

Unit 4B Chemical Bonding & Molecular Interactions SG

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Chemical Bonding Continuum Notes

- Noble Gas Envy
 - Noble gases have a full valence shell
 - All noble gases except helium have 8 valence electrons
 - Helium has only two
 - Most transition and inner transition metals have 2 (because s-sublevel is the highest principal energy level, and they end at s₂), but there are exceptions (mostly occurring in the d and f block)
 - The Octet Rule states that elements tend to react and bond with other atoms in order to achieve a full valence shell of 8 valence electrons
 - Exceptions: H, He, Li, Be, B -> want to achieve 2 electrons (closest to He configuration)
 - Atoms can obtain an octet by losing electrons, gaining electrons, or sharing electrons through chemical bonding
- Types of Bonds
 - Ionic Bond - Electrons are transferred. Tend to occur between metals that form cations and nonmetals that form anions
 - Coulombic attraction until 1 crystal lattice arrangement, called a formula unit
 - Covalent Bond - electrons are shared, or more accurately, fought over. Tends to occur between nonmetals.
 - Metallic Bond - electrons are delocalized and form a sea of electrons around metal nuclei
 - Results in metallic properties like being malleable, conductive, ductile
- Electronegativity (EN)
 - When an atom is bonded to another atom, it is the tendency of the atom to attract or pull a shared pair of electrons in a bond to itself that weren't originally theirs
 - The type of bond formed can be predicted by the difference in electronegativity
 - Each element is assigned an electronegativity value
 - Higher value -> more electronegative, and the greater the ability for an atom to attract electrons when it is bonded to another atom
 - Fluorine = most EN (from periodic trends, & remember that noble gases can't form bonds); nitrogen, oxygen, and halogens are the most electronegative elements. Their atoms attract strongly in compounds.
 - Lower value -> less electronegative
 - Across a period, electronegativity **increases**, down a group electronegativity **decreases**
- Electronegativity Values (will be given/referenced to on the test)

H 2.1																	He ---
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne ---
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar ---
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 2.6
Cs 0.7	Ba 0.9	La-Lu 1.1-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn ---
Fr 0.7	Ra 0.9	Ac-No 1.1-1.7															

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- Bonding Continuum & Electronegativity Difference
 - The sharing is a **continuum** (always happening), and there are different degrees of sharing (maybe one is able to pull the electrons more strongly to the other, unequal sharing)
 - The type of bond that forms between atoms can be predicted based on the electronegativity difference between the atoms
 - Very large EN difference
 - The more electronegative element will take one or more electrons away from the less electronegative element and form an ionic bond
 - Very similar / exact same EN \rightarrow almost 0 EN difference
 - End up “sharing” the electrons to some degree & form a covalent bond
 - Not really sharing; no element is strong enough to take an electron from the other one.
- Electronegativity Difference
 - $\Delta EN = |EN_1 - EN_2|$
 - ΔEN (covalent - electrons shared) $< 2.0 \leq \Delta EN$ (ionic - electrons transferred)
 - Remember the value 2.0. Furthermore, this is the cutoff for chem H, may be different for other sources
 - Bonding is not just either ionic or covalent \rightarrow happens on a continuum. There are general cutoffs that we can use to predict the type of bond that will occur between two atoms
 - If $\Delta EN \geq 2.0$, the more electronegative element is so strong that it will remove the electron(s) from the less electronegative element and form an ionic bond.
 - If $\Delta EN < 2.0$, the elements are not strong enough to remove the electrons and they will instead share them, forming a covalent bond
- General ΔEN cutoffs (different degrees of “sharing”) - Memorize
 - $0 \leq \Delta EN < 0.5$ = **nonpolar** covalent bond (roughly equal EN), equal sharing
 - $0.5 \leq \Delta EN < 2.0$ = **polar covalent** bond, unequal sharing
 - One electron orbits the more EN element more than the other
 - $2.0 \leq \Delta EN$ = **ionic** bond (i.e. very polar), electrons transferred
- Other Properties
 - Ionic Bonds

- Strong bond
 - Large ΔEN , electrons transferred which form an anion and cation (cation + anion), electrostatically bonded, form ionic crystals called salts
 - Solid at room temperature because intermolecular forces (molecule \leftrightarrow molecule forces) within substances are strong
 - Extremely polar and will **dissolve** well in polar-covalent compounds like water
 - Do NOT conduct electricity in solid form, but **will conduct** electricity in an **aqueous** (water-like) form
- Covalent Bonds
 - Smaller ΔEN , “sharing” electrons, molecules instead of salts
 - At room temperature, covalent bonds can be solids, liquids, or gases, depending on the size and mass and the shape and polarity which result in varying intermolecular force strength
 - Like dissolves like
 - Polar covalent compounds will dissolve in polar covalent solvents
 - Nonpolar covalent compounds will dissolve in nonpolar solvents
 - Do **NOT** conduct electricity in ANY form
 - No electrons moving
- Metallic Bonds
 - Electrons are relatively free to move throughout the 3D structure (i.e. delocalized, electrons can move to nuclei freely)
 - Metal atoms are bonded to several neighboring atoms
 - All metallic substances are solid at room temperature except mercury
 - Highly conductive through a metal, malleable, ductile, and lustrous
- Miscellaneous
 - Larger noble gases can fight over electrons with VERY electronegative elements, so you **CAN** measure a value for the larger noble gases
 - Distilled water (pure, deionised) does NOT conduct electricity
 - Tap water (with minerals) DO conduct electricity

How to Draw Lewis Structures (Pt. 1)

- When we draw out the structures of compounds, we only represent the valence electrons, which are determined by the highest principal energy level & the s&p sublevels since d&f are always 1, 2 principal energy levels behind
 - Which group (column) you are in determines how many valence electrons you have (unless you are Helium, in which you have only 2)
- Lewis Structures (Electron Dot Diagrams)
 - Only valence electrons are represented
 - Electrons represented by dots are placed around the element symbol
 - You place one dot on each side before a second (similar to Hund’s rule)
 - The side you start putting electrons on does not matter

- However, do not put electrons in the corner
- Covalent Bonds and Unpaired Electrons
 - In covalent molecules, atoms need to share **PAIRS** of electrons
 - Always in PAIRS
 - In order to gain a full valence shell, UNPAIRED electrons in Lewis dot diagram need to bond with other atoms and pair up
 - The number of unpaired electrons = # of covalent bonds these elements TEND to form (there are exceptions)
 - There are exceptions to this rule, but atoms are **MOST stable** and most likely to occur in nature when they follow the rule
- Covalent Lewis Structures
 - Pair up unpaired electrons using circles to make the covalent bond
 - Element that wants to form the most bonds -> put in center
 - Atoms can be drawn next to each other and shared pairs of electrons can be represented as a line
 - Each line = 1 covalent bond, TWO shared electrons
 - Unshared pairs of electrons are called lone pairs (that have to be drawn), and are included to show how each atom has a FULL valence shell (satisfy the octet rule)
 - Each atom needs to satisfy the octet rule UNLESS they are Hydrogen or Helium which are satisfied at 2 valence electrons
- **HONC1234**
 - Hydrogen/Halogens form 1 bond, Oxygen forms 2 bonds, Nitrogen forms 3 bonds, Carbon forms 4 bonds
 - The element that forms the **most** bonds goes to the **center**
 - This is what happens normally/usually and is most stable
- Tips and helpful reminders
 - Carbon is always a **CENTRAL** atom with 4 bonds
 - Hydrogen only wants 2 valence electrons
 - Hydrogens (ALWAYS) and halogens (usually) are **terminal atoms** (at the end, NEVER central) that make only ONE bond.
- The first atom (least electronegative) in the formula is usually the **CENTRAL** atom
 - There are also sometimes MULTIPLE central atoms
- A formula can tell you information about where to put what
 - For example: CH₃SH: Put C and S at center, bonded by a line, then put 3 H's around the C and the H around the S, and then fill in as required
- Double and Triple Bonds
 - Atoms can share multiple pairs of electrons when needed
 - 1 pair shared -> single bond, 2 pairs shared -> double bond, 3 pairs shared -> triple bond)

How to Draw Lewis Structures (Pt. 2)

- Steps for drawing ANY Lewis Structures for covalent compounds

- Count the # of valence electrons for each atom and add them up together
 - ADD electrons if overall an anion, charge (-)
 - SUBTRACT electrons if overall a cation, charge (+)
- Draw a skeleton structure with lines for shared electrons (draw lines before dots)
 - In general, the LEAST electronegative element goes in the center, but never put H in the center)
- Add electrons around atoms (as lone pairs) until they are all used up (start with most electronegative element) and each has 8 electrons that surround it
 - Exceptions: hydrogen wants to get 2 electrons, Be wants to get 4, B wants to get 6
 - Add to outside (most electronegative) first, then inside
- Possible scenarios
 - Just enough electrons
 - Not enough electrons: use lone pairs and use them to make double & triple bonds until all have 8 electrons
 - Too many electrons: atoms may have expanded octets (More than 8) and put extra electrons around the central atoms (least electronegative atom)
- If your structure has a charge, **DO NOT FORGET** to put BRACKETS around the structure with the **CHARGE** on top. Ions stay ions
- In order to maintain SYMMETRY, make other elements take turns having a lone pair
 - E.g.: you don't want to take 2 bonds from one element and leave 2 electrons on the left element and 6 electrons on the right element. You want to make 1 bond from the left, 1 bond from the right, etc. until one is satisfied
 - You want to avoid having something like 3 bonds on one side and 1 on the other -> not symmetrical
- Fewer octets broken -> more stable
- Examples with multiple central atoms
 - You will also see formulas where there is more than one central atom
 - In N_2H_4 if one nitrogen is made the central atom it will not be able to bond with the remaining 5 atoms, so both nitrogens are at the center
 - Formulas are sometimes written in the order that the atoms connect
 - CH_3OH indicates that the carbon is bound to 3 hydrogen, then to the oxygen. The remaining hydrogen is bound to the oxygen
 - Remember that hydrogen is always a TERMINAL ATOM -> ONE bond
 - H can NEVER go in the center
- Formal Charge
 - Do when there seem to be multiple correct structures for a compound that satisfy the octet rule.
 - Most stable is when $FC = 0$ OR least HONC1234 broken.
 - The **MOST FC's of 0's** is the most stable configuration. It is not the TOTAL SUM of all the formal charges = 0, but rather the MOST 0's.
 - $FC = \# \text{ of valence electrons before bond (e.g. carbon: 4)} - \# \text{ of assigned electrons}$

- $FC = \# \text{ of valence electrons by itself} - \# \text{ of lone pair electrons} - \frac{1}{2} * \# \text{ of bond pair electrons}$
- $FC = 0 \rightarrow$ most stable (follow HONC1234)
- The one with most 0's of formal charge / **LEAST** # of HONC1234's broken \rightarrow the one that's most likely to exist in nature

Resonance

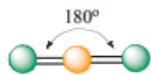

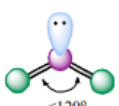
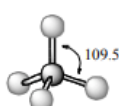
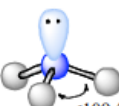
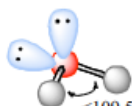
- Arises when more than one pair of electrons needs to be shared between two atoms AND more than one atom has the ability to do the sharing
- Each resonance shows the electron distribution of the molecule or ion @ a particular time
 - Use \leftrightarrow (double headed arrows) to show resonance
 - You **MUST** remember to do this when there are multiple correct configurations
 - All atoms are in the same relative positions
 - The electrons are distributed differently, but there are the same # of electron pairs in each structure
- Molecule is **constantly changing** between the different configurations in resonance

Molecular Geometry & VSEPR Notes

- VSEPR Theory: Valence Shell Electron Pair Repulsion Theory
 - A model that predicts the 3D shape of a molecule based on interactions between electron groups around the CENTRAL ATOM \rightarrow everything is about this central atom
 - The question: how many single, double, triple bonds, and lone pairs are around the central atom/
 - If there are TWO central atoms, you have to answer the VSEPR theory question twice.
 - Result: Electron groups REPEL each other because they are both negatively charged
 - However, they are held together by the central atom and the nucleus so they space out as evenly as possible around the central atom
 - We classify molecules by the # of electron domains (regions of electrons) around the central atom to determine the electron geometry.
 - Then, determine which of those elements are bonding electrons and which are lone pairs to determine the molecular geometry.
- Molecular Geometry
 - Shape of the molecule, only taking into account the bonds and how elements are connected, while ignoring lone pairs
- Electron Geometry
 - Considers lone pairs, the shape of the molecule given all the electron domains around the central atom
- Molecular Geometry and Electron Geometry will be the same when there are no lone pairs. They will differ when there are lone pairs around the **CENTRAL** atom

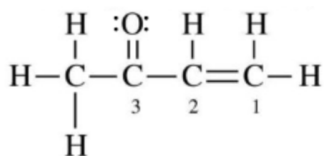
- If there are lone pairs but not around the central atom, MG and EG will still be the same
- Effect of Lone Pairs
 - Lone Pairs tend to take up **MORE SPACE** than a bond, and require more space than bonding pairs and reduces the angles of the bonding pairs (e.g. makes the bond angle from 107 deg to 105 deg)
 - They do this by REPELLING and forcing bonding groups closer together
- Note
 - A bond is not simply a line, but rather a region of space between two atoms where electrons are shared, formed by the overlap of atomic orbitals

VSEPR Table

Electron Groups	Electron Geometry (Hybridization)	Bonding Groups NOT # of Bonds	Lone Pairs	Molecular Geometry (VSEPR Class)	Predicted Bond Angle	Actual Bond Angle	Diagram	Polarity
2	Linear (sp)	2	0	Linear (AX_2)	180°	180°		Nonpolar
3	Trigonal Planar (sp^2)	3	0	Trigonal Planar (AX_3)	120°	120°		Nonpolar
		2	1	Bent (AX_2E)		119°		Polar Always
4	Tetrahedral (sp^3)	4	0	Tetrahedral (AX_4)	109.5°	109.5°		Nonpolar
		3	1	Trigonal Pyramid (AX_3E)		107°		Polar Always
		2	2	Bent (AX_2E_2)		105°		Polar Always

- A double bond counts as **ONE BONDING GROUP!!!**

- For example:

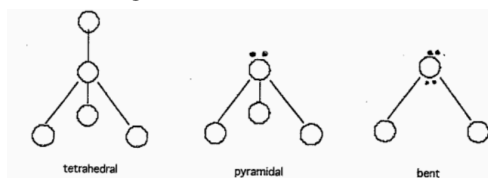


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- C-1 has 3 bonding GROUPS, not 4, because the double bond counted as one
- You should **memorize** the above
- Note: a double bond counts as one bounding group
 - In 2 bonding groups and 0 pairs, the groups want to be as far away as possible so they form a 180 degree angle
 - 2 bonding groups, 1 lone pair: polar always because the lone pair makes MG asymmetrical, so vectors can never cancel out to 0
- Polar: **ALWAYS**, because they have a non pair
- Nonpolar: could also be polar, depending on the electronegativity difference & depends if **different atoms** are around the central atom

Drawing Molecular Geometry

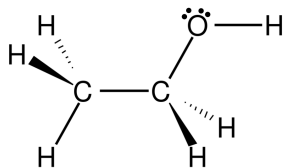
- Hand Drawing Molecular Geometry
 - Simplified



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- Bent **CAN** be drawn in 2 dimensions.

- Wedges & Dashes
 - Dark wedge represents the bond coming forward out of the plane of the paper.
 - Dashes represent the bond going out the back of the plane of the paper.

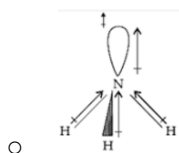


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- Make sure you **LABEL** the bond angles in diagram!!
- On a central atom...
 - It doesn't matter if it's a lone pair/ single bond / double bond/ triple bond, it is 1 electron domain/group
- Lone pair: do not draw a balloon, it is just a lewis structure but you now have to draw the bond angles and correct "real" configuration of the compound in nature
 - The same except lines are moved.

Molecule Polarity

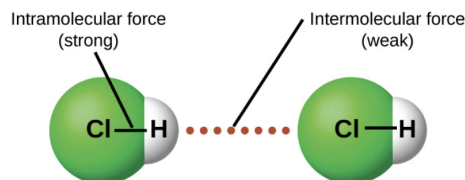
- Bond Polarity
 - Both a bond and a molecule can be a dipole
 - Caused by a difference of electronegativity of bonded atoms (unequal sharing)
 - The more EN atom pulls electrons in a bond closer to it, resulting in a **partial negative** charge (δ^-)
 - "Hogs" the electrons
 - The less EN atom ends up with a **partial positive** charge (δ^+)
 - A polar bond has two poles of opposite charge, so it is called a **dipole**
 - Resulted from unequal distribution
- Molecule Polarity
 - When a molecule has a δ^+ partially positive side and a δ^- partially negative side
 - Option 1: Caused when a molecule has 1 or more polar bonds AND an asymmetrical shape (molecular geometry) that makes one end of the molecule δ^+ and the other end δ^-
 - Option 2: Caused when there are lone pairs on the central atom AND an asymmetrical shape (molecular geometry) that makes one end of the molecule δ^+ and the other end δ^-
 - Because a molecule has two poles of opposite charge, it is also called a dipole
- Not all molecules with polar bonds are polar molecules
 - Because even if there are polar bonds, the molecular geometry (shape) might not make one end of the **whole molecule** overall δ^+ and δ^- (no opposite poles of charge, and poles of each bond cancel out)
 - The vectors need to not cancel out for there to be an overall polarity / for the molecule to be polar
 - So, even if a molecule has polar bonds, that doesn't necessarily mean that the whole molecule is polar.
- Bent geometry is asymmetrical -> water is asymmetrical
- Dipole arrows
 - Instead of δ^+ and δ^- , dipole arrows with a (+) on the opposite end of the arrowhead can be drawn to indicate polar bonds and polar molecules
 - In a polar bond, the arrow points toward the more EN atom
 - For a polar molecule, an arrow is drawn next to the molecule parallel to the molecule polarity
- **Vector addition** makes the most sense here
- Example of vector addition: horizontal components cancel out, so only a vertical component of polarity (hence big arrow is vertical)



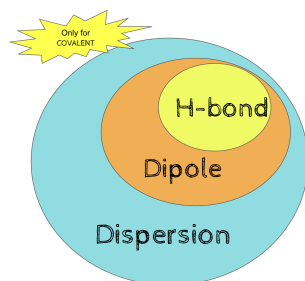
- H & C barely have any EN \rightarrow nonpolar ($0.4 < 0.5$ so nonpolar covalent, no arrow)
 - **Look at EN difference** to see if a **NP** or a **P** bond is formed!
 - You find EN difference from looking at the EN table and subtracting the two numbers
- Vectors add to 0 in all directions \rightarrow overall nonpolar
 - This is why atoms of the same element around the central atom at 180 deg atoms cancel out, which is the “symmetry” argument. Same magnitude, opposite in direction \rightarrow overall 0 polarity
- Vectors add to something non zero \rightarrow overall polar
- Overall polarity drawn using a big arrow

Intermolecular Forces & Properties

- Intramolecular vs Intermolecular forces
 - Intramolecular forces - forces WITHIN a molecule (e.g. covalent bond)
 - **Intermolecular** force (IMF) - force BETWEEN molecules
 - Our focus
 - The glue between molecules
 - Stronger intermolecular force \rightarrow more stable
 - Affects **properties** of compound
 - State of matter, volatility, boiling and melting points, solubility
 - IMFs are **WEAKER** than intramolecular forces



- Types of Intermolecular Forces
 - Dispersion forces
 - Dipole forces
 - Hydrogen bonds

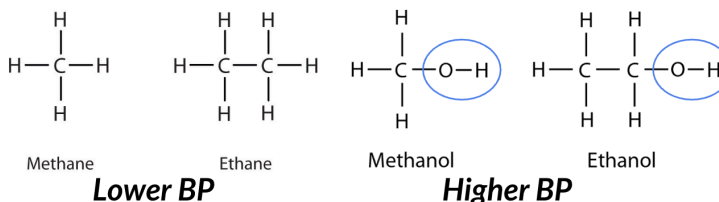


- - Molecules that experience H-bonds will **ALSO EXPERIENCE** dipole forces and dispersion forces
- The type of force (IMF) holding molecules together depends on the polarity of the molecule

- The strength of IMFS determine properties such as state of matter & boiling point
- (London) Dispersion Forces
 - Arises from temporary dipoles which is when a random shift in the electron density (location) creates a δ^+ and δ^- end of the molecule
 - Briefly attracted to other dipoles
 - Generally the **WEAKEST** of the intermolecular forces, but it can be quite strong, depending on the size & structure of the substance
 - Occurs in **ALL TYPES** of molecules
 - The ONLY IMF exhibited by **nonpolar** compounds (EN difference < 0.5)
- Strength of the Dispersion Force
 - Larger substance -> more polarisable -> stronger dispersion force if more electrons are briefly on one side
 - As the mass of the compound increases, the strength of the dispersion forces increases, because it takes longer for temporary dipoles to recover. This means that it will take more energy to separate the molecules from each other
 - Therefore, **LARGER** nonpolar molecules have **stronger** dispersion forces and thus higher **boiling points** than **smaller** nonpolar molecules
 - Dispersion forces are weaker than dip-dip & H-bond forces in general, so nonpolar compounds that experience only dispersion forces will have lower boiling points than those who experience other forces as well.
- Dipole-dipole forces
 - Arises in molecules that have a permanent dipole
 - Polar molecules (because of EN difference that is large enough to create a polar covalent bond and molecular geometry) have PERMANENT dipoles and exhibit dispersion forces **AS WELL AS** dipole forces
 - Exhibited by the venn diagram above
 - Dipole-dipole forces are generally stronger than dispersion forces (since they are the result of a PERMANENT dipole)
- Hydrogen Bond (H-bond)
 - Special type of dipole force, & not a bond despite its name
 - **STRONGEST IMF**
 - H is very small in size compared to other elements, and when there is a big EN difference, this leads to highly concentrated partial charges -> strong force
 - Occurs between molecules in which the Hydrogen atom of a H-F, H-O, or H-N bond can be attracted by a lone pair of electrons on a N, O, or F of another molecule
 - Arises due to F, O, and N being the most EN atoms
 - Molecules that experience H-bonds **ALSO HAVE** dispersion forces and dipole forces
- Strength of IMFs & Boiling Point
 - The boiling point of a substance is influenced by the strength of IMFs experienced by a substance.

- Stronger IMFs, like dipole-dipole forces or H-bonds require more energy to overcome/break to separate the molecules from each other, leading to a **higher boiling point** temperature.

- Hence molecules like H_2O , HF , & NH_3 (all of which can H-bond, which is a strong force) have significantly HIGHER boiling points than similarly sized but nonpolar molecules which only have dispersion forces (weak)



- Alcohols** like methanol and ethanol have significantly higher boiling points because of H-bonding and are therefore liquid at room temperature instead of gas, like their hydrocarbon counterparts (methane and ethane)
 - H-bonding is a stronger IMF -> more stick -> more heat/higher temperature to get ethanol molecules to separate
- Molecule Polarity and Solubility
 - Like dissolves like**
 - Polar substances tend to dissolve in polar solvents
 - Hydrophilic, "water loving"
 - Ionic and polar covalent compounds dissolve in water (which is a polar solvent due to the lone pairs)
 - Nonpolar substances tend to dissolve in nonpolar solvents
 - Hydrophobic, "water fearing"
 - Nonpolar substances do NOT dissolve in water (because it is polar)
 - The more similar the IMFs, the more likely one substance is to be soluble in another
 - Hence, like dissolves like
- Miscellaneous
 - Strong bonds -> more of that liquid that can be put on a penny, since the bonds hold each other more strongly