_5^2
$S_5^3 = \sigma C_5^3$	S_5^3
$S_5^4 = C_5^4$	C_5^4
$S_5^5 = \sigma$	σ
$S_5^6 = C_5$	C_5
$S_5^7 = \sigma C_5^2$	S_5^7
$S_5^8 = C_5^3$	C_5^3
$S_5^9 = \sigma C_5^2$	S_5^9
$S_5^{10} = E$	E

Can you derive all the series of improper rotation in an eclipse ethane and then determine their equivalent operations

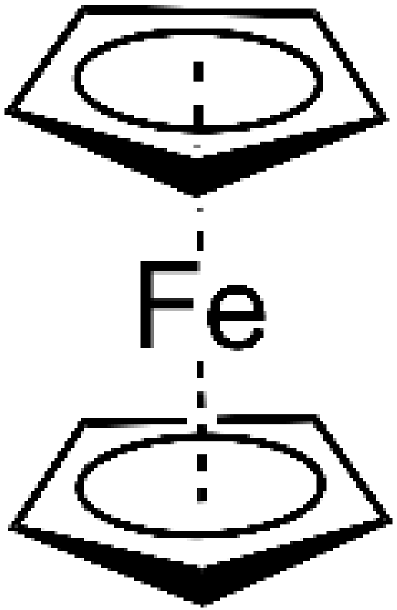
https://www.chemtube3d.com/symethaneecld3h/

Generally for improper rotations S$_n$ when **n** is EVEN, there are n operations $\{S_n^1, S_n^2, \dots \dots S_n^n\}$, while when **n** is ODD, there are 2n operations $\{S_n^1, S_n^2, \dots \dots S_n^{2n}\}$.

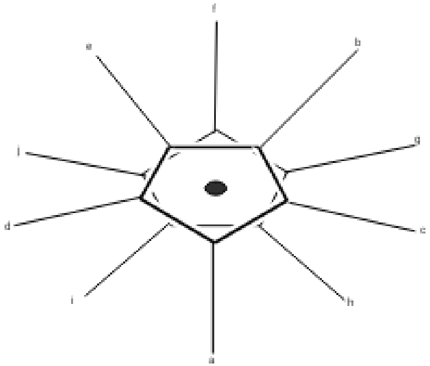
For an improper rotation S_n^m when m is even an alternative route of operation can be found e.g. $S_6^2 = C_6^2$ but when m is odd it the regular improper operation occurs $S_6^5 = \sigma C_6^5$.

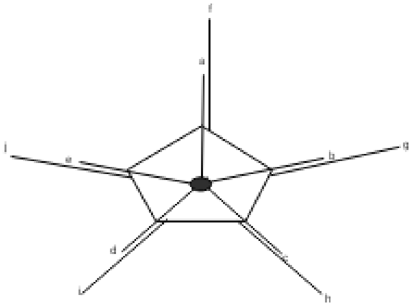


Staggered ferrocene



Eclipsed ferrocene





END OF UNIT THREE

UNIT FOUR

Point Group

- The collection of symmetry elements present in a molecule forms a group and is technically called a **Point Group.** It called point group because all the symmetry elements (points, lines and planes) will intersect at a single point.
- Let’s take water for example water has the following symmetry element E, C_2, $2\sigma_v$ and it belongs to C_{2v} point group. Another molecule that belongs to the C_{2v} group is the boat conformation of cyclohexane.
- Even though they have different shapes they belong to the same point group. Therefore, molecules can be classified according to their symmetry.

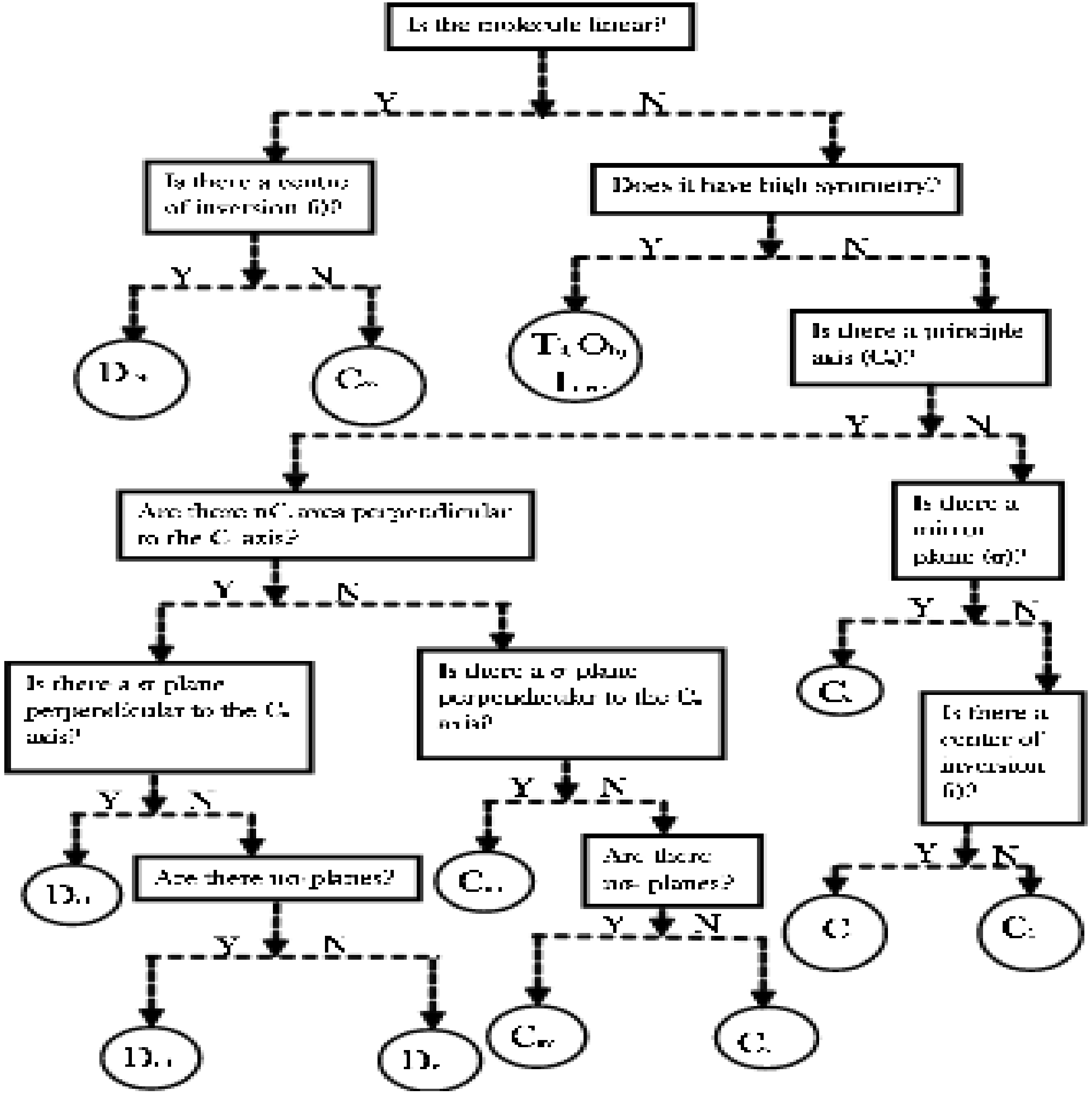
Point Group	Elements
$C_{\infty v}$	C_{∞}, E, σ_v
$D_{\infty h}$	C_{∞}, E, σ_v, σ_h
C_1	E
C_i	E , i
C_s	E , σ
C_n	E , C_n
C_{nv}	E, C_n , σ_v
C_{nh}	E, C_n , σ_h
D_n	E, C_n, C_2 ($\perp C_n$)
D_{nh}	E, C_n, C_2($\perp C_n$), σ_h
D_{nd}	E, C_n, C_2($\perp C_n$), σ_d
S_n	E, S_n axis
T_d	$4C_3$, $3C_2$, $6\sigma_d$
T	$4C_3$, $3C_2$
T	4C, 3C, i

That is the symbol for perpendicular

It is possible to determine the point group by finding the entire symmetry elements and then look up in set of tables called the character table until a match is found.

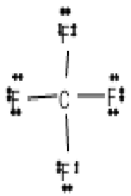
There are however molecules that have many symmetry elements an example is methane which has 24 symmetry elements.

So chemists have developed various flow chats that make the process simplier. See sample of chat below.


Is the molecule linear?
Y
N
Is there a centre of inversion (i)?
Y
N
$D_{\infty h}$
$C_{\infty v}$
Does it have high symmetry?
Y
N
T_d, O_h, I_h
Is there a principle axis (C_n)?
Y
N
Are there nC_2 axes perpendicular to the C_n axis?
Y
N
Is there a σ plane perpendicular to the C_n axis?
Y
N
D_{nh}
Are there $n\sigma_d$ planes?
Y
N
D_{nd}
D_n
Is there a σ plane perpendicular to the C_n axis?
Y
N
C_{nh}
Are there $n\sigma_v$ planes?
Y
N
C_{nv}
C_n
Is there a mirror plane (σ)?
Y
N
C_s
Is there a center of inversion (i)?
Y
N
C_i
C_1

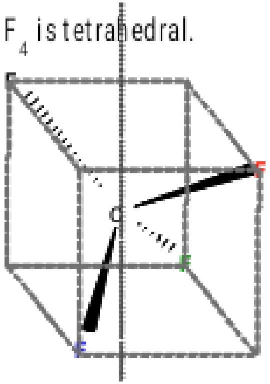
Determine the point group of CF_4

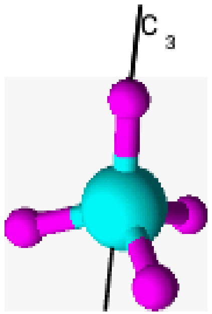
C		4e
4F	4x7e =	28e
Total		32e

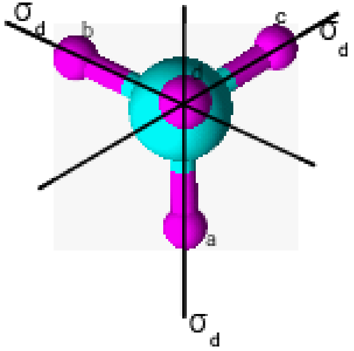


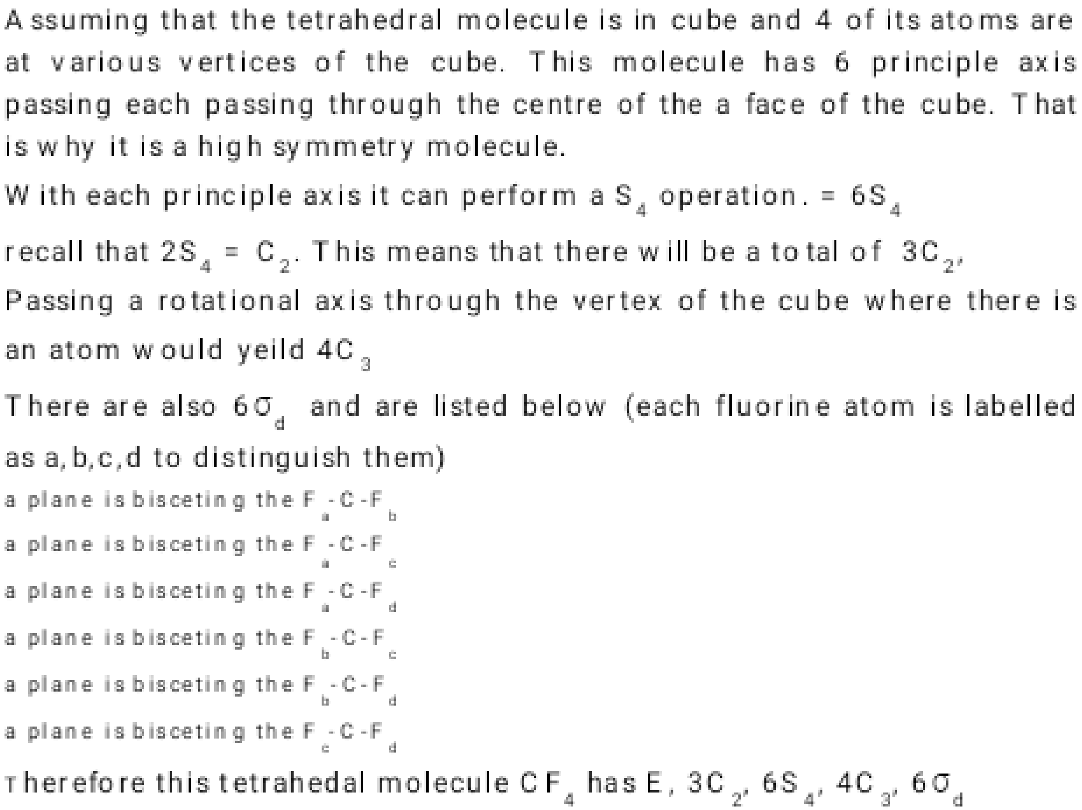
Around C there are 4bp and no lp.

The shape of CF_4 is tetrahedral.









Assuming that the tetrahedral molecule is in cube and 4 of its atoms are at various vertices of the cube. This molecule has 6 principle axis passing each passing through the centre of the a face of the cube. That is why it is a high symmetry molecule.

With each principle axis it can perform a S_4 operation. = $6S_4$

recall that $2S_4 = C_2$. This means that there will be a total of $3C_2$,

Passing a rotational axis through the vertex of the cube where there is an atom would yeild $4C_3$

There are also $6\sigma_d$ and are listed below (each fluorine atom is labelled as a, b, c, d to distinguish them)

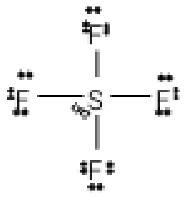
a plane is bisceting the F_a-C-F_b
a plane is bisceting the F_a-C-F_c
a plane is bisceting the F_a-C-F_d
a plane is bisceting the F_b-C-F_c
a plane is bisceting the F_b-C-F_d
a plane is bisceting the F_c-C-F_d

Therefore this tetrahedal molecule CF_4 has E, $3C_2$, $6S_4$, $4C_3$, $6\sigma_d$

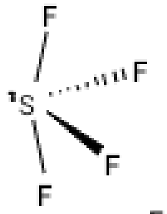
Following the chart
Is this molecule linear – No
Does it have a high symmetry – Yes, it can be with T_d, O_h, I_h.
It is a tetrahedral molecule it would belong to the **T_d point group** since it has σ_d.

Determine the point group of SF_4

S		6e
4F	4x7e =	28e
Total		34e



Around S there are 4bp and 1lp.
The shape of SF_4 is see-saw.



Following the point group chart
Is the molecule linear? – No
Does it have high symmetry? – No
Is there a principle axis? – Yes (C_2)

SF_4 has a C_2 that passes through the F_2-S-F_3 angle as well as the F_1-S-F_4 angle

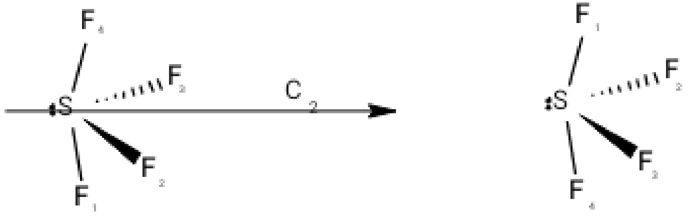
Are there nC_2 axes perpendicular to the C_n? – No
Is there σ_h a perpendicular to the C_n? – No
Are there nσ_v planes – Yes

It has a mirror plane parallel to the C_2, bisecting the F_2-S-F_3 angle and lie along F_1-S-F_4 (σ_v)

It has another mirror plane lie along F_2-S-F_3 angle but bisects the F_1-S-F_4 angle (σ_v)

The point group is C_{nv}, since the principle axis is C_2 then SF_4 belongs to C_{2v} point group

A



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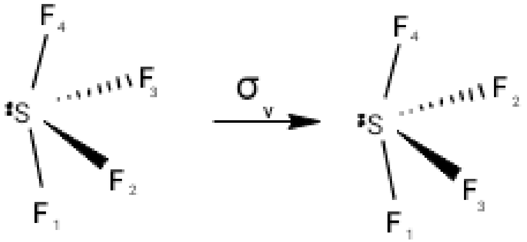
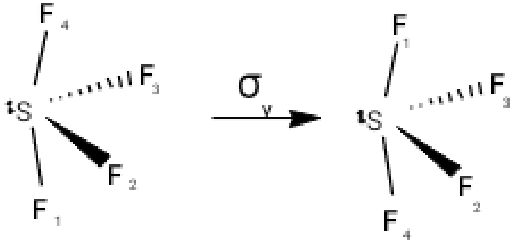
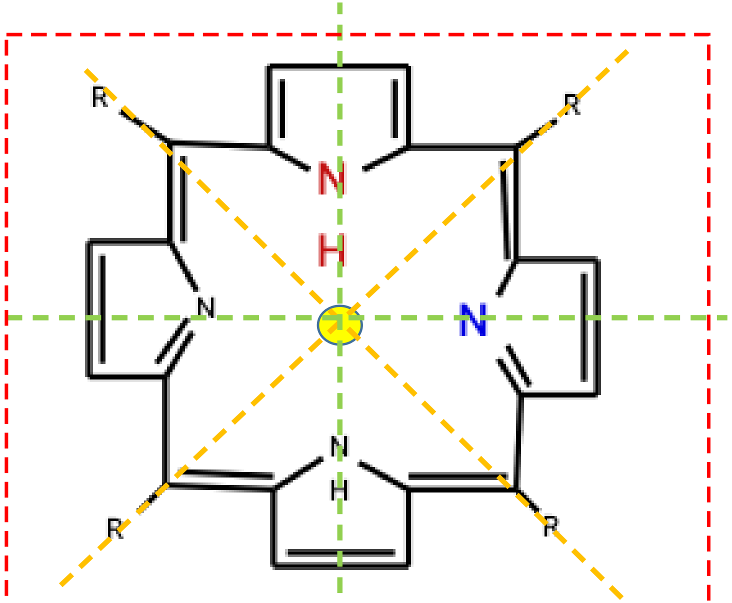
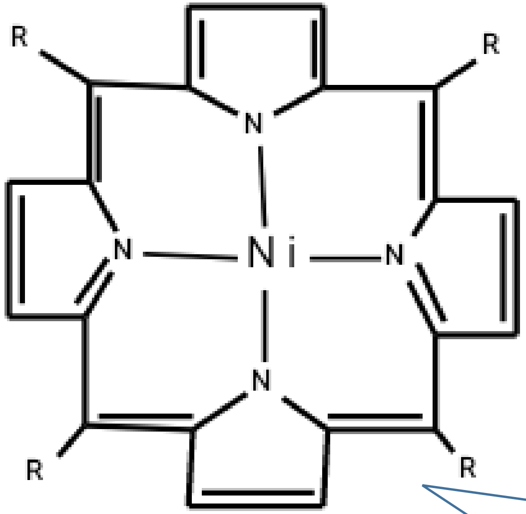


C





a. Free base Porphyrin



b. Metalloporphyrin

Try figuring the point group of the metalloporphyrin

Following the point group chart
Is the molecule linear? – No
Does it have high symmetry? – No
Is there a principle axis? – Yes (C_2)
Are there nC_2 axes perpendicular to the C_n? – Yes
Is there σ_h a perpendicular to the C_n? – Yes
The point group is D_{nh}, since the principle axis is C_2 then free base porphyrin belongs to **D_{2h}** point group

MODULE THREE

INTRODUCTION TO COORDINATION COMPOUDS (II)

- **Unit One –** What are coordination compounds?
- **Unit Two –** Naming coordination compounds
- **Unit Three –** (A) Coordination number and molecular structure

  (B) Types of ligands
- **Unit Four –**Isomerism in coordination compounds
- **Unit Five –** Crystal field theory

UNIT ONE

What are Coordination Compounds?

Coordination complexes are compounds which consist of a central metal atom or ions surrounded by a definite number of electron donating molecules or ions

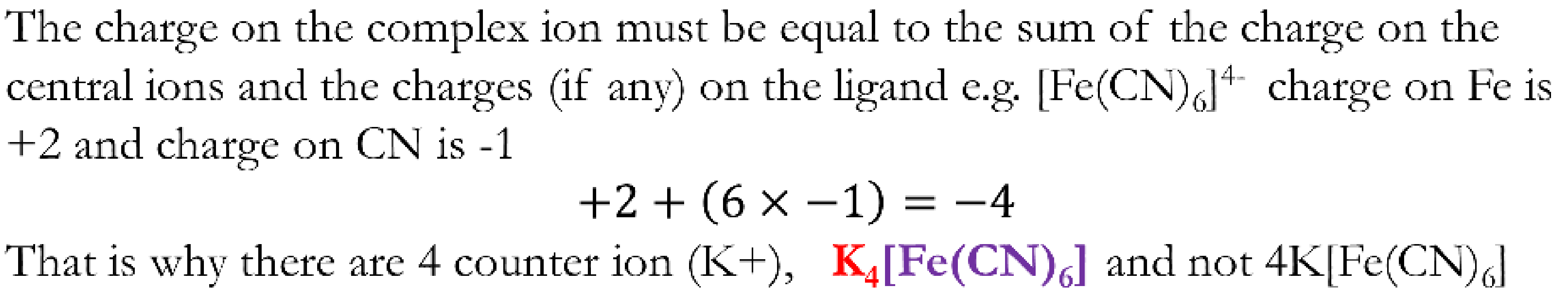
These molecules or ions surrounding the metals are referred to as **ligands**.
The central metal is usually **transition metals** this is because of the presence of vacant d or f orbitals for the ligands to donate their electrons.

A coordination complex maybe a neutral molecule or an ion and if it is positively charged it is called a cationic complex while the negatively charged complex is called an anionic complex.

Coordination compound are coloured. They exhibit magnetic properties such as being diamagnetic (no unpaired electrons) or paramagnetic (one or more unpaired electrons).

Double salts vs Coordination complexes

- Double salts and coordination complexes can appear similar especially in writing their formulae e.g. KCl. MgCl.6H_2O and $Fe(CN)_2$.4KCN.
- However, KCl.MgCl.6H_2O is a double salt when it's dissolved in water it gives rise to K^+, Mg^+, Cl^- ions.
- Whereas $Fe(CN)_2$.4KCN when dissolved in water does not form K^+, Fe^{2+}, and CN^- ions but rather K^+ and $[Fe(CN)_6]^{4-}$.
- $[Fe(CN)_6]^{4-}$ is a complex ion, hence $Fe(CN)_2$.4KCN is a coordination compound and is better written as $K_4[Fe(CN)_6]$.



The charge on the complex ion must be equal to the sum of the charge on the central ions and the charges (if any) on the ligand e.g. $[Fe(CN)_6]^{4-}$ charge on Fe is +2 and charge on CN is -1

$$+2 + (6 \times -1) = -4$$

That is why there are 4 counter ion (K+), $K_4[Fe(CN)_6]$ and not $4K[Fe(CN)_6]$

The number of ligands surrounding the central metal is called the **coordination number** of the complex and this is different from oxidation number of the complex.

$$[Fe(CN)_6]^{4-}$$

-4 is the oxidation number of the complex ion

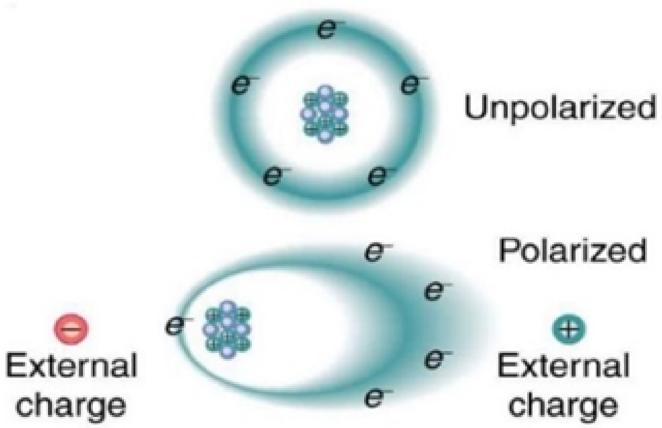
6 is the coordination number.

Oxidation number is referred to as the Primary/Principle Valence while coordination number is referred to as Secondary/Auxiliary valence

Hard and Soft Acids and Bases in Transition Metal Complexes.

- The interaction between the metal atom and the ligands are considered to be Lewis acid – base reactions.
- A Lewis base is an electron pair donor while Lewis acids are electron pair acceptor.
- So ligands are Lewis bases and the central metals are Lewis acids.
- The acids and the bases are classified as hard or soft.
- Hardness means that acid or base is not easily polarized.
- Softness means that they are easily polarized.

		oft
Acid	Mn^{2+}, Zn^{2} etc	+, Pd^{+}, Fe^{2+}, Co^{2+}, Cu^{2}
Base	F^{-}, Cl^{-}, NH	

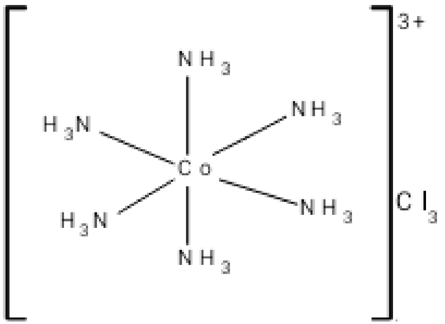


Hard acids soft acids to soft bases.

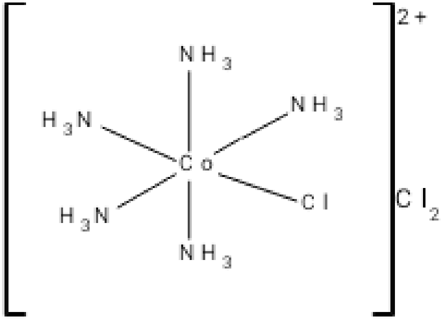
WERNER'S THEORY OF COORDINATION COMPOUNDS

Alfred Werner got the Nobel prize of chemistry in 1913 for his coordination theory of transition metal-amine complexes.

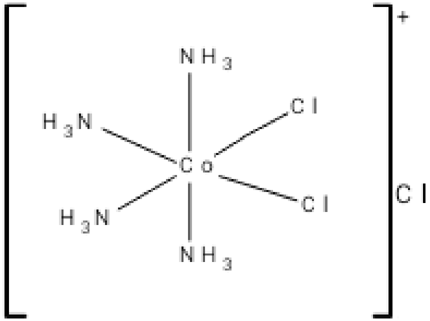
$$\boxed{CoCl_3 + XNH_3 \rightarrow aminecobalt\ complex}$$



In solution 3 moles of Cl^- is produced



In solution 2 moles of Cl^- is produced



In solution 1 mole of Cl^- is produced

Just like NaCl will dissociate in water to produce Na^+ and Cl^- same thing with $AlCl_3$

$Al^{3+} + 3Cl^-$ →

Postulate of Werner’s theory

- In coordination compounds, the central metal atoms exhibit primary valence and secondary valence. The primary valence is ionizable and the secondary one is not. The primary valence corresponds to oxidation state the secondary valence corresponds to the coordination number.
- Every metal atom has a fixed number of secondary valences (coordination number(s)).
- The metal atom tends to satisfy both its primary valence as well as the secondary valence. The primary valence is satisfied by negative ions because the metal ion has positive charge whereas the secondary valence is satisfied either by negative ions or by neutral molecules.
- The secondary valences are always directed towards the fixed position in the space and this lead to definite geometry of the coordination compound.

Limitation of Werner’s theory

- It failed to explain why all elements do not form coordination compounds.
- It failed to explain the directional properties of bond in coordination compounds.
- It does not explain the colour, magnetic and optical properties of these compounds.

END OF UNIT ONE

Naming Coordination Complexes

The rules for naming coordination compounds are as following:

1. The **cation** is named before the anion. This rule holds whether the complex ion is negatively charged or positively charge. For example, in $K_4[Fe(CN)_6]$ and $[Co(NH_3)_4Cl_2]Cl$; K^+ and $[Co(NH_3)_4Cl_2]^+$ are the cations and are named first.

2. Within a complex ion the ligands are named first, and the metal ion is named last.

3. The names of the anionic ligand end with the letter o, whereas a neutral ligand is usually called by the name of the molecule except for H_2O, CO, and NH_3.

4. When there are more than one ligands present, we use the Greek prefixes di-(2), tri-(3), tetra-(4), penta-(5), and hexa- (6) to name. For example $[Co(H_2O)_6]^{3+}$ will be *hexaaquocobalt or hexaaquacobalt.*

5. When there are different ligands the ligands are names in alphabetical order. Thus the ligands in the cation $[Co(NH_3)_4Cl_2]^+$ are "*tetraamminedichloro*".

6. If the name of the ligand contains a Greek prefix, we use the prefixes *bis-*(2) , tris-(3), and tetrakis-(4) to indicate the number of ligands present. For example, the ligand *ethylene**di**ammine* already contain the word '*di*' which is a Greek word therefore if two of such ligands are present, the name will be *bis(ethylene**di**ammine).*

7. The oxidation number of the metal in Roman numerals following the name of the metal. For example the Roman numerals III is used to indicate the +3 oxidation state of Co in $[Co(NH_3)_4Cl_2]^+$ which is called *tetraaminedichlorocobalt(III) ion.* (no space between the name of the metal and its oxidation state).

8. If the complex is an anion, its name ends in –**ate**. For example, in $K_4[Fe(CN)_6]$, the anion $[Fe(CN)_6]^{4-}$ is called hexacyanoferrate(II) ion. Note that the Roman numeral II indicates the oxidation state of iron.

9. In writing the name of the **complex ion** there must be **no space between the name.**

10. In writing the chemical formula of a complex the ligands are writing is a circle brackets ( ) while the complex ion is written in square brackets [ ].

11. The counter ion (if present) are written outside the square brackets – before the square brackets if it is a cation e.g. $K_3[Fe(CN)_6]$ and after the square brackets if it is an anion e.g. $[Cr(H_2O)_6]Cl_3$.

12. Structurally the complex ion is drawn showing all bonds between the metal and the ligands. This are then placed a large square bracket forming what is called the coordination sphere while its counter ion placed before or after the bracket (outside the coordination sphere).

$[Cr(H_2O)_6]Cl_3$

Hexaaquochronium(III) chloride

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

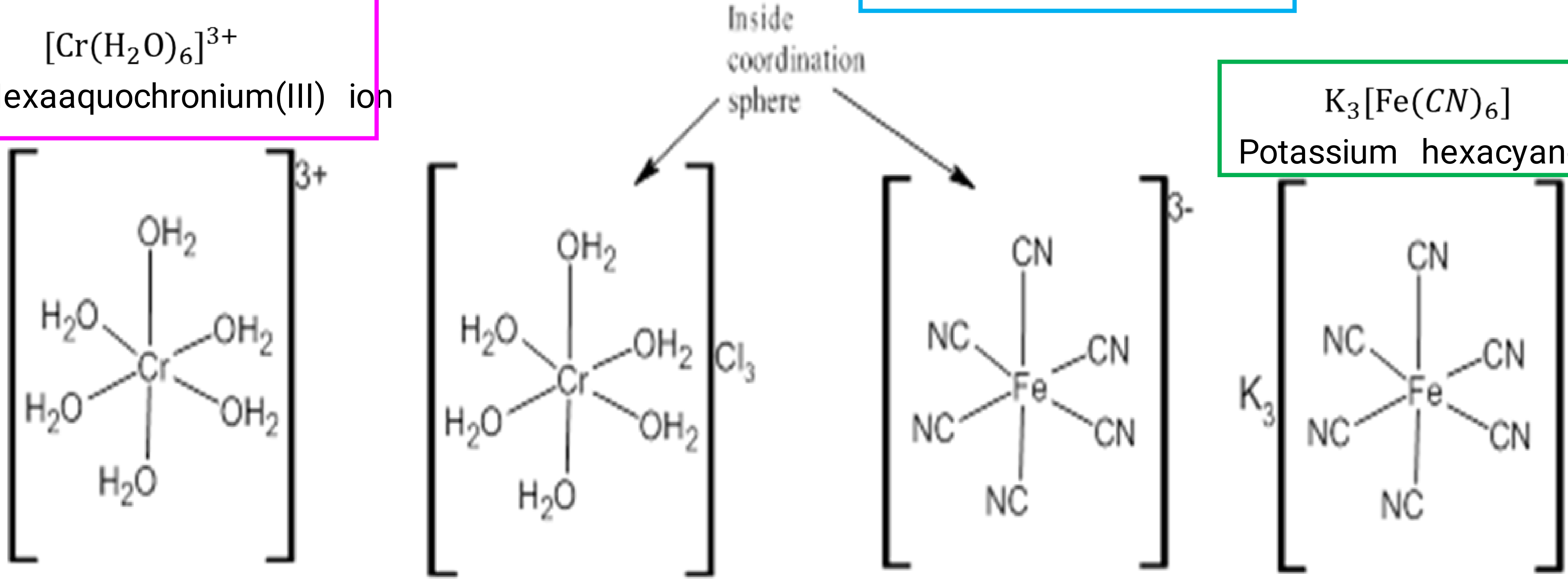
Hexacyanoferrate(III) ion

$[Cr(H_2O)_6]^{3+}$

Hexaaquochronium(III) ion

$K_3[Fe(CN)_6]$

Potassium hexacyanoferrate(



Cationic complex

Complex salt

Anionic complex

Complex salt

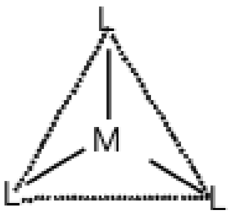
END OF UNIT TWO

UNIT THREE

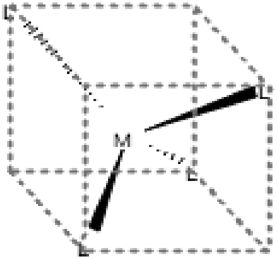
(A) Coordination Number and Molecular Structure

L —— M —— L

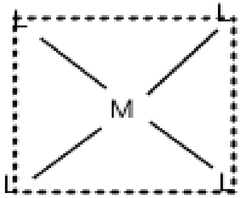
Coordination nọ = 2
Shape = Linear



Coordination nọ = 3
Shape = Trigonal Planar

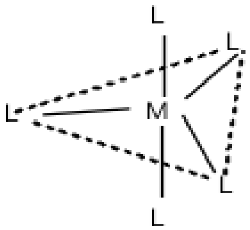


Tetrahedral

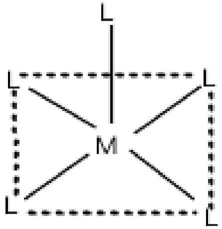


Square Planar

Coordination nọ = 4

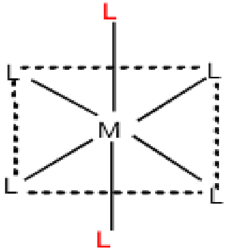


Trigonal bipyramidal

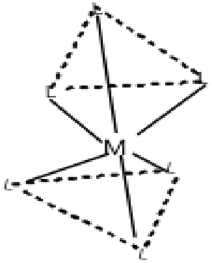


Square-based pyramid

Coordination nọ = 5



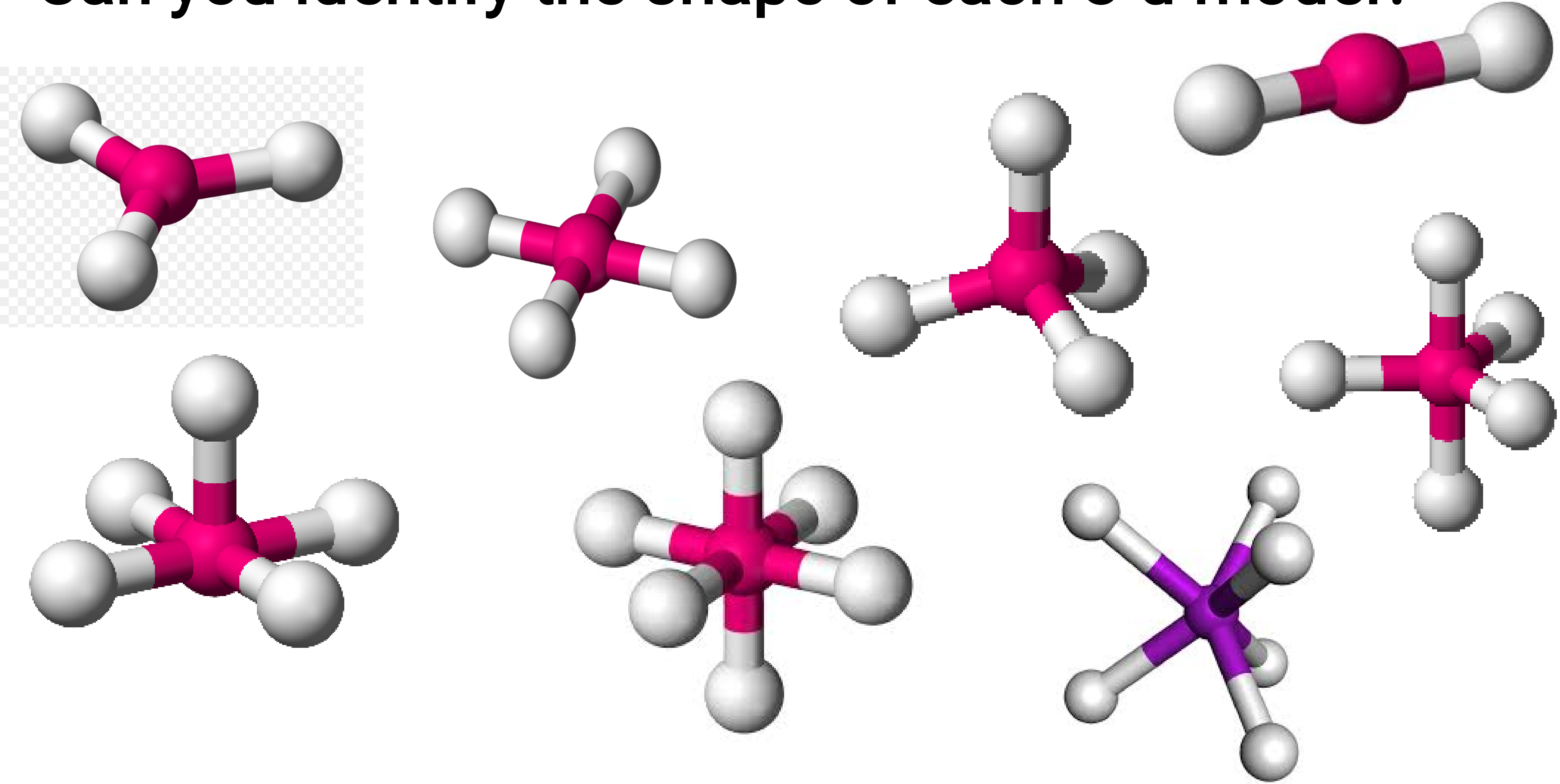
Octahedral



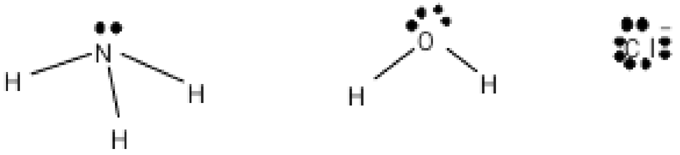
Trigonal prism

Coordination nọ = 6

Can you identify the shape of each 3-d model?

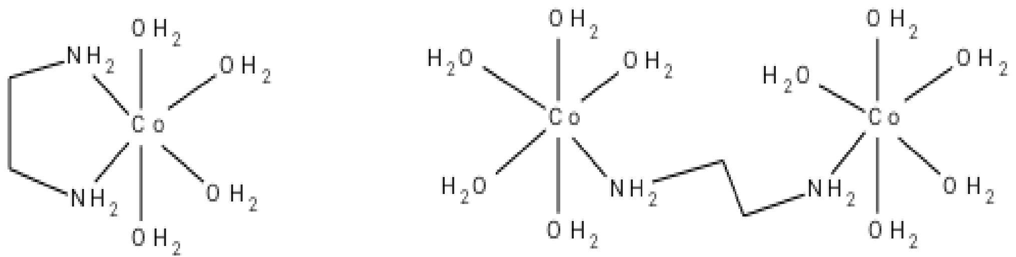


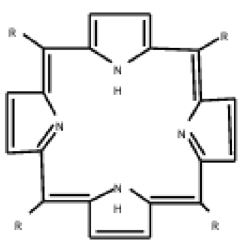
(B) Types of Ligand



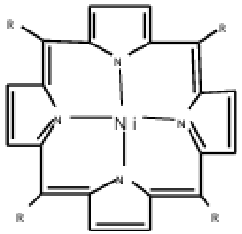
Monodentate ligand

Polydentate ligands

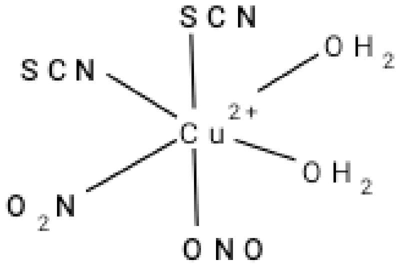




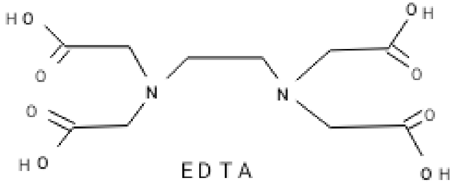
a. Porphyrin



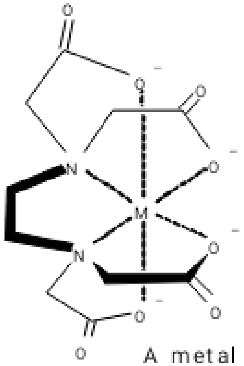
b. Metalloporphyrin



Ambidiedante ligand



EDTA



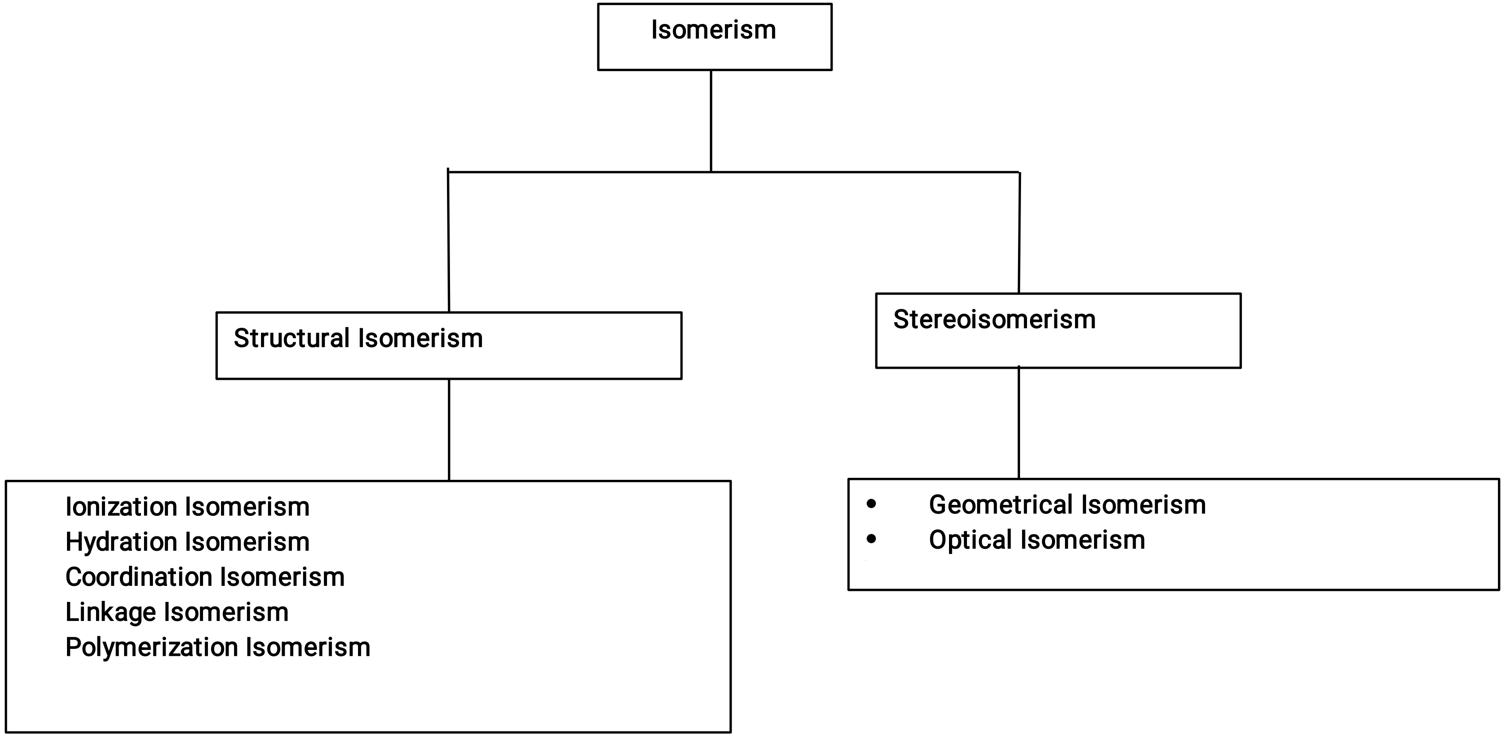
A metal coordianted to the EDTA, forming a chelate

Chelating ligands

END OF UNIT THREE

UNIT FOUR

Isomerism in Coordination Compounds

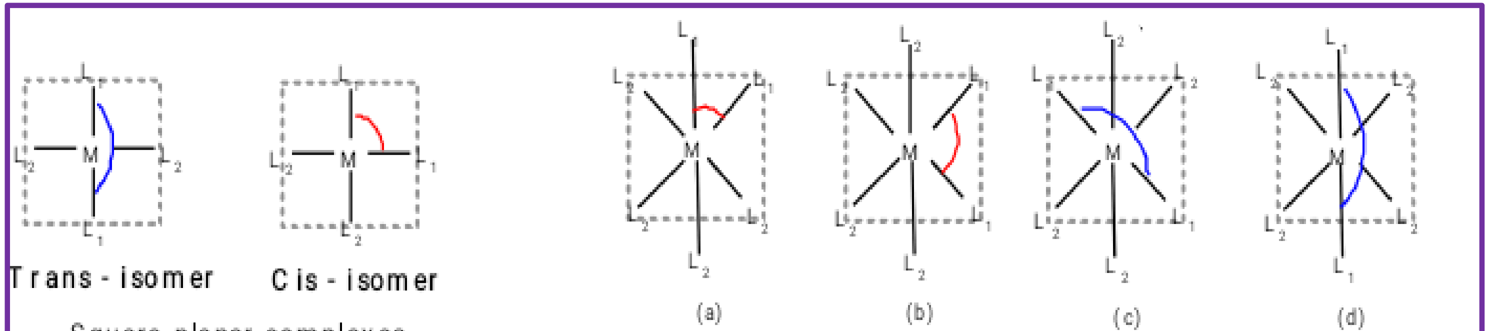


- Isomerism
  - Structural Isomerism
    - Ionization Isomerism
    - Hydration Isomerism
    - Coordination Isomerism
    - Linkage Isomerism
    - Polymerization Isomerism
  - Stereoisomerism
    - Geometrical Isomerism
    - Optical Isomerism

Structural Isomerism

Type of isomerism	Examples
Ionization Isomerism	$[Co(NH_3)_5\mathbf{Br}]\mathbf{SO_4}$ (violet in colour) $[Co(NH_3)_5\mathbf{SO_4}]\mathbf{Br}$ (red in colour)
Hydration Isomerism	$[Cr(H_2O)_4Cl_2]Cl\cdot 2H_2O$ – Green $[Cr(H_2O)_5Cl]Cl_2\cdot H_2O$ – Blue green $[Cr(H_2O)_6]Cl_3$ – Violet
Coordination Isomerism	$[Co(NH_3)_6]$ $\mathbf{[Cr(CN)_6]}$ and $[Cr(NH_3)_6]$ $\mathbf{[Co(CN)_6]}$ $[Co(NH_3)_6]$ $\mathbf{[Co(NO_2)_6]}$ and $[Co(NH_3)_4(NO_2)_2]$ $\mathbf{[Co(NH_3)_2\ (NO_2)_4]}$
Linkage Isomerism	Co–NCS Isothiocyanate Co–SCN Thiocyanate
Polymerization Isomerism	$[Pt(NH_3)_2(Cl)_2]$ $(Pt_nN_{2n}H_6Cl_{2n})$ {n =1} $[Pt(NH_3)_4]\ [Pt\ (Cl)_4]$ $(Pt_nN_{2n}H_6Cl_{2n})$ {n =2}

Geometrical Isomerism



Trans - isomer

Cis - isomer

Square planar complexes

Cis - isomer

Trans - isomer

Octahedral complexes

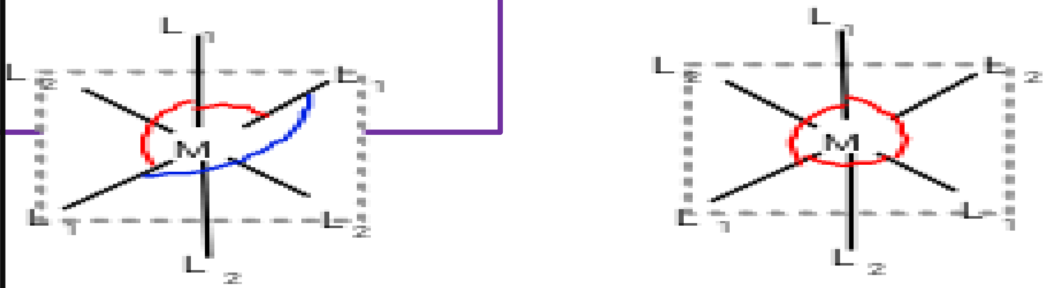
M - central metal

L_1 and L_2 are different ligands

Using L_1 as reference point

90° - represented in red

180° - represented in blue



mer -

fac-

M - central metal

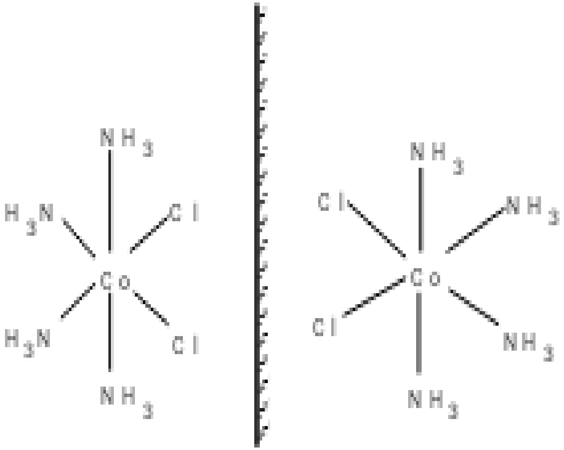
L_1 and L_2 are different ligands

Using L_1 as reference point

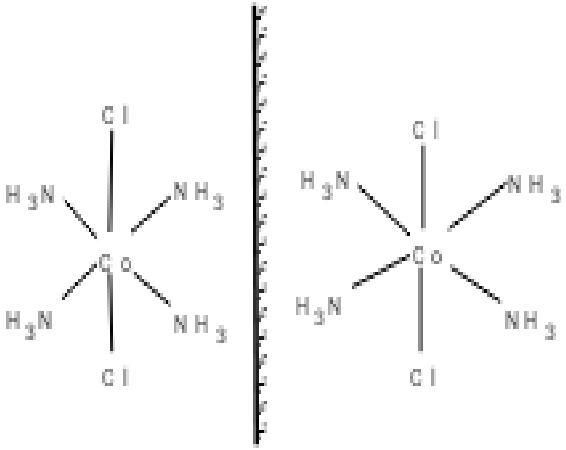
90° - represented in red

180° - represented in blue

Optical Isomerism



These are non-superimposable mirror image hence they are optically active and are enantiomers

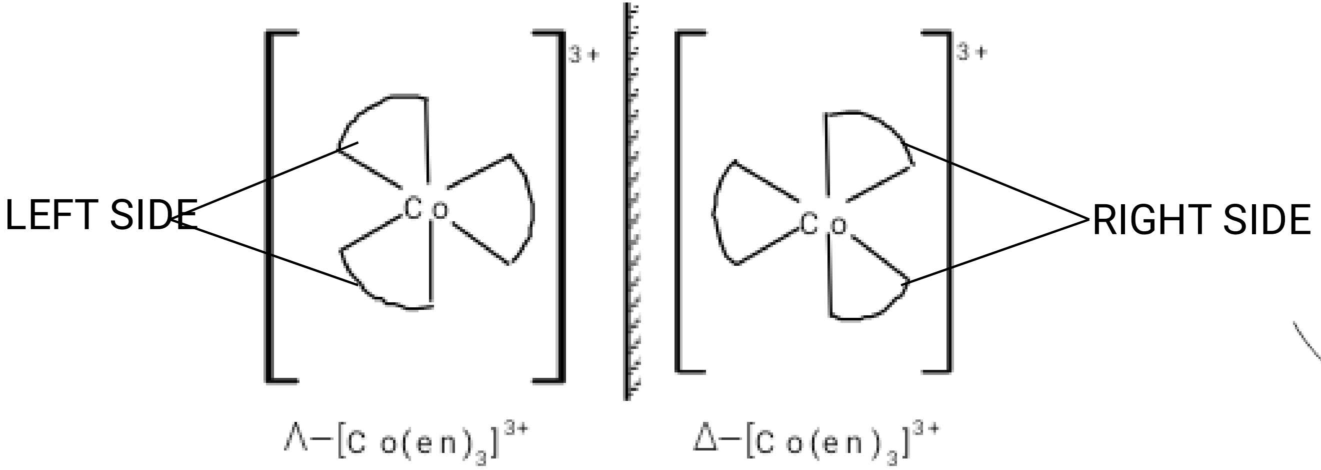


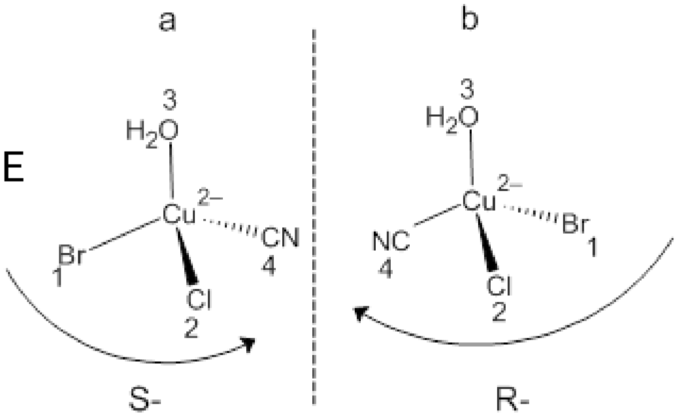
These are superimposable mirror image therefore are not optically active and are diastereomers

One rotates towards the left would be labeled as (l)-[Co(NH_3)$_4$(Cl)$_2$] or (-)-[Co(NH_3)$_4$(Cl)$_2$]

The one that rotate right would be labeled as (d)-[Co(NH_3)$_4$(Cl)$_2$] or (+)-[Co(NH_3)$_4$(Cl)$_2$]

More on Optical Isomerism





Λ- and Δ- isomerism

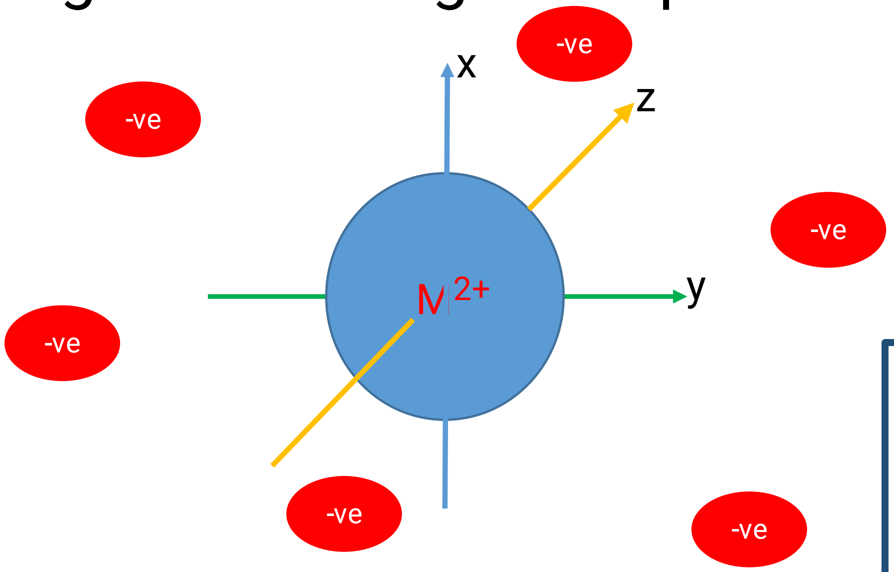
R- and S- isomerism

END OF UNIT FOUR

UNIT FIVE

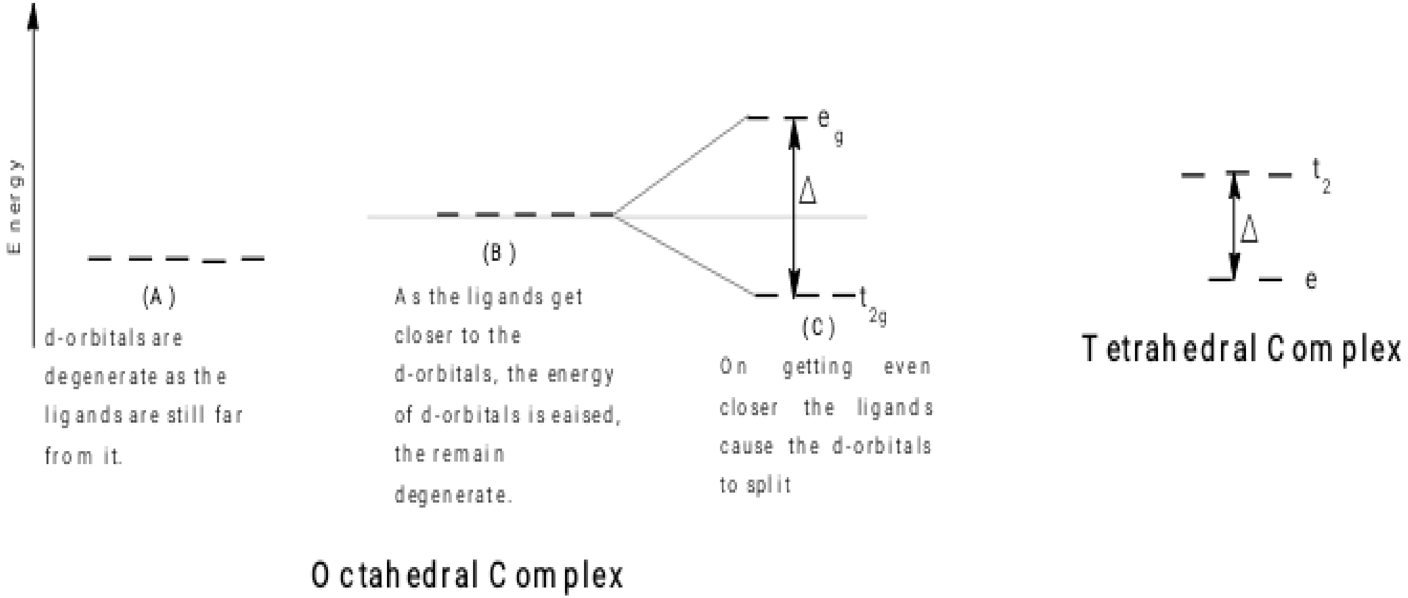
Crystal Field Theory (CFT)

This theory explains the bonding between metals and ligands to be electrostatic where the metal is positively charged and the ligands are negative spherical point charge.



***Valence Bond theory (VBT)** describes the bonds between the metal and the ligand as coordinate bond, where the ligand donates loan pair(s) of electrons to the vacant d or f orbital of the metal.

***Ligand Field theory (LFT)** describes the bonds between metal and ligand overlapping of the atomic orbitals of metal with ligand group of orbitals to form molecular orbitals. It is based on molecular orbital theory. It takes into account both ionic and covalent interactions.



d-orbitals are degenerate as the ligands are still far from it.

As the ligands get closer to the d-orbitals, the energy of d-orbitals is eaised, the remain degenerate.

On getting even closer the ligands cause the d-orbitals to split

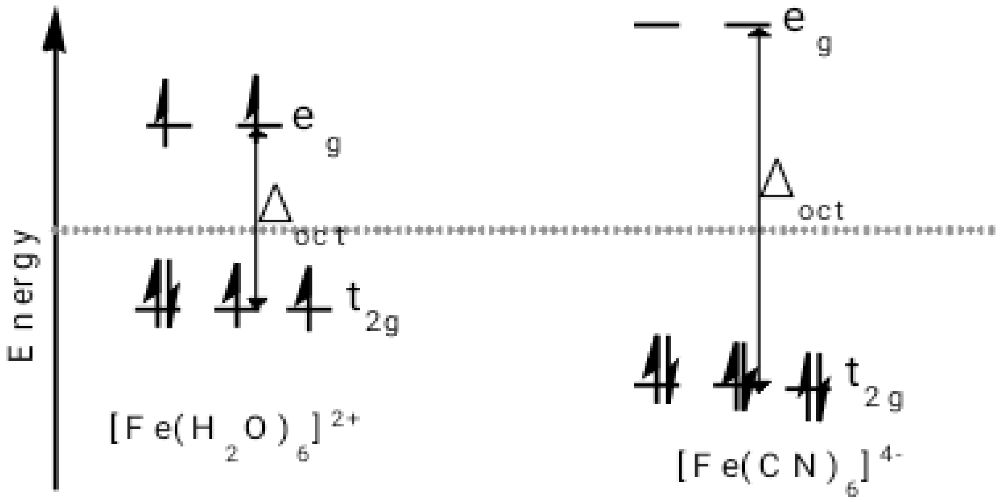
A. Before the ligands approach the metal the d-orbitals are degenerate (i. e. equal in energy).
B. Although the electrons of the ligands are attracted to the central ion but as the ligands approach closer to the metal ion there is also repulsion between the electrons in d-orbitals and the electrons of the ligands.
C. This effect raises the energy of the d-orbital and consequently split them. The direction of approach of the ligand to the d-orbitals affect the type of splitting that occurs.

- **The magnitude (size) of Δ depends on the strength of the ligands.**

$I^- < Br^- < [NCS]^- < Cl^- < F^- < [OH]^- < [ox]_2^- \approx H_2O < [NCS]\text{-} < NH_3 < en < bpy < phen < [CN]\text{-} \approx CO$

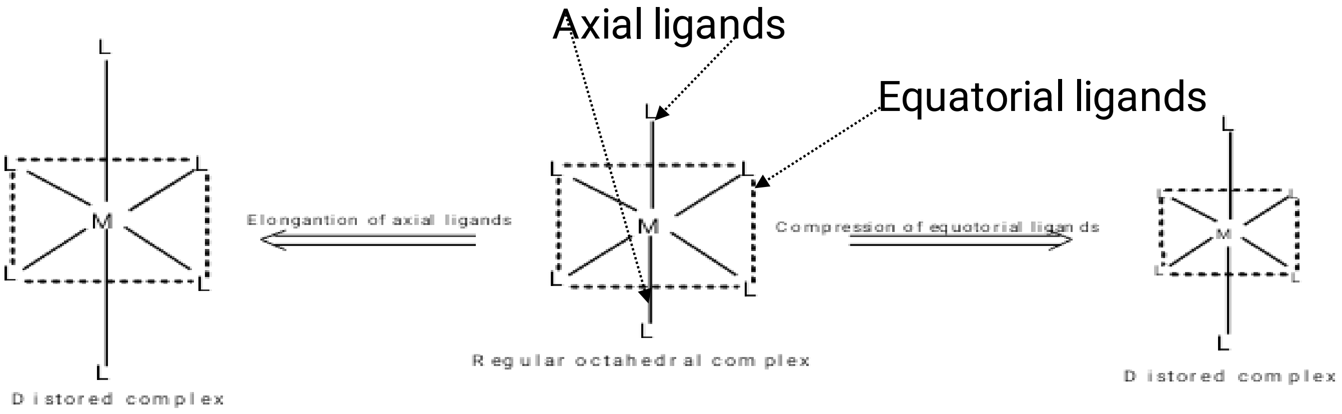
Weak field ligands ← → Strong field ligands

- **Strong field ligands force**



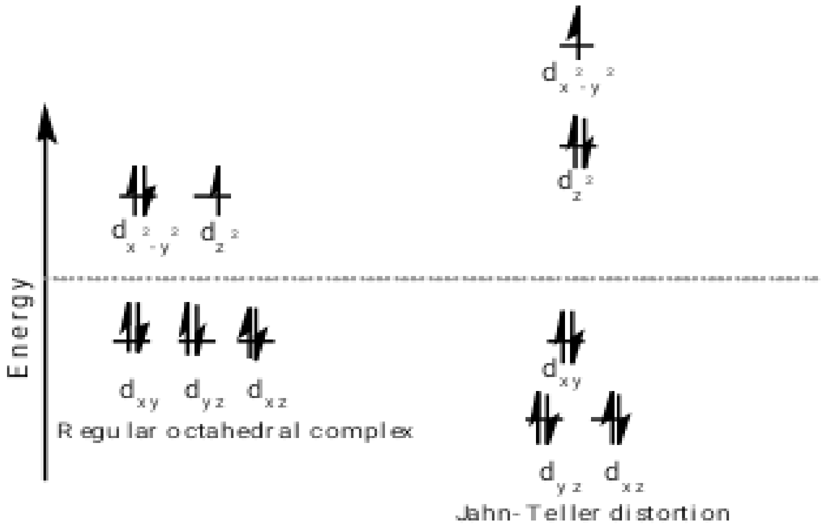
- **In the presence of weak field ligands the complex is high spin because there is no force pairing**
- **In strong field ligands which then forces pairing the complex is described as being low spin.**

Jahn-Teller Distortion



Axial ligands

Equatorial ligands



The asymetrical filling of the e_g orbital caused the distortion

Lability and Inertness

- If the crystal field splitting is wide an incoming ligand will not be able to substitute it such a complex is inert.
- chelating ligand cause inertness.
- The more filled the d-orbitals the more labile hence d^{10} ion of Zn^{2+}, Cd^{2+} and Hg^{2+} are very labile.
- Across the 3d period, M^{2+} ions are labile and Cu^{2+} is most labile due to distortions.
- d-metal complexes with d^3 (Cr^{3+}), and low-spin d^6 configuration like Fe^{2+} and Co^{3+} are inert.
- High charge and small size results in inertness.

THE END

MODULE THREE

INTRODUCTION TO COORDINATION COMPOUNDS II

- **Unit One –** What are coordination compounds?
- **Unit Two –** Naming coordination compounds
- **Unit Three –** (A) Coordination number and molecular structure
  (B) Types of ligands
- **Unit Four –**Isomerism in coordination compounds
- **Unit Five –** Crystal field theory

UNIT ONE: What are Coordination Compounds?

Double salts and coordination complexes can appear similar especially in writing their formulae e.g. KCl.MgCl.6H_2O and $Fe(CN)_2$.4KCN. However, KCl.MgCl.6H_2O is a double salt when it's dissolved in water it gives rise to K^+, Mg^+, Cl^- ions. Whereas $Fe(CN)_2$.4KCN when dissolved in water does not form K^+, Fe^{2+}, and CN^- ions but rather K^+ and $[Fe(CN)_6]^{4-}$. $[Fe(CN)_6]^{4-}$ is a complex ion, hence $Fe(CN)_2$.4KCN is a coordination compound and is better written as $K_4[Fe(CN)_6]$.

Coordination complexes are compounds which consist of a central metal atom or ions surrounded by a definite number of electron donating molecules or ions. These molecules or ions surrounding the metals are referred to as ligands. The central metal is usually transition metals this is because of the presence of vacant d or f orbitals for the ligands to donate their electrons. A coordination complex maybe a neutral molecule or an ion and if it is positively charged it is called a cationic complex while the negatively charged complex is called an anionic complex.

The interaction between the metal atom and ligand are considered to be as Lewis acid-base reaction. Lewis bases are electron pair donor while Lewis acids are electron pair acceptor. So the ligands are Lewis base and the central metals are Lewis acid.

The charge on the complex must be equal to the sum of the charge on the central ions and the charges (if any) on the ligand e.g. $[Fe(CN)_6]^{4-}$ charge on Fe is +2 and charge on CN is -1

$$+2 + (6 \times -1) = -4$$

The number of ligands surrounding the central metal is called the **coordination number** of the complex and this is different from oxidation number of the complex.
$[Fe(CN)_6]^{4-}$

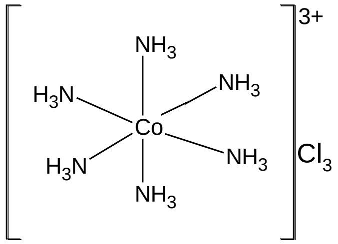
-4 is the oxidation number of the complex ion

6 is the coordination number.

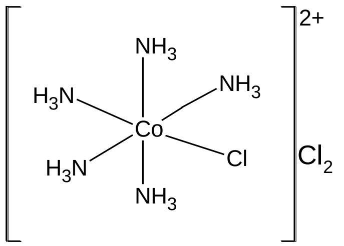
Oxidation number is referred to as the Primary/Principle Valence while coordination number is referred to as Secondary/Auxiliary valence. Primary valences are non-directional while secondary valences are directional.

Werner's Theory of Coordination Compounds

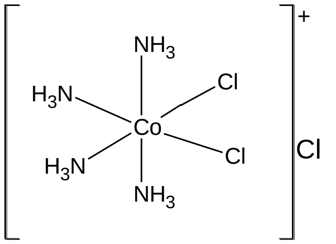
Alfred Werner got the Nobel prize of chemistry in 1913 for his coordination theory of transition metal-amine complexes. He carried out a series of experiments with reacting $CoCl_3$ and various concentrations of ammonia form various amminechlorocobalt(III) complexes then titrating against $AgNO_3$ to determine the amount of chloride in the solution. For 3 different solutions he found that each had varied concentration of chloride ion. One had an equivalent of 3 moles of chloride ion, the other 2 moles and another just 1 mole. He concluded that the structure of these complexes were as



In solution 3 moles of Cl^- is produced



In solution 2 moles of Cl^- is produced



In solution 1 mole of Cl^- is produced

Postulate of Werner's theory

1. In coordination compounds, the central metal atoms exhibit primary valence and secondary valence. The primary valence is ionizable and the secondary one is not. The primary valence corresponds to oxidation state the secondary valence corresponds to the coordination number.
2. Every metal atom has a fixed number of secondary valences (coordination number(s)).
3. The metal atom tends to satisfy both its primary valence as well as the secondary valence. The primary valence is satisfied by negative ions because the metal ion

has positive charge whereas the secondary valence is satisfied either by negative ions or by neutral molecules.

4. The secondary valences are always directed towards the fixed position in the space and this lead to definite geometry of the coordination compound.

Limitation of Werner's theory

1. It failed to explain why all elements do not form coordination compounds.
2. It failed to explain the directional properties of bond in coordination compounds.
3. It does not explain the colour, magnetic and optical properties of these compounds.

UNIT TWO - Naming Coordination Compounds

The rules for naming coordination compounds are as following:

1. The cation is named before the anion. This rule holds whether the complex ion is negatively charged or positively charge. For example, in $K_4[Fe(CN)_6]$ and $[Co(NH_3)_4Cl_2]Cl$; K^+ and $[Co(NH_3)_4Cl_2]^+$ are the cations and are named first.

2. Within a complex ion the ligands are named first, in alphabetical order, and the metal ion is named last.

Ligand	Abbreviation	Name of ligand in coordination compound
Bromide Br^-		Bromo
Chloride Cl^-		Chloro
Cyanide $\mathbf{C}N^-$		Cyano
Hydroxide $\mathbf{O}H^-$		Hydroxo
Oxide O^{2-}		Oxo
Carbonate CO_2^{3-}		Carbonate
Nitrite NO^{2-}		Nitro
Oxalate $C_2O_4^{2-}$	$[ox]^{2-}$	Oxalato
Ammonia $\mathbf{N}H_3$		Ammine
Carbon monoxide $C\mathbf{O}$		Carbonyl
Water $H_2\mathbf{O}$		Aquo
Ethylenediamine $H_2\mathbf{N}CH_2CH_2\mathbf{N}H_2$	en	Ethylenediamine
Acetylacetonate $CH_3C\mathbf{O}CH_2C\mathbf{O}CH_3$	$[acac]^-$	Acetoacetate
Ethylenediaminetetraacetate $(^-\mathbf{O}OC)_2\mathbf{N}CH_2CH_2\mathbf{N}(CO\mathbf{O}^-)_2$	$[EDTA]^{4-}$	Ethylenediaminetetraacetate

3. The names of the anionic ligand end with the letter o, whereas a neutral ligand is usually called by the name of the molecule except for H_2O, CO, and NH_3.

4. When there are more than one ligands present, we use the Greek prefixes di-(2), tri-(3), tetra-(4), penta-(5), and hexa- (6) to name. For example $[Co(H_2O)_6]^{3+}$ will be *hexaaquocobalt.*

5. When there are different ligands the ligands are names in alphabetical order. Thus the ligands in the cation $[Co(NH_3)_4Cl_2]^+$ are "*tetraamminedichloro*".

6. If the name of the ligand contains a Greek prefix, we use the prefixes *bis*-(2), tris-(3), and tetrakis-(4) to indicate the number of ligands present. For example, the ligand *ethylenediammine* already contain the word '*di*' which is a Greek word therefore if two of such ligands are present, the name will be *bis(ethylenediammine)*.

7. The oxidation number of the metal in Roman numerals following the name of the metal. For example the Roman numerals III is used to indicate the +3 oxidation state of Co in $[Co(NH_3)_4Cl_2]^+$ which is called *tetraaminedichlorocobalt(III) ion*.

8. If the complex is an anion, its name ends in –ate. For example, in $K_4[Fe(CN)_6]$, the anion $[Fe(CN)_6]^{4-}$ is called hexacyanoferrate(II) ion. Note that the Roman numeral II indicates the oxidation state of iron.

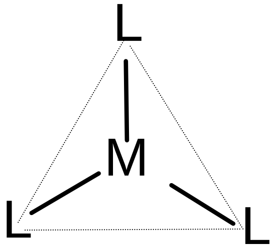
Metal	**Names of metal in anionic complex**
Aluminum	Aluminate
Chromium	Chromate
Cobalt	Cobaltate
Copper	Cuprate
Gold	Aurate
Iron	Ferrate
Lead	Plumbate
Manganese	Manganate
Molybdenum	Molybdate
Nickel	Nickelate
Silver	Argentate
Tin	Stannate
Tungsten	Tungstate
Zinc	Zincate

UNIT THREE – (A) Coordination Number and Molecular Structure

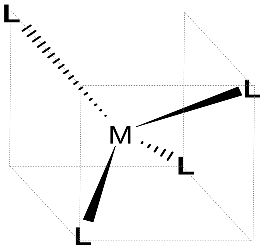
With the coordination number it is possible to predict the shape/structure of a complex. However further experimental data will be required to confirm the structure. Note here we will discuss only coordination number 2 - 6, however there are high coordination numbers up to 10.

Coordination number 2: They are uncommon and generally restricted to Cu(I), Ag(I), Au(I), and Hg(II) and all are d^{10} ions e.g. $[CuCl_2]^-$, $[Ag(NH_3)_2]^{2+}$, $[Au(CN)_2]^-$, $Hg(CN)_2$. The shape is LINEAR.

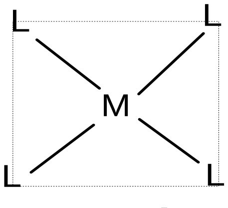
Coordination number 3: Their shape is TRIGONAL PLANAR e.g. $[Cu(CN)_3]^{2-}$, $[HgI_3]^-$



Coordination number 4: The shape is usually TETRAHEDRAL or SQUARE PLANAR but the tetrahedral is more common e.g. $[CoCl_4]^{2-}$, $[MnCl_4]^{2-}$ -tetrahedral geometry, $[PdCl_4]^{2-}$, $[AuCl_4]^-$ $[PtCl_4]^{2-}$ square planar.

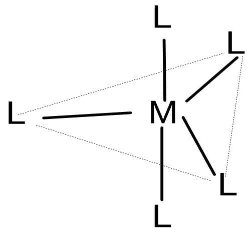


Tetrahedral

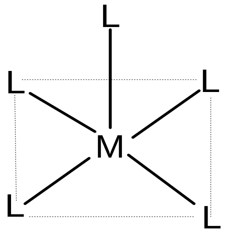


Square Planar

<u>Coordination number 5:</u> The usual shape is TRIGONAL BIPYRAMID or SQUARE BASED PYRAMID. For example, $[CdCl_5]^{3-}$, $[CuCl_5]^{3-}$ - trigonal bipyramid, $[WCl_4O]^-$, $[TcCl_4N]^-$ - square based pyramid.

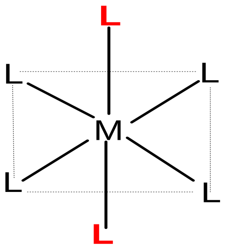


Trigonal bipyramidal

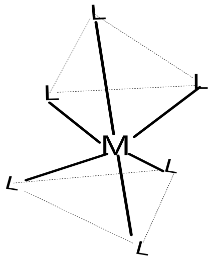


Square-based pyramid

<u>Coordination number 6:</u> This is another common coordination number. There shapes are usually OCTAHEDRAL or TRIGONAL PRISM. For example, $[TiF_6]^{2-}$, $[Ti(OH_2)_6]^{3+}$, $[Co(OH_2)_6]^{2+}$ - octahedral, $[Zr(CH_3)_6]^{2-}$ - trigonal prism



Octahedral



Trigonal prism

In octahedral complexes the 4 ligands (in black) that lie in the plane are the equatorial ligands and the two that are above and below the plane (in red) are axial ligands. The most commonly studied complexes are the octahedral, square planar and tetrahedral complexes

(B) TYPES OF LIGAND

<u>Monodentate Ligands</u>: these are ligands that use only I pair of electrons to bond to the central metal, for example H_2**O**, **N**H_3, Cl^- etc.

<u>Ambidientate Ligands:</u> are monodentate ligands that can bond to the central atom through either of the two or more donor atoms e.g. NO_2^- it can bond through the oxygen (ONO- nitrito) or through the nitrogen (NO_2 nitro). Another example is CSN^-

. This can bond through the Nitrogen ($\underline{\mathbf{N}}CS^-$ isothiocyanate) or through the sulphur ($\underline{\mathbf{S}}CN^-$ thiocyanate).

Polydentate Ligands: These ligands donate two or more pairs of electrons from different atoms in the ligand and to different sites in the structure of the complex. The specific names of such ligands are based on the number of donating sites. Below are few examples

a. Bidentate Ligands: the ligands donate two pairs of electrons e.g. ethylenediamine $H_2\underline{\mathbf{N}}CH_2CH_2\underline{\mathbf{N}}H_2$, oxalate ion $^-\underline{\mathbf{O}}_2C\text{-}C\underline{\mathbf{O}}_2^-$.

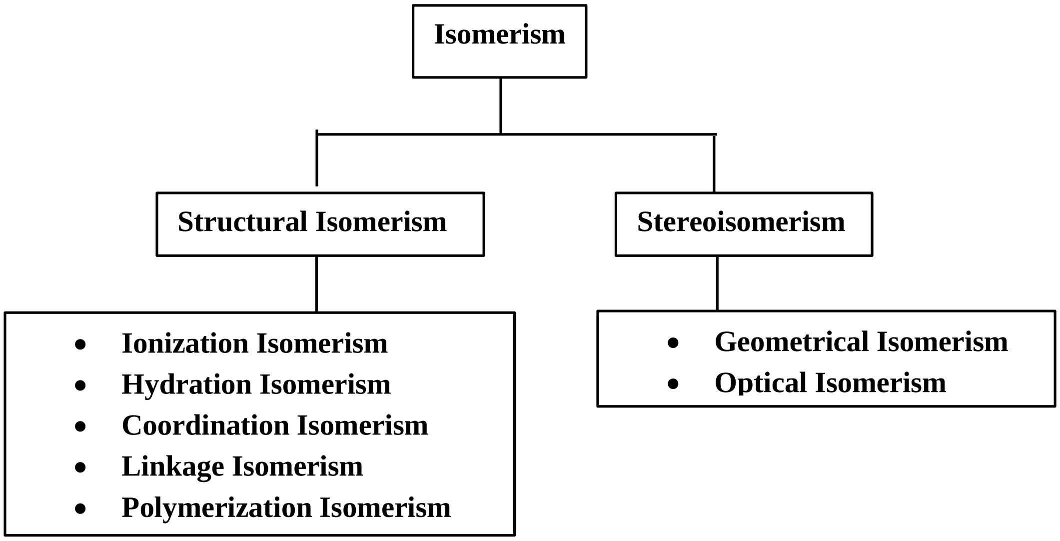
b. Tridentate Ligand: 3 pair of electrons e.g. diethylenetriamine $H_2\underline{\mathbf{N}}CH_2CH_2\underline{\mathbf{N}}HCH_2CH_2\underline{\mathbf{N}}H_2$

c. Tetradentate Ligand: Porphyrin

d. Hexadentate Ligand: 6 pairs of electron e.g. ethylenediaminetetraacetate ion (EDTA) $[(^-\underline{\mathbf{O}}OCCH_2)_2\underline{\mathbf{N}}CH_2CH_2\underline{\mathbf{N}}(CH_2CO\underline{\mathbf{O}}^-)_2]^{4-}$

Chelating Ligands: When a ligand attaches to the same central metal by two or more atoms forming a ring structure. The complex formed is called a chelate. Chelating ligands increase the stability of the complex.

UNIT FOUR - Isomerism in coordination compounds



Ionization Isomer: This occurs when there is an interchange of an anionic ligand that is inside the coordination sphere with another anionic ligand outside the coordination sphere e.g.

- $[Co(NH_3)_5Br]SO_4$ (violet in colour)
- $[Co(NH_3)_5SO_4]Br$ (red in colour)

Hydration Isomer: This arises when there is an interchange of H_2O and another ligand between the coordination sphere and outside of it e.g.

- $[Cr(H_2O)_4Cl_2]Cl \bullet 2H_2O$ – Green
- $[Cr(H_2O)_5Cl]Cl_2 \bullet H_2O$ – Blue green
- $[Cr(H_2O)_6]\ Cl_3$ – Violet

Coordination Isomer: These isomers are formed from the interchange of ligand between 2 different metal centers and can only happen if the salts which form the cation and anions are themselves complex ions e.g.

- $[Co(NH_3)_6]$ **$[Cr(CN)_6]$** and $[Cr(NH_3)_6]$ **$[Co(CN)_6]$**
- $[Co(NH_3)_6]$ **$[Co(NO_2)_6]$** and $[Co(NH_3)_4(NO_2)_2]$ **$[Co(NH_3)_2\ (NO_2)_4]$**

Linkage Isomer: this arises when one or more ligands can coordinate to a metal ion in more than one way e.g.

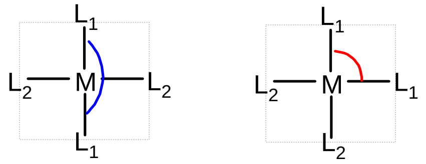
- $[Co(NH_3)_5(CSN)]Cl_2$ coordination can occur through S – atom or N – atom of the CSN ligand
  Co–**N**CS Isothiocyanate
  Co–**S**CN Thiocyanate
- $[Co(NH_3)_5(NO_2)]Cl_2$ coordination can occur through O – atom or N – atom of the NO_2 ligand
  Co–**O**NO Nitrito
  Co–**N**O_2 Nitro

Polymerization Isomer: These isomers have the same empirical formulae but different molecular masses e.g.

- $[Pt(NH_3)_2(Cl)_2]$ $(Pt_nN_{2n}H_6Cl_{2n})$ {n =1}
- $[Pt(NH_3)_4]$ $[Pt(Cl)_4]$ $(Pt_nN_{2n}H_6Cl_{2n})$ {n =2}

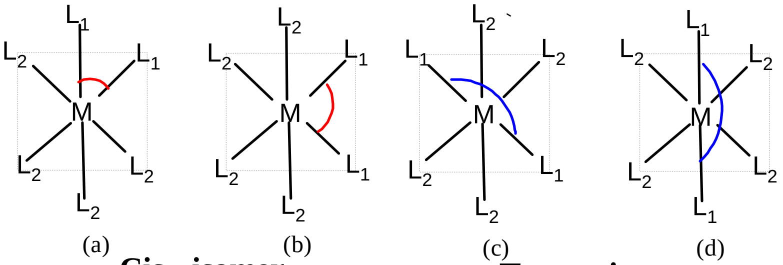
Geometrical Isomer: They have the same molecular formulae but different arrangement of their ligands in space. For coordination complexes there are two kinds.

a. Cis-Trans isomerism: here is the spatial arrangement of only 2 of the ligand especially in square planar and octahedral complexes.
   - For the cis- isomer the two ligands are at 90° to each other with respect to the central atom and so the bond angle between the 2 ligands is 90°.
   - Trans- isomers have the 2 ligands at 180° to each other i.e. opposite each other.



Trans - isomer **Cis - isomer**

Square planar complexes

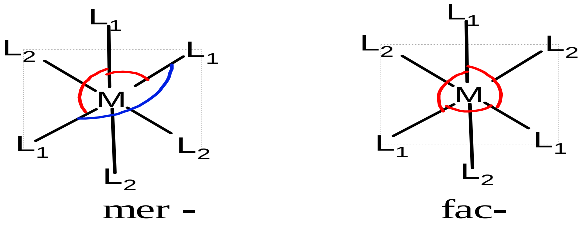


Cis - isomer **Trans - isomer**

Octahedral complexes

M - central metal
L_1 and L_2 are different ligands
Using L_1 as reference point
90^o - represented in red
180^o - represented in blue

b. Mer-Fac isomerism: here the spatial arrangement involves only 3 of the ligands and occurs in only octahedral complexes. For the fac- isomer the 3 ligands are at 90° to each other. For the mer- isomer 2 of the ligand would be at 90° to each other while the third one will be at 180° to one of the other 2.

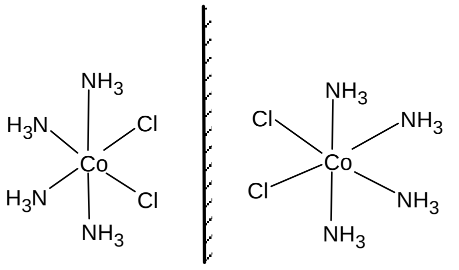


M - central metal
L_1 and L_2 are different ligands
Using L_1 as reference point
90° - represented in red
180° - represented in blue

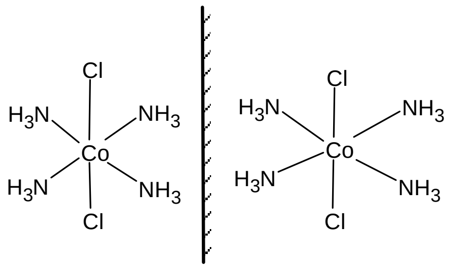
<u>Optical Isomers:</u> these are two complexes that are mirror images of each other. When these mirror images are not superimposable they are called enantiomers and if they are superimposable they are called diastereomer.

The mirror images can be distinguished by the direction they rotate in the presence of polarized light. The one that rotate towards the left direction is called Laevorotatory (l or -) and other will rotate toward the right called Dextrorotatory (d or +). The degree of rotation of enantiomers will be the same but in opposite direction (left and right) hence are optically active.

While for diasteromers they would move in the same direction and therefore optically inactive. So if $[Co(NH_3)_4(Cl)_2]$ is an enantiomer and have a degree of rotation of 24°, the one that rotate towards the left would be labeled as (l)-$[Co(NH_3)_4(Cl)_2]$ or (-)-$[Co(NH_3)_4(Cl)_2]$ and the one that rotate right would be labeled as (d)-$[Co(NH_3)_4(Cl)_2]$ or (+)-$[Co(NH_3)_4(Cl)_2]$

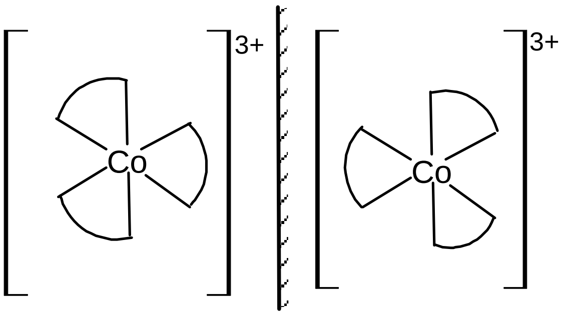


These are non-superimposable mirror image hence they are optically active and are enantiomers



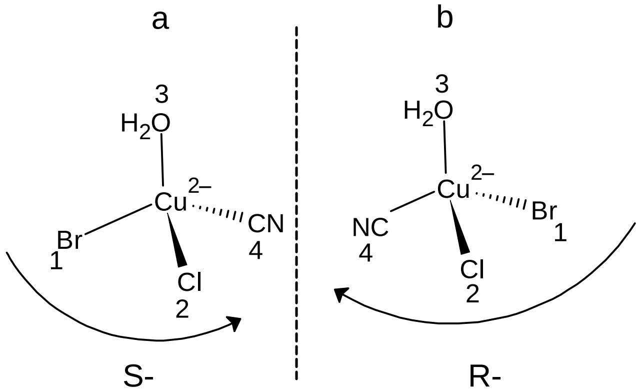
These are superimposable mirror image therefore are not optically active and are diastereomers

For octahedral chelating ligand containing 3 equivalent ligands the prefix would be Δ (delta) right handedness and Λ (lamda) for left handedness.



Λ–$[Co(en)_3]^{3+}$ Δ–$[Co(en)_3]^{3+}$

R and S prefixes is the convention for labelling tetrahedral complexes with four different groups attached. The four groups attached to metal atom are prioritized according to the atomic number of the attached atoms, highest priority being assigned to highest atomic number and the one with the lowest atomic number has the lowest priority and it is ignored. Here the atoms attached directly to the metal (Cu) are Br (35), Cl (17), O (8) and C (6). These atoms have been labelled 1 to 4 from highest to lowest. In 'a' moving from 1 to 3 is anticlockwise and in 'b' it is clockwise. The R- and S-labels for the enantiomers refer to a clockwise (rectus) and anticlockwise (sinister) moving from high to low priority:

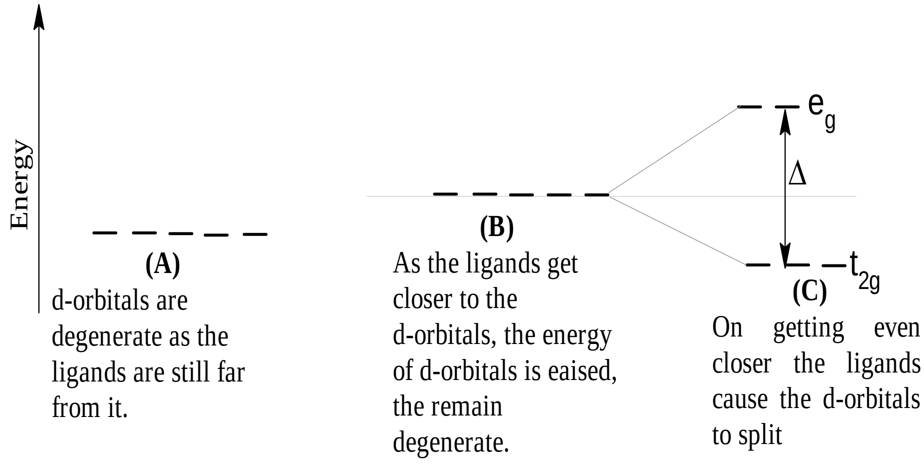


UNIT FIVE – Crystal Field Theory (CFT)

This is one of the theories used to explain the bonding in Transition metal complexes. Most of what has been discussed above is based on another theory, which is the Valence Bond theory (VBT). VBT describes the bond between the metal and the ligand as coordinate bond, where the ligand donates loan pair(s) of electrons to the vacant d or f orbital of the metal.

In CFT the bond described to be purely electrostatic. Here the metal being positively charged is attracts the ligands which are negatively charged spheres. Ligands of course are usually ions (Cl^-, Br^- etc) but for neutral ligands like ammonia or water, they dipoles. N and O are more electronegative that H and would draw the electron they share more towards themselves giving them a partial –ve charge (-δ) and the H would have a partial +ve charge (+δ). The –ve charged portion would now be attracted to the central metal (which is a cation).

A. Before the ligands approach the metal the d-orbitals are degenerate (i.e. equal in energy).
B. Although the electrons of the ligands are attracted to the central ion but as the ligands approach closer to the metal ion there is also repulsion between the electrons in d-orbitals and the electrons of the ligands.
C. This effect raises the energy of the d-orbital and consequently split them. The direction of approach of the ligand to the d-orbitals affect the type of splitting that occurs.

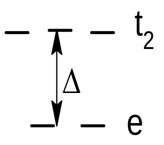


(A) d-orbitals are degenerate as the ligands are still far from it.

(B) As the ligands get closer to the d-orbitals, the energy of d-orbitals is eaised, the remain degenerate.

(C) On getting even closer the ligands cause the d-orbitals to split

Octahedral Complex



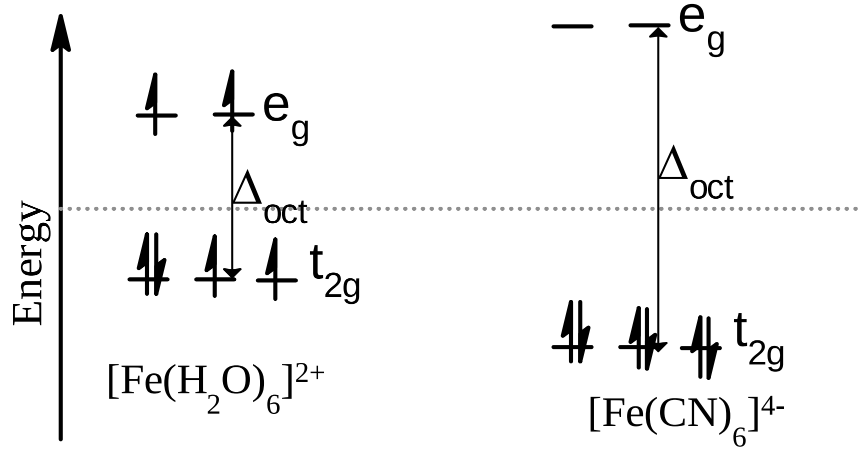
Tetrahedral Complex

The magnitude (size) of Δ depends on the strength of the ligands. Ligands that result in large values of Δ are referred to as strong field ligands and those that result in small values of Δ are called weak field ligands. The arrangement of ligands according to their field strength is called the spectrochemical series

$$I^- < Br^- < [NCS]^- < Cl^- < F^- < [OH]^- < [ox]^{2-} \approx H_2O < [NCS]^- < NH_3 < en < bpy < phen < [CN]^- \approx CO$$

Weak field ligands Strong field ligands

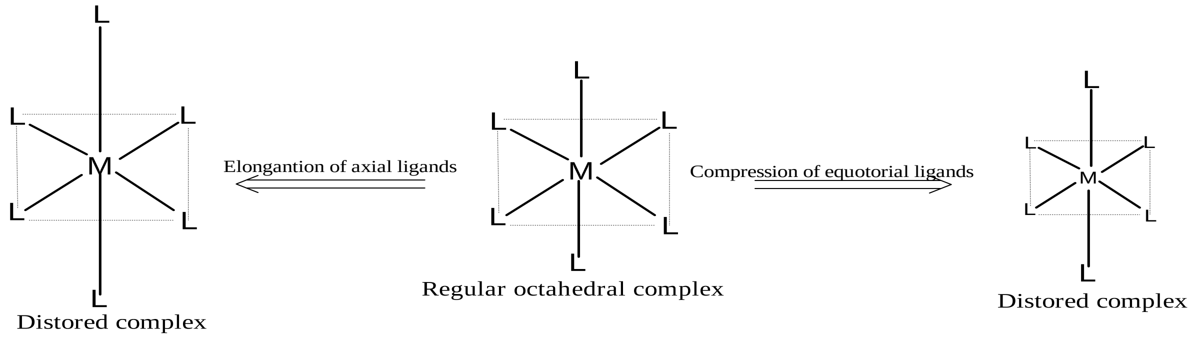
An increase in the crystal field splitting would result in force the electrons to pair. Strong field ligands force pairing because they cause the crystal field to split very wide such the electrons cannot move into e_g-orbitals and would rather be forced to pair in the t_{2g}. The same is applicable in a tetrahedral environment only this time instead of Δ_{oct}; Δ_{tet} would be used. (Remember to reverse the orbitals i.e. e comes down and t_2 goes up).



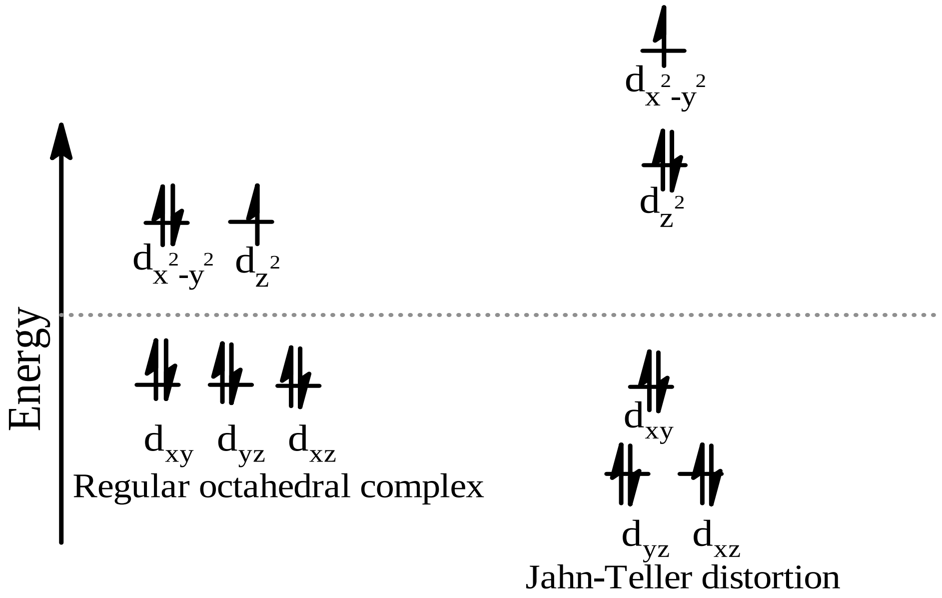
Coordination compound apart from being coloured they exhibit magnetic properties such as being diamagnetic (no unpaired electrons) or paramagnetic (one or more unpaired electrons). In the presence of weak field ligands the complex is said to have high spin however due to effect of strong field ligands which then forces pairing the complex is described as being low spin.

Jahn-Teller Distortion

Sometimes an octahedral complex undergoes distortion in its shape. This distortion can take place either by the elongation of the axial ligands or the compression of equatorial ligands.



This distortion is a manifestation of the Jahn-Teller effect and its referred to as tetragonal distortion. This effect occurs when the ground electronic configuration is asymmetrically filled making the geometry unstable and in order to bring about stability the distortion occurs. A common example is d^9 complexes of Cu(II).



The asymetrical filling of the e_g orbital caused the distortion

Lability and Inertness

Any metal complex that's undergoes reactions with $t_{\frac{1}{2}} \leq 1 \text{ min}$ at ordinary conditions (room temperature and about 0.1 M solution) is described as being kinetically labile. If the reaction takes significantly longer than this, the complex is kinetically inert. For example, iron(II) chloride was dissolved in water gives green solution on addition of few drops of cyanide solution it changes to purple. If conc NH_3 is added or water, there will be no change in the colour of the solution. This is because the cyano complex is inert and the aqou complex is labile.

1. If the crystal field splitting is wide an incoming ligand will not be able to substitute it such a complex is inert.
2. Very small ions are often less labile because they have greater M-L bond energy and it becomes sterically difficult for incoming ligands to approach the metal ion
3. chelating ligand cause inertness
4. d^{10} ion of Zn^{2+}, Cd^{2+} and Hg^{2+} are very labile
5. Across the 3d period, M^{2+} ions are labile and Cu^{2+} is most labile due to distortions.
6. d-metal complexes with d^3 and low-spin d^6 configuration like Cr^{3+}, Fe^{2+} and Co^{3+} are inert
7. High charge and small size results in inertness.
8. The more filled the d-orbitals the more labile.

CHM201

ACIDS AND BASES

Definition

- There are several theories to define the terms acids and bases
- The most relevant is a function of the system considered

[1] Arrhenius theory: Substances that produce Hin aqueous medium are called acids and those producing OH are bases

e.g $HCl \leftrightharpoons H + Cl$; $NaOH \leftrightharpoons Na + OH$

- Hydrogen ion concentration may be given in terms of pH

$pH = -\log[H]$

- Consider: $2H_2O \leftrightharpoons H_3O^+ + OH^-$
- $K_a = [H_3O^+] + [OH^-] / [H_2O]^2$ (K_a =equilibrium const)
- $K_w = [H_3O^+] + [OH^-] = 1 \text{ X } 10^{-14}\ mol^2L^{-2}$ ($[H_2O]$ is constant)
- Similarly the $pK_a = -logK_a$
- pK_a may also serve as a measure of the strength of an acid
- High acid strength= large K_a = small value of pK_a

- Variations in acid strength

i. Strength increases on moving from left to right on the PT

E,g:	methyl	ammonia	water	hydrogen fluoride
pK_a	46	35	16	3

ii. Acid strength increases on moving down a group

	HF	HCl	HBr	HI
pK_a	3	-7	-9	-10

iii. For oxoacids that contain more than one hydrogen atom, successive dissociation constant become more positive

Jv. When an element forms a series of oxoacids the more the oxygen atom the more acidic it is

[2] Bronwsted Lowry theory: Acids are proton donors and bases are proton acceptors

- This extends to non-aqueous systems e.g liquid NH_3 e.g: $NH_4Cl + NaNH_2$ ’n NaCl + $2NH_3$

- Identify the acid/base in the above reaction with reasons

- Conjugate pairs are species that differ in composition only by a proton

e.g in $HCl + H_2O \leftrightharpoons H_3O^+ + Cl^-$

Here Cl^- is the conjugate base of HCl and H_3O^+ is the conjugate acid of H_2O

- Acids are classified by the number of hydrogen ions available to be donated.
- *Monoprotic acids* have one hydrogen ion to donate.
- *Polyprotic acids* have two or more hydrogen ions to donate.

- All polyprotic acids donate one hydrogen ion at a time.

E.g:

$H_2SO_4(aq) + H_2O(l)\ H_3O^+(aq) + HSO^{4-}(aq)$ Ka = very large

- Homework:

1. Compare and contrast both theories
2. Give two limitations of the Bronsted-Lowry theory
3. List four examples of

i. Strong acids
ii. Weak acids
iii. Strong bases
iv. Weak bases

4. Suggest reasons why you classified each compound in question 3 above as such.

5. Consider the CHM 201 past questions and answers booklet and give answers to questions 48-54 for 2019/2020 session in your own words.

6. Consider question 53 and arrange the solutions given assuming:

  a. the acids are in aqueous solutions

  b. in concentrated forms

Give reasons to buttress your point.

NB: Kindly submit answers to the questions on or before 14th February to your individual class reps; who in turn should submit them to the Secretary to the Department of Chemistry to place them in my

Levelling and differentiating solvents

- Levelling solvents are solvents in which the strength of any acid or base in them are the same strength.
- ❖ As an example oxalic, sulphuric and nitric acid all ionize in water and have varying acid strength
- o However, in liquid ammonia, they all ionize completely.
- o ie they are all levelled (have similar strength) in liquid ammonia
- In differentiating solvents acids/bases dissociate to varying degrees, ie, they exhibit different strength.
- Eg, acetic acid; many mineral acids ionize partially in it,
- o However, (usual) bases, e.g NaOH ionize completely in it.
- o Therefore we may infer that a differentiating solvent for acids will act as a levelling solvent for bases and vise versa.

Lewis definition for acids and bases

- Acids are substances which accept electron pairs

These include:

a. Positive ions : Cu^{2+} , Ag^{+} , Co^{2+}
b. Molecules formed by elements in the first row of the periodic table with incomplete octet: BF_3 , $BeCl_2$
c. Compounds in which the central atom may exceed its octet by use of d-orbital, $TiCl_{4,}$ $SiCl_{4,}$

- Bases donate electron pairs

a. Negative ions F^{-} , OH^{-} , CN^{-}
b. molecules with lone pairs of electrons, e-g ammonia
c. molecules with C-C multiple bonds, $CH_2=CH_2$

Hard and soft acids and bases

- This theory proposes that soft acids react faster and form stronger bonds with soft bases. And hard acids react faster and form stronger bonds with hard bases, all other factors being equal.
- Hard acids have the following characteristics:
- Small atomic/ionic radius
- High oxidation state
- Polarizing in nature
- Eg: Ti^{4+} , Cr^{3+}, BF_3 , Cr^{6+}
- Hard bases : have high electronegativity, slightly polarizable: NH_3, CO_3^{2-} , F^- , OH^- , CH_3COO^-
- The affinity of hard acids and hard bases for each other is mainly ionic in nature.

- Soft acids and bases tends to have the following characteristics:
- Large atomic/ ionic radius
- Low/zero oxidation state
- Acids: negligible polarizability and bases: highly polarizable
- Low electronegativity (bases)
- Soft acids: Ag^{+} , CH_3Hg^{+} , $BH_{3,}$ Cd^{2+} , Pt^{2+} , Pd^{2+} , Hg^{2}
- Soft bases: I^{-} , H^{-} , SCN^{-} , R_3P

The affinity of soft acids and bases for each other is mainly covalent in nature

Oxidation and Reduction

- Many reactions occur by formal loss of electron by one atom and gain of electron by another.
- The process of electron gain is called reduction while that of loss of electron is known as oxidation
- Both are jointly called redox reaction
- Species that supply electrons are called reducing agent
- While the one that receives electrons is called oxidizing agent (Oxidant)
- $Zn_{(s)} + Cu^{2+}_{(aq)}$ ″ $Zn^{2+}_{(aq)} + Cu_{(S)}$

  $Zn_{(s)}$ ′n $Zn^{2+}_{(aq)}$ (oxidation; o.s of 0 to +2)

  $Cu^{2+}_{(aq)}$′n $Cu_{(S)}$ (reduction; o.s of +2 to 0)

Electrochemical cell

- An electrochemical cell is a device that produces an electric current from energy.
- They are of two types

I. Converts chemical energy to electrical energy: galvanic cell

II. Converts electrical energy chemical energy: electrolytic cell

- Galvanic cell
- Consists of two conductive electrode (the anode and cathode)
- Anode is the electrode where oxidation occurs
- Cathode is where reduction occurs
- In between both electrode is the electrolyte that contains free moving ions.
- The metal of the anode oxidize from 0 to a positive oxidation state
- The metal ion in solution will accept electrons from the cathode and the o.s of the ions becomes zero; resulting in solid metal deposited on the cathode.

- The two electrodes are electrically connected to each other allowing for a flow of electrons that leave the metal of the anode and flow through this connection to the ions at the surface of the cathode.
- A voltameter measures the change of electrical potential between the anode and cathode, this voltage is termed emf .
- The path of electrons in an electrochemical cell is shown using a cell diagram

  e.g $Zn | Zn^{2+}$ (1M) || Cu^{2+} (1M) | Cu

H/W

1. Draw an annotated diagram of a galvanic cell (Daniel cell) using the cell diagram shown above.

2.What does the double line (||) and (1M) from the ell diagram above represent

Electrode Potential and Standard Electrode Potential

- The potential difference between a metal and a solution containing its own ions (in equilibrium) is called electrode potential of that metal (electrode).
- The magnitude of the electrode potential of a metal is a measure of its relative tendency to lose or gain electrons.
- This implies that it is a measure of the relative tendency of the metal to undergo oxidation or reduction.
- Depending on the tendency of a metal to lose or gain electrons the electrode potential maybe of two types namely oxidation potential and reduction potential
- Oxidation potential of a metal indicates its electron losing tendency, while reduction potential represents the electron gaining capacity of the metal.
- However, according to IUPAC convention electrode potential are given as reduction potentials.
- The unit of the electrode potential is the volt.

- Factors affecting the magnitude of electrode potential

a. The nature of metal or electrode: metals have different tendency to lose or accept electrons.

b. Concentration of metal ions in solution

E.g Zn^{2+} ″ $Zn + 2e^-$

As the concentration of Zn^{2+} ions increases the equilibrium will shift to the left side and the electrode potential decrease. Similarly as the concentration of Zn^{2+} ions decreases electrode potential increases.

c,Temperature

d. Complexation: Complex formation may also bring down the effective concentration of one of the species involved in an electrode process, thereby altering the potential of the system

e. pH: When hydrogen or hydroxyl ions are involved in a half-cell reaction, their concentrations appear in the Nerst equation and accordingly the potential is influenced by the pH of the medium.

- Standard electrode potential (E^o) may be defined as the potential difference between the standard hydrogen half cell and the half cell that is been studied, provided that:

i. All the dissolved species are at unit concentration (1M)
ii. Gases are at 1 atm pressure.
iii. All solid are in their most stable form
Iv The temperature is maintained at 25 °C

The standard emf of a given cell (E^o_{cell}) is equal to the difference of standard reduction potential of the cathode ($E^o_{cathode}$) and the standard reduction potential of the anode (E^o_{anode}).

- $E^o_{cathode} - E^o_{anode} = E^o_{cell}$
- The emf of any cell can be calculated using the Nerst equation
- E,g $M^{n+} + ne^- ″ \quad M^-$
- $E= E^o + RT/nF \ln(1/a_m^{n+})$

If both oxidized and reduced form are in solution

- $E= E^o + RT/nF \ln(a_{oxidized}/a_{reduced})$
- Where: R= gas constant; T= absolute temperature; a_m^{n+} = the activity of the ion in solution; n= valency of the ion; F= Faraday.
- NB: a_m^{n+} may be replaced by the concentration of the ions in solution

- Emf is also related to the free energy change of a system by the equation
- $\Delta G = -nFE$
- Or standard electrode potential: $\Delta G^o = -nFE^o$
- An arrangement of element in order of increasing E^o values is called the electrochemical series
- In this series the most electropositive elements are at the top and the least electropositive at the bottom
- Couples containing powerful reducing agents have negative potentials
- Strong oxidizing agents have positive potentials.
- E^o value is affected by complexation
- In certain cases E^o also depends on pH.

Electrode potential and equilibrium constant

- The force energy change of a chemical reaction is dependent on the activity of the reactant and products.
- Accordingly the emf of a cell should also depend on the activity of the species taking part in the cell reaction.
- $\Delta G^o = -nFE^o$
- $\Delta G^o = -RT\ln K$
- Therefore; $RT\ln K = nFE^o$
- $\ln K = nFE^o/RT$
- Or $2.303\log K = nFE^o/RT$
- Hence if E^o is known K can be obtained for an equation
- Furthermore,
- $E = E^o + RT/nF \ln[ox]/[redu.]$
- $= E^o + 0.059/n \log [\text{oxidized form}]/[\text{reduced form.}]$ At 298K

- Using this for the two half cell reactions. At equilibrium net emf must be zero. Therefore the net emf is zero.
- Example: MnO_4^- + $5Fe^{2+}$ + $8H^+$″ Mn^{2+} + $5Fe^{3+}$ + $4H_2O$
- For MnO_4^- / Mn^{2+}
- $E_1 = E_1^\circ + 0.059/5 \log [MnO_4^-][H^+]/[Mn^{2+}]$
- For Fe^{2+}/Fe^{3+}
- $E_2 = E_2^\circ + 0.059/5 \log [Fe^{3+}]^5/[Fe^{2+}]^5$
- However, at equilibrium $E_1 = E_2$
- $E_1^\circ - E_2^\circ = \{0.059/5 \log [Fe^{3+}]^5/[Fe^{2+}]^5\} - \{0.059/5 \log [MnO_4^-][H^+]/[Mn^{2+}]\}$
- $= 0.059/5 \log[Fe^{3+}]^5[Mn^{2+}]/[Fe^{2+}]^5[MnO_4^-][H^+]$
- $=0.059/5 \log K$
- But $E_1^\circ = 1.51$ and $E_2^\circ = 0.77$
- $\log K = 5(1.51 - 0.77)$
- $K = 10^{62.6}$ H/W suggest the implication of the K value obtained.

- Assignment

1. Give 3 properties of hard and soft acids and bases each.
2. Give 4 examples each of hard and soft acids and bases
3. Predict whether Fe will be oxidized to Fe^{2+} by the reaction with 1.0 HCl (Fe/Fe^{2+})
4. Define an acid in terms of the following theories:

I. Arrhenius

II. Bronsted Lowry

III. Lewis

4. Distinguish between levelling and differentiating agents and give two examples of each.
5. Give two possible practical applications of electrochemistry.
6. Balance the equation representing the redox reaction of the reduction of potassium permanganate solution to manganous salt in acidic medium by hydrogen peroxide.

Balancing redox equation

- Redox reactions involves the transfer of electrons from reducing agent to oxidizing agent,
- Balancing redox equations may be carried out using either of two ways

a. The oxidation no method
b. The ion-electron method

a. Oxidation no method

- Step1: Ascertain the mole ratio of the oxidant and reductant
- Step 2: All the species appearing on the reactant and product side are considered; adjustment is made for atoms which do not undergo any change of oxidation number. Acid, alkali or water may be inserted depending on the condition and medium of the reaction.

- Step 3: The balancing is closed by inspection of the reactant and product side, i.e that it is balanced.
- Example: manganese dioxide oxidizes concentrated hydrochloric acid to chlorine, manganous chloride and water.
- Step 1
- MnO_2 ʹn $MnCl_2$

+4 +2

HCl ʹn ½ Cl_2

-1 0

$MnO_2 + 2HCl$ ʹn $MnCl_2 + Cl_2$

- Step 2

$MnO_2 + 2HCl + 2HCl$ ʹn $MnCl_2 + Cl_2 + H_2O$

- Step3 : $MnO_2 + 4HCl$ ′n $MnCl_2 + Cl_2 + 2H_2O$

b. Ion-electron method

This method is based on the electronic theory of oxidation of and reduction. However, it is particularly limited to ionic reactions in aqueous solutions.

- Step 1 : The product of the reaction are ascertain and the loss of electrons by the reductant and the gain of electron by the oxidant are expressed separately by partial equations
- Step 2: The individual partial equation are balanced separately with respect to different atoms as well as with respect to the electrical charge on both sides . H^+ and OH^- are inserted as appropriate. For electrical balance the total charge of all the ions appearing on the two sides of the half reactions are considered and the difference adjusted by adding electrons on the appropriate side.
- Step 3: The two partial equations obtained ae multiplied by suitable factors to equalize the number of electrons in them. These are added after the electrons cancel out. The ions are replaced by molecules with necessary adjust.

- Example: Cupric sulfide dissolves in hot nitric acid forming cupric nitrate , nitric oxide and sulphur
- NO_3^- ′n NO

  CuS ′n $S + Cu^{2+}$
- NO_3^- ′n $NO + 2H_2O$
- $NO_3^- + 4H^+ + 3e^-$ ′n $NO + 2H_2O$
- CuS ′n $S + Cu^{2+} + 2e^-$
- $2NO_3^- + 8H^+ + 6e^-$ ′n $2NO + 4H_2O$

  $3CuS$ ′n $3S + 3Cu^{2+} + 6e^-$
- $2NO_3^- + 8H^+ + 3CuS$ ′n $3Cu^{2+} + 2NO + 4H_2O + 3S$
- Step 3 $3CuS + 8HNO_3$ ″ $3Cu(NO_3)_2 + 2NO + 3S + 4H_2O$
- H/W: balance the equation $Zn + Cr_2O_7^{-2} + H^+$ ′n $Zn^{2+} + Cr^{3+} + H_2O$

CORROSION

- Corrosion can be defined as the deterioration of materials by chemical processes. The most important by far is electrochemical corrosion of metals, in which the oxidation process $M \rightarrow M^+ + e^-$ is facilitated by the presence of a suitable electron acceptor, sometimes referred to in corrosion science as a **depolarizer**.
- Examples of corrosion include the rusting of iron, tarnishing of silver, development of green coating on copper and bronze.
- It causes enormous damage to buildings, bridges, ships and to all objects made of metals especially that of iron.
- A lot of money is lost every year on account of corrosion.

- The economic aspects of corrosion are far greater than most people realize; according to a report published in 2001, the cost of corrosion in the U.S. alone was $276 billion per year. Of this, about $121 billion was spent to control corrosion, leaving the difference of $155 billion as the net loss to the economy.
- Corrosion of iron (commonly known as rusting) occurs in presence of water and air. The chemistry of corrosion is quite complex but it may be considered essentially as an electrochemical phenomenon.
- At a particular spot of an object made of iron, oxidation takes place and that spot behaves as anode and we can write the reaction
- Anode: $Fe(s) \rightarrow Fe^{+2}(aq) + 2e^-$

Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in the presence of H^+ (which is believed to be available from H_2CO_3 formed due to dissolution of carbon dioxide from air into water).

- Hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere.
- This spot behaves as cathode with the reaction

Cathode: $O_{2(g)} + 4H^{+}_{(aq)} + 4e$ ’n $2H_2O_{(l)}$

- The overall reaction being:

$2Fe(s) + O_2(g) + 4H^+(aq)$ ’n $2Fe^{+2}(aq) + 2H_2O(l)$

- **E_0cell = E_0cathode - E_0anode = 1.23 V - (-0.44V) = + 1.67 V**

The ferrous ions are further oxidized by atmospheric oxygen to ferric ions

- which come out as rust in the form of hydrated ferric oxide (Fe_2O_3. x H_2O) and with further production of hydrogen ions.
- Prevention of corrosion is of prime importance. It not only saves money but also helps in preventing accidents such as a bridge collapse or failure of a key component due to corrosion.
- One of the simplest methods of preventing corrosion is to prevent the surface of the metallic object to come in contact with atmosphere. This can be done by covering the surface with paint or by some chemicals (e.g. bisphenol).
- Another simple method is to cover the surface by other metals (Sn, Zn, etc.) that are inert or react to save the object.
- An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn, etc.) which corrodes itself but saves the object.

Assignment

- “In a sense, corrosion can be viewed as the spontaneous return of metals to their ores.” Suggest reasons why this statement may be correct.
- The special characteristic of most corrosion processes is that the oxidation and reduction steps occur at separate locations on the metal. What characteristic of metals enables this to occur?

BATTERIES

- A battery serves as a source of electrical energy
- It is basically a galvanic cell where the chemical energy of the redox reaction is converted into electrical energy.
- They are usually a series or pile of cells that can be used as a source of direct current at a constant voltage
- However, for a battery to be of practical use it should be reasonably light, compact and its voltage should not vary appreciably during its use.

a. **The Mercury Battery**
   Consists of *amalgamated* zinc anode and a stainless steel casing which supports the mercuric oxide

- cathodic material. Only the solid components change, not the electrolyte, keeping volume and internal pressure constant.
- It is used in high-end applications where removing battery is inconvenient.

Anode: $Zn(Hg) + 2OH^{-}(aq)$ ʹn $ZnO(s) + H_2O(l) + 2e$ (plus unchanged Hg)

Cathode: $HgO(s) + H_2O + 2e$ ʹn $Hg(l) + 2OH^{-}(aq)$

b. **The Lead Storage Battery**

- It is commonly used in automobiles and invertors.
- It consists of a lead anode and a grid of lead packed with lead dioxide (PbO2) as cathode. A 38% solution of sulphuric acid is used as an electrolyte.

Anode: $Pb(s) + SO^{-}_{4}{}^{2}(aq)$ ʹn $PbSO_4(s) + 2e$

- Cathode: $PbO(s) + 4H^{+} + SO_{4}{}^{-2}(aq) + 2e$ ʹn $PbSO_4(s) + 2H_2O(l)$

Overall cell reaction :

- It can be recharged by passing current
- On charging the battery the reaction is reversed and $PbSO_4(s)$ on anode and cathode is converted into Pb and PbO_2, respectively

Assignment

a. Give two other examples of batteriesand their uses.

REVISION OF ATOMIC THEORY

INTRODUCTION

1. constituents of the nucleus
2. electrostatic interactions
3. isotopy
4. excitation during heating e.g. flame test
5. spectroscopy

Review of Experiments Associated with atomic structure

1. Rutherford experiment (Geiger-Marsden Experiment)
2. J.J Thompson
3. Millikan
4. Moseley's Law

Assignment: In one page, review the contributions of the above scientists to the atomic theory. Assignment due in one week.

From some of the previous suggestions on the composition of an atom, Bohr highlighted some problems:

1. electrons may slow down after a time

2. what makes electrons move in defined orbit

3. electrons may move into the nucleus later

To find a way round these observations, Bohr postulated that:

1. electrons do not radiate energy if the orbit is maintained, so will not slow down

2. energy is absorbed or radiated when electrons change orbits

3. electrostatic attraction/centrifugal force must be balanced to keep electrons in their orbits.

All these deficiencies were put together in the development of other theories that better give the description of atoms and some of the observations recorded.

Find below two slides from the previous discussion:
1. relating the centrifugal force to the columbic force of attraction in the third of Bohr’s postulates
2. a calculation from de Broglie equation

Note: You can forward your questions to me by email: aayeni@oauife.edu.ng e's in their orbit. In balance can throw out an e^- or cause collapse into the nucleus.

centrifugal force = $\frac{mv^2}{r}$ * energy tend to throw e^- out of orbit

Coulombic attractive force (c.a.f) = $\frac{Ze^2}{4\pi\varepsilon_0 r^2}$

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\varepsilon_0 r^2}$$

$$v^2 = \frac{Ze^2}{4\pi\varepsilon_0 mr}$$

other important theory is Planck's quantum theory

viewed as discrete and not continuous i.e en

$$\frac{mv^2}{2m} = ev$$

Calculate the wave length of electrons accelerated from rest through a potential difference of 80 kV.

$$\lambda = \frac{h}{p}$$

Kinetic energy $= \frac{1}{2}mv^2$

$$\frac{p^2}{2m_e} = eV \quad ; \quad p = \sqrt{(2m_e eV)}$$

$$\therefore \quad x = \frac{h}{\sqrt{(2m_e eV)}}$$

$$x = \frac{6.626 \times 10^{-34}\,Js}{\left(2 \times (9.109 \times 10^{-31}\,kg) \times (1.609 \times 10^{-19}\,C) \times 8.0 \times 10^{4}\,V\right)^{1/2}}$$

$$= 4.36 \times 10^{-12}\,m$$

wavelength in nm

Electron

Rutherford gave

While Niels Bohr

by electrons (account

described e's as

Further experi

ways as

ELECTRON: PARTICLE OR WAVE

Rutherford gave the planetary theory of the atom while Bohr describe the nucleus as surrounded by electrons. These two describe electrons as particles.
Further experiments however showed electrons behave in some ways as waves.

Phenomena like diffraction/interference can only be explained by assuming that light behaves like waves.

!!! Do not forget that light comes as packets or quanta (each quantum is $h/2\pi$) where h is Planck's constant.

De Broglie described the wave particle duality of matter.
$\lambda = h/p$ (i.e. it relates wavelength to momentum (p)

Heisenberg Uncertainty Principle

Studies using the Bohr's model requires precise information on the position of the electron and its velocity
But electrons are difficult to study when stationary, they must be perturbed.

E.g X-ray techniques (i.e hitting electrons/matter with another particle)
or photoelectric/thermoelectric effect

All these techniques affect the position/velocity of electrons

Heisenberg stated that the more precisely we can define the position of an electron, the less certainly we are able to define its velocity and vice versa. And that leads to the equation below:

$$\Delta x \cdot \Delta v \geq h/4\pi$$

Therefore, the earlier concept of electrons in orbits with defined position and velocity is no longer valid, it must be replaced by a probability of locating an electron in a particular position or rather volume of space.

This led to the birth of the Schrodinger wave equation which when solved gives wave functions (ψ). The probability of finding an electron at a point in space with coordinates x, y, z is $\psi^2_{(x,y,z)}$

Schrodinger Wave Equation (SWE)

For a wave equation to have acceptable solutions, it must meet the following conditions:

1. ψ must be continuous
2. ψ must be finite
3. ψ must be single valued
4. the integration of ψ^2 from - ∞ to + ∞ over all space i.e. $\int \psi^2$ dxdydz must be equal to 1. this means that the probability of finding an electron over all space must be equal to one.

SWE has only been solved for hydrogen atom and one electron ions like He^+, Li^{2+} (list further examples). By approximation, information on polyelectronic atoms can be obtained.
The filling of orbitals is the order of increasing n+l.
Few exceptions exist like Cu with $3d^{10}4s^1$ instead of $3d^9 4s^2$ due to increased stability of evenly filled orbitals.

Molecular Orbital Theory

Atoms combine to give molecules,
thus atomic orbitals remain after molecules are formed.
We have Linear Combination of Atomic orbitals (LCAO)
MOs are developed by a case of single valence electrons associated with two atoms

e.g.

H_2^+ where two 1s atomic orbitals are involved in bonding

Li_2^+ - two 2s orbitals

LiH^+ - 1s and 2s orbitals

for Li_2^+ and LiH^+ an approximation is made that $1s^2$ closed shells are not involved in bonding

SWE may be put as

$$\left[V - h^2/8\pi^2 m(\delta^2\psi/\delta x^2 + \delta^2\psi/\delta y^2 + \delta^2\psi/\delta z^2)\right] \psi = E\psi$$

can be further represented as

$H\psi = E\psi$ (H is Hamiltonian operator)

$$\int \psi H \psi \, d\tau = E \int \psi^2 \, d\tau$$

$$E = \int \psi H \psi \, d\tau \, / \int \psi^2 \, d\tau$$

E is the energy

For two atoms with wavefunctions ψ_A and ψ_B

$\psi_{AB} = N(C_1\psi_A + C_2\psi_B)$

N is normalizing constant chosen to ensure that the probability of finding an electron in the whole space is unity.

C_1 and C_2 are constants chosen to give minimum energy for ψ_{AB}

$\psi^2 dv$ is the probability of finding an electron in a volume of space (V), so the probability density for the combination of two atoms is

$\psi^2_{AB} = (C_1\psi_A + C_2\psi_B)^2$

$\psi^2_{AB} = C_1^2\psi^2_A + 2C_1C_2\psi_A\psi_B + C_2^2\psi_B^2$

$C_1C_2\psi_A\psi_B$ is called overlap integral and represents the main difference between the electron clouds of individual atoms. The larger this term the stronger the bond.

Criteria for Stable Molecular Orbital

1. The energies of the atomic orbitals must be comparable
2. The atomic orbitals must be positioned so that good overlap can occur
3. The atomic orbitals must have same or approximately the same symmetry with respect to the bond axis.

Schrodinger Wave Equation and Quantum Numbers

Schrodinger proposed a differential equation that relates energy of a system to the space coordinates of the constituent particles e.g. electrons

In the equation:
ψ has properties analogous to the amplitude of the wave
ψ is proportional to the probability of finding the particles at x,y,z coordinates

Applying the SWE to the hydrogen atom or any system with one electron and one nucleus yields 3 integration constants.

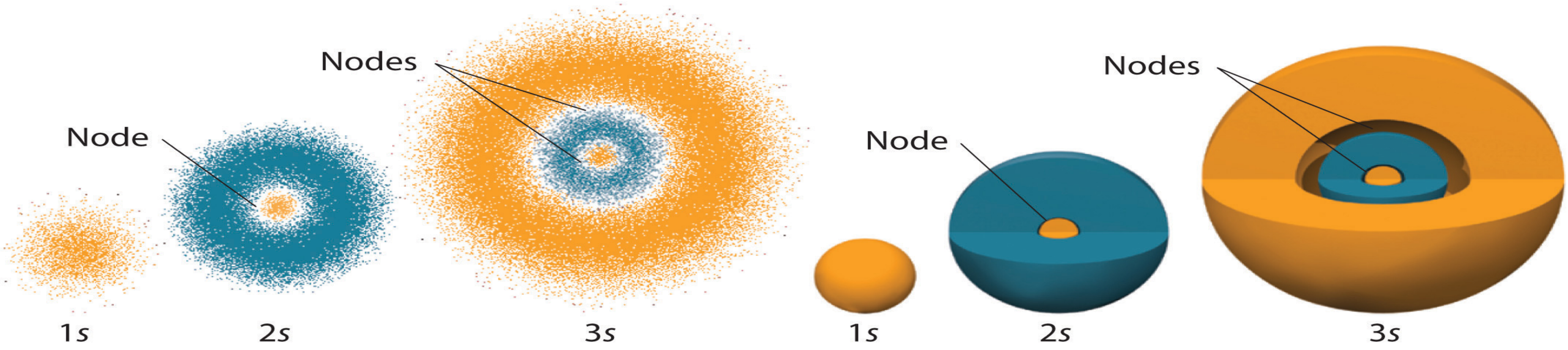
These solutions are known as quantum numbers n,l, m_l and m_s

Hydrogen atom-orbital shapes and energies

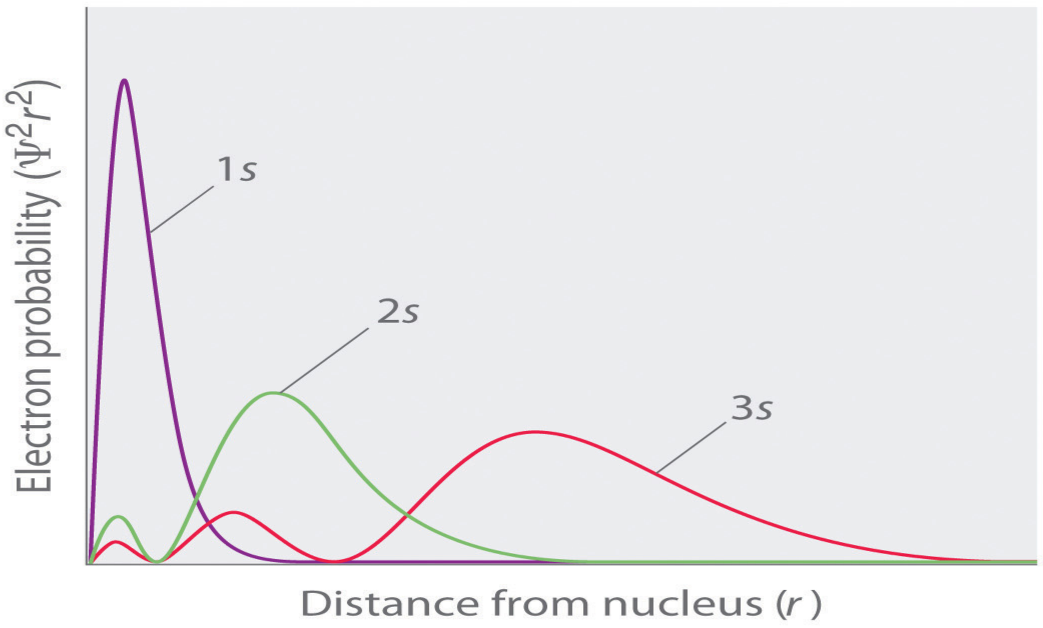
it is possible to express wave-functions in terms of polar coordinates
i.e. we can draw the orbitals.

$$\Psi(r, \theta, \phi) = R(r) \cdot \Theta(\theta) \cdot \Phi(\phi)$$

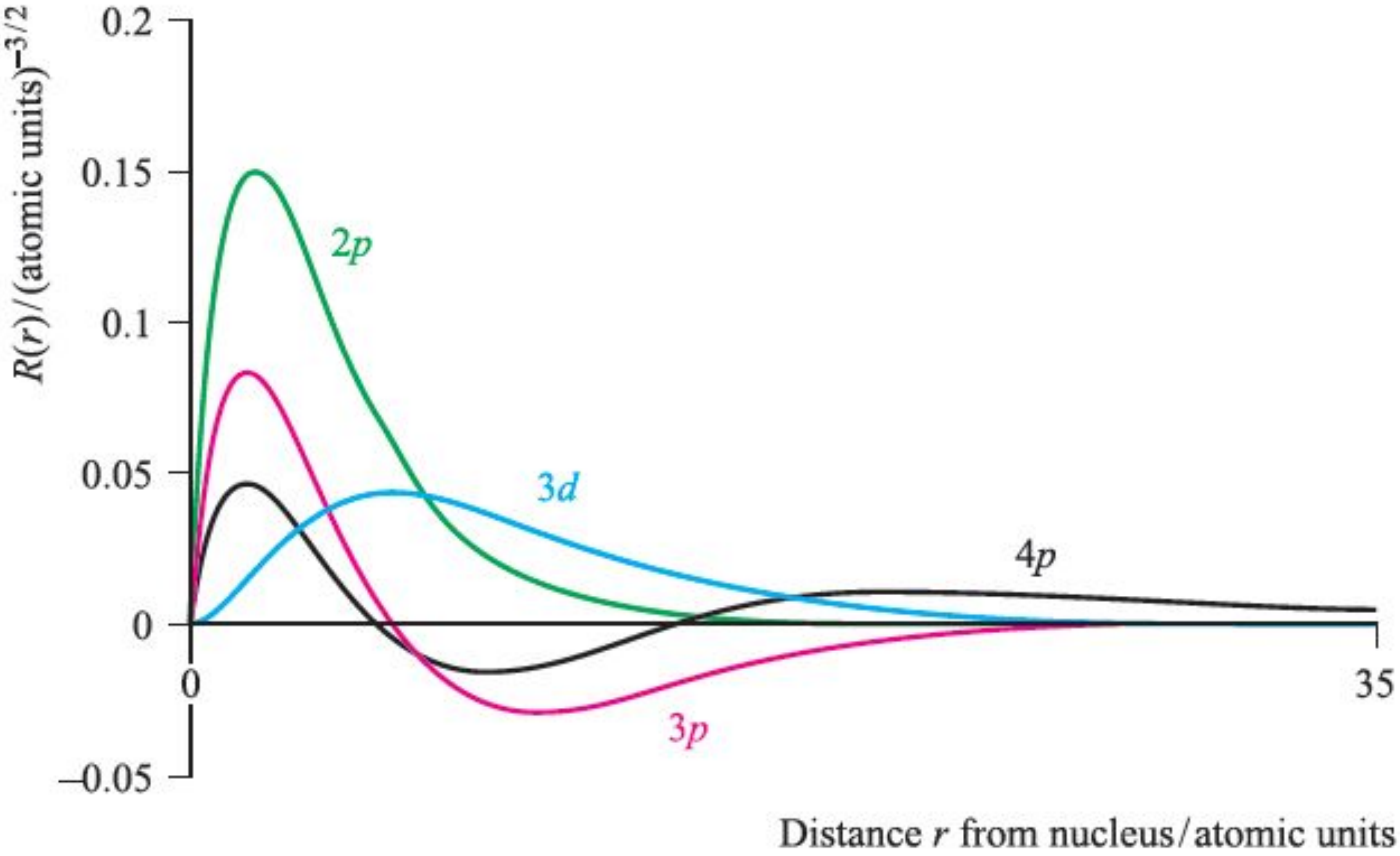
See the examples for s- and p- orbitals below



(a) Electron probability **(b) Contour probability**



(c) Radial probability


$R(r)/(\text{atomic units})^{-3/2}$
0.2
0.15
0.1
0.05
0
−0.05
0
35
2p
3d
4p
3p
Distance r from nucleus/atomic units

All the above plots are that of R against r
where R = radial wave function
r = distance from the nucleus for n = 1, 2 and 3

Note the following:
1. magnitude of the wave function is highest at the nucleus
2. for n>1, the wave function is zero in certain regions called nodes (as a general rule, the are n-1 nodes in an atomic wave function
3. the sign of R changes from +ve to –ve as it passes through a node
R is not directly related to any experimental measured quantity, R2 is proportional to electron density.

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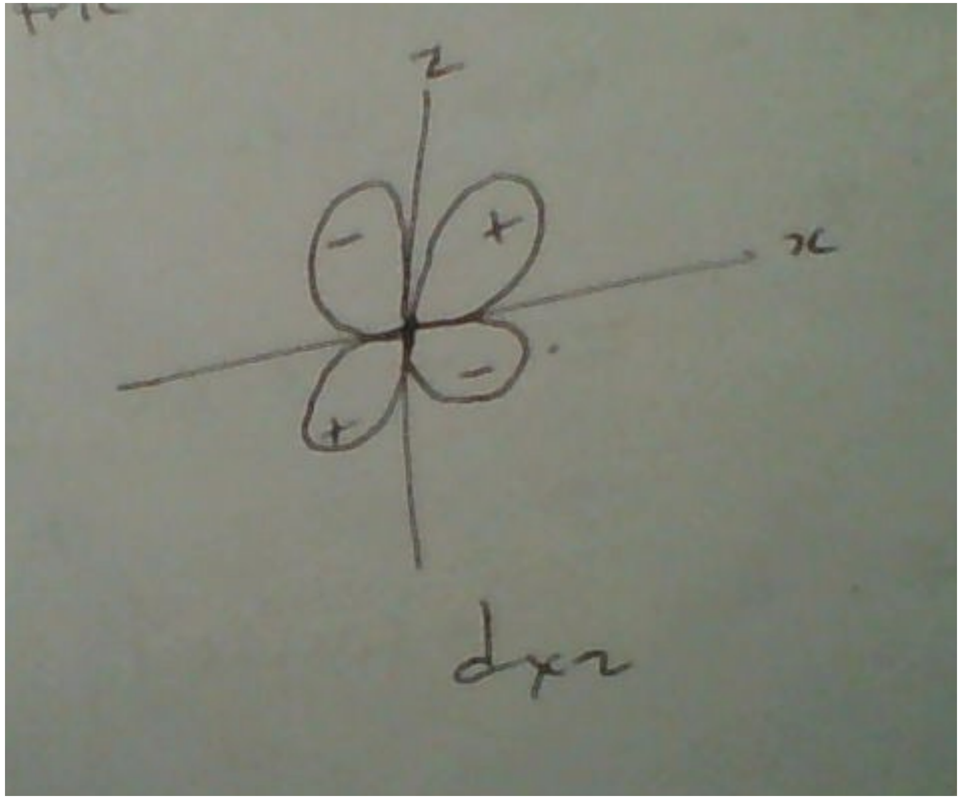
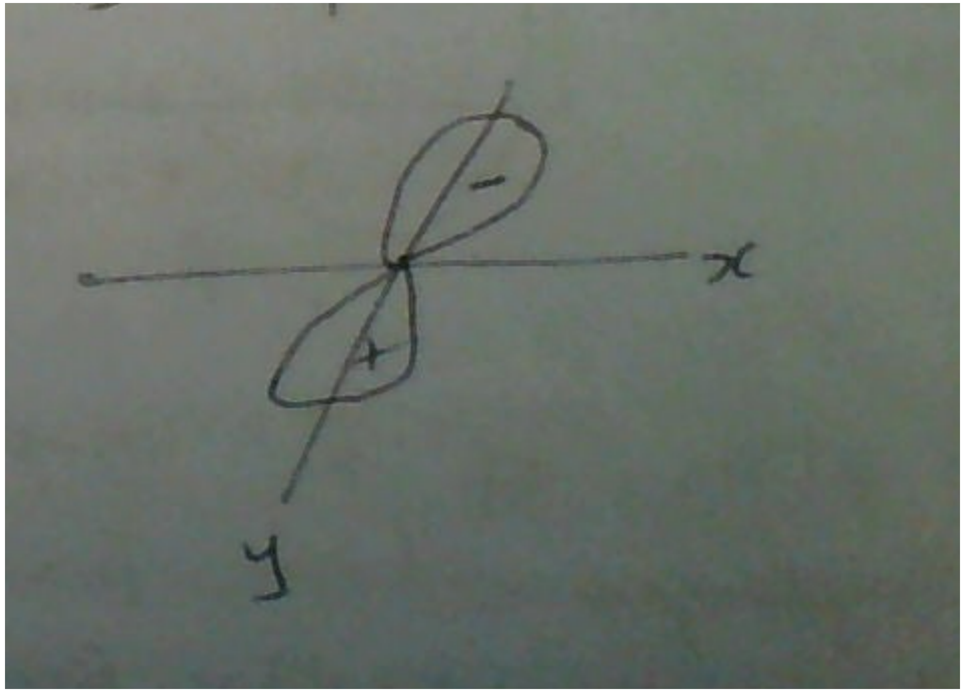




In the figure in above; left is d_{xz} orbital while right is p_y orbital
The + and – signs refer to the sign of the original wave function.

Classwork: Study these patterns and draw for other p and d orbitals.
Also study the radial plots for s and p orbitals.

Orbitals may be classified according to the symmetry with respect to inversion through the centre (nucleus).

Where inversion i.e. simply changing the sign of the x,y,z coordinates causes no change in the sign of ψ the orbital and its wave function are described as *gerade* (German word for even)

where inversion causes a change in sign, the orbital or wave function is described as *ungerade* (odd)

therefore: s and d orbital – *gerade*

p – orbital - *ungerade*

Solving the SWE for the energy levels of the H-atom or one electron ion gives
E = energy relative to the infinitely separated electron and nucleus
$E = -2\pi^2 m Z^2 e^4 / n^2 h^2$

putting the values for the constants give
$E = -13.60 Z^2 / n^2$

Unit of energy is (eV)
therefore E is independent of l and ml and only dependent on n (principal quantum number)
Absolute energy increases as the distance from the nucleus increases

Diatomic Molecules

Just like you have electronic configuration, we can write the filling of orbitals for molecules.

Molecular orbitals can be considered as the overlap of valence shell s- and p- orbitals in a homonuclear diatomic molecule.

The sequence determined from spectroscopic data is as follows

$\sigma 1s, \sigma^{*}1s, \sigma 2s, \sigma^{*}2s, \sigma 2p_x \begin{cases} \pi 2p_y \\ \pi 2p_z \end{cases} \begin{cases} \pi^{*}2p_y \\ \pi^{*}2p_z \end{cases}, \sigma^{*}2p_x$

From the sequence, both 2py and 2pz atomic orbitals give π bonding and π* antibonding molecular orbitals. The ones in the open brackets are doubly degenerate

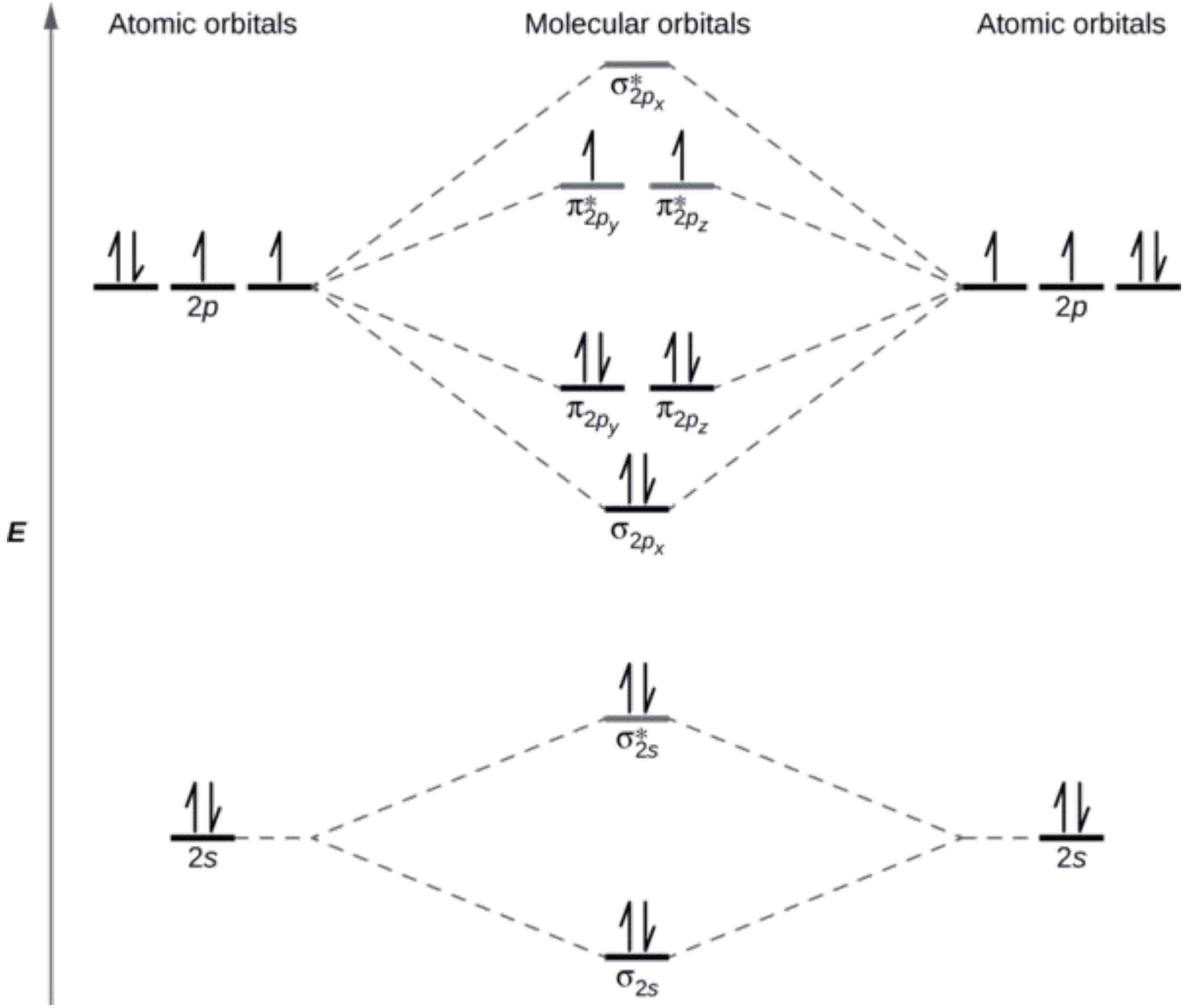
The energies of σ2p and π2p MO's are close. The order presented above is correct for oxygen and heavier elements . Because the pπ overlap is poorer than pσ overlap

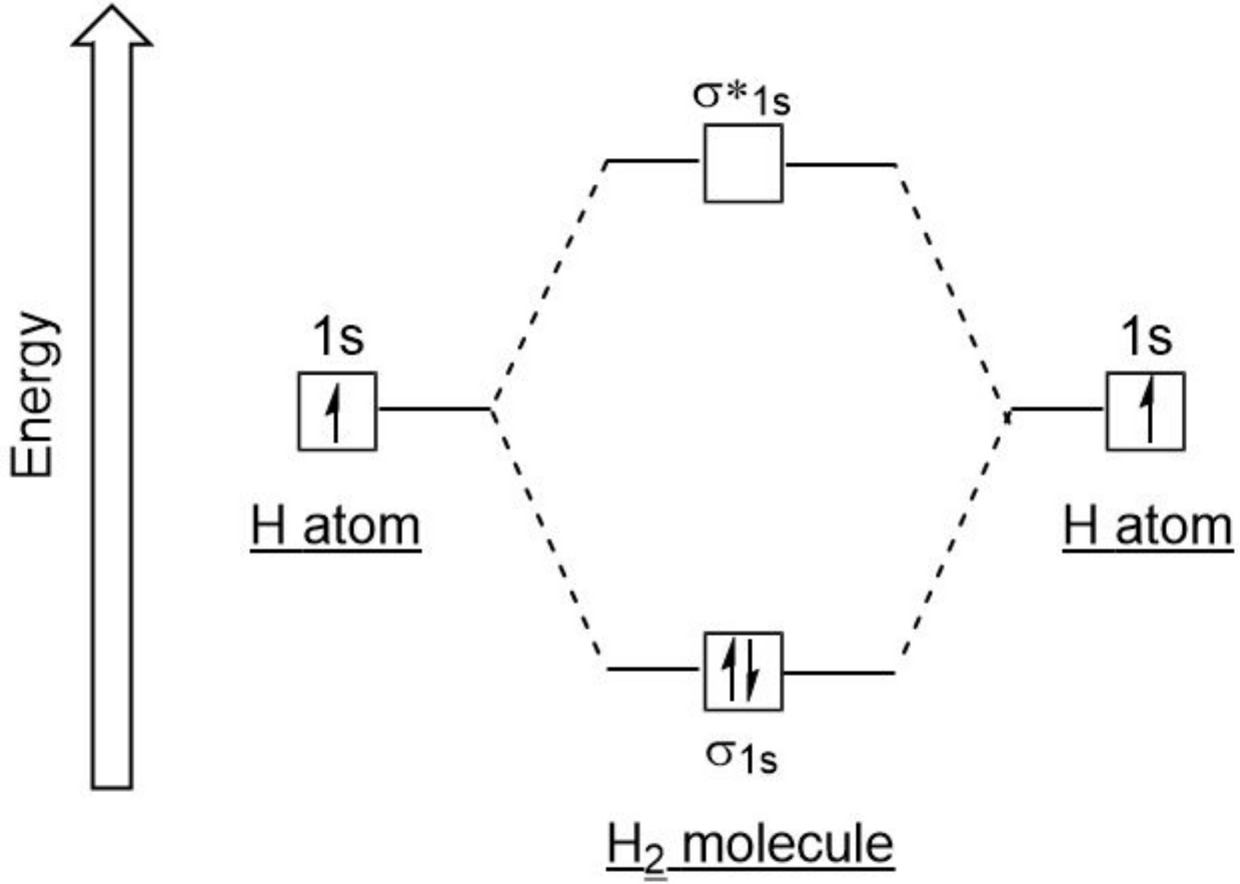
i.e. $\boldsymbol{\beta}_{p\sigma} > \boldsymbol{\beta}_{p\pi}$

where $\boldsymbol{\beta}$ is the interaction energy

Therefore, for lighter elements B,C and N, the $\pi 2p_y$ and $\pi 2p_z$ are lower than $\sigma 2p_x$, and we have the following

$$\sigma 1s,\ \sigma^{*}1s,\ \sigma 2s,\ \sigma^{*}2s,\ \left\{\begin{matrix}\pi 2P_y\\ \pi 2P_z\end{matrix}\right.\quad \sigma 2px\ ,\sigma{*}2px\quad \left\{\begin{matrix}\pi^{*}2P_y\\ \pi^{*}2P_z\end{matrix}\right.$$


Atomic orbitals
Molecular orbitals
Atomic orbitals
$\sigma^*_{2p_x}$
$\pi^*_{2p_y}$
$\pi^*_{2p_z}$
2p
2p
π_{2p_y}
π_{2p_z}
σ_{2p_x}
E
σ^*_{2s}
2s
2s
σ_{2s}


Energy
σ^*_{1s}
1s
1s
H atom
H atom
σ_{1s}
H_2 molecule

To draw the orbital diagram, all the elctrons in a molecule must be considered.
For lithium – 6electrons
Oxygen - 16 electrons
Some gains from this theory,
- it will provide information on the number of unpaired electrons and predict magnetic properties
- bond order and strength of bonds
- correlate expected dissociation energy with bond order/distance
Those orbitals without star (*) sign are bonding orbitals
Those orbitals with star (*) sign are anti- Those orbitals without star (*) sign are bonding orbitals bonding orbitals

Bond order = $(N_a - N_{ab})/2$

N_a = number of electrons in bonding orbital

N_{ab} = number of electrons in anti-bonding orbital

For Oxygen, we have (10 - 6)/2 = 2

Note:

1. The higher the bond order, the shorter the bond
2. The shorter the bond, the shorter the bond distance
3. The shorter the bond distance, the stronger the bond.

Practice question

Rationalize the following bond distances

O_2^+ - 1.22 Å

O_2 – 1.21 Å

O_2^- - 1.28 Å

O_2^{2-} - 1.49 Å

Steps

1. Determine the total number of electrons
2. Write the Molecular orbital configuration
3. Determine the bond order
4. Determine the bond distance and compare your answer with the trend given.

CONCEPT OF EFFECTIVE NUCLEAR CHARGE

- The concepts of electron shielding, orbital penetration and effective nuclear charge can now quantitatively estimated with the aid of Slater Rules and electron shielding/effective nuclear charge taken into consideration.

- The general principle behind Slater's Rule is that the actual charge felt by an electron is equal to what you'd expect the charge to be from a certain number of protons, but minus a certain amount of charge from other electrons.

Slater's Rules

- **Step 1**: Write the electron configuration of the atom in the following form:
- (1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p) . . .
- **Step 2**: Identify the electron of interest, and ignore all electrons in higher groups (to the right in the list from Step 1). These do not shield electrons in lower groups
- **Step 3**: Slater's Rules is now broken into two cases:
  - the shielding experienced by an s- or p- electron,
    - electrons within same group shield **0.35**, except the 1*s* which shield **0.30**
    - electrons within the n-1 group shield **0.85**
    - electrons within the n-2 or lower groups shield **1.00**

1. What is the shielding constant experienced by a 2*p* electron in the nitrogen atom?

Step 1: Write the electronic configuration of Nitrogen and group according to the quantum number

N: $(1s^2)\ (2s^2,2p^3)$

S[2p] = 0.85(2) the 1s electrons + 0.35(4) the 2s and 2p electrons

=3.10

The shielding constant can now be used to calculate the effective nuclear charge as seen in the next example.

2. What is the effective nuclear charge experienced by a valence *p*-electron in boron?

B: $(1s^2)(2s^2,2p^1)$

$S[2p] = 0.85(2) + 0.35(2) = 2.40$

$Z = 5$

Zeff = (5 – 2.40) = 2.60

We can go a step further to calculate the energy involved in the electronic interaction.

3. Calculate the energy for an electron in ($n=3$, $n^* = 3$) in Sulphur

Sulphur has the configuration grouped as follows

$1S^2$ ($2S^2$ $2p^6$) ($3S^2$ $3P^4$)

Effective screening = $2 \times 1.00 + 8 \times 0.85 + 5 \times 0.35$

$= 10.55$

$Z_{eff} = 16 – 10.55 = 5.45$

$E\ (3S^2\ 3P^4) = -\ (Z_{eff}/n)^2 \times 13.6$ eV $= -\ (5.45/3)^2 \times 13.6$

$= -45.05$ eV

PERIODICITY OF CHEMICAL PROPERTIES

PREFACE TO PERIODICITY OF CHEMICAL PROPERTIES

The science of chemistry touches on every aspect of our Lives. It is also important in the successful pursuit of many careers.

- **Elements are the basic constituents of matter**

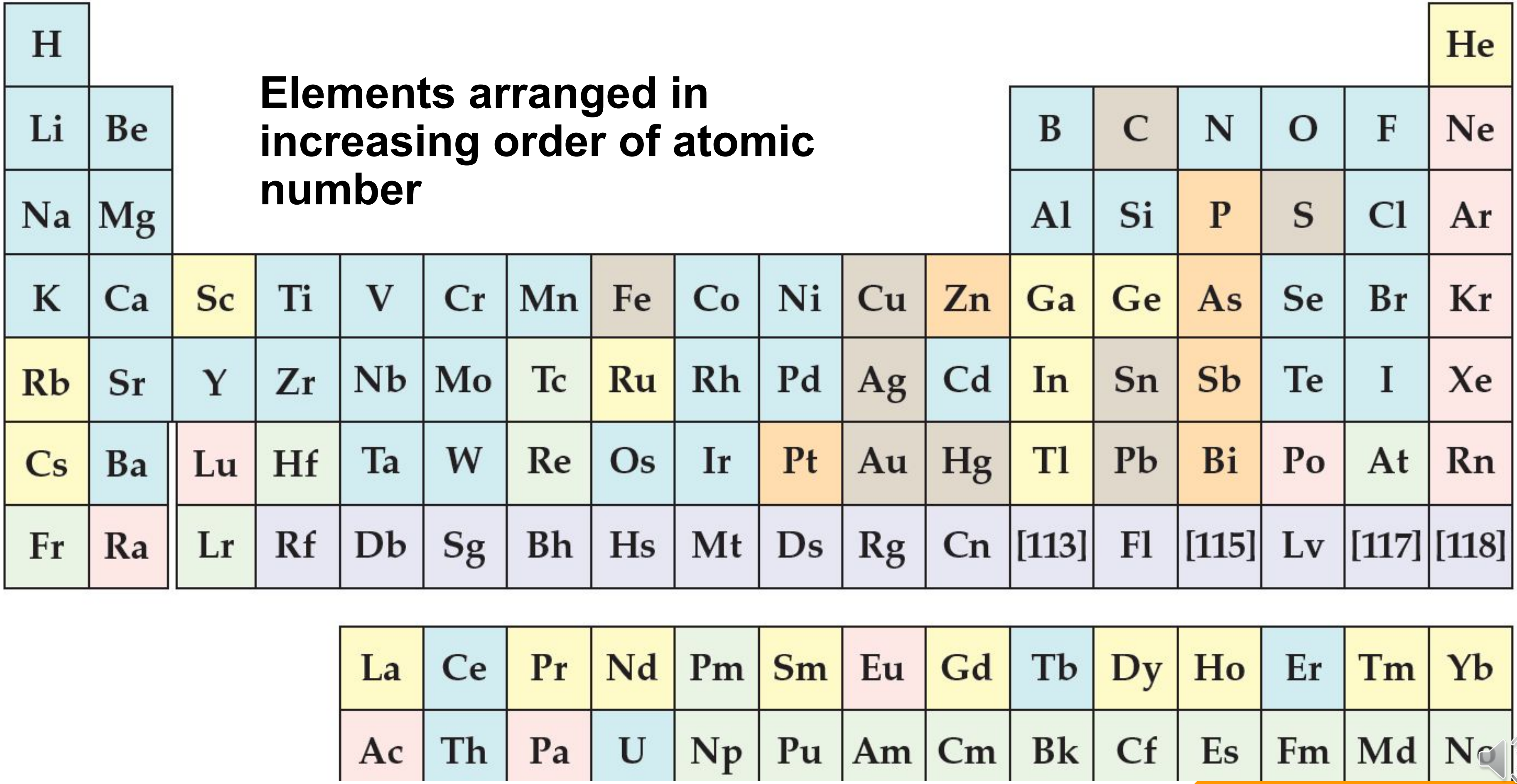
PREFACE TO PERIODICITY OF CHEMICAL PROPERTIES

- Life full of patterns

- Presence of repeating patterns common throughout nature

PERIODIC TABLE

Elements arranged in increasing order of atomic number



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	[113]	Fl	[115]	Lv	[117]	[118]
				La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
				Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

THE EARLIEST VERSION OF THE CURRENT PERIODIC TABLE WAS PRESENTED BY DIMITRI MENDELEEV & LOTHAR MEYER

MENDELEEF’S PERIODIC LAW AND MENDELEEV’S PERIODIC TABLE

- Mendeleev law state that: The properties of elements are a periodic function of their atomic weights
- Mendeleev arranged elements in increasing order of their atomic weights to obtain a Mendeleev Periodic Table

MAIN DEFECTS OF MENDELEEF’S PERIODIC TABLE

- Anomalous position of hydrogen. Mendeleev placed hydrogen in Grp 1A with alkali metals; hydrogen also resembles halogens
- Position of isotopes: arranging elements in increasing atomic weights will give no different position to isotopes.
- Similar pairs of elements placed in different groups and dissimilar in the same group
- Group does not represent Valency. Elements in Grp 8 do not have a valency of 8 except Osmium

MAIN DEFECTS OF MENDELEEF'S PERIODIC TABLE

- Position of 4 anomalous pairs of elements with 4 lower atomic weights placed after the element with a higher atomic weight against his law. The pairs: Ar {Z=18; at wt=40} and K{Z=19; at wt=39}; Co{Z=27; at wt=58.9} and Ni{Z=28; at wt=58.6}; Te{Z=52; at wt=127} and I {Z=53; at wt=126.9}; Th {Z=90; at wt=323.12} and Pa{Z=91; at wt=231}.
- Non-classification of metals and non-metals
- Non-placement of the Lanthanides (58 to 103) and Actinides (90 to 103) in the periodic table; given separate table below the table.

MOSELY'S PERIODIC LAW: MODERN PERIODIC LAW

- Mosely's experiment revealed that atomic number, NOT atomic weight is the criterion for the periodic arrangement of atoms.
- This observation formed the basis of the modern periodic table.
- This observation also led Mosely to predict the disappearance of most of the defects of Mendeleev's periodic table if the basis for clarifications is changed to atomic number

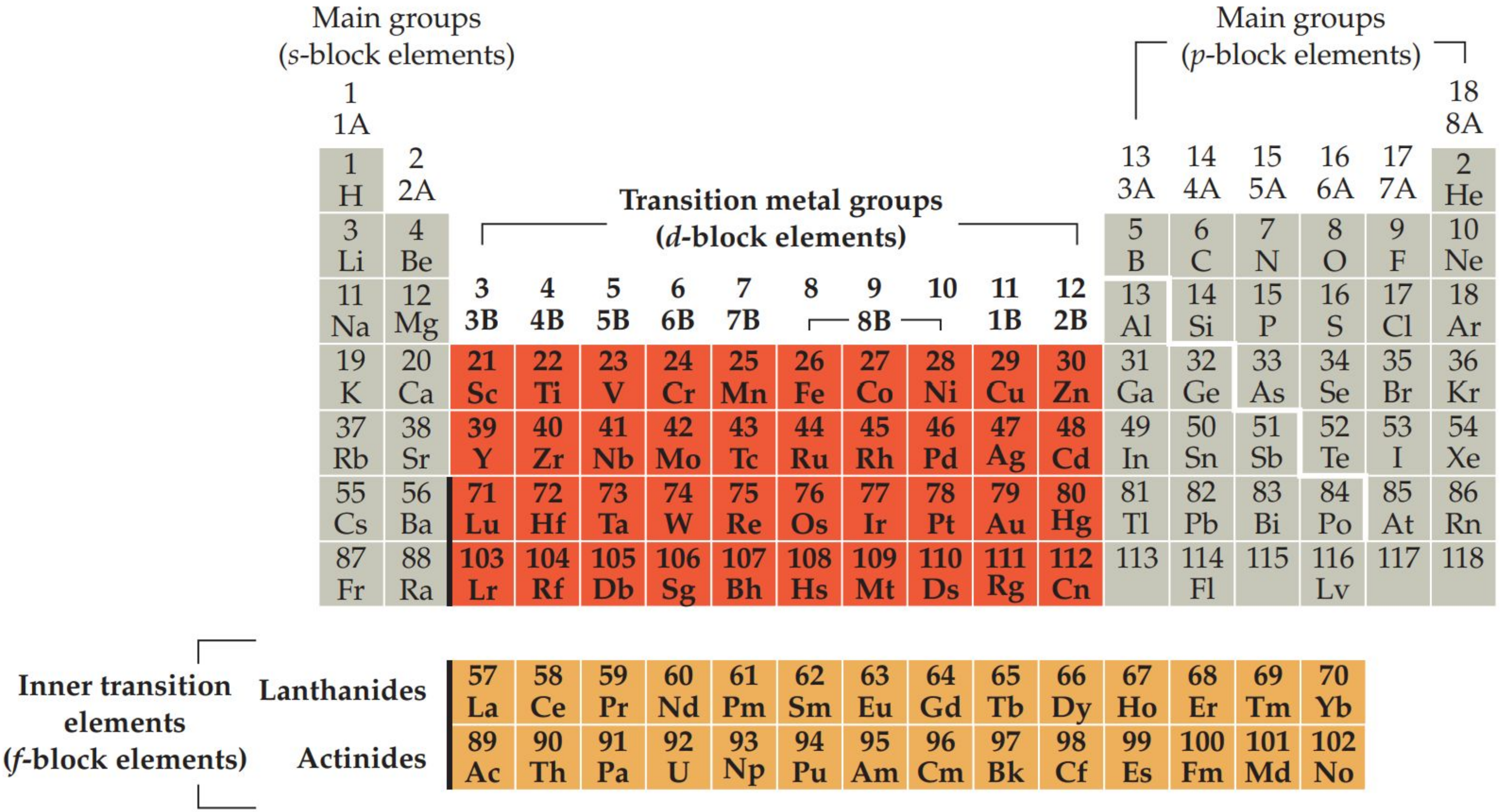
MOSELY’S PERIODIC LAW: MODERN PERIODIC LAW

- Mosely put forward the modern periodic law which states that: The properties of elements are a periodic function of their atomic number i.e. if the elements are arranged in the increasing order of their atomic numbers, the properties of the elements (i.e. similar elements) are repeated after definite regular intervals or period.

MODERN PERIODIC LAW

- Bohr gave a modern periodic table in which elements are arranged based on Mosely’s suggestions- according to increasing atomic number.
  - the arrangement addresses many defects of Mendeleev’s Periodic Table.
- Two major defects remained unresolved:
  - Position of hydrogen
  - Lanthanides and Actinides are still not accommodated in the main body of the periodic table

PERIODICITY OF PROPERTIES



Main groups (*s*-block elements)

Transition metal groups (*d*-block elements)

Main groups (*p*-block elements)

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
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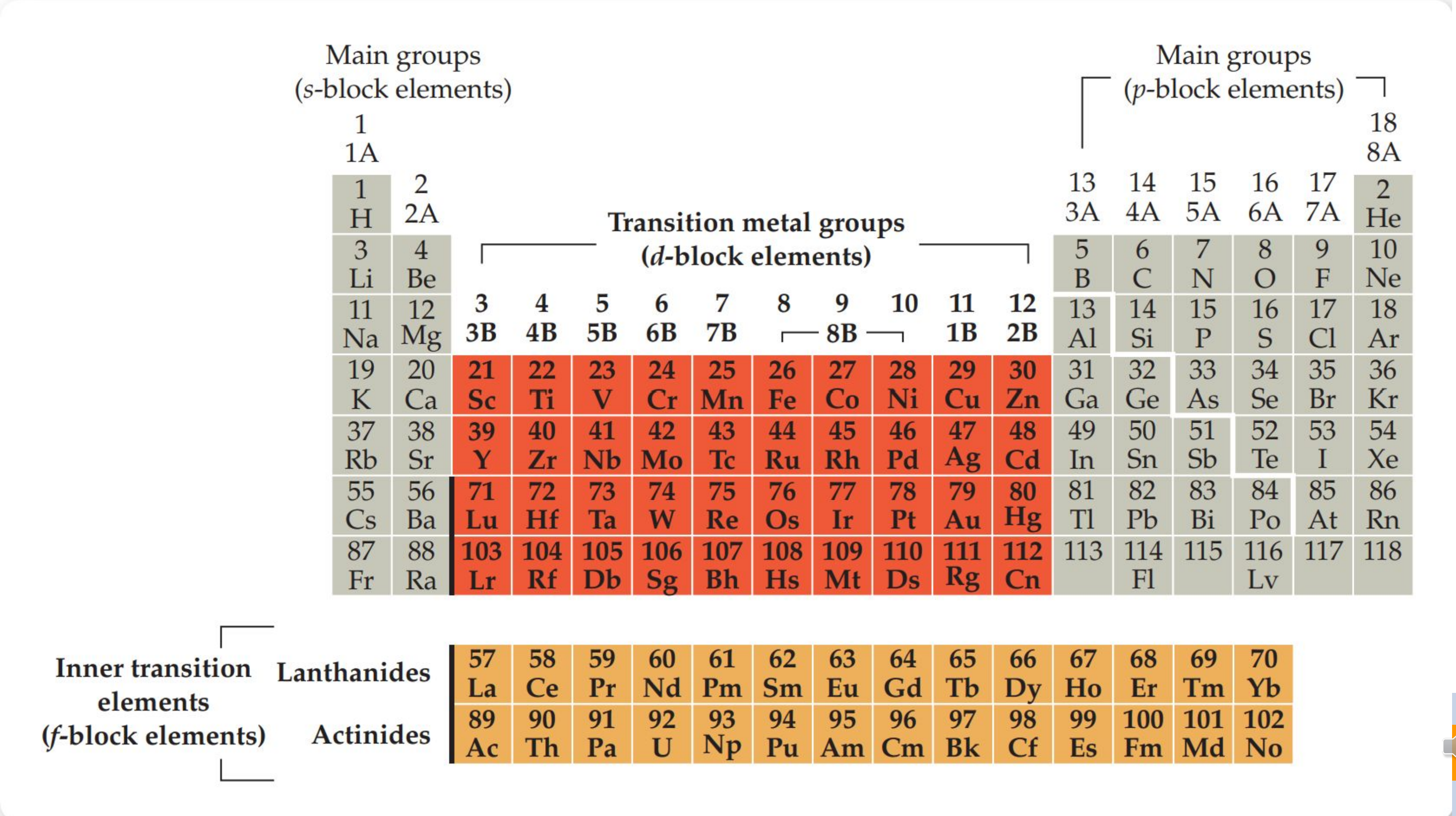
Inner transition elements (*f*-block elements)

Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

CAUSE OF PERIODICITY OF PROPERTIES



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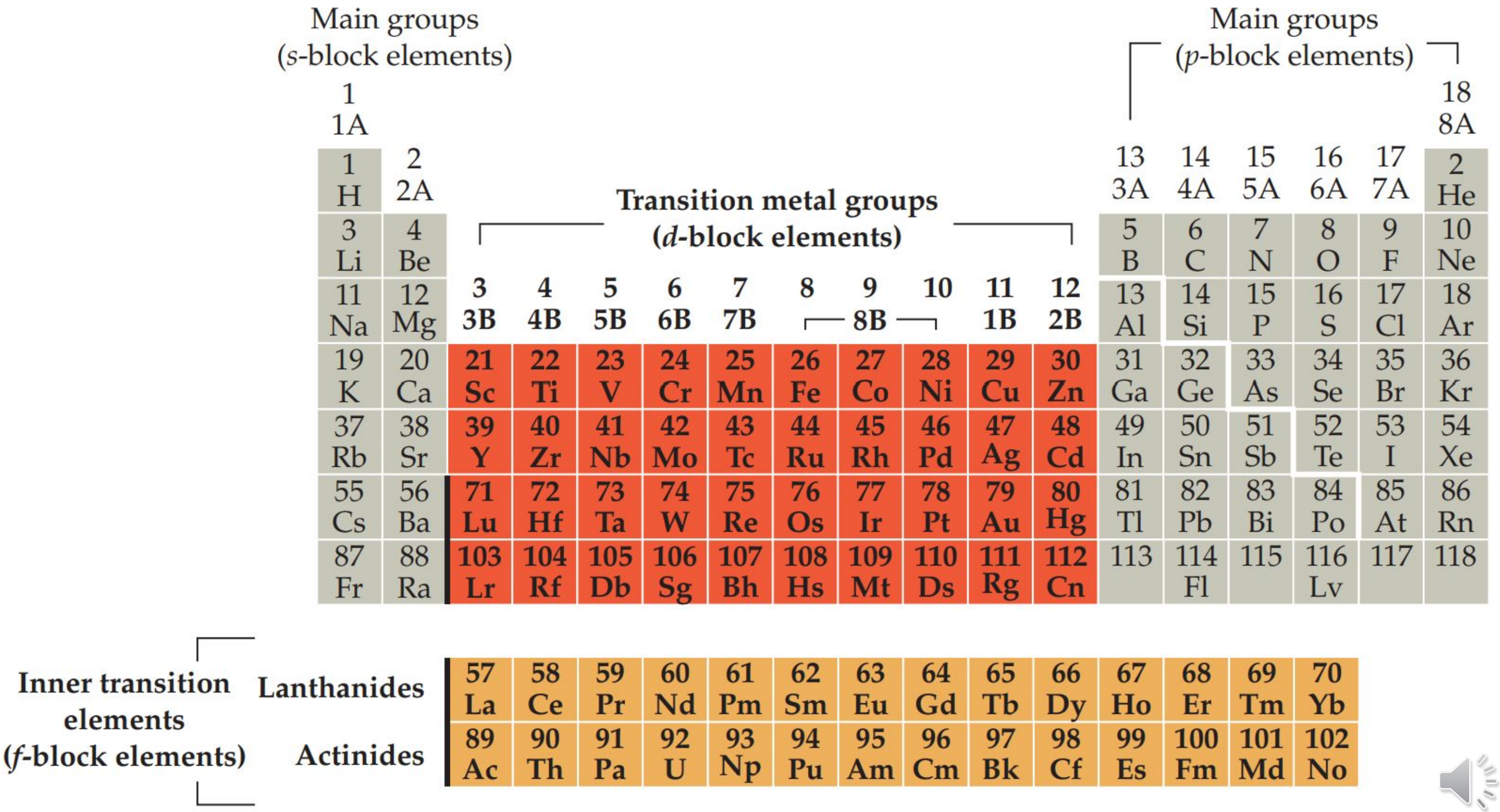
PERIODIC TABLE & PERIODIC LAW

Periodic law- physical and chemical properties are functions of atomic number



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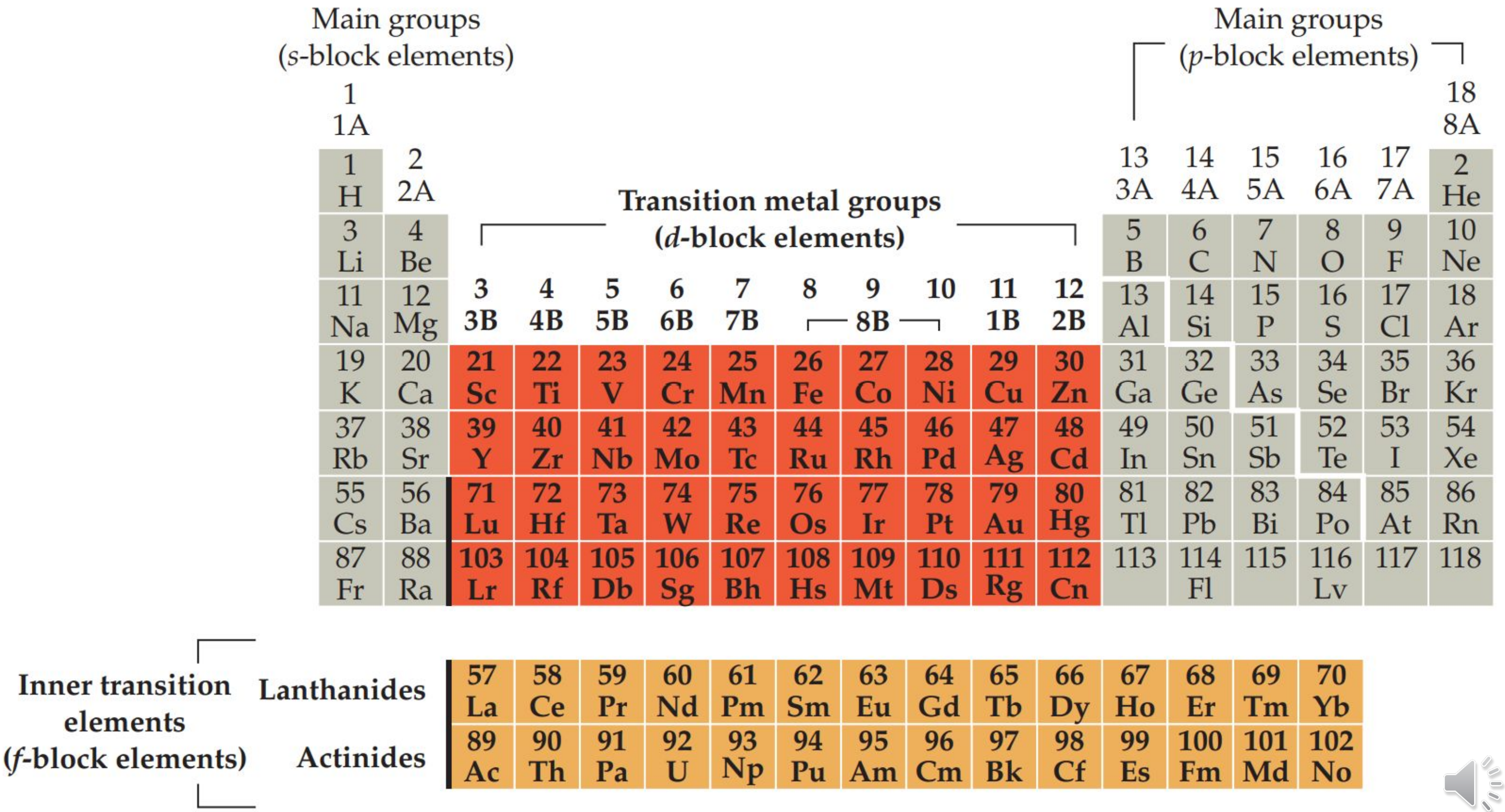

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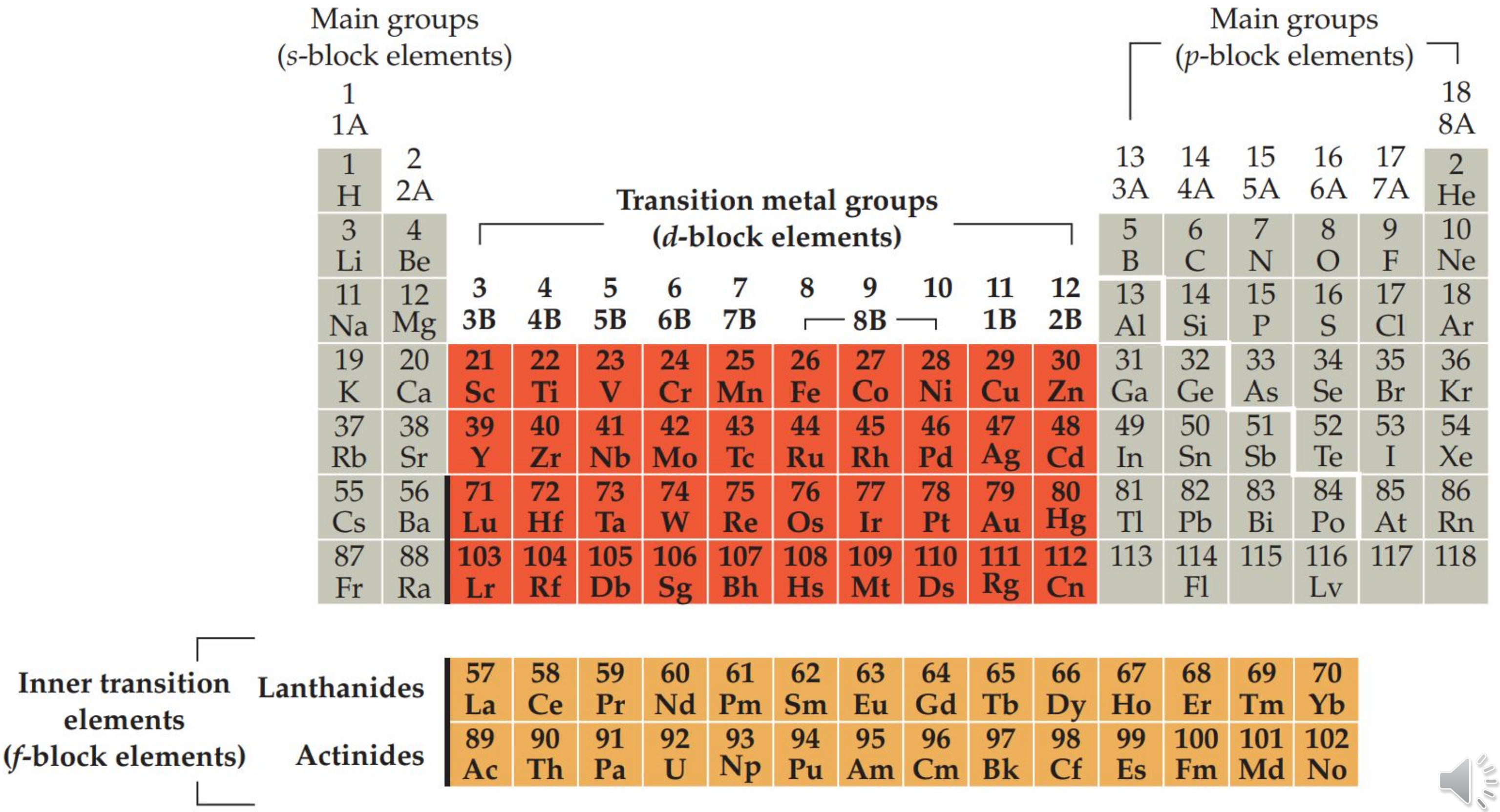

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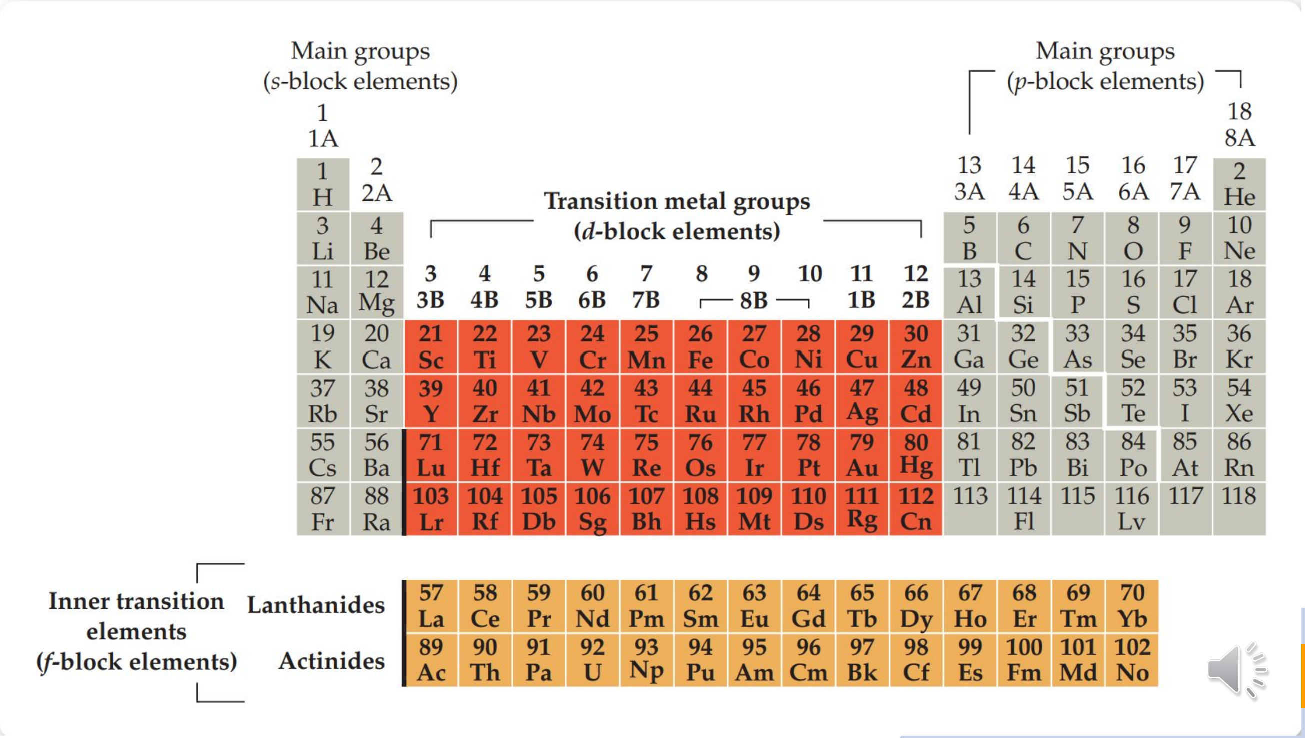
PERIODIC TABLE & PERIODIC LAW

Pd = [Kr] $5s^0 4d^{10}$; Na = [Ne] $3s^1$; C = [He] $2s^2 2p^2$; Cu = [Ar] $4s^1 3d^{10}$; Cr = [Ar] $4s^1 3d^5$

- Electronic configuration reveals block, period and the group of an elements
- Block of the elements is the orbital that accommodates the last electron
- Period – principal quantum number of the outermost shell.



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PERIODICITY OF CHEMICAL PROPERTIES II

PERIODIC TRENDS IN PROPERTIES

ATOMIC AND IONIC RADII

The atomic or Ionic radius is determined primarily by the

1. The arrangement of electrons around the nucleus
2. The strength of the nucleus pulls on the electrons towards the nucleus

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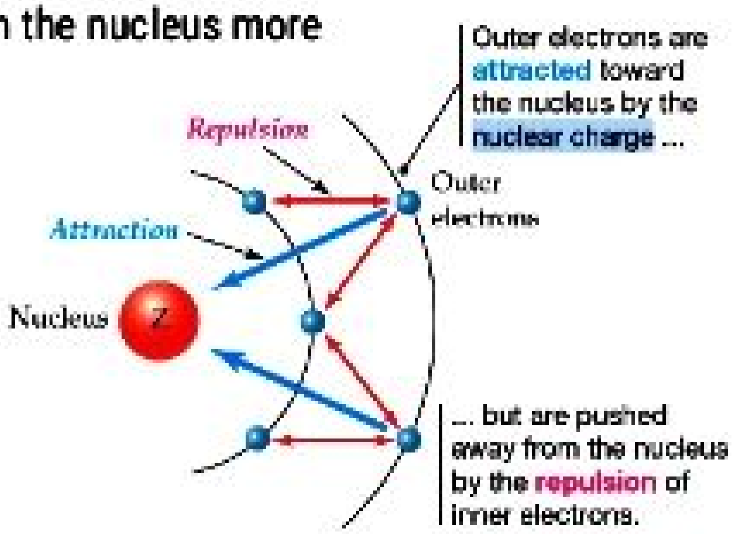
ATOMIC AND IONIC RADII

NUCLEAR CHARGE

Penetration effect is the increase in the nuclear charge that acts on electrons that approach the nucleus more closely.

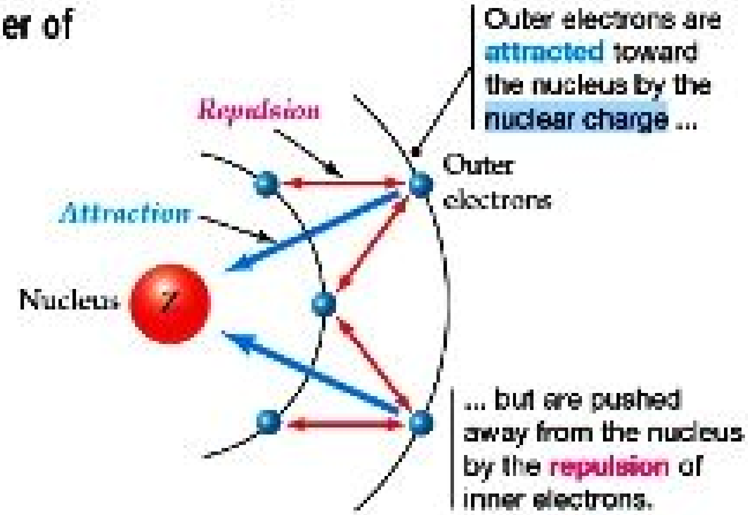

Outer electrons are attracted toward the nucleus by the nuclear charge ...

... but are pushed away from the nucleus by the repulsion of inner electrons.

ATOMIC AND IONIC RADII

NUCLEAR CHARGE

the degree of penetration by an electron rest on the orbital the electron occupies and it decreases in the order of



PERIODIC VARIATION OF ATOMIC AND IONIC RADII

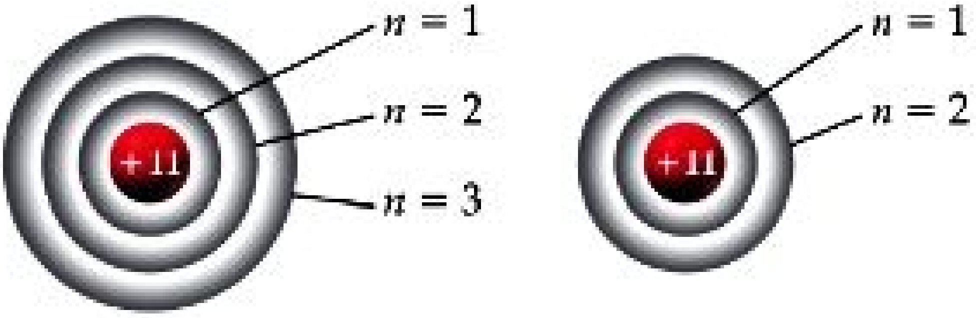
In representative (s- and p- block) elements:

Atomic radius decrease across a period due to increasing effective nuclear charge (Zeff). The increasing Zeff constantly draws the valence electrons closer to the nucleus, as a result, causes a reduction in the bonding atomic radius. If all are van der Waals radii, then Li>Be>B>C>N>O>F>Ne

The atomic radius for d-block elements decreases, remain constant and increases again.

ATOMIC AND IONIC RADII

NUCLEAR CHARGE

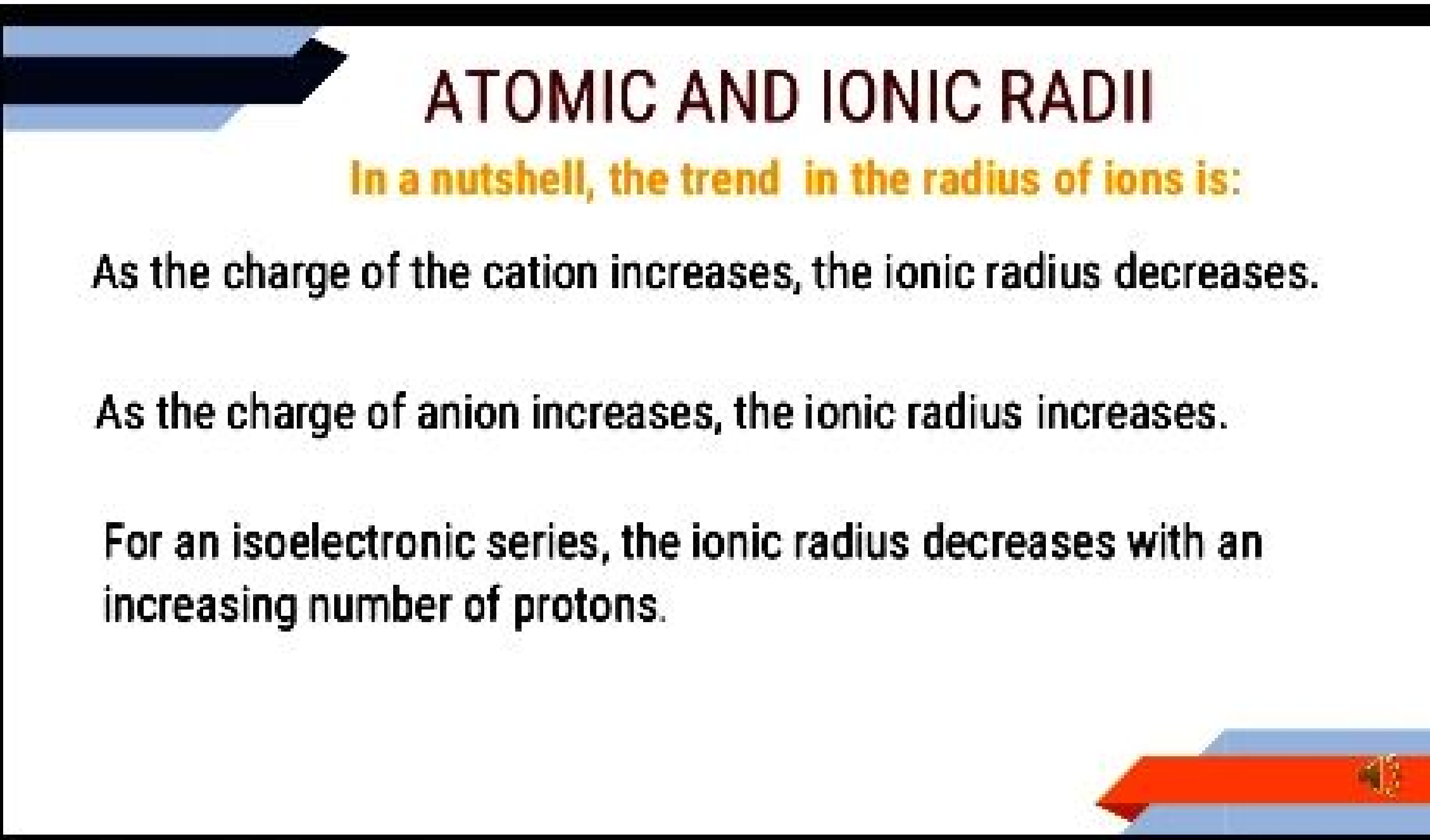


$\mathbf{Na:}\ 1s^2\,2s^2\,2p^6\,3s^1 \xrightarrow{-e^-} \mathbf{Na^+:}\ 1s^2\,2s^2\,2p^6$ or [Ne]

ATOMIC AND IONIC RADII

NUCLEAR CHARGE

$\mathbf{Cl:}\ [\mathrm{Ne}]\,3s^2\,3p^5 \xrightarrow{+e^-} \mathbf{Cl^-:}\ [\mathrm{Ne}]\,3s^2\,3p^6$



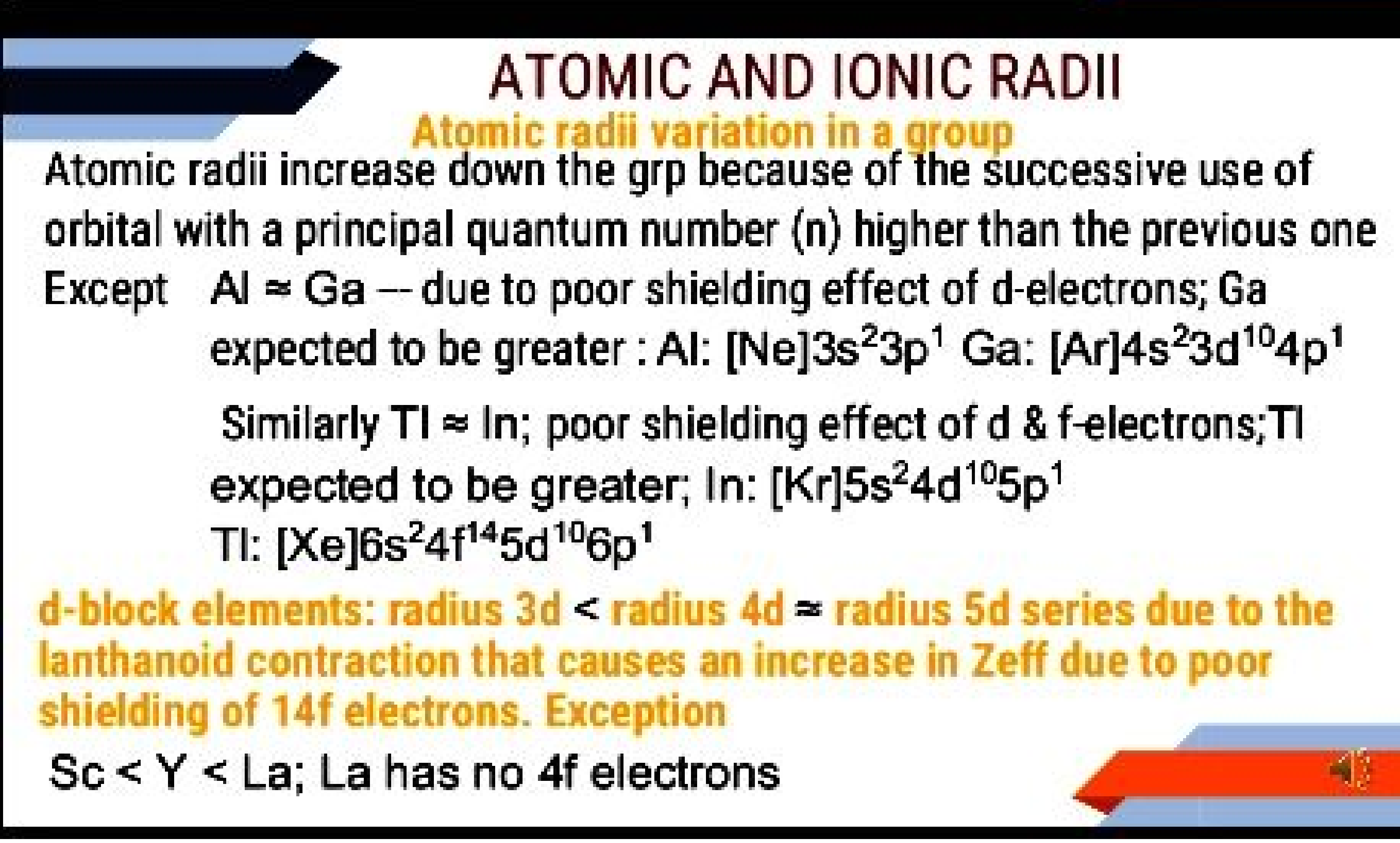
ATOMIC AND IONIC RADII

In a nutshell, the trend in the radius of ions is:

As the charge of the cation increases, the ionic radius decreases.

As the charge of anion increases, the ionic radius increases.

For an isoelectronic series, the ionic radius decreases with an increasing number of protons.



ATOMIC AND IONIC RADII

Atomic radii variation in a group

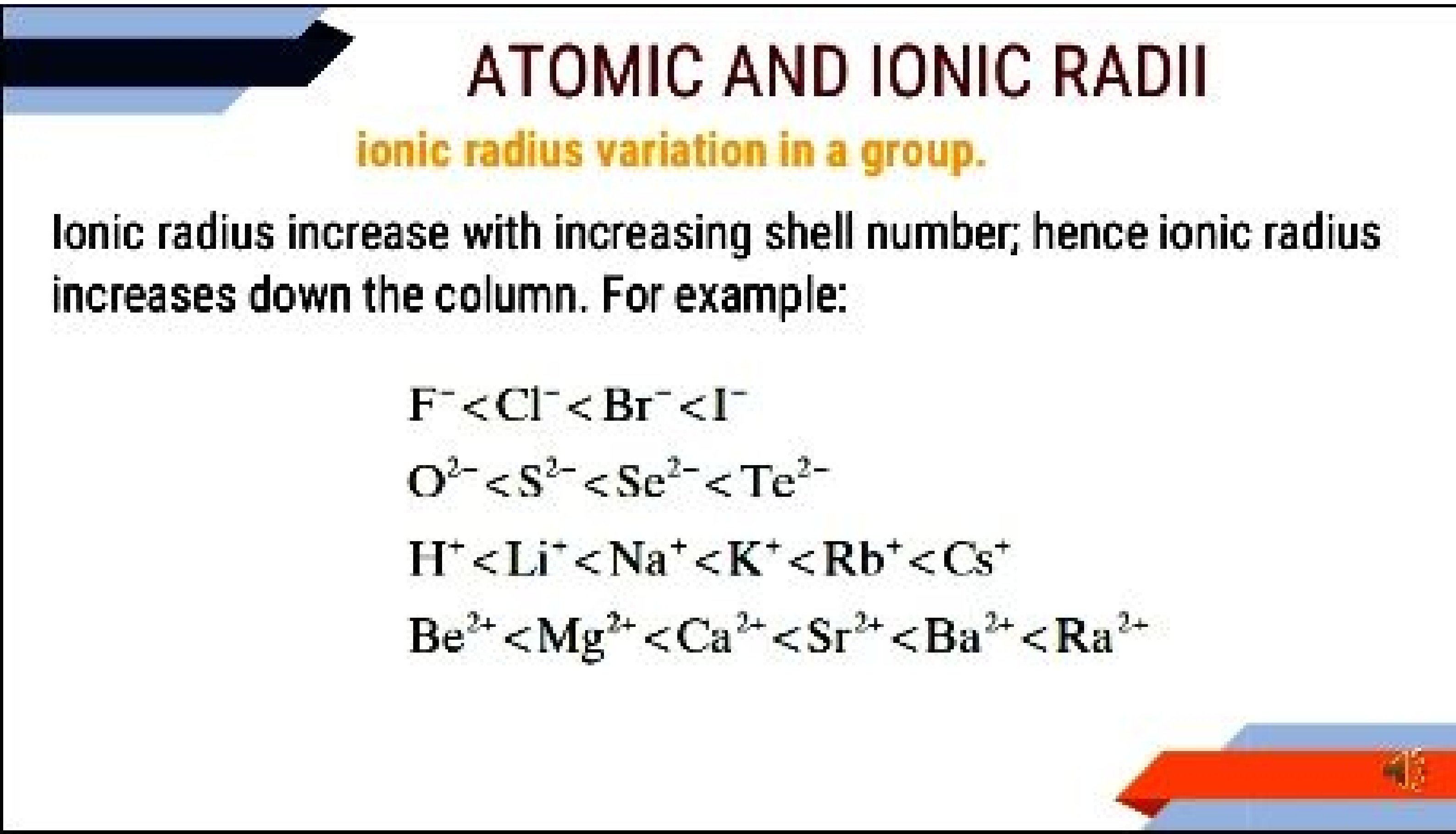
Atomic radii increase down the grp because of the successive use of orbital with a principal quantum number (n) higher than the previous one

Except Al ≈ Ga -- due to poor shielding effect of d-electrons; Ga expected to be greater : Al: [Ne]$3s^2 3p^1$ Ga: [Ar]$4s^2 3d^{10} 4p^1$

Similarly Tl ≈ In; poor shielding effect of d & f-electrons;Tl expected to be greater; In: [Kr]$5s^2 4d^{10} 5p^1$
Tl: [Xe]$6s^2 4f^{14} 5d^{10} 6p^1$

d-block elements: radius 3d < radius 4d ≈ radius 5d series due to the lanthanoid contraction that causes an increase in Zeff due to poor shielding of 14f electrons. Exception

Sc < Y < La; La has no 4f electrons



ATOMIC AND IONIC RADII

ionic radius variation in a group.

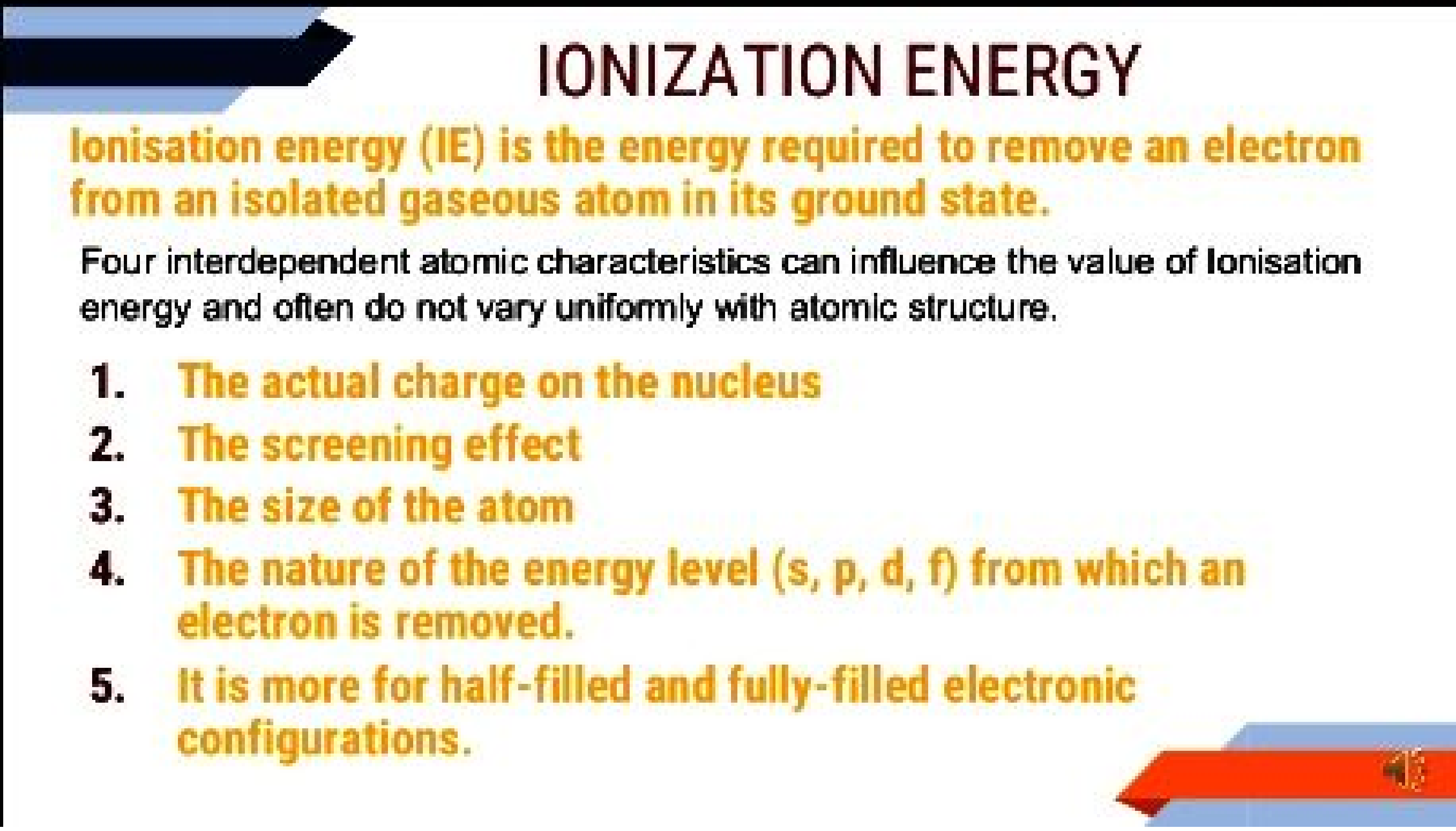
Ionic radius increase with increasing shell number; hence ionic radius increases down the column. For example:

$$F^- < Cl^- < Br^- < I^-$$

$$O^{2-} < S^{2-} < Se^{2-} < Te^{2-}$$

$$H^+ < Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$$

$$Be^{2+} < Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+} < Ra^{2+}$$

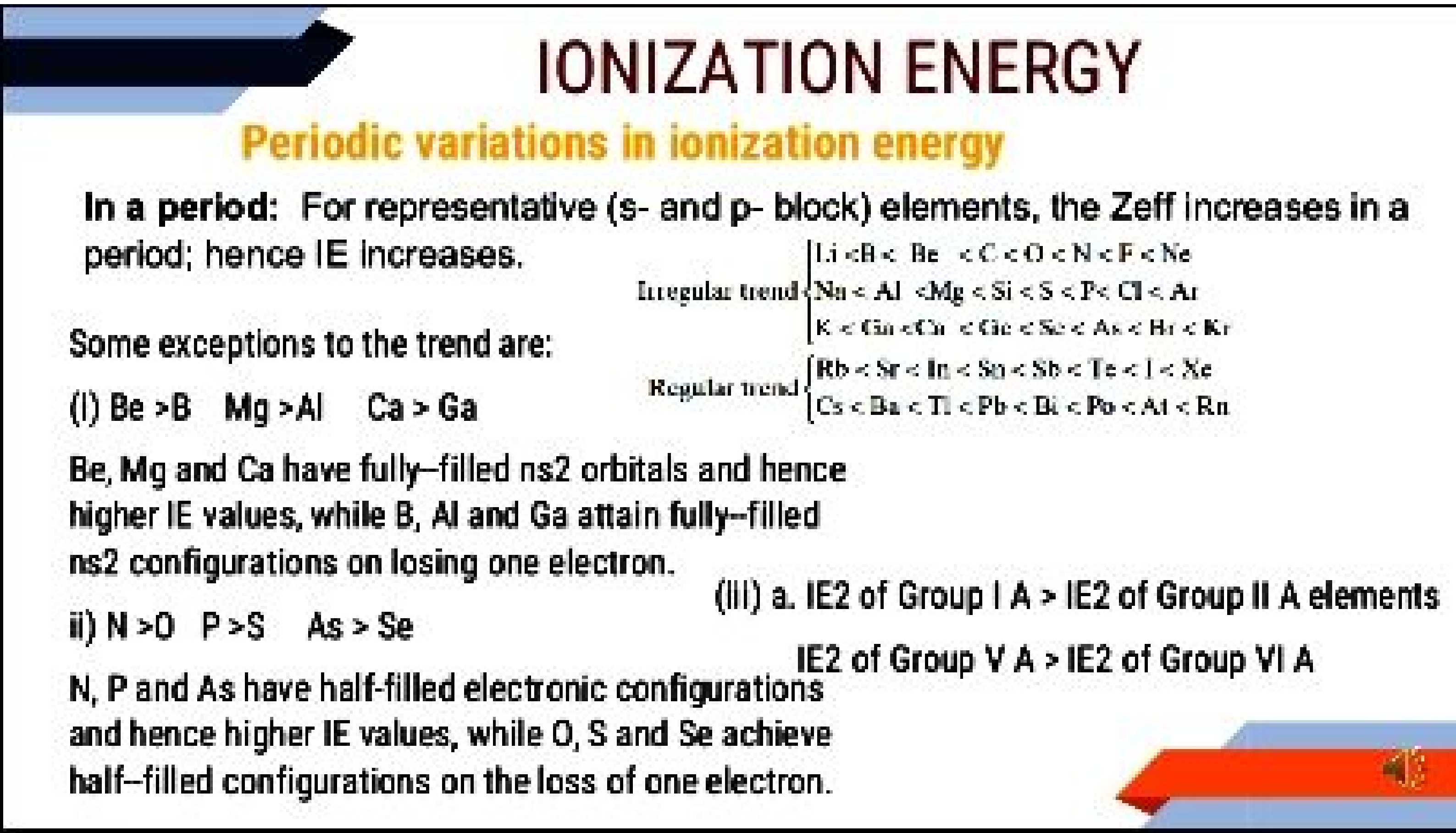


IONIZATION ENERGY

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

Four interdependent atomic characteristics can influence the value of Ionisation energy and often do not vary uniformly with atomic structure.

1. **The actual charge on the nucleus**
2. **The screening effect**
3. **The size of the atom**
4. **The nature of the energy level (s, p, d, f) from which an electron is removed.**
5. **It is more for half-filled and fully-filled electronic configurations.**



IONIZATION ENERGY

Periodic variations in ionization energy

In a period: For representative (s- and p- block) elements, the Zeff increases in a period; hence IE increases.

Irregular trend
$$\begin{cases} Li < B < Be < C < O < N < F < Ne \\ Na < Al < Mg < Si < S < P < Cl < Ar \\ K < Ga < Ca < Ge < Se < As < Br < Kr \end{cases}$$

Regular trend
$$\begin{cases} Rb < Sr < In < Sn < Sb < Te < I < Xe \\ Cs < Ba < Tl < Pb < Bi < Po < At < Rn \end{cases}$$

Some exceptions to the trend are:

(i) Be >B Mg >Al Ca > Ga

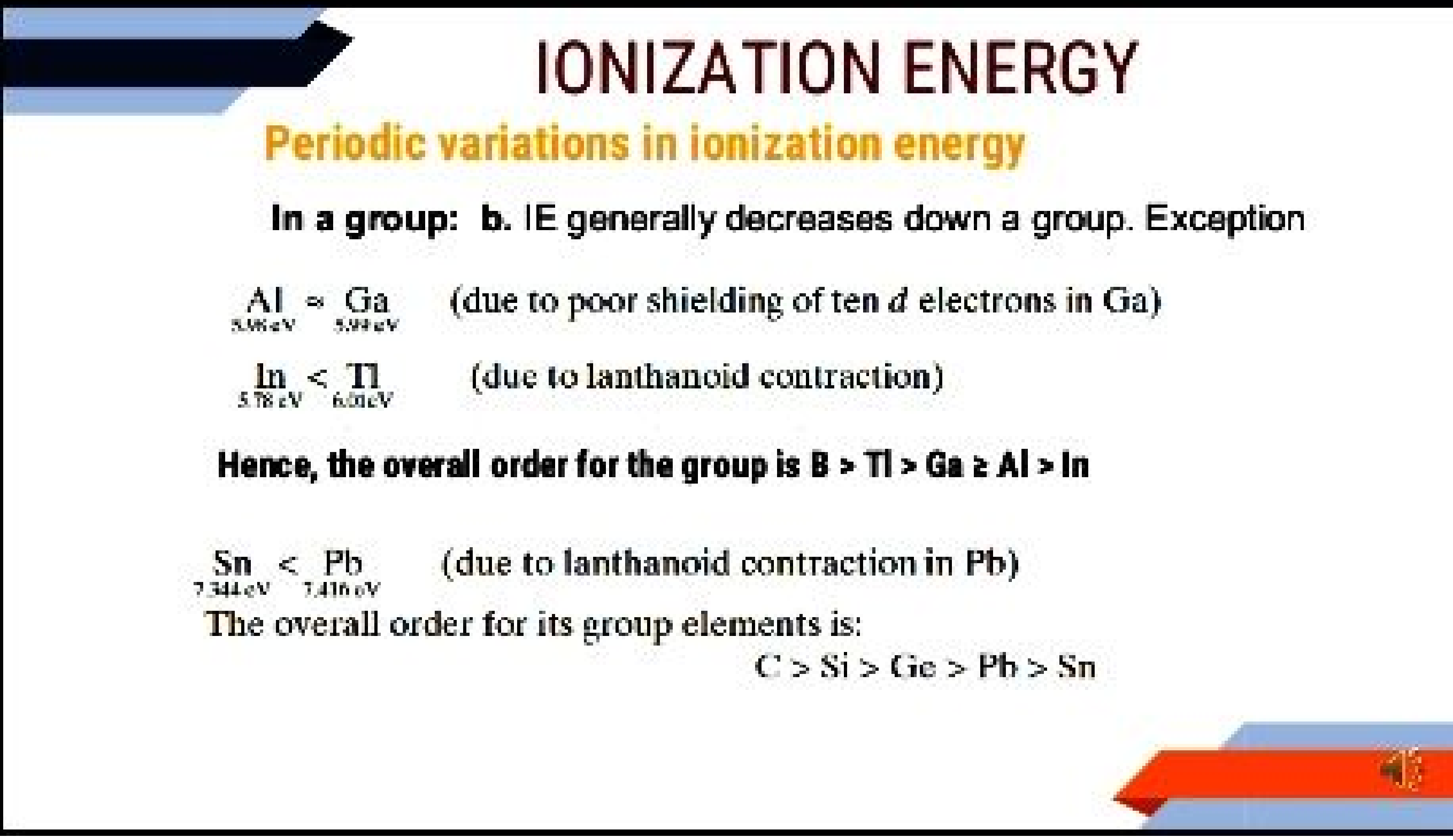
Be, Mg and Ca have fully–filled ns2 orbitals and hence higher IE values, while B, Al and Ga attain fully–filled ns2 configurations on losing one electron.

ii) N >O P >S As > Se

N, P and As have half-filled electronic configurations and hence higher IE values, while O, S and Se achieve half–filled configurations on the loss of one electron.

(iii) a. IE2 of Group I A > IE2 of Group II A elements

IE2 of Group V A > IE2 of Group VI A



IONIZATION ENERGY

Periodic variations in ionization energy

In a group: **b.** IE generally decreases down a group. Exception

$\underset{5.98\,eV}{Al} \approx \underset{5.99\,eV}{Ga}$ (due to poor shielding of ten *d* electrons in Ga)

$\underset{5.78\,eV}{In} < \underset{6.08\,eV}{Tl}$ (due to lanthanoid contraction)

Hence, the overall order for the group is B > Tl > Ga ≥ Al > In

$\underset{7.344\,eV}{Sn} < \underset{7.416\,eV}{Pb}$ (due to lanthanoid contraction in Pb)

The overall order for its group elements is:

C > Si > Ge > Pb > Sn

IONIZATION ENERGY

Periodic variations in ionisation energy

For d-block elements: In a period, IE increases slightly due to an increase in Zeff across the period but is not prominent. The sudden jump from Cu to Zn, Silver to cadmium and gold to mercury due to fully-filled configurations.

In a group: IE1 of 3d series ≈ IE1 of 4d series while IE1 of 4d series < IE1 of 5d series due to lanthanide contraction. The exception to the trend is: $\underset{6.54\ \text{eV}}{\text{Sc}} > \underset{6.38\ \text{eV}}{\text{Y}} > \underset{5.57\ \text{eV}}{\text{La}}$

Note that lanthanide contraction is not observed in the case of lanthanum.

Ionisation energies are always positive – energy is always added to separate a negatively charged electron from the resultant positively charged cation. Electron affinities, however, are generally negative - energy is usually released when a neutral atom adds an electron.

ELECTRON AFFINITIES

Electron Affinity (Eea)- is the energy change that occurs when an electron is added to an isolated atom in the gaseous state. The more negative the Eea, the greater the tendency of the atom to accept an electron and the more stable the anion that results. EA1 > EA2

Factors that influence electron affinity

1. **Zeff; Eea increases with increasing Zeff**
2. **The size of the atom: with constant Zeff, Eea decreases with increasing atomic radius**
3. **Electronic configuration**
4. **EA of half-filled and full-filled electronic configuration is less**
5. **EA order of adding electron** s > p > d > f **for same principal quantum number.**

ELECTRON AFFINITIES TRENDS

In a group: EA decrease, but for p-block elements, the EA1 of second-period element < EA1 of the third-period element.

b. In a period: EA increases across the period with increasing Zeff (except inert gases). Some exceptions to the trend are: (i) EA of alkali metals > EA of alkaline earth metals

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ELECTRONEGATIVITY

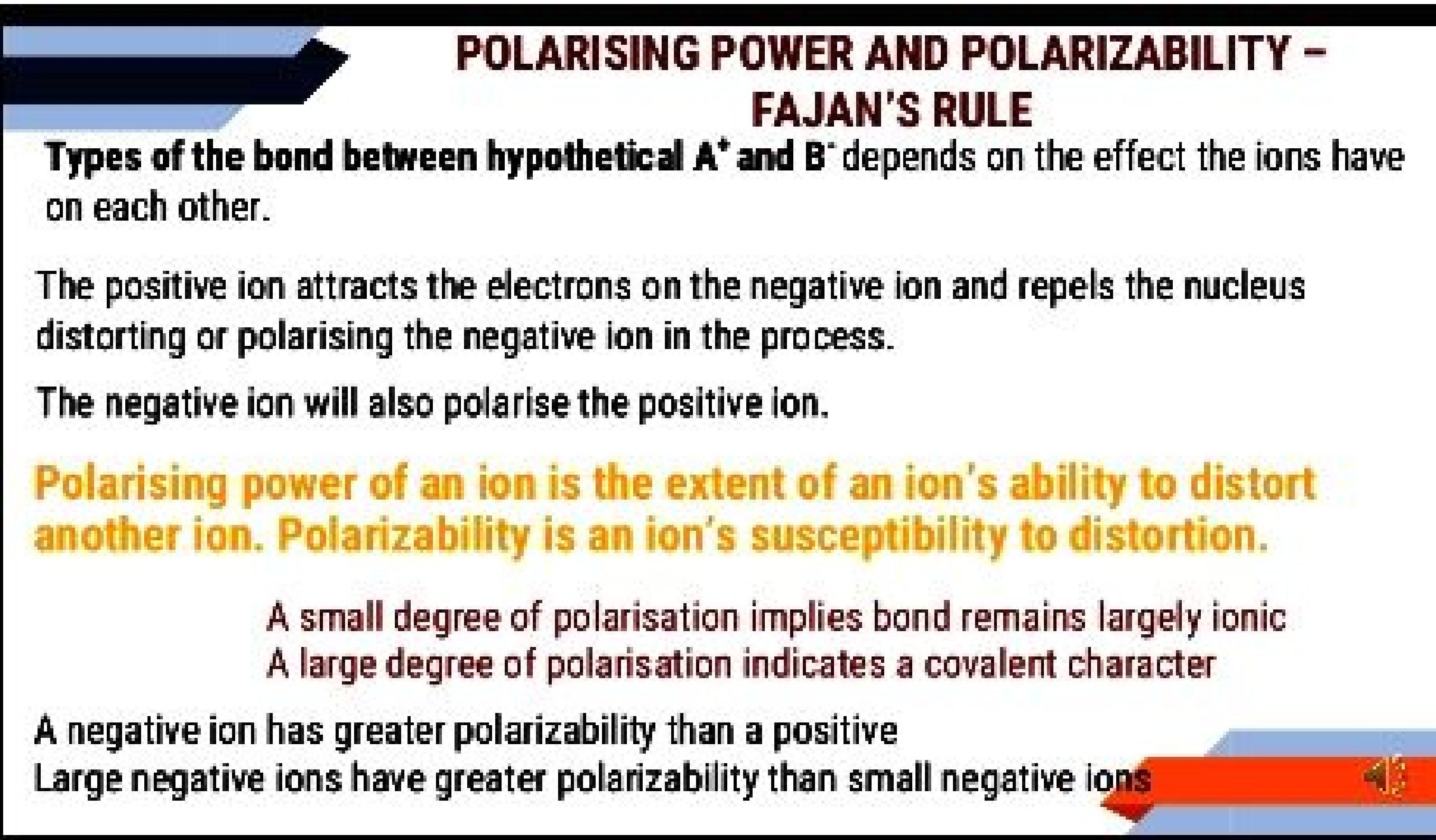
In a period, the electronegativity increases from left to right as Zeff increases.
In a group, the electronegativity decreases in general.

Electronegativity depends on the following factors.

1. It decreases when the radius increases.
2. It increases when Zeff increases.
3. It decreases when s (shielding constant) increases.
4. It increases when the oxidation state of an element increases.
5. It increases as the percentage of s character in hybrid orbital increases.

Important points

1. Fluorine has the highest electronegativity in the periodic table, and Caesium has the lowest electronegativity (excluding the radioactive element Fr).
2. Alkali metals have the lowest electronegativity in their respective period.
3. Halogens have the highest electronegativity in their respective period.
4. Electronegativity of inert gases is zero.



POLARISING POWER AND POLARIZABILITY – FAJAN'S RULE

Types of the bond between hypothetical A^+ and B^- depends on the effect the ions have on each other.

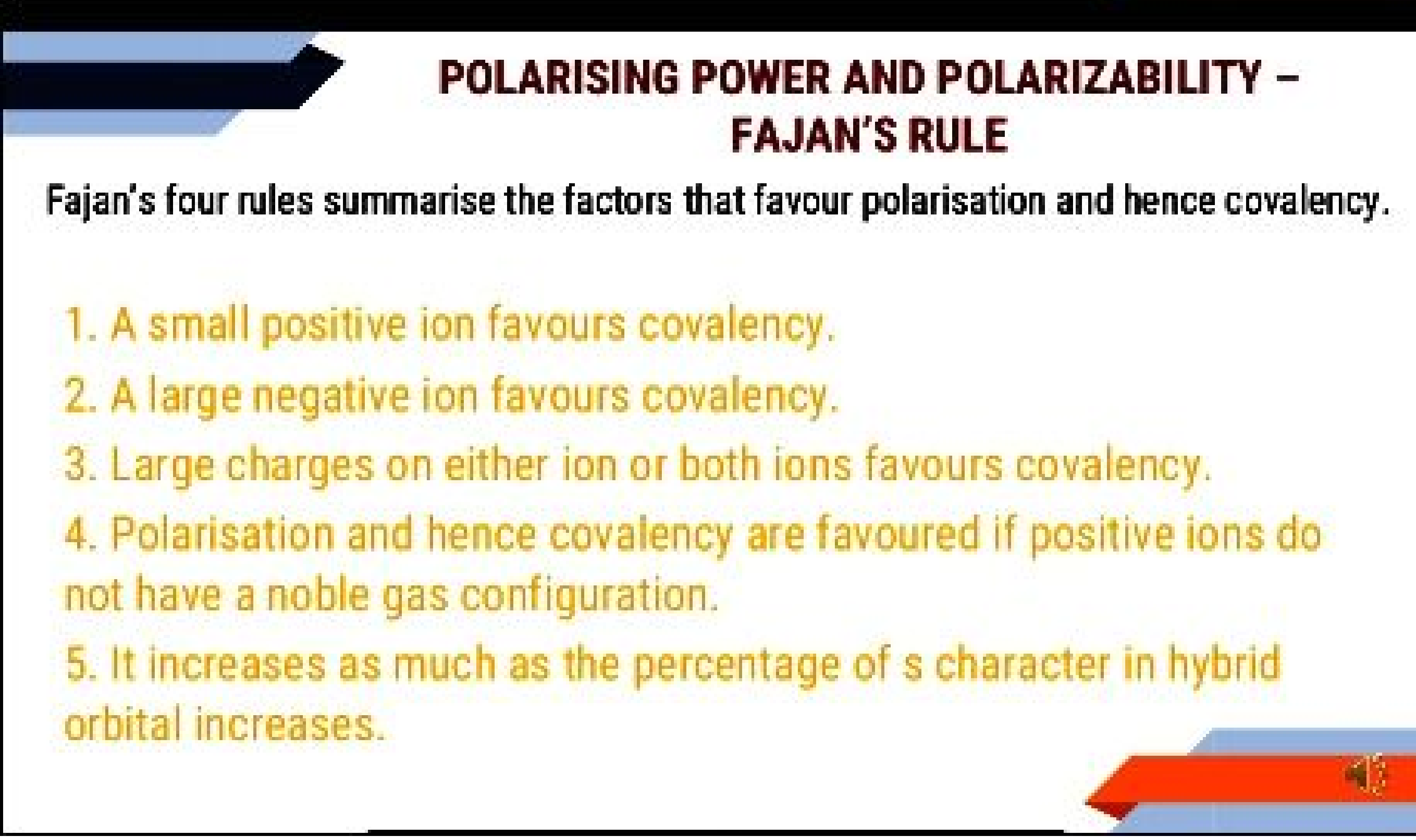
The positive ion attracts the electrons on the negative ion and repels the nucleus distorting or polarising the negative ion in the process.

The negative ion will also polarise the positive ion.

Polarising power of an ion is the extent of an ion's ability to distort another ion. Polarizability is an ion's susceptibility to distortion.

A small degree of polarisation implies bond remains largely ionic
A large degree of polarisation indicates a covalent character

A negative ion has greater polarizability than a positive
Large negative ions have greater polarizability than small negative ions



POLARISING POWER AND POLARIZABILITY – FAJAN'S RULE

Fajan's four rules summarise the factors that favour polarisation and hence covalency.

1. A small positive ion favours covalency.
2. A large negative ion favours covalency.
3. Large charges on either ion or both ions favours covalency.
4. Polarisation and hence covalency are favoured if positive ions do not have a noble gas configuration.
5. It increases as much as the percentage of s character in hybrid orbital increases.

CHEMICAL BONDING III

CHEMICAL BONDING

How and why do atoms combine to form molecules? Why do atoms form bonds?

A molecule will only be formed if it is more stable and has lower energy than the individual atoms; otherwise, the bond will not be formed.

Note that only valence electrons of an atom are involved in bond formation.

Bond formation aimed at achieving a stable configuration

A chemical bond is a force that acts strongly enough between two atoms or groups of atoms to hold them together in a different, stable species having measurable properties.

TYPES OF CHEMICAL BOND

Three basic types of chemical bonds: ionic, covalent and metallic.

Atoms attain stable configuration in 3 ways: losing electrons (electropositive elements), gaining electrons (electronegative elements), and sharing electrons (those with little tendency to lose or gain electrons)

3 basic types of intramolecular chemical bonds are possible:

(a) Ionic bond: electropositive and electronegative elements combined
(b) Covalent bond: 2 electronegative elements combined
(c) Metallic bond: 2 electropositive elements combined

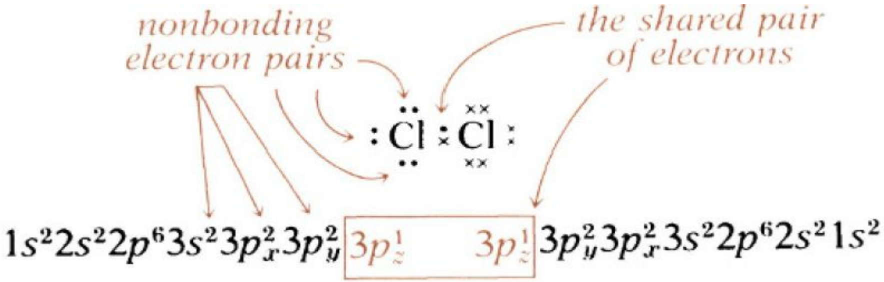
TYPES OF CHEMICAL BOND

Ionic bond: outright loss of one or more electrons to another. The +ve & -ve ions formed are held by the force of electrostatic attraction. Consider NaCl as an example.

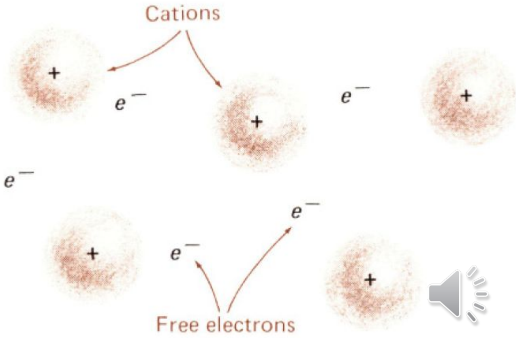
$$Na + Cl \longrightarrow Na^+Cl^-$$

$1s^2\,2s^2\,2p^6\,3s^1$ $\quad 1s^2\,2s^2\,2p^6\,3s^2\,3p^5$ $\quad 1s^2\,2s^2\,2p^6$ $\quad 1s^2\,2s^2\,2p^6\,3s^2\,3p^6$

Covalent bond: a pair of electrons shared between atoms, Cl_2 as an example; dative if the shared pair comes from one atom; identical



Metallic bond: based on valence electrons that are free to move around throughout the crystal. Metallic is the attraction between positive metal ions and surrounding freely mobile electrons.

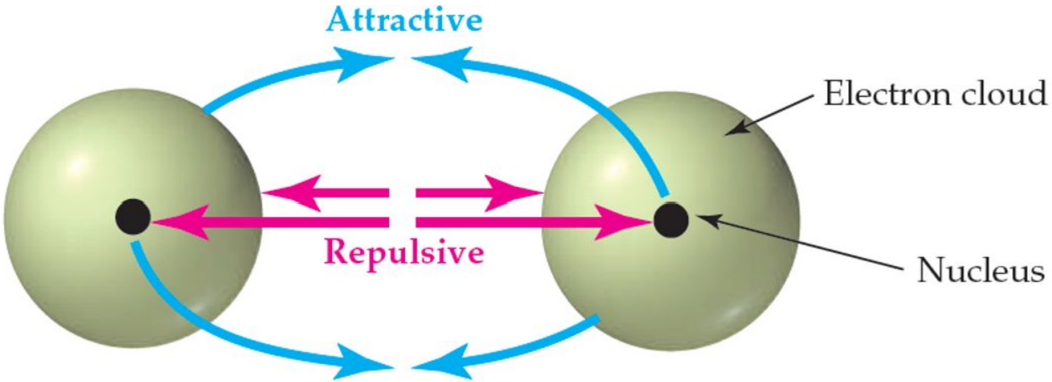


COVALENT BOND IN MOLECULES

SIMPLE COVALENT

Covalent bonding is based on electron-pair sharing and is the attraction between atoms that share electrons, formed when the gain or loss of e^- is not easy.

Consider H-H



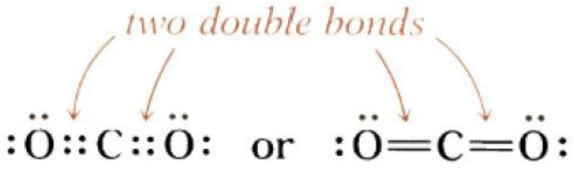
The nucleus-electron attractions are greater than the nucleus-nucleus and electron-electron repulsions, resulting in a net attractive force that binds the atoms together

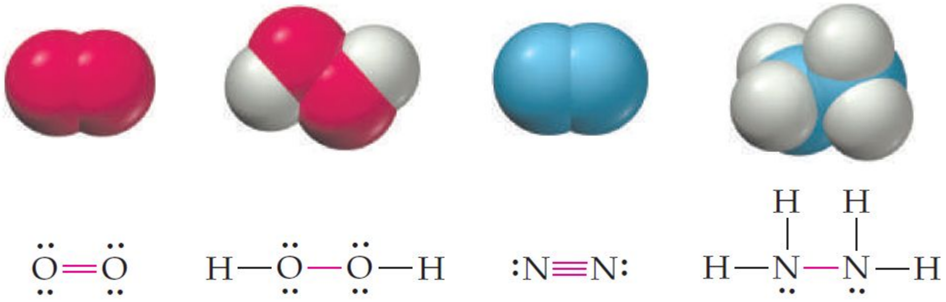
COVALENT BOND IN MOLECULES

MULTIPLE COVALENT BONDS

Double bond: 2 pairs of electrons shared; Triple bond: 3 pairs of electrons share

Multiple bonds are shorter and stronger than their corresponding single bond.





Bond length:	121 pm	148 pm	110 pm	145 pm
Bond strength:	498 kJ/mol	213 kJ/mol	945 kJ/mol	275 kJ/mol

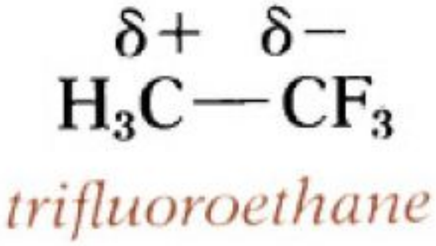
COVALENT BOND IN MOLECULES

POLAR COVALENT BONDS: ELECTRONEGATIVITY

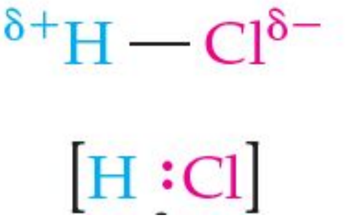
Non-polar covalent bond: electrons shared equally, e.g. Cl_2, H_2 N_2
Polar covalent bond: unequal sharing of electrons, e.g. HCl, H_2O, CH_3CF_3

Bond polarity: caused by differences in electronegativity

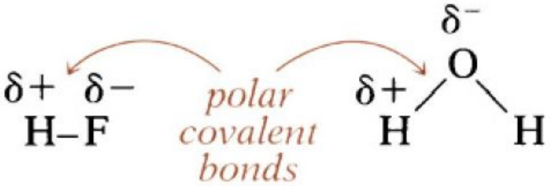
Polar covalent bonds: unsymmetrical electron distribution; bonding electrons more strongly attracted by one atom than the other


$\overset{\delta+}{H_3C}—\overset{\delta-}{CF_3}$

trifluoroethane


$^{\delta+}H—Cl^{\delta-}$

$[H:\ddot{Cl}]$



GENERAL PROPERTIES OF COVALENT BOND

As molecular weight increases, melting and boiling points increase for similar covalent compounds

Most covalent substances have relatively low melting & boiling points; low heat of vapourisation and fusion

Exists as gases, liquids & solids; insoluble in polar solvents but soluble in non-polar solvent

Solids are usually soft, brittle, waxy, and easily broken

Melting & boiling point are much lower than those of ionic and metallic.

How high or low the properties do not depend on the force of the covalent bond itself.

A few substances display covalent characteristics but are hard and have high melting points due to a network of covalent bonds, e.g. quartz, borazon, and diamond.

COORDINATE COVALENT BOND

Electrons pair shared come from one atom or molecule.

Once the coordinate covalent bond is formed, it becomes identical to a typical covalent bond.

Have all the characteristics of normal covalent bonds

Melting & boiling point are relatively higher than those of normal covalent bonds but lower than those of ionic and metallic.

IONIC BOND

Ionic bonding: Electron transfer between positive and negative ions.

High melting & boiling points; high heat of vaporisation and fusion.
Generally exist as crystalline solids.
Ionic crystalline substances are hard; however, ionic solids are brittle
Solid ionic compounds are poor conductors of electricity and heat.
Conductive when dissolved in water or when in a molten state.
They are highly polar, soluble in polar solvents but insoluble in non-polar solvents, and most are soluble in water.

METALLIC BONDS

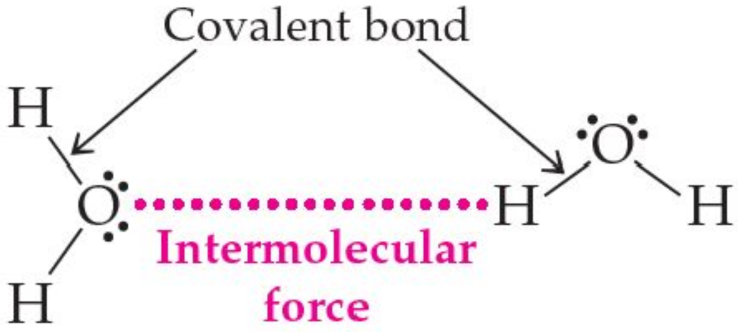
Metallic bond: based on valence electrons that are free to move around throughout the crystal. Metallic is the attraction between positive metal ions and surrounding freely mobile electrons.

- High melting & boiling points; high heat of vaporisation and fusion.
- High melting & boiling points are higher for metals with a larger number of valence electrons which also affects other properties.
- Exceptionally good conductors of electricity and heat
- High malleability (can be hammered into shape) and ductility (can be drawn out into wires).
- Metallic lustre in the liquid state but could be dull when metal oxide layer formed on the surface.

INTERMOLECULAR FORCES

They influence macroscopic properties such as melting & boiling points and solubility

They are weaker than ionic and covalent bonds



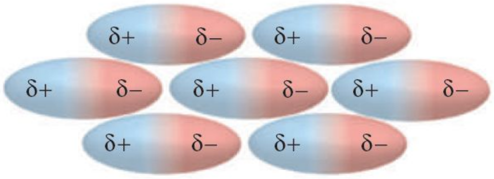
They are called van der Waals forces

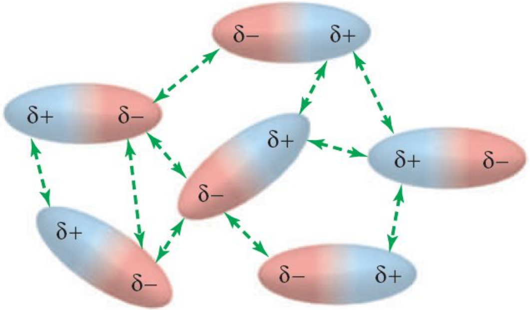
Forces include dipole-dipole forces and hydrogen bonds

DIPOLE-DIPOLE FORCES

They influence macroscopic properties such as melting & boiling points and solubility.

..polar molecules attract one another when they orient with unlike charges close together





..they repel when they orient with like charges together…

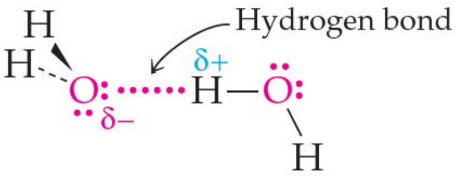
Example: SiH_4 is non-polar, H_2S has a dipole moment twice that of PH_3; SiH_4 has the lowest melting & boiling points, and H_2S has the highest.

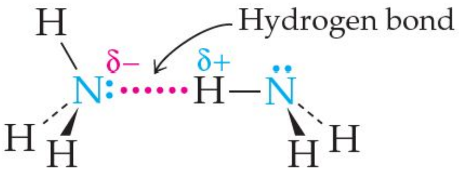
..the more polar the substance, the greater the strength of its dipole-dipole interactions …

HYDROGEN BONDS

A hydrogen bond is an electrostatic interaction between a hydrogen atom bonded to a very electronegative atom.

..stronger than ordinary dipole-dipole interactions





..influence melting & boiling points

Example: HF, HCl, HBr & HI; boiling points will regularly increase from HCl, HBr to HI, with HF having the highest boiling points due to hydrogen bonding.

..strongest when hydrogen is directly bonded to O, N, F