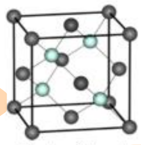
Lesson #6: Polarity & Intramolecular Forces

May 23, 2018 4:31 PM

G. MOLECULAR SHAPE AND POLARITY

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: **covalent crystals**. Examples of these substances include diamond, silicon carbide and boron nitride. The covalently bonded atoms form a **crystal lattice** or **network**.



Structure of diamond

Silicon carbide saw blade
(used to cut tile and stone)

Structure of **diamond**

- Note the very high melting temperatures:
  - Boron nitride (BN) ~ 2700 °C
  - Silicon carbide (SiC) ~ 2750 °C
  - Diamond (C) ~ 3500 °C

> Note: an *allotrope* is a structural variation of an element within the same state. Most elements do not exhibit allotropy. The most well-known allotropic elements include phosphorus (white and red), oxygen (O_2 & O_3) and carbon (coal, diamond, graphite and the fullerenes).

Example
C (carbon)
· diamond
· coal
· graphite

- What would you conclude about the strength of the covalent bonds in covalent crystals?
  covalent bonds are VERY strong.

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

Examples: CH_4 ~ -184 °C O_2 ~ -219 °C F_2 ~ -220 °C

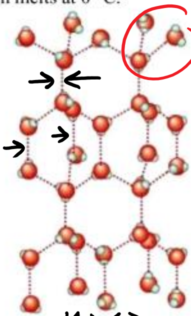
What explains this fact? It turns out that there are other types of bonding responsible for the phases of these substances. Consider H_2O which melts at 0 °C.

covalent

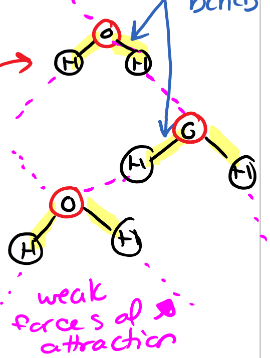
O
H H

$H_2O(l)$

Freezing
0 state
melting



$H_2O(s)$

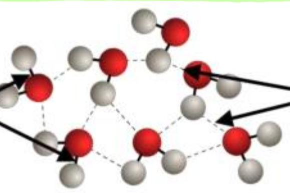


So when ice melts, it is the weak forces of attraction BETWEEN the molecules that break (NOT the covalent bonds)

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

O–H

covalent
strong bonds within molecules



weak bonds "
between
molecules

"forces of attraction"

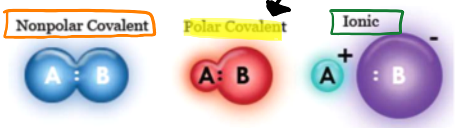
28

Types of Covalent Bonds:

We have discussed the two extreme cases of bonding: complete e^- transfer - **ionic bonding**

And **covalent bonds** with completely equal sharing of e^-

Between these extremes are covalent bonds which involve UNEQUAL electron sharing.



When atoms with different electronegativities form covalent bonds, those **ΔEN** ($\Delta\chi$) **values** may be minimal or significant.

In math & science, the Greek letter delta is used as a prefix and has two meanings: Δ means change while δ means partial (used for "partial charge")

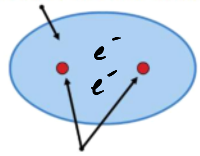
$\Delta\chi = 0$ non-polar covalent

Table 6.3.3 *Relationship of ΔEN and Bond Designation*

ΔEN	Bond Designation
0	non-polar covalent
< 0.4	mostly covalent
0.4 – 1.7	polar covalent
> 1.7	ionic

Non-Polar Covalent: $\Delta\chi = 0$

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



all diatomic molec. eg. O_2 H_2 F_2...

This results in a symmetrical distribution of e^- density around the two atoms.

Bonding in diatomic molec. (all. HOFBrINCl) (for example O_2 or Cl_2) is non-polar covalent because the electronegativity of the atoms in each molecule is the same.

Mostly Covalent bonds

If *ΔEN is* $0 < 0.4$, the bonding electrons ($\rightarrow e^-$ pair) between the two atoms spend no more of their time nearer one nucleus than the other.

Such bonds are designated as being "mostly covalent" because ΔEN appears to be so small it is insignificant.

Another way to characterize this is to say that these bonds have "little ionic character"

how "like" an ionic bond is it.

29

↑ electroneg. { ↑ ionization E. ↑ e⁻ affinity } Cl is MORE electronegative.

Polar Covalent Bonds (*aka polar bonds*)

Definition: A polar covalent bond is one that has one or more electron pairs are ***unequally shared.***

Polar Covalent Bond

e⁻ more "drawn" to Cl

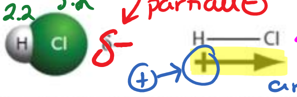
- occurs between two atoms when $0.4 < \Delta \chi < 1.7$
- the electron density is enriched around the more electronegative element and is deficient around the less electronegative element.

e⁻ are closer to ↑ electroneg.

Electronegativity and Polar Covalent Bonds

partially ⊕ δ^+ 2.2 e⁻ 3.2 partially ⊖ δ^-

"Bond Dipole" $\Delta\chi = 1.0$



arrow points to ⊖

Figure 6.3.4 *Polar covalent bond depictions. The bond dipole is in the direction of the chlorine.*

As ΔEN 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 (δ) 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.

↳ ⊕ end and ⊖ end

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:

H–F

$\Delta\chi = 4.0 - 2.2 = 1.8$

(χ)

Element	H	F	Cl	Br	I
Pauling elecronegativities	2.2	4.0	3.2	3.0	2.7

($\Delta\chi$)

Molecule	H–F	H–Cl	H–Br	H–I
Electronegativity difference between atoms	1.8	1.0	0.8	0.5

decreasing polarization

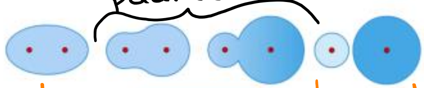
Ionic or covalent?

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

polar covalent

Less polar bonds have more covalent character.

equal sharing of e⁻



increasing polarization

non-polar covalent

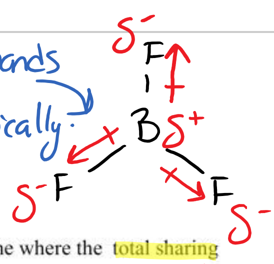
ionic : complete transfer of e⁻

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

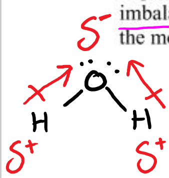
30

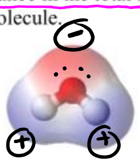
Polar & Non-Polar Molecules

polar bonds arranged symmetrically



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

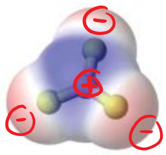




To be a polar molecule requires the presence of polar covalent bonds and that those bonds are arranged ASYMMETRICALLY

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

either: NO polar bonds. or polar bonds symm.



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

Polar molecules

Key Point:

(+/- charges cancel)

Non-polar molecules

If the polar bonds are arranged **symmetrically**, the partial charges cancel out and the molecule is non-polar.

δ^- δ^+ δ^-

O=C=O

Polar molecules

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

δ^-

δ^+ O δ^+

H H

Key Point:

Polar molecules are those that contain polar covalent bonds and are Asymmetrical

Non-polar molecules either

i) have no polar covalent bonds

or

ii) have polar covalent bonds but the molecule is symmetrically to the charges cancel.

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

↳ good idea to calculate the $\Delta\chi$

Example Verify that the following molecules contain polar covalent bonds:

a) HCl

Cl H

δ^- δ^+

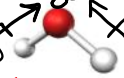
$\Delta\chi = 3.0 - 2.1 = 0.9$

polar covalent bond.

b) H_2O

$\delta\ominus$

$\delta\oplus$ $\delta\oplus$

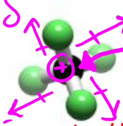


$\Delta\chi = 3.5 - 2.1 = 1.4$

polar covalent bond.

c) CF_4

δ^- δ^- δ^+ δ^- δ^-



$\Delta\chi = 4.0 - 2.5 = 1.5$

polar covalent bond.

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

a) HCl is a Polar molecule due to asymmetry

b) H_2O is a Polar molecule due to asymmetry

c) CF_4 is a NON-polar molecule due to symmetry.

Are the bonds Polar?

Yes → sym. → non-polar molecule

Yes → Asym. → polar molecule

NO → non-polar molecule

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

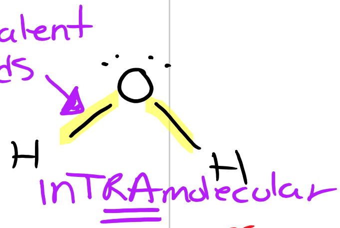
H_2O best solvent

- polar, it can dissolve ionic comp.

H. INTERMOLECULAR FORCES OF ATTRACTION

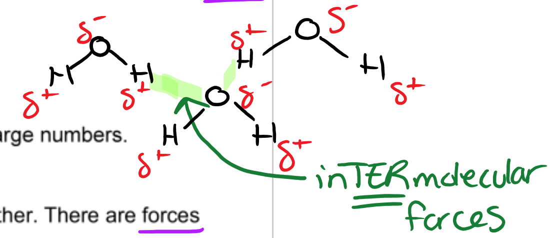
Intramolecular Forces are forces that act **within** molecules.

- The covalent bonds within a molecule are the most obvious example. or ionic
- 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

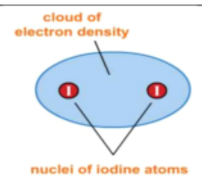
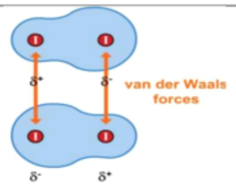
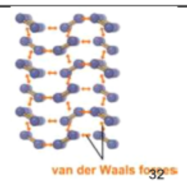
The molecules in simple covalent substances are not entirely isolated from one another. There are forces of attraction between them. These are called inTERmolecular, “inter” means “between”, or **Van der Waals forces**.

There are three main types of intermolecular forces:

Intermolecular Forces

- London Forces – temporary dipolar attractions between neighbouring atoms, for example, between I_2 molecules in iodine crystals.
- Permanent dipole-dipole for example, found between HCl molecules in hydrogen chloride.
- Hydrogen "bonds" – for example, found between H_2O 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.	

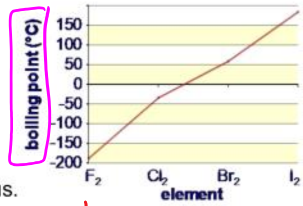
32

(London Forces)

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. down P.T.

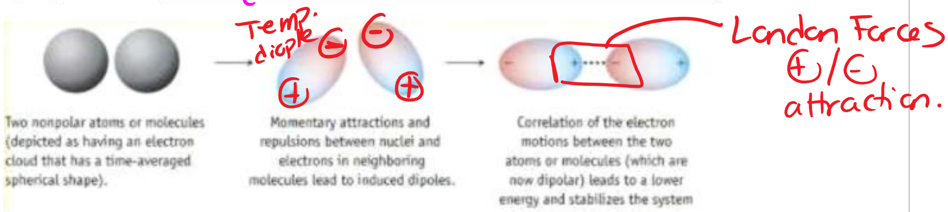


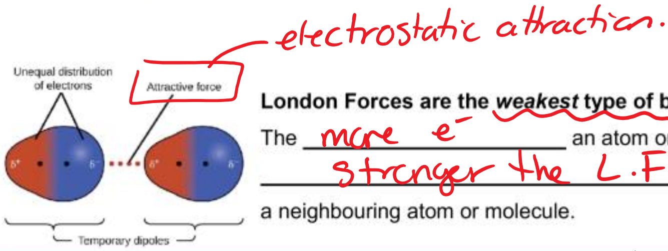
Atomic radius increases down the group, so the outer e^- become further from the nucleus.

e^- "They" are attracted less strongly by the nucleus and so temporary dipoles are easier to induce. (occur more often)

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

1. **London Forces** are weak attractive forces between non-polar molecules (temporary dipoles).
   - are the weakest of all intermolecular forces
   - * strength grows with as # of e^-s 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. H_2, O_2, S_8, CF_4, etc) can form Liquids and solid





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. *

(Permanent)

2. Dipole-dipole Forces are forces of attraction between "polar molecules" (permanent dipoles).

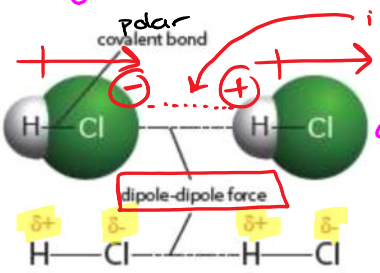
- dominant intermolecular force between all polar molecules
- the strongest of these is the **Hydrogen Bond**.
  - only capable between molecules containing H-N, H-F, H-O bonds.

** why do these three bond types have such strong polarity? N, O, F have very ↑ χ values

Within any substance containing Polar molecules, each molecule has a positive and a negative pole — a ⊕ → ⊖ molecular dipole

Because of these partial charges, the molecules in the liquid and solid phases will *naturally orient themselves* so that the positive pole of one molecule **will be next to and** attract to the negative pole of the next molecule.

intermolecular force: "dipole-dipole" $\delta^+ \rightarrow \delta^-$

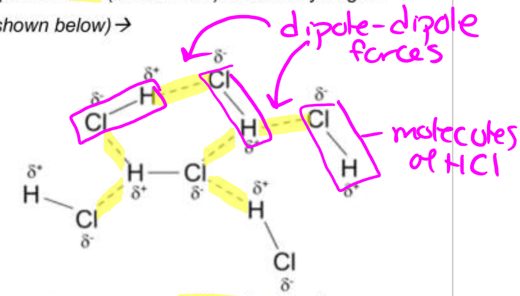


If molecules contain bonds with a permanent dipole, the molecules may align so there is electrostatic +/- attraction between the opposite charges on neighbouring molecules.

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

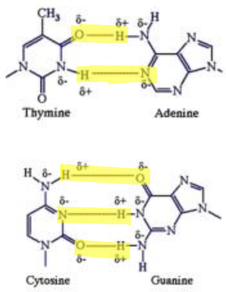
This network of dipole-dipole forces will result in higher melting + boiling points because more energy will be **required to overcome the attractions** between the molecules.

The permanent dipole–dipole forces are approximately 1/100 the strength of a covalent bond.



Examples

Hydrogen bonds are responsible for water being sticky and its ability to act as a solvent for many things. They are also why it has surface tension and forms raindrops.



Hydrogen bonds are the intermolecular forces that hold the double helix together in DNA.

GC pairings (3 H bonds) provide a stronger force than AT pairings (2 H bonds).

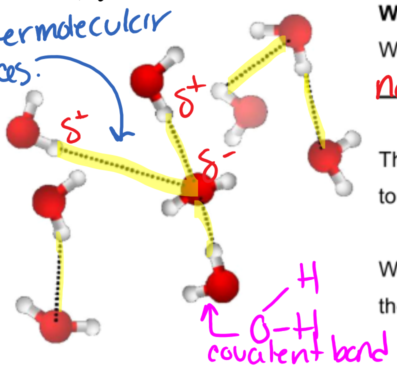
Thermophilic bacteria (naturally live in very hot water) have a lot of GC pairings in their DNA.

*This understanding led an oligonucleotide chemist to develop the **Polymerase Chain Reaction** (PCR) which now allows us to amplify DNA.*

34

Hydrogen "bonds" in H_2O

Intermolecular forces.



3. Hydrogen "bond" (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.

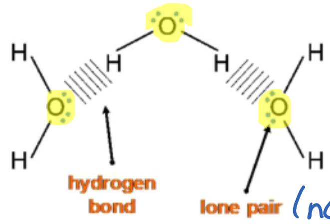
This is because these atoms (N, F, O) are highly electronegative due to their ↑ nuclear charge. and small size.

When these atoms bond to hydrogen, electrons are withdrawn from the H atom, making it δ+ (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 e^- on nitrogen or oxygen is attracted to the slight positive charge on the hydrogen on a neighbouring molecule.

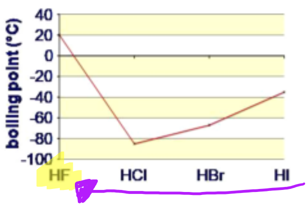


(non-bonding)

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

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

Boiling points of the hydrogen halides



The boiling point of hydrogen fluoride HF (halogen) 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.

MORE energy is therefore required to separate the molecules of hydrogen fluoride.

Summary of IntERmolecular (van der waals) forces:

weakest ← London Forces (temp. dipole) ex. I_2 — ex. HCl Permanent Dipole-Dipole — Hydrogen "bonds" eg. water, DNA H-N, H-O, H-F → strongest

35

Homework **Assignment ~~#6~~** 7 (Last Assignment) *can be completed in the space provided below*

Do HIGHLIGHTED Questions only.

Chemical Bonding Exercises Set 2

1. What explains the fact that at room temperature F_2 is a gas while I_2 is a solid?

2. Write the number of valence electrons possessed by each of the following species:

   a) Ge ___ b) Y ___ c) W^{4+} ___ d) Sn^{2+} ___ e) Bi ___

3. Which substance has a lower melting temperature: $CaBr_2$ (s) or SrI_2 (s)? Explain why.

4. Write the valence for each: a) S ___ b) B ___ c) Ca ___ d) Xe ___ e) Ga ___ f) Bi ___

5. ~~Write the number of open and closed shells for each of the species given below.~~

   a) At^{3+} _____, _____ b) Ba _____, _____ c) I^{5+} _____, _____ d) V^{+} _____, _____

6. 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.

7. 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)

8. 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)

9. ~~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.

10. Define “allotrope”. Name the allotropes of carbon.

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

12. 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) BCl_3 ***vs.*** BCl_2F b) NH_3 ***vs.*** SbH_3

c) $CH_3CH_2CH_3$ ***vs.*** $CH_3CH_2CH_2CH_2CH_2CH_3$ d) $CH_3CH_2CH_3$ ***vs.*** CH_3OH