Lesson #6: Polarity & Intramolecular Forces

Let’s reconsider covalent molecules in a little more detail:

- When a whole network of atoms are covalently bonded together, we have a special case of covalent bonding called covalent crystals. Examples of these substances include diamond, silicon carbide, and boron nitride. The covalently bonded atoms form a crystal lattice or network.

- Note the very high melting temperatures:
  - Boron nitride (BN) – 2700°C
  - Silicon carbide (SiC) – 2850°C
  - Diamond (C) – 3500°C

What would you conclude about the strength of the covalent bonds in covalent crystals?

Q: Is it surprising that many covalent compounds do not have very high melting points?

Examples: CH₄ – 184°C  O₂ – 181°C  F₂ – 220°C

What explains this fact? It turns out there are other types of bonding responsible for the phases of these substances. Consider H₂O which melts at 0°C.

So when ice melts, it is the weak forces of attraction between the molecules that break (not the covalent bond).

The covalent bonds within these molecules are strong but the bonds between molecules are weak and easy to break.

Example: C (carbon)  diamond  coal  graphite
Types of Covalent Bonds:
We have discussed the two extreme cases of bonding: \textbf{complete e⁻ transfer} - ionic bonding
And \textbf{covalent bonds} with completely \underline{\textbf{equal sharing of e⁻}}
Between these extremes are covalent bonds which involve \underline{\textbf{UNEQUAL}} electron sharing.

When atoms with \underline{different electronegativities} form covalent bonds, those \textbf{\(\Delta EN\)} \(\Delta X\)
values may be minimal or significant.

In math & science, the Greek letter \textit{delta} is used as a prefix and has two meanings: \(\Delta\) means \underline{\textit{change}} while \(\delta\) means \underline{\textit{partial}} (used for "partial charge").

\[\Delta X = 0 \quad \text{for} \quad \text{non-polar covalent} \]
\[\Delta X \neq 0 \quad \text{for} \quad \text{polar covalent} \]

If the electronegativity of both atoms in a covalent bond is \underline{identical}, the electrons in the bond will be \underline{equally attracted} to both of them, and form a \underline{non-polar covalent bond}.

This results in a \underline{symmetrical} distribution of e⁻ density around the two atoms.

Bonding in \underline{diatomic molecules} (for example O₂ or Cl₂) is \underline{non-polar covalent} because the electronegativity of the atoms in each molecule is \underline{the same}.

Mostly Covalent bonds
If \(\Delta EN\) is \(0 < 0.4\) the bonding electrons between the two atoms spend no more of their time near one nucleus than the other.

Such bonds are designated as being \underline{"mostly covalent"}, because \(\Delta EN\) appears to be \underline{so small} it is \underline{insignificant}.

Another way to characterize this is to say that these bonds have \underline{"little ionic character\)} now \underline{"like\) an ionic bond is it.}
Polar Covalent Bonds (aka polar bonds)

Definition: A polar covalent bond is one that has one or more electrons unequally shared.

- occurs between two atoms when $0.4 < \Delta \gamma < 1.7$
- the electron density is enriched around the more electronegative element and is deficient around the less electronegative element.

Electronegativity and Polar Covalent Bonds

As $\Delta \gamma$ increases beyond 0.4, the pair of bonding electrons will be drawn closer and closer to the nucleus of the atom with the higher electronegativity.

This unequal distribution of electron density will give that end of the bond a partially negative “pole” and the other a partially positive “pole.” A bond dipole is said to exist and the bond itself is known as a polar covalent bond.

Effect of electronegativity on polarization

The greater the electronegativity difference between the two atoms in a bond the greater the polarization of the bond.

This can be illustrated by looking at the hydrogen halides:

$$\Delta \gamma = 4.6 - 2.2 = 1.8$$

Less polar bonds have more covalent character.

Ionic or covalent?

Rather than saying that ionic and covalent are two distinct types of bonding, it is more accurate to say that they are at the two extremes on a scale.

More polar bonds have more ionic character. The more electronegative atom attracts the electrons in the bond enough to ionize the other atom.

Polar & Non-Polar Molecules

A polar molecule is one where there is an imbalance in the total sharing of electrons within the molecule.

To be a polar molecule requires the presence of polar covalent bonds and that these bonds are arranged asymmetically.

A non-polar molecule is one where the total sharing of electrons is balanced.

To be a non-polar molecule requires either the absence of any polar covalent bonds or that any polar covalent bonds are arranged symmetrically (± charges cancel).
**Non-polar molecules**
If the polar bonds are arranged symmetrically, the partial charges cancel out and the molecule is non-polar.

\[ \delta^- \quad \delta^- \quad \delta^- \quad O \quad C \quad O \]

**Polar molecules**
If the polar bonds are arranged asymmetrically, the partial charges do not cancel out and the molecule is polar.

\[ \delta^- \quad \delta^- \quad \delta^+ \quad O \quad \delta^- \quad \delta^- \quad H \quad H \]

**Key Point:**
- **Polar molecules** are those that contain polar covalent bonds and are *Asymmetrical*.
- **Non-polar molecules** either
  1. have no polar covalent bonds
  2. have polar covalent bonds but the molecule is *symmetrically* arranged so that the charges cancel.

**The presence of polar covalent bonds is necessary but not sufficient for a molecule to be a polar molecule.**

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**Example**
Verify that the following molecules contain polar covalent bonds:

a) HCl
\[ \delta^- \quad \delta^+ \]
\[ \Delta \chi = 3.0 - 2.1 = 0.9 \]

b) H₂O
\[ \delta^- \quad \delta^- \quad \delta^+ \]
\[ \Delta \chi = 2.5 - 2.1 = 1.4 \]

c) CF₄
\[ \delta^- \quad \delta^- \quad \delta^- \quad \delta^- \]
\[ \Delta \chi = 4.0 - 2.5 = 1.5 \]

**Example**
Classify the molecules in the previous example as polar or non-polar:

a) HCl is a **Polar molecule** due to asymmetry.
b) H₂O is a **Polar molecule** due to asymmetry.
c) CF₄ is a **Non-polar molecule** due to symmetry.

**Why is this important?**
- The more polar a molecule is, the more attractive it is to other polar molecules.
- The melting and boiling temperatures of all covalent compounds depend on forces of attraction between molecules.

When dissolving, "like dissolves like". **Polar solvents dissolve other polar solutes**. Non-polar solvents dissolve other non-polar solutes.

H₂O best solvent for polar, it can dissolve ionic comp.
H. INTERMOLECULAR FORCES OF ATTRACTION

Intramolecular Forces are forces that act within molecules.
- The covalent bonds within a molecule are the most obvious example.
- Disulfide bonds (which cross-link proteins) are another example.

Intermolecular Forces are attractive forces between molecules.
- Due to molecules being permanently, or temporarily, polar (see below...)
- Much weaker than ionic and covalent bonds but can be very significant in large numbers.

Types of intermolecular force
The molecules in simple covalent substances are not entirely isolated from one another. There are forces of attraction between them. These are called intermolecular, "inter" means "between", or Van der Waals forces.

There are three main types of intermolecular forces:
- **London Forces** — temporary dipolar attractions between neighbouring atoms, for example, between I₂ molecules in iodine crystals.
- **Permanent dipole-dipole** — for example, found between HCl molecules in hydrogen chloride.
- **Hydrogen "bonds"** — for example, found between H₂O molecules in water.

Van der Waals forces (animation)

**London Forces**

How do Van der Waals forces hold Molecules together?
Electrons are constantly moving...

At any one time the electrons may not be evenly distributed

The temporary dipole in one molecule can...

The dipole induction occurs between all neighboring molecules.
Strength of van der Waals forces
The strength of van der Waals forces **increases** as molecular size increases.
This is illustrated by the **boiling points** of group 7 elements.
*Atomic radius* decreases down the group, so the **outer e⁻** become further from the nucleus.
They are attracted *less strongly* by the nucleus and so **dipoles** are easier to induce. (occur more often)

3) The Two Types of Intermolecular Forces (*a.k.a.* van der Waals Forces)

1. **London Forces** are weak attractive forces between non-polar molecules (temporary dipoles).
   - *strength grows with # of e⁻ increases, the more e⁻ in an atom/molecule the stronger the force*
   - *always present, but significant only when no other forces present*
   - *only way to explain why Noble gases (He, Ne, Ar, ...) and non-polar molecules (e.g. H₂, O₂, S₈, CF₄, etc) can form liquids and solids*

   ![London Forces](image)

   - **London Forces** are the weakest type of bonding.*
   - The more e⁻ an atom or molecule has altogether, the *stronger the L.F* existing between it and a neighbouring atom or molecule.

   The greater the atomic number (#e⁻), the stronger the **London Forces** experienced.*
2. Dipole-dipole Forces are forces of attraction between polar molecules (permanent dipoles).

- dominant intermolecular force between all polar molecules
- the strongest of these is the Hydrogen Bond.
  - only capable between molecules containing ____________ bonds.

** Why do these three bond types have such strong polarity? ____________ have very high X values.**

Within any substance containing ____________ molecules, each molecule has a ____________ and a ____________ pole. ____________ molecular dipole

Because of these ____________ partial charges, the molecules in the liquid and solid phases will ____________ themselves so that the ____________ pole of one molecule will be next to and ____________ to the ____________ pole of the next molecule.

If molecules contain bonds with a ____________ the molecules may align so there is ____________ attraction between the opposite charges on neighbouring molecules.

Permanent dipole–dipole forces (dotted lines) occur in hydrogen chloride (HCl) gas →(shown below) →

This network of dipole-dipole forces will result in ____________ melting and boiling points because more energy will be required to overcome the attractions between the molecules.

The permanent dipole–dipole forces are approximately ____________ the strength of a covalent bond.

Examples

Hydrogen bonds are the ____________ forces that ____________ hold the double helix together in DNA.
3. Hydrogen “bonds” (Type of Intermolecular Force)

What is hydrogen bonding?
When hydrogen bonds to nitrogen, oxygen or fluorine, a larger than normal dipole than in other polar bonds.

N, F, O are highly electronegative due to their 9 nuclear charge and small size.

When these atoms bond to hydrogen, electrons are withdrawn from the H atom, making it $\delta^+$ (slightly positive).

The H atom is very small so the positive charge is more concentrated, making it easier to link with other molecules.

*Hydrogen bonds are therefore particularly STRONG examples of permanent dipole-dipole forces. (stronger than London forces)

In molecules with OH or NH groups, a Lone Pair of $\text{e}^-$ on nitrogen or oxygen is attracted to the slight positive charge on the hydrogen on a neighbouring molecule.

Hydrogen bonding makes the melting and boiling points of water higher than might be expected.

It also means that alcohols (OH groups) have much higher boiling points than alkanes of a similar size.

**Boiling Points of the Hydrogen Halides**

The boiling point of hydrogen fluoride is much higher than that of other hydrogen halides, due to fluorine’s high electronegativity ($\chi=4.0$).

The means that hydrogen bonding between molecules of hydrogen fluoride is much stronger than the permanent dipole-dipole forces between molecules of other hydrogen halides. is therefore required to separate the molecules of hydrogen fluoride.

**Summary of Intermolecular (Van der Waals) Forces:**

- London Forces
  - ev. HCl
  - Hydrogen “bonds”

- Permanent Dipole-Dipole
  - eg. water, DWA
  - H-H, H-C, H-F

Weakest $\rightarrow$ Strongest

(temp. dipole) $\rightarrow$ Permanent Dipole-Dipole

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Chemical Bonding Exercises Set 2

1. Write the number of valence electrons possessed by each of the following species:
   a) Ge
   b) Y
   c) W
   d) Sn
   e) Bi

2. Which substance has a lower melting temperature: CaBr₂ (s) or SrI₂ (s)? Explain why.

3. Write the valence for each: S, B, Ca, Xe, Ga, Bi

4. Write the number of open and closed shells for each of the species given below:
   a) Ar
   b) Ba
   c) I
   d) V

5. Although oxygen and fluorine molecules are roughly the same size, each oxygen atom shares four electrons with its neighbour while each fluorine atom shares only two electrons with its neighbour. Which bond should be stronger? Explain.

6. Which types of bonds or forces increase in strength going down a group in the periodic table? (I only want you to consider bonds/forces between atoms or molecules of the same element)

7. Which types of bonds or forces decrease in strength going down a family in the periodic table? (Again, only in terms of bonds/forces between atoms or molecules of the same element)

8. Provide brief explanations for the following facts:
   a) the melting temperatures of the noble gases increase going down the periodic table.
   b) the reactivity of the alkali metals increases going down the periodic table.
   c) the reactivity of the noble gases increases going down the periodic table.
   d) the melting temperature of the alkali metals decreases going down the periodic table.
   e) the reactivity of the halogens decreases going down the periodic table.
Define “allotrope”. Name the allotropes of carbon.

If a noble gas could form a +1 cation, which noble gas would do so most easily? Why?

Molecule “M” has closed outer shells as a result of pure covalent bonding within its structure. What type of bond would attract molecules of “M” to each other?

13. Briefly explain the difference between ionic bonding, covalent bonding, and metallic bonding.

14. Use your periodic table to classify each of the bonds as covalent, polar covalent, or ionic. Then predict the formula of the compound based on the valence each type of atom.
   a) Ba and Br
   b) Mg and P
   c) Si and N
   d) As and F
   e) Ga and Se
   f) B and Te

15. For each pair of compounds, state which should have the higher boiling points. Why?
   a) BCl₃ vs. BCl₃F
   b) NH₃ vs. SbH₃
   c) CH₃CH₂CH₃ vs. CH₃CH₂CH₂CH₂CH₃
   d) CH₃CH₂CH₃ vs. CH₃OH