Lesson 2 : Covalent Bond and Molecular Geometry

Lesson Objectives

At the end of this lesson, you will be able to:

- describe the valence shell electron pair repulsion theory (VSEPR).
- distinguish between the bonding pairs and non-bonding pairs of electrons.
- describe how electron pair arrangements and shapes of molecules can be predicted from the number of electron pairs
- explain why double bonds and lone pairs cause deviations from ideal bond angles
- explain the term dipole moment with the help of a diagram.
- describe the relationship between dipole moment and molecular geometry.
- describe how bond polarities and molecular shapes combine to give molecular polarity
- predict the geometrical shapes of some simple molecules on the bases of hybridization and the nature of electron pairs
- construct models to represent shapes of some simple molecules.
- define intermolecular forces
- name the different types of intermolecular forces.
- explain dipole-dipole interactions.
- give examples of dipole-dipoleinteraction
- define hydrogen bonding.
- explain the effect of hydrogen bondo nthe properties of substances.
- give reasons why hydrogen bonding is stronger than ordinary dipole-dipole interactions.
- explain dispersion (London)forces.
- give examples of dispersion forces.
- predict the strength of intermolecular.forces for a given pair of molecules.

Brainstorming Questions

- Can two non-metal atoms combine together? How?
- Why doesn't a hydrogen atom lose an electron and form an ionic bond?
- Give one main difference between ionic and covalent bonds.
- Explain the formation of polar covalent and coordinate covalent bonds.

key terms/Concepts

- Molecular geometry
- Electron set arrangement
- Lewis Structure
- VSEPR theory

Molecular geometry refers to the three-dimensional arrangement of atoms in a molecule and the spatial relationships between these atoms. It is determined by the arrangement of bonding electron pairs and lone pairs of electrons around the central atom(s) in a molecule. The geometry influences various physical and chemical properties of molecules, including their reactivity, polarity, and biological activity

- Intermolecular force
- Hydrogen bond
- Dipole moment
- Dispersion Force

Intermolecular forces (IMFs) are the attractive or repulsive forces that exist between molecules and atoms, influencing the physical properties and behavior of substances. These forces are weaker than chemical bonds within molecules but are essential in determining many properties of liquids and solids. Here's an overview of the main types of intermolecular forces:

Types of Intermolecular Forces:

1. **London Dispersion Forces (Van der Waals Forces)**:

- **Nature**: London dispersion forces are the weakest type of IMF and occur due to temporary fluctuations in electron distribution that create temporary dipoles.
- **Effect**: These forces exist between all molecules and atoms, regardless of polarity, and increase with molecular size.

2. **Dipole-Dipole Interactions**:

- **Nature**: Dipole-dipole interactions occur between polar molecules where the positive end of one molecule is attracted to the negative end of another.
- **Effect**: They are stronger than London dispersion forces and contribute to the higher boiling points and melting points of polar substances.

3. **Hydrogen Bonding**:

- **Nature**: Ion-dipole interactions occur between an ion and a polar molecule.
- **Effect**: They are significant in solutions where ionic compounds dissolve in polar solvents, such as water dissolving salt (NaCl).

Importance of Intermolecular Forces:

- **Physical Properties**: IMFs determine properties such as boiling point, melting point, viscosity, and surface tension of substances.
- **Phase Changes**: They affect the transition between solid, liquid, and gas phases.
- **Chemical Reactions**: IMFs influence the solubility and reaction rates of substances in solution.
- **Biological Systems**: IMFs play a role in the structure and function of biological molecules and interactions within biological systems.

Examples:

- **Water (H_2O)**:
- **IMFs**: Hydrogen bonding between water molecules contributes to its high boiling point and surface tension.
- **Ethanol (CH_3CH_2OH)**:

- **IMFs**: Dipole-dipole interactions and hydrogen bonding between ethanol molecules contribute to its ability to dissolve in water (polar solvent).
- **Methane (CH_4)**:
- **IMFs**: London dispersion forces are the primary IMFs between methane molecules due to its non-polar nature.

Covalent Bond theories

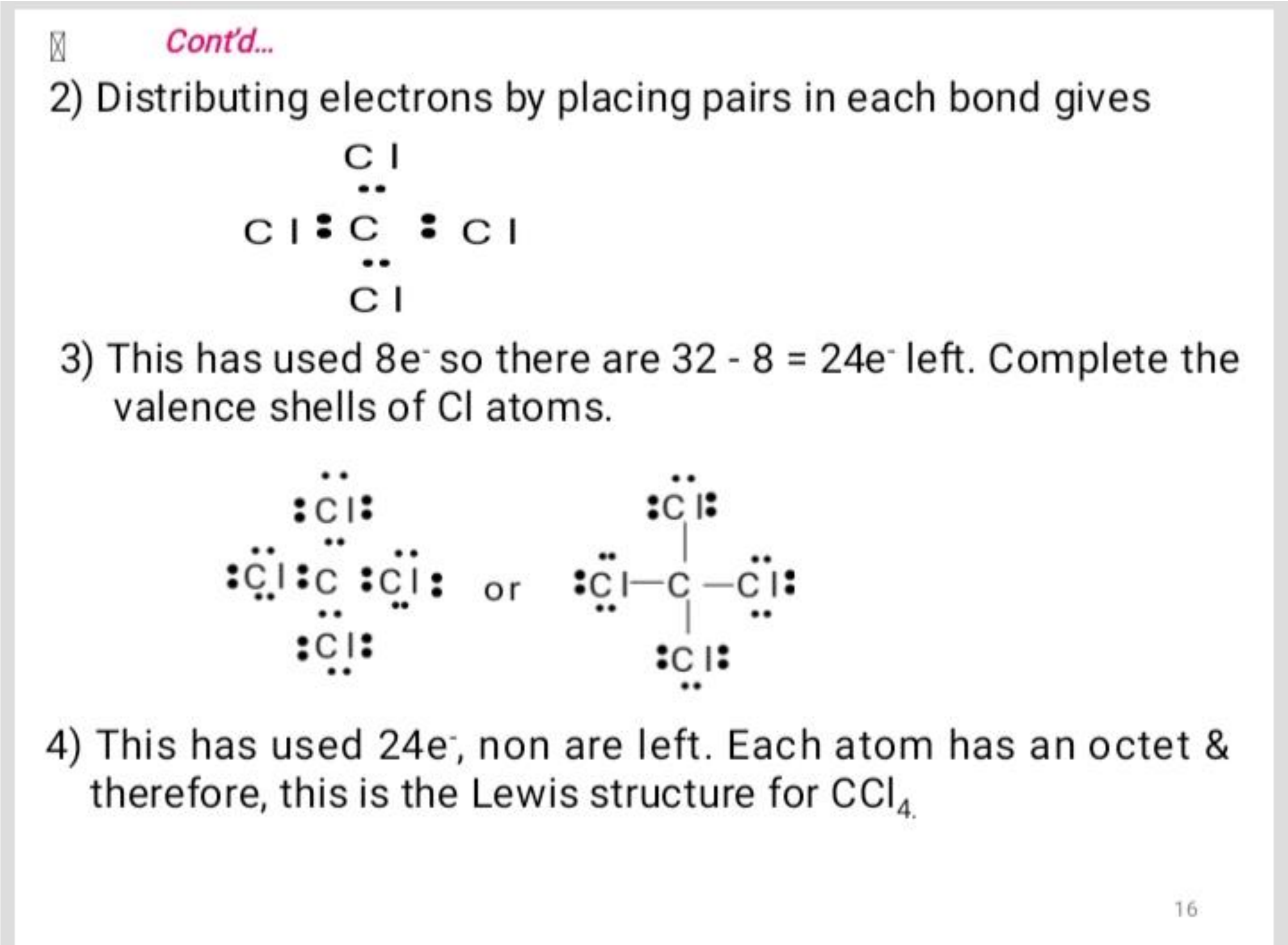
2.3.1 Lewis structure of Covalent compound

- The Lewis structure (or Lewis formula)- is two-dimensional structural formula consists of electron-dot symbols that depict each atom and its neighbors.
- The bonding pairs that hold them together, and the lone pairs that fill each atom's outer level (valence shell) – octet rule.
  Steps to assign Lewi's dot formula.

- Write the electron configuration of the combining atoms.
- determine the valence shell electrons of each atom.
- Add the valence shell electrons of all combining atoms
- (charge on the molecule:
  if the molecule is positively charged, subtract the number of charges from the total valence electrons;
  if the molecule is negatively charged add the number of charge to the total valence shell electrons.
- Decide the central atom:
  The atom with fewer numbers is taken as central atom. Large sized and relatively electropositive atoms are always selected as central atom. Example H, O and halogens are always selected as surrounding atoms.
  O and C have a tendency to form O-O and C-C chain respectively
- a pair of electron between central atom and surrounding atom (form a temporary single bond).
- Complete the octet starting from the surrounding atom.
- Put any remaining as after the surrounding atoms complete their octet is put as lone pair on the central atom.
- If the central atom has less than an octet, you must form multiple bonds so that each atom has an octet
  what is the Lewis structure for CCl_4 ?

- Solution
  1) We count the valence electrons
  Carbon is group IVA contributes 4e-,
  Chlorine Group IIIA contributes 7* 4=28e-
  total valance electron =32
- Distributing electrons by placing pairs in each bond gives:

.This has used 8e- so there are 32 – 8 = 24e- left. Complete the valence shells of Cl atoms



2.3. 2 Valence Shell Electron Pair Repulsion (VSEPR) Theory

- This theory was proposed for the first time by Sidewick and Powell in 1940 and developed by Gillespie and Nyholm in 1957.
  This theory is very useful in predicting the geometry or shape of polyatomic molecules or ions of non-transition elements.
  According to this theory, "the shape of a given species (molecule or ion) depends on the number and nature of electron pairs surrounding the central atom of the species.
- Molecular Geometry is the general shape of a molecule as determined by the relative position of atomic nuclei.
  The valence shell electron pairs are arranged about each atom so that electron pairs are kept as far away from one another as possible, thus minimizing the electron pair repulsion.

Basic principle of VSEPR Theory

- Electron pairs will arrange themselves to be as far apart as possible so that the repulsion between them is at minimum.
- Lone pair of electrons takes more room on the surface of atom than that of bonding pairs.
- According to the VSEPR theory, the repulsion of electron pair is in the following order:Lp-Lp >Lp -Bp > Bp -Bp
- The repulsive force decreases sharply with increasing bond angle.

Molecular Geometry:
Molecular geometry refers to the spatial arrangement of atoms in a molecule. It describes the actual three-dimensional shape of the molecule, taking into account the positions of all atoms relative to each other.

Molecular geometry is determined primarily by the positions of atoms, regardless of whether they are bonded directly to the central atom or not.

Example: For example, in a molecule like methane (CH_4), the molecular geometry is tetrahedral, meaning the carbon atom is at the center with four hydrogen atoms positioned at the vertices of a tetrahedron.

Electron Set Arrangement (Electron Pair Geometry):
Electron set arrangement (or electron pair geometry) refers to the spatial arrangement of all electron pairs (both bonding and non-bonding) around the central atom in a molecule.

Electron set arrangement is determined by the total number of electron pairs (bonding pairs + lone pairs) around the central atom.

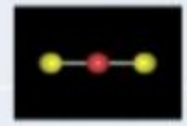
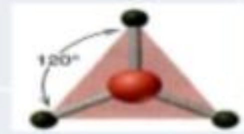
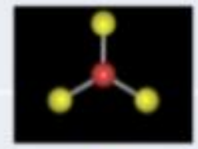
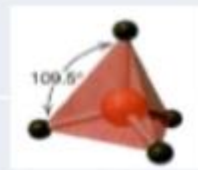
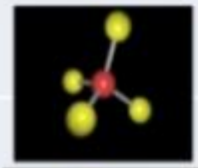
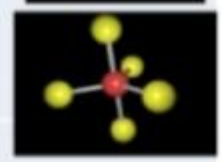
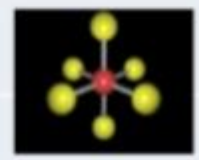
Example: Continuing with the example of methane (CH_4), the electron set arrangement around the central carbon atom is tetrahedral because there are four regions of electron density (four bonding pairs of electrons).

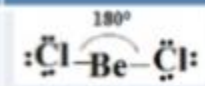
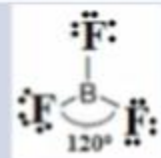
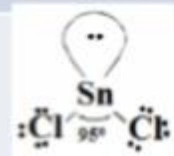
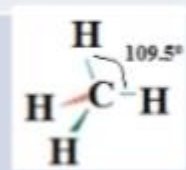
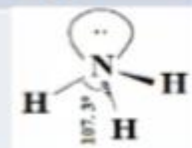
Differences:
Molecular geometry focuses on the actual positions of atoms in space, providing information about the shape of the molecule. Where as Electron set arrangement considers all electron pairs around the central atom, including both bonding pairs and lone pairs, providing a broader perspective on electron distribution.

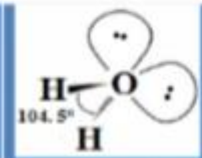
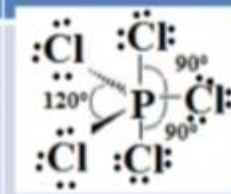
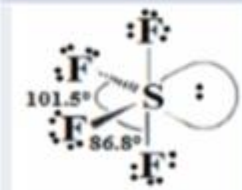
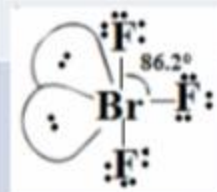
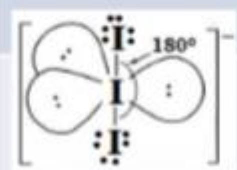
Relationship:
The molecular geometry is often a subset or specific manifestation of the electron set arrangement. For example, in molecules with no lone pairs on the central atom (like methane), the molecular geometry and electron set arrangement are the same (tetrahedral). However, in molecules with lone pairs, the molecular geometry describes the actual shape of the molecule, while the electron set arrangement describes the overall arrangement of electron pairs around the central atom.

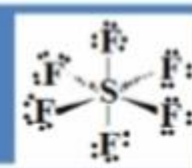
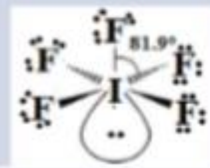
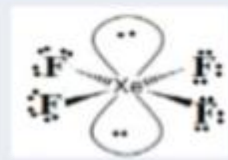
- based on the lewis structure , the shape of molecules is expressed as follow.

Geometry .

Geometrical description	General formula	Angles	Examples	3-D view of geometry	2-Dview
Linear	AX_2	180^0	$BeCl_2$, CO_2, CS_2		
Trigonal-planar	AX_3	120^0	BCl_3,CO_3^{2},SO_3		
Tetrahedron	AX_4	109.5	CH_4,CCl_4,NH_4^+, SiF_4,BF_4^-, ClO_4, PO_4^{3-}		
Trigonal bipyramid	AX_5	90^0,120^0	PF_5, PCl_5,AsF_5		
Octahedron	AX_6	90^0	SF_6,SeF_6,PF_6^-, SiF_6^{2-}		

Electro pairs			Electro pair geometry	Molecular Geometry	Example	Other Examples
Total	Bonding pair	Lone pair				
2	2	0	Linear	Linear		BeF_2, HCN, CS_2, CO_2
3	3	0	Trigonal planar	Trigonal planar		SO_3, NO_3^-, CO_3^{2-}
	2	1	Trigonal planar	Bent(V-shape)		SO_2, $PbCl_2$, $SnBr_2$, O_3 $SnCl_2$
4	4	0	Tetrahedral	Tetrahedral		$SiCl_4$, SO_4^{2-}, ClO_4^-
	3	1	Tetrahedral	Trigonal pyramidal		PF_3, ClO_3^-, H_3O^+

4	2	2	Tetrahedral	Bent (angular)		OF_2, SCl_2
5	5	0	Trigonal bipyramidal	Trigonal bipyramidal		PF_5, AsF_5, SOF_4
	4	1	Trigonal bipyramidal	Distorted tetrahedral(See Saw)		SF_4, IF_4^+, XeO_2F_2, $IO_2F_2^-$
5	3	2	Trigonal bipyramidal	T-shape		ClF_3, $BrCl_3$
	2	3	Trigonal bipyramidal	Linear		XeF_2, IF_2^-

6	6	0	Octahedral	Octahedral		IOF_5, SCl_6
	5	1	Octahedral	Square pyramidal		TeF_5^-, BeF_5, XeF_5^+
	4	2	Octahedral	Square planar		ICl_4^-

- Generally the **electron pair geometry** depends on the **number of electron pairs** around central atom.
- Where as, the **Molecular geometry** depends on both the number of electron pairs and the nature (**bonding** and **lone pair) of electron pairs** around central atom.

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Merits of Knowing Shape of Covalent Compounds

- Knowing the shape (geometry) of covalent molecules is a key to understand its physical and chemical behavior.
  One of the most important and far-reaching effects of molecular shape is molecular polarity, which can influence melting and boiling points, solubility, chemical reactivity, and even biological function.
- Bond Polarity In general, a covalent bond is:
  polar if it occurs between two different atoms.
- non polar if it occurs between two identical atoms
  Dipole Moments

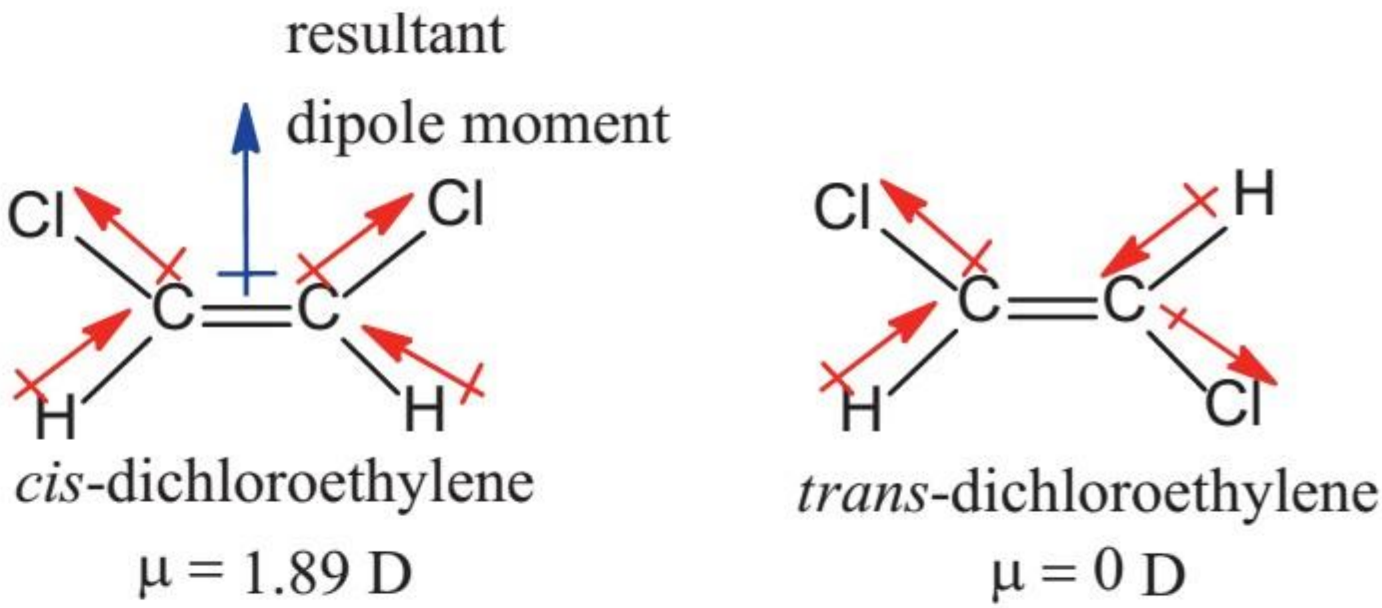
- – It is a measure of the polarity of a bond.- Is often represented by a special arrow.

$$H^{\delta+} - F^{\delta-}$$

Diatomic Molecules – molecules made of only two atoms.
If atoms are the same, molecule is nonpolar.

If atoms are diff., molecule is polar.
NOTE: Polar does not mean charged.
Is Cl_2 polar or nonpolar?
Is CO polar or nonpolar?
Molecules With 3 or More Atoms

- A molecule with 3 or more atoms is:
  Polar if its central atom has lone pairs OR
  If the outer atoms are not all the same.
  Non-polar
- if its central atom has no lone pairs and All the outer atoms are identical.
- Example: CO_2 vs. H_2O
  i) Consider the Lewis structure of CO_2:
  This molecule is non-polar, and water is polar
  Nonpolar and polar molecules



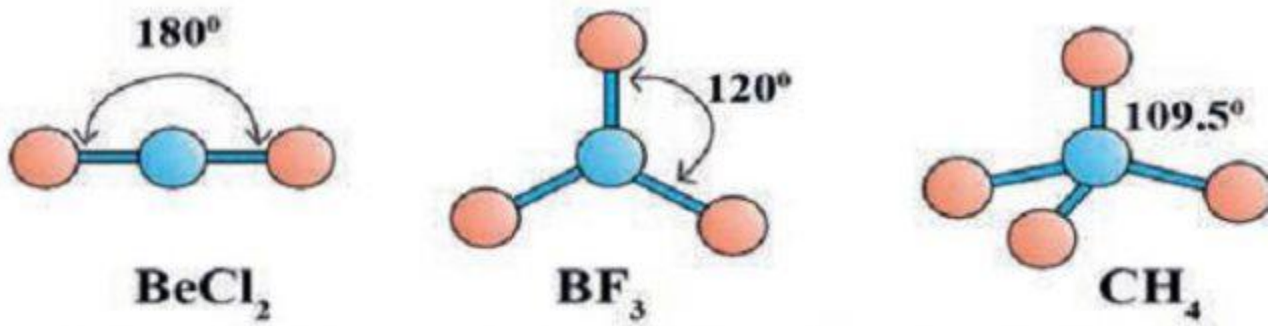
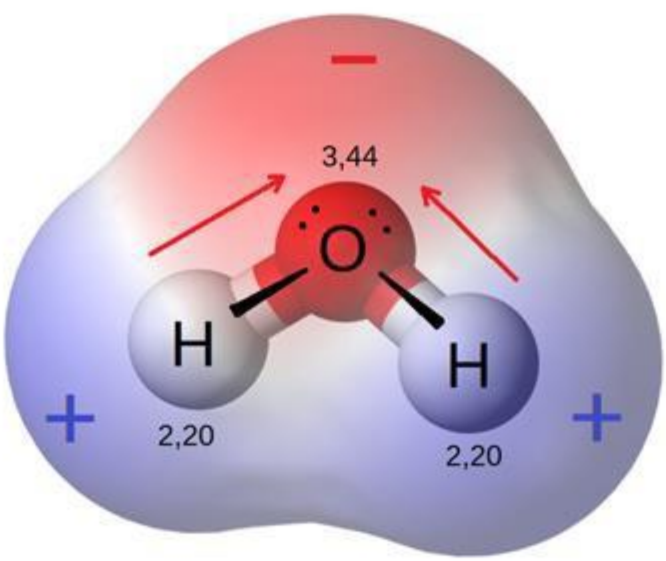


Figure 2.7: The shapes of molecules in which the centr



Intermolecular Force in the covalent bond

- Thereare two types of force that holds matter together.Theseare
- intramolecular forces
- intermolecularforces.
- Intramolecular force is a chemical bond (ionic, covalent or metallic)that exists within a particle (molecule or polyatomic ion) and affects the chemical property of the species.
- Intermolecular force are those bonds that hold particles (ions or molecules) together.
- Aglassofwaterforexample,containsmanymoleculesofwater.
- These molecules are held together by intermolecular forces, whereas the intramolecular forces hold the two hydrogen atoms to the oxygen atom in each molecule of water.
- Intermolecular forces are relatively weak as compared to intramolecular forces,because they typically involve lower charges that are farther apart.However, the strength of the intermolecular forces is important because they affect physical properties of the species such as melting point and boiling point.
- Three typesof attractive force are known toexist between neutral molecules:
- Dipole–dipole forces
- London(ordispersion)forces,
- Hydrogen bonding
  The term vander Waals Forces area general term for those intermolecular forces that include dipole–dipole and London forces.

- Van derWaals forces are the weak attractive forces in a large number of substances, including Cl2, and Br2.
  Dipole-Dipoleforces

- Dipole-dipole forces act between the molecules possessing permanent dipole.
- When polar molecules are brought near one another, their partial charges act as tiny electric fields that orient them and give rise to dipole-dipole forces; the partially positive end of one molecule attracts the partially negative end of another.
- Ends of the dipoles possess “partial charges” and these charges are shown by Greek letter delta (δ).
  Dispersion or London Forces

- Usually,theelectronsinanon-polarcovalentmoleculearedistributed symmetrically.
- However, the movement of the electrons may place more of them in onepart of the molecule than another, which forms a temporary dipole.
- These momentary dipoles align the molecules so that the positive end ofone molecule is attracted to the negative end of another molecule.
- This interaction is stronger than the London forces but is weakerthanion-ion interaction because only partial charges are involved.
- The attractive force decreases with the increase of distance between the dipoles.
  Hydrogen Bonding

- Polar molecules containing hydrogen atoms bonded to highly electronegative atoms of nitrogen, oxygen, or fluorine form especially strong dipole–dipole attractions
- Hydrogen bonds are the strongest type of attractive forces between polar covalent molecules

Question

- identify intermolecular forces
- H – F,O,N_ hydrogen bond
- polar molecule _dipole -dipole force
- Non-polar molecules_dipersion forces

Which type of intermolecular force is dominant ?

A. CH3COOH

B. CH4

C. CH3OH

D.HI ,

E. CH3OH

F. .NH2

SOLUTION

A, E, F_hydrogen bond

B -nonpolar

D.polar

Lewis Structures:

Lewis structures, also known as Lewis dot structures, are diagrams that show the bonding between atoms in a molecule and the lone pairs of electrons that may exist in the molecule.

- **Purpose**: They provide a simple way to understand how atoms are connected in a molecule and predict the basic shape of the molecule.

Steps to Draw:

1. **Count Valence Electrons**: Determine the total number of valence electrons for all atoms in the molecule.
2. **Connect Atoms**: Use single bonds (pairs of electrons) to connect atoms, satisfying the octet rule (except for hydrogen, which follows the duet rule).
3. **Place Remaining Electrons**: Distribute remaining electrons as lone pairs on outer atoms to satisfy their octets, and then on the central atom.

4. **Formal Charge Check**: Check formal charges to ensure they are minimized or zeroed out, if possible.

- **Examples**:
- **Water (H_2O)**:
  - Central atom: Oxygen (6 valence electrons), Hydrogen (1 each).
  - Structure: H-O-H with 2 lone pairs on oxygen.
- **Carbon dioxide (CO_2)**:
  - Structure: O=C=O, with double bonds between carbon and oxygen.

Molecular Geometry:

Molecular geometry refers to the three-dimensional arrangement of atoms in a molecule and the spatial relationships between these atoms.

Determining Factors:

- **VSEPR Theory**: Predicts the geometry based on minimizing electron pair repulsion around the central atom.
- **Electron Pair Arrangement**: Bonding pairs and lone pairs around the central atom determine the geometry.

Common Geometries:

- **Linear**: 180° bond angle, e.g., CO_2.
- **Trigonal Planar**: 120° bond angle, e.g., BF_3.
- **Tetrahedral**: 109.5° bond angle, e.g., CH_4.
- **Trigonal Bipyramidal**: 90° and 120° bond angles, e.g., PCl_5.
- **Octahedral**: 90° bond angles, e.g., SF_6.

VSEPR Theory (Valence Shell Electron Pair Repulsion Theory):

VSEPR theory predicts the molecular geometry based on the idea that electron pairs (bonding and lone pairs) repel each other and position themselves as far apart as possible to minimize repulsion.

Steps to Predict Geometry:

1. **Identify Central Atom**: Determine the central atom in the molecule.
2. **Count Electron Domains**: Count the number of bonding pairs and lone pairs around the central atom (electron domains).
3. **Predict Geometry**: Choose the molecular geometry based on the arrangement of electron domains and lone pairs, considering their repulsive forces.

Example:

- **Ammonia (NH_3)**:
  - Central atom: Nitrogen (5 valence electrons), Hydrogen (1 each).
  - Electron domains: 4 (3 bonding pairs, 1 lone pair).
  - Predicted geometry: Trigonal pyramidal.

Intermolecular Forces:

Intermolecular forces (IMFs) are attractive or repulsive forces between molecules or atoms that determine the physical properties of substances.

Types of IMF:

1. **London Dispersion Forces**: Weakest IMF due to temporary dipoles.
2. **Dipole-Dipole Interactions**: Between polar molecules with permanent dipoles.
3. **Hydrogen Bonding**: Strong IMF between a hydrogen atom and a highly electronegative atom (N, O, F).
4. **Ion-Dipole Interactions**: Between an ion and a polar molecule.

Effects:

- Influence boiling points, melting points, and phase changes.
- Determine solubility in different solvents.
- Play a role in biological processes and molecular recognition.

Example:

- **Water (H_2O)**:
  - Exhibits hydrogen bonding between water molecules, which contributes to its high boiling point and surface tension.
- Lewis electron-dot formulas are simple representations of the valence-shell electrons of atoms in molecules and ions.
- An ionic bond is a strong attractive force holding ions together. An ionic bond can form between two atoms by the transfer of electrons from the valence shell of one atom to the valence shell of the other.
- Covalent bond is a strong attractive force that holds two atoms together by their sharing of electrons. These bonding electrons are attracted simultaneously to both atomic nuclei, and they spend part of the time near one atom and part of the time near the other.
- In some cases of covalent bonding, one atom appears to provide both electrons in the bonding pair; the bond is known as coordinate-covalent bond or dative bond.