

# Unit 2

## CHEMICAL BONDING

### Introduction to Chemical Bonding

In Grade 9, you were introduced to the fundamental concepts of chemical bonding, including ionic, covalent, and metallic bonds. In this unit, we will build on that foundation by exploring additional concepts such as intermolecular forces, molecular geometry, and advanced theories of chemical bonding.

A **chemical bond** is the attractive force that holds atoms, ions, or molecules together. These forces can be classified into **intramolecular forces**, which affect the chemical properties and physical states of a substance.

#### Activity :

1. **Why do some atoms combine while others do not?**
  - Atoms combine to achieve stability, often by attaining a full valence shell, such as the noble gases. For example, sodium (Na) readily loses an electron to achieve a stable configuration, while neon (Ne) is already stable and does not readily form bonds.
2. **Why do different atoms form different types of bonds?**
  - The type of bond formed depends on the nature of the elements involved, such as metals and non-metals, which form ionic bonds due to the transfer of electrons. Non-metals typically share electrons to form covalent bonds.

### Octet Rule and Exceptions

Noble gases are known for their stability due to having complete valence electron shells, typically following the **octet rule**. This rule states that atoms tend to gain, lose, or share electrons to have eight electrons in their outermost shell, similar to the electron configuration of noble gases. There are exceptions to this rule, such as compounds where the central atom does not adhere strictly to eight electrons.

### Types of Chemical Bonds

1. **Ionic Bonds:** Formed by the electrostatic attraction between positively charged ions (cations) and negatively charged ions (anions). This type of

bonding is common between metals and non-metals, where one atom donates electrons, and another atom accepts them.

**Example:** Sodium chloride (NaCl) is formed when sodium (Na) loses an electron to become  $\text{Na}^+$ , and chlorine (Cl) gains an electron to become  $\text{Cl}^-$ .

## Understanding Ionic Bonds

- **Formation of Ionic Bonds:** An ionic bond is created when one or more electrons are transferred from one atom to another, resulting in the formation of cations and anions.
- **Properties of Ionic Bonds:** Ionic compounds typically have high melting and boiling points, conduct electricity when molten or dissolved in water, and form crystalline solids.

## Lattice Energy and the Born-Haber Cycle

**Lattice energy** is the energy released when ions come together to form a crystalline ionic solid. It can be indirectly calculated using the Born-Haber cycle, which applies Hess's law to sum the enthalpy changes involved in forming an ionic compound from its elements.

**Example:** The lattice energy of sodium chloride (NaCl) is calculated by considering the steps in the Born-Haber cycle, which includes the vaporization of sodium, ionization, and electron affinity of chlorine.

## Factors Affecting Ionic Bond Formation

1. **Ionization Energy:** Lower ionization energy favors cation formation.
2. **Electron Affinity:** Higher electron affinity favors anion formation.
3. **Lattice Energy:** Higher lattice energy favors the stability of ionic compounds, depending on the charge and size of the ions involved.

## Exceptions to the Octet Rule

1. **Less than Octet:** Atoms like hydrogen, lithium, and beryllium do not require eight electrons to be stable and often have fewer.
2. **More than Octet:** Transition metals and post-transition elements may have more than eight electrons due to the involvement of d-orbitals, following the 18-electron rule.

## Properties of Ionic Compounds

1. **High Melting and Boiling Points:** Ionic compounds typically have high melting and boiling points due to the strong electrostatic forces between the oppositely charged ions.
2. **Hard and Brittle:** Ionic compounds are usually hard, but they are also brittle. When enough force is applied, the ions of like charge can be forced together, causing the crystal to shatter.
3. **Electrical Conductivity:** In their solid state, ionic compounds do not conduct electricity because the ions are fixed in place within the lattice. However, when melted or dissolved in water, the ions are free to move, allowing the compound to conduct electricity.
4. **Solubility in Water:** Many ionic compounds are soluble in water. The polar nature of water molecules helps to separate the positive and negative ions, leading to dissolution.
5. **Formation of Crystals:** Ionic compounds form crystalline structures, which are orderly and repeat in a three-dimensional pattern, contributing to their physical properties.

## Covalent Bonds and Molecular Geometry

1. **Covalent Bonds:** Covalent bonds form when two atoms share a pair of electrons. This type of bond typically occurs between non-metal atoms. Covalent bonds can be single, double, or triple, depending on the number of shared electron pairs.
2. **Molecular Geometry:** The shape of a molecule is determined by the number of bonds and lone pairs around the central atom, following the Valence Shell Electron Pair Repulsion (VSEPR) theory. The geometry influences the molecule's physical and chemical properties.
3. **Polar and Non-Polar Covalent Bonds:**
  - o **Non-Polar Covalent Bonds:** Occur when the bonding electrons are shared equally between the two atoms, as seen in molecules like  $\text{H}_2$  and  $\text{O}_2$ .
  - o **Polar Covalent Bonds:** Occur when the electrons are shared unequally, leading to a partial positive charge on one atom and a partial negative charge on the other, as seen in  $\text{H}_2\text{O}$ .
4. **Resonance Structures:** Some molecules, like ozone ( $\text{O}_3$ ), can be represented by more than one valid Lewis structure. The actual structure is a hybrid of these resonance forms, with electrons delocalized across the molecule.
5. **Exceptions to the Octet Rule:**
  - o **Incomplete Octet:** Some molecules, such as  $\text{BF}_3$ , have a central atom with fewer than eight electrons.

- **Expanded Octet:** Elements in the third period or below, like  $\text{SF}_6$ , can have more than eight electrons around the central atom.
- **Odd Number of Electrons:** Some molecules, such as  $\text{NO}$ , have an odd number of electrons, leading to free radicals.

## Activity

1. **Combination of Non-Metal Atoms:** Non-metal atoms can combine together by sharing electrons, forming covalent bonds.
2. **Hydrogen and Ionic Bond Formation:** A hydrogen atom does not easily lose its electron because it would leave behind a bare proton, which is highly unstable in isolation.
3. **Difference Between Ionic and Covalent Bonds:** Ionic bonds involve the transfer of electrons from one atom to another, while covalent bonds involve the sharing of electrons between atoms.
4. **Polar Covalent and Coordinate Covalent Bonds:**
  - **Polar Covalent Bonds:** Form when atoms with different electronegativities share electrons unequally.
  - **Coordinate Covalent Bonds:** Form when one atom donates both electrons to the bond, as seen in the ammonium ion ( $\text{NH}_4^+$ ).

## Molecular Geometry and VSEPR Theory

**Molecular Geometry** refers to the three-dimensional arrangement of atoms in a molecule. The geometry is determined by the number of electron pairs surrounding the central atom, which includes both bonding pairs (shared electrons between atoms) and lone pairs (non-bonding electrons). The shape of a molecule significantly influences its chemical properties, such as reactivity, polarity, and interactions with other molecules.

**Valence Shell Electron Pair Repulsion (VSEPR) Theory** is a model used to predict the geometry of molecules based on the repulsion between electron pairs in the valence shell of the central atom. The key idea is that electron pairs will arrange themselves as far apart as possible to minimize repulsive forces. This model allows us to determine the shape of the molecule by considering the number of bonding pairs and lone pairs of electrons around the central atom.

## Electron Pair Arrangement and Molecular Shape

- **Electron Pair Arrangement** is the orientation of both bonding and lone pairs around the central atom. This arrangement determines the general geometry of the molecule.
- **Molecular Shape** is determined by the positions of the atomic nuclei and can differ from the electron pair arrangement, especially when lone pairs are present. Lone pairs exert greater repulsion than bonding pairs, which can cause deviations in bond angles.

## Predicting Molecular Geometry

### 1. Molecules without Lone Pairs:

- **Linear (AB<sub>2</sub>):** Molecules like BeCl<sub>2</sub> have two bonding pairs and no lone pairs, resulting in a linear shape.
- **Trigonal Planar (AB<sub>3</sub>):** Molecules like BF<sub>3</sub> have three bonding pairs and no lone pairs, resulting in a trigonal planar shape.
- **Tetrahedral (AB<sub>4</sub>):** Molecules like CH<sub>4</sub> have four bonding pairs and no lone pairs, resulting in a tetrahedral shape.
- **Trigonal Bipyramidal (AB<sub>5</sub>):** Molecules like PCl<sub>5</sub> have five bonding pairs and no lone pairs, resulting in a trigonal bipyramidal shape.
- **Octahedral (AB<sub>6</sub>):** Molecules like SF<sub>6</sub> have six bonding pairs and no lone pairs, resulting in an octahedral shape.

### 2. Molecules with Lone Pairs:

- **Bent (AB<sub>2</sub>E):** In molecules like SO<sub>2</sub>, the presence of a lone pair results in a bent shape rather than a trigonal planar shape.
- **Trigonal Pyramidal (AB<sub>3</sub>E):** In molecules like NH<sub>3</sub>, the lone pair causes the shape to be trigonal pyramidal instead of tetrahedral.
- **Bent (AB<sub>2</sub>E<sub>2</sub>):** In water (H<sub>2</sub>O), two lone pairs result in a bent shape, with a bond angle less than the tetrahedral angle.
- **See-Saw (AB<sub>4</sub>E):** In SF<sub>4</sub>, one lone pair causes a distortion from the trigonal bipyramidal shape to a see-saw shape.

## Molecular Shape and Polarity

Molecular polarity is influenced by the molecular shape and the distribution of bond dipoles. If the bond dipoles do not cancel each other out, the molecule will have a net dipole moment and be polar. For example:

- **Water (H<sub>2</sub>O):** Has a bent shape, making it polar with a net dipole moment.

- **Carbon Dioxide (CO<sub>2</sub>):** Despite having polar bonds, it has a linear shape, and the bond dipoles cancel each other out, resulting in a non-polar molecule.

## Bond Polarity and Dipole Moment

- **Dipole Moment:** A measure of the polarity of a molecule, represented by the separation of charge. Molecules like HCl, with atoms of different electronegativities, have dipole moments and are polar.
- **Non-Polar Molecules:** Molecules like O<sub>2</sub>, with atoms of the same element, have no dipole moment and are non-polar.

## Key Points

- **Lone pairs exert more repulsion** than bonding pairs, affecting bond angles and molecular shape.
- **Molecular shape** determines many physical and chemical properties, including polarity.
- **Polar molecules** tend to have higher boiling points and different solubilities compared to non-polar molecules of similar molecular mass.

## Formation of Metallic Bonding

### *Understanding Metallic Bonding*

Metallic bonding occurs in metals like copper, iron, and aluminum, where atoms are bonded together in a unique way. Here's a clear breakdown of how metallic bonding forms:

1. **Characteristics Leading to Metallic Bonding:**
  - **Metallic Elements:** Metals are typically characterized by having few electrons in their outermost shell and the ability to lose these electrons easily. This allows them to form metallic bonds.
  - **Lattice Structure:** In metals, atoms arrange themselves in a regular, repeating pattern known as a lattice.
2. **Delocalized Electrons:**
  - **Definition:** Delocalization refers to the free movement of electrons within a metal. These electrons are not bound to any specific atom but move freely throughout the metal lattice.
  - **Electron-Sea Model:** This model visualizes the metal as a sea of electrons surrounding positively charged metal ions. The electrons are delocalized and move freely, which contributes to many of the physical properties of metals.

### 3. Comparison with Other Bonds:

- **Metallic vs. Covalent Bonds:** In covalent bonds, electrons are shared between specific pairs of atoms. In contrast, metallic bonds involve a collective sharing of electrons among many atoms.
- **Metallic vs. Ionic Bonds:** Ionic bonds involve a transfer of electrons from one atom to another, creating positively and negatively charged ions. In metallic bonds, electrons are delocalized and shared among a lattice of metal cations.

## Strength and Properties of Metallic Bonds

### 1. Strength Factors:

- **Number of Delocalized Electrons:** More delocalized electrons increase the bond strength and result in higher melting points.
- **Packing Arrangement:** The closer the metal atoms are packed, the stronger the bond and the higher the melting point.

### 2. Physical Properties Explained by Metallic Bonding:

- **Electrical and Thermal Conductivity:** Delocalized electrons can move freely, making metals good conductors of electricity and heat.
- **Malleability and Ductility:** The regular arrangement of metal ions and the mobility of delocalized electrons allow metals to be shaped without breaking. They can be bent or stretched into wires without shattering.

### 3. Comparison with Ionic Compounds:

- **Conductivity:** Ionic compounds do not conduct electricity in solid form because their ions are fixed in place. However, when dissolved in water, they dissociate into ions, allowing them to conduct electricity. Metals conduct electricity in both solid and liquid forms due to their free-moving electrons.

### 4. Melting and Boiling Points:

- **Example:** Gallium melts at 29.8°C but boils at 2403°C. This is because breaking the metallic bond requires more energy at higher temperatures compared to breaking the bonds to reach the boiling point.

Metallic bonding involves a lattice of metal cations surrounded by a "sea" of delocalized electrons. This bonding gives metals their characteristic properties, such as high electrical and thermal conductivity, malleability, and ductility. The strength of metallic bonds is influenced by the number of delocalized electrons and the packing arrangement of metal atoms.

## Hybridization of Orbitals

**Concept of Hybridization:** Hybridization is a concept used to explain the bonding in molecules and the geometry of molecules. It involves the mixing of atomic orbitals in an atom to form new hybrid orbitals of equivalent energy and shape. This mixing helps to explain the observed molecular geometries and bond angles that cannot be predicted by considering atomic orbitals alone.

## Carbon Atom and Covalent Bonding:

- **Ground State of Carbon:** The carbon atom has the electronic configuration  $1s^2 2s^2 2p^2$ . In this state, carbon has two unpaired electrons in the 2p orbitals.
- **Excited State of Carbon:** To form four bonds, carbon promotes one of its 2s electrons to an empty 2p orbital, resulting in the electronic configuration  $1s^2 2s^1 2p^3$ . This leads to the formation of four unpaired electrons, which is ideal for forming four bonds.

## Types of Hybridization:

### 1. $sp$ Hybridization:

- **Formation:** Mixing of one s orbital and one p orbital results in two equivalent  $sp$  hybrid orbitals.
- **Geometry:** Linear arrangement with a bond angle of  $180^\circ$ .
- **Example:** Beryllium chloride ( $BeCl_2$ ). The Be atom forms two  $sp$  hybrid orbitals that overlap with chlorine's p orbitals to create two Be-Cl sigma bonds.

### 2. $sp^2$ Hybridization:

- **Formation:** Mixing of one s orbital and two p orbitals results in three equivalent  $sp^2$  hybrid orbitals.
- **Geometry:** Trigonal planar arrangement with a bond angle of  $120^\circ$ .
- **Example:** Boron trichloride ( $BCl_3$ ). The B atom forms three  $sp^2$  hybrid orbitals that overlap with chlorine's p orbitals to create three B-Cl sigma bonds.

### 3. $sp^3$ Hybridization:

- **Formation:** Mixing of one s orbital and three p orbitals results in four equivalent  $sp^3$  hybrid orbitals.
- **Geometry:** Tetrahedral arrangement with a bond angle of  $109.5^\circ$ .
- **Example:** Methane ( $CH_4$ ). The C atom forms four  $sp^3$  hybrid orbitals that overlap with hydrogen's s orbitals to create four C-H sigma bonds. For  $NH_3$  and  $H_2O$ ,  $sp^3$  hybridization explains their pyramidal and V-shaped geometries respectively.



## Hybridization in Molecules with d-Orbitals:

### 1. $sp^3d$ Hybridization:

- **Formation:** Mixing of one s, three p, and one d orbital results in five  $sp^3d$  hybrid orbitals.
- **Geometry:** Trigonal bipyramidal arrangement with bond angles of  $120^\circ$  (equatorial) and  $90^\circ$  (axial).
- **Example:** Phosphorus pentachloride ( $PCl_5$ ). The P atom forms five  $sp^3d$  hybrid orbitals that overlap with chlorine's p orbitals.

### 2. $sp^3d^2$ Hybridization:

- **Formation:** Mixing of one s, three p, and two d orbitals results in six  $sp^3d^2$  hybrid orbitals.
- **Geometry:** Octahedral arrangement with bond angles of  $90^\circ$ .
- **Example:** Sulfur hexafluoride ( $SF_6$ ). The S atom forms six  $sp^3d^2$  hybrid orbitals that overlap with fluorine's p orbitals.

## Multiple Bonds and Hybridization:

- **Double Bonds:** Consist of one sigma ( $\sigma$ ) bond and one pi ( $\pi$ ) bond. In ethene ( $C_2H_4$ ), each carbon uses  $sp^2$  hybrid orbitals to form  $\sigma$  bonds, with unhybridized p orbitals forming the  $\pi$  bond.
- **Triple Bonds:** Consist of one sigma ( $\sigma$ ) bond and two pi ( $\pi$ ) bonds. In acetylene ( $C_2H_2$ ), each carbon uses  $sp$  hybrid orbitals for  $\sigma$  bonds and unhybridized p orbitals for two  $\pi$  bonds.

## Key Points:

- Hybridization helps explain molecular shapes and bond angles that are not easily predicted by atomic orbitals alone.
- The number of hybrid orbitals equals the number of atomic orbitals mixed.
- $sp$ ,  $sp^2$ , and  $sp^3$  hybridizations correspond to linear, trigonal planar, and tetrahedral geometries respectively.
- Hybridization involving d orbitals leads to more complex geometries like trigonal bipyramidal and octahedral.

This approach of hybridization provides a clear and practical framework to predict and understand the bonding and geometry of molecules.

## Molecular Orbital Theory (MOT)

**Introduction to MOT:** Molecular Orbital Theory (MOT) provides a deeper insight into molecular bonding than Valence Bond Theory (VBT). It proposes that when atoms combine to form molecules, their atomic orbitals overlap and transform into new orbitals known as molecular orbitals (MOs). These MOs extend over the

entire molecule and are critical for understanding molecular structure and bonding.

### Atomic vs. Molecular Orbitals:

- **Atomic Orbitals (AOs):** Describe the regions around a single nucleus where electrons are likely to be found.
- **Molecular Orbitals (MOs):** Result from the overlap of atomic orbitals from different atoms. These orbitals are delocalized over the entire molecule.

### Bonding and Antibonding Orbitals:

- **Bonding Molecular Orbitals:** Formed by the constructive interference of atomic orbitals. Electrons in bonding MOs increase electron density between nuclei, lowering the system's energy and stabilizing the molecule.
- **Antibonding Molecular Orbitals:** Formed by the destructive interference of atomic orbitals. Electrons in antibonding MOs decrease electron density between nuclei and increase the system's energy, destabilizing the molecule. They contain a node, a region where electron density is zero, between the nuclei.

**Bond Order Calculation:** The bond order indicates the strength and stability of a bond. It is calculated using the formula:

$$\text{Bond Order} = \frac{(\text{Number of electrons in bonding MOs} - \text{Number of electrons in antibonding MOs})}{2}$$

A higher bond order means a stronger and more stable bond. For example, in the hydrogen molecule ( $\text{H}_2$ ):

- There are 2 electrons in the bonding  $\sigma_{1s}$  orbital and 0 electrons in the antibonding  $\sigma_{1s}^*$  orbital.
- Bond Order =  $\frac{(2-0)}{2} = 1$ , indicating a single bond.

**Electron Configuration of Diatomic Molecules:** Electrons are filled into molecular orbitals following the Aufbau principle, Pauli Exclusion Principle, and Hund's rule. For example:

- In  $\text{H}_2$ , electrons fill the lower-energy  $\sigma_{1s}$  orbital first.

## Molecular Orbital Diagrams:

- Diagrams show the relative energies of molecular orbitals and the distribution of electrons among them. For homonuclear diatomic molecules with fewer than 14 electrons, the order is:  
 $\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \pi_{2p} < \pi_{2p}^* < \sigma_{2p}$  .
- For molecules with more than 14 electrons, the  $\pi_{2p}$  and  $\pi_{2p}^*$  orbitals come after  $\sigma_{2p}$  .

## Magnetic Properties:

- Molecules with unpaired electrons exhibit paramagnetism (attraction to a magnetic field), while those with all electrons paired exhibit diamagnetism (repulsion from a magnetic field). For example,  $O_2$  has unpaired electrons in its  $\pi_{2p}^*$  orbitals, making it paramagnetic.

## Comparison with VBT:

- **VBT (Valence Bond Theory):** Focuses on the overlap of atomic orbitals and is less effective at explaining some aspects of bonding, such as the magnetic properties of molecules.
- **MOT (Molecular Orbital Theory):** Provides a more comprehensive explanation of bonding and magnetic properties, successfully predicting the paramagnetism of  $O_2$ , which VBT cannot.

## Types of Crystalline Solids:

1. **Ionic Crystals:** Formed by ions held together by ionic bonds. They have high melting points and are poor conductors of electricity in solid form but can conduct when molten or dissolved.
2. **Molecular Crystals:** Composed of discrete molecules with intermolecular forces (e.g., hydrogen bonding). They generally have lower melting points and are poor conductors of heat and electricity.
3. **Covalent Network Crystals:** Atoms are covalently bonded in a continuous network. These crystals, like diamond, have very high melting points and are typically non-conductors.
4. **Metallic Crystals:** Atoms are held together by metallic bonds, characterized by a "sea of electrons." They are good conductors of electricity and heat and have variable melting points.

**Summary:** Molecular Orbital Theory offers a detailed understanding of molecular structure and bonding by examining the formation and energy levels of molecular orbitals, providing insights that extend beyond the capabilities of Valence Bond Theory.

