

Lewis Diagrams

A **Lewis symbol** is a symbol in which the electrons in the valence shell of an atom or simple ion are represented by dots placed around the letter symbol of the element. Each dot represents one electron.

Hydrogen $1s^1$ H·

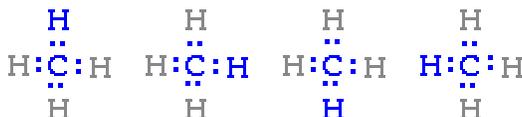
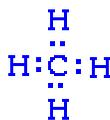
Oxygen $1s^2 2s^2 2p^4$ · \ddot{O} ·

Chlorine $1s^2 2s^2 2p^6 3s^2 3p^5$: \ddot{Cl} ·

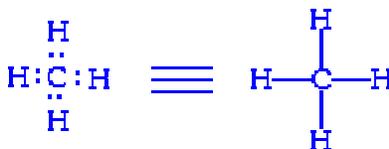
Chloride ion $1s^2 2s^2 2p^6 3s^2 3p^6$: \ddot{Cl} :

A **covalent bond** is a chemical bond formed by the sharing of a pair of electrons between two atoms.

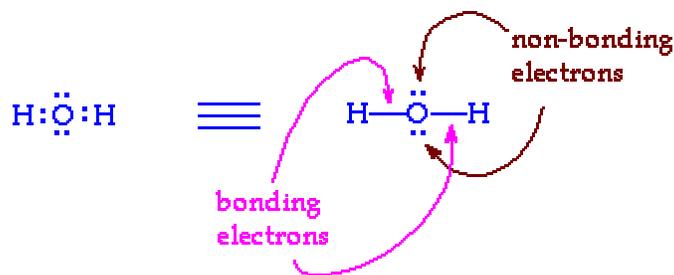
The **Lewis structure** of a covalent compound or polyatomic ion shows how the valence electrons are arranged among the atoms in the molecule to show the connectivity of the atoms.



Instead of using two dots to indicate the two electrons that comprise the covalent bond, a line is substituted for the two dots that represent the two electrons.



Below is shown the Lewis structure for water. Two hydrogen atoms (H) are separately covalently bonded to the central oxygen (O) atom. The **bonding** electrons are indicated by the dashes between the oxygen (O) and each hydrogen (H) and the other two pairs of electrons that constitute the octet for oxygen, are called **non-bonding** electrons as they are not involved in a covalent bond.



1. The first step in drawing Lewis structures is to determine the number of electrons to be used to connect the atoms. This is done by simply adding up the number of valence electrons of the atoms in the molecule.

Consider carbon dioxide CO_2

carbon (C) has four valence electrons \times 1 carbon = $4 e^-$

oxygen (O) has six valence electrons \times 2 oxygens = $12 e^-$

There are a total of $16 e^-$ to be placed in the Lewis structure.

2. Connect the central atom to the other atoms in the molecule with single bonds.

Carbon is the central atom, the two oxygens are bound to it and electrons are added to fulfill the octets of the outer atoms.



3. Complete the valence shell of the outer atoms in the molecule.



4. Place any remaining electrons on the central atom.

There are no more electrons available in this example.

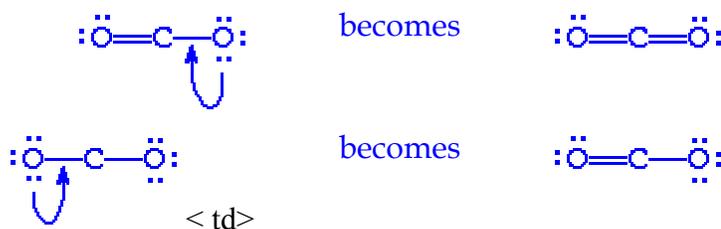
- If the valence shell of the central atom is complete, you have drawn an acceptable Lewis structure.

Carbon is electron deficient - it only has four electrons around it. This is not an acceptable Lewis structure.

- If the valence shell of the central atom is not complete, use a lone pair on one of the outer atoms to form a double bond between that outer atom and the central atom. Continue this process of making multiple bonds between the outer atoms and the central atom until the valence shell of the central atom is complete.



The central atom is still electron deficient, so share another pair.



5. Double check to make sure that you have used the correct number of electrons in the Lewis structure **and** that no atom that cannot exceed its valence shell, does not.

The best Lewis structure that can be drawn for carbon dioxide is:

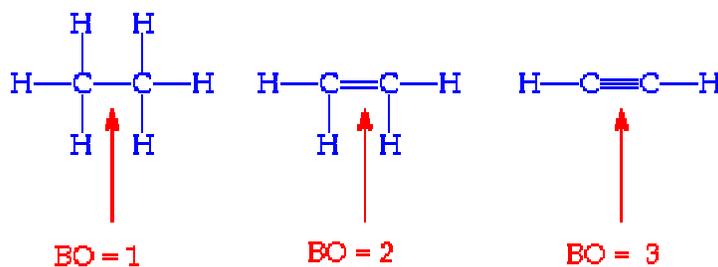
The best Lewis structure that can be drawn for carbon dioxide is:



Bond Order and Bond Length

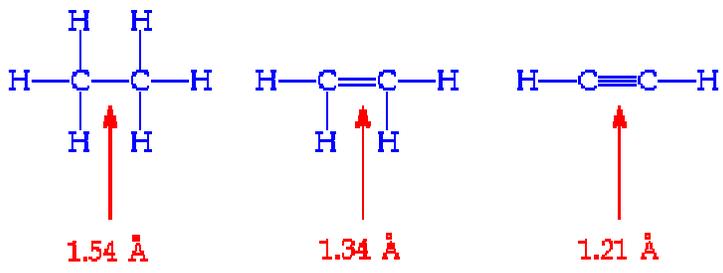
The **bond order** is equal to the number of bonds between two atoms.

Bond Order (BO) = # bonds between two atoms



The **bond length** is the distance between those two atoms. The greater the number of electrons between two atoms, the closer the atoms can be brought towards one another, and the shorter the bond.

The BO is an indication of the bond length, the greater the bond order, the shorter the bond.



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BONDING

- Some atoms are very reluctant to combine with other atoms and exist in the air around us as single atoms. These are the **Noble Gases** and have **very stable electron arrangements** e.g. **2**, **2.8** and **2.8.8** and are shown in the diagrams below. All other atoms therefore, bond to become electronically more stable, that is to become like Noble Gases in electron arrangement. Atoms can do this in two ways
- **Ionic and Covalent**
- **Cation** is smaller than the corresponding metal atom because the excess of protons in the ion draws the outer electrons in closer to the nucleus. In the example above, Na^+ is smaller than Na.
- **Anion** is larger than corresponding neutral (charge less) atom. The extra electron in the anion adds to the repulsion between outer electrons. Also, the added negative charge dilutes the nuclear charge onto more electrons, weakening its effect. In the example above Cl^- is larger than Cl.

	Structure	State	Forces between molecules	Melting and boiling points	Solubility in water	Conducts electricity	Examples
Covalent	Molecular	Liquids & Gases	Weak intermolecular	Low	Insoluble exceptions include HCl, Sugar, NH_3	No	H_2O , O_2 , CH_4
Ionic	Giant lattice	Solids	Strong intramolecular	High	Soluble	When molten (melted) and when dissolved in water.	CaO , NaCl, MgO

Ionic Bonds

The central idea of an ionic bond is that electrons (one or more, depending on the element) were transferred between the outer rings (shells) of adjacent atoms. For example, consider Na and Cl. Na would lose one electron and become positively charged and the Cl would gain one electron becoming negatively charged. The positive/negative charge attraction would hold the two ions together.

- Ionic bonds occur between metals and non-metals on the periodic table.

Three points

1. All transition metals and rare earth metals act as positives in ionic bonding.

- Hydrogen can be involved in ionic bonding. It will act as a nonmetal with a negative one charge. It is named hydride.
- There are more complex ionic bonding situations which will remain for later. For example, the bond between NH_4^+ and Cl^- in ammonium chloride is an ionic bond.
 - Metals bonding with non-metals
 - Involves transfer of electrons from metal to non-metal, so that both species obtain full outer shell electron configurations (Noble gas configuration).
 - Metals lose electrons to form positive ions (Cations).
 - Non-metals gain electrons to form negative ions (Anions).
 - The ions are held together by strong forces of electrostatic attraction. The ions are held in a giant three-dimensional regular lattice.

Properties

- The ions in an ionic solid are arranged in an orderly way in a giant ionic lattice shown in the diagram on the left. The ionic bond is the strong electrical attraction between the positive and negative ions next to each other in the lattice. Salts and metal oxides are typical ionic compounds.
- This strong bonding force makes the structure hard (if brittle) and have high melting and boiling points. Unlike covalent molecules, ALL ionic compounds are crystalline solids at room temperature.
- Many ionic compounds are soluble in water, but not all.
- The solid crystals DO NOT conduct electricity because the ions are not free to move to carry an electric current. However, if the ionic compound is melted or dissolved in water, the liquid will now conduct electricity, as the ion particles are now free.

Covalent Bonding

- Between non-metals and non-metals
- Involves the sharing of electrons. Atoms share electrons, so that both can achieve a full outer shell electron configuration.
- The covalent bonding is caused by the mutual electrical attraction between the two positive nuclei of the two atoms of the bond, and the electrons between them.
- One **single covalent bond** is a sharing of **1 pair of electrons**, two pairs of shared electrons between the same two atoms gives a double bond and it is possible for two atoms to share 3 pairs of electrons and give a triple bond.

Properties

- High melting point and boiling points — the atoms are packed close together and the bonds holding them are very strong. The energy needed to melt the metals is high.
- Conduct heat and electricity — electrons in the “sea” are mobile. A current (flow of electrons) can pass.
- Insoluble in water and organic solvents, but may react with water.

Metallic Bonds

The **crystal lattice of metals consists of ions** *NOT atoms*. The outer electrons (-) from the original metal atoms are free to move around between the positive metal ions formed (+). These free or 'delocalized' electrons are the 'electronic glue' holding the particles together. There is a **strong electrical force of attraction between these mobile electrons and the 'immobile' positive metal ions** - this is the **metallic bond**.

- This **strong bonding** generally results in **dense, strong materials with high melting and boiling points**.
- Metals are **good conductors of electricity** because these 'free' electrons carry the charge of an electric current when a potential difference (voltage!) is applied across a piece of metal.
- Metals are also **good conductors of heat**. This is also due to the free moving electrons. Non-metallic solids conduct heat energy by hotter more strongly vibrating atoms, knocking against cooler less strongly vibrating atoms to pass the particle kinetic energy on. In metals, as well as this effect, the 'hot' high kinetic energy electrons move around freely to transfer the particle kinetic energy more efficiently to 'cooler' atoms.
- Typical metals also have a **silvery surface** but remember this may be easily tarnished by corrosive oxidation in air and water.

VSEPR

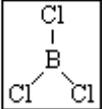
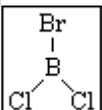
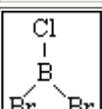
- VSEPR stands for Valence Shell Electron Pair Repulsion.
- Electrons will come in several flavors:
 - a) bonding pairs - this set of two electrons is involved in a bond, so we will write the two dots BETWEEN two atoms. This applies to single, double, and triple bonds.
 - b) nonbonding pairs - this should be rather obvious.
 - c) single electrons - in almost every case, this single electron will be nonbonding.

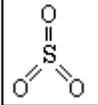
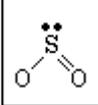
Geometry	Similar Regions
Linear	Ends
Trigonal Planar	Corners of the triangle
Tetrahedral	corners of the tetrahedron
Trigonal Bipyramidal	two axial positions as a set three equatorial positions as a set
Octahedral	Corners of the octahedron
Pentagonal Bipyramidal	two axial positions as a set five equatorial positions as a set

Linear Examples

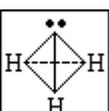
H ₂	H - H	Both ends are the same. Nonpolar.
HCl	H - Cl	Both ends are not the same. Polar. Cl more electronegative than H. Polarity direction towards Cl.
CS	C [triple bond] S	Both ends are not the same. Polar. C and S have the same electronegativity. C has a -1 formal charge Polarity towards C

Trigonal Planar Examples

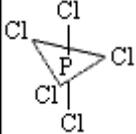
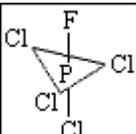
BCl ₃		all triangle corners are the same. Nonpolar.
BCl ₂ Br		all triangle corners are not the same. Polar. Cl more electronegative than Br. since there are two Cl, polarity direction towards Cl.
BClBr ₂		all triangle corners are not the same. Polar. with two Br versus one Cl, the polarity direction is expected

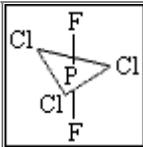
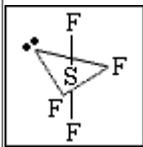
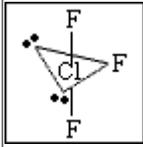
		towards the Br.
SO ₃		all triangle corners are the same. Nonpolar.
SO ₂		all triangle corners are not the same. Polar. the lone pair on the S versus two O would make a reasonable polarity direction difficult even with O more electronegative than S

Tetrahedral Examples

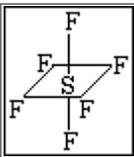
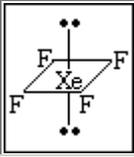
CH ₄		all tetrahedron corners are the same. Nonpolar.
CH ₃ F		all tetrahedron corners are not the same. Polar. Even with three H versus one F, the polarity direction would likely be toward F
NH ₃		all tetrahedron corners are not the same. Polar. with three H versus one N, but N more electronegative than H and a N lone pair, polarity direction would be toward the lone pair
H ₂ O		all tetrahedron corners are not the same. Polar. with two H versus one O, but O more electronegative than H and two O lone pairs, polarity direction would be toward the lone pairs

Trigonal Bipyramidal Examples

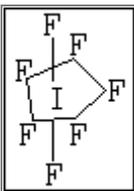
PCl ₅		two axial positions are the same, and three equatorial positions are the same. Nonpolar.
PCl ₄ F		two axial positions are not the same. three equatorial positions are the same. Polar. Since the three equatorial positions cancel each other for polarity, the polarity direction would be toward the axial F.

PCl_3F_2		the two axial positions are the same the three equatorial positions are the same. Nonpolar.
SF_4		the two axial positions are the same the three equatorial positions are not the same. Polar. Polarity direction would be quite difficult to predict with two F versus a lone pair.
ClF_3		the two axial positions are the same the three equatorial positions are not the same. Polar. With two lone pairs versus one F, polarity direction would likely be toward the lone pairs.

Octahedral Examples

SF_6		all octahedron corners are the same. Nonpolar.
XeF_4		all octahedron corners are not the same. All opposite corners are the same; symmetry takes precedence. Thus, there is no preferred polarity direction. Nonpolar.

Pentagonal Bipyramidal Examples

IF_7		The two axial positions are the same. the five equatorial positions are the same. Nonpolar.
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VSEPR TABLE

Molecular Type	# of Electron Pairs	# of single bonding electron pairs	# of unshared electron pairs	Name/Angle	Example	Lewis	3-D Structure
AX ₂	2	2	0	linear (180°)	BeH ₂		
AX ₃ ²⁻	3	3	0	trigonal planar (120°)	BCl ₃		
AX ₂ E	3	2	1	Non-Linear	SO ₂		
AX ₄	4	4	0	tetrahedral (109.5°)	CH ₄		
AX ₃ E	4	3	1	trigonal pyramidal	NH ₃		
AX ₂ E ₂	4	2	2	Non-Linear 104.5°	H ₂ O		
AX ₅	5	5	0	Trigonal bipyramid (90°, 120°)			
AX ₄ E	5	4	1	see-saw			
AX ₃ E ₂	5	3	2	T-shaped			
AX ₂ E ₃ ⁻	5	2	3	Linear			
AX ₆	6	6	0	Octahedral	SF ₆		
AX ₅ E ⁻	6	5	1	Square pyramidal	BrF ₅		
AX ₄ E ₂	6	4	2	square planar	XeF ₄		

INTERMOLECULAR FORCES

Three types of force can operate between covalent molecules:

- Dispersion Forces
also known as London Forces (named after Fritz London who first described these forces theoretically 1930) or as Weak Intermolecular Forces or as van-der- Waals' Forces (named after the person who contributed to our understanding of non-ideal gas behaviour).
- Dipole-dipole interactions
- Hydrogen bonds

Relative strength of Intermolecular Forces:

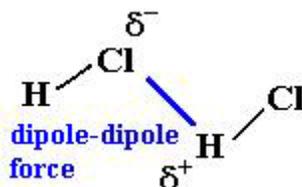
- Intermolecular forces (dispersion forces, dipole-dipole interactions and hydrogen bonds) are much weaker than intramolecular forces (covalent bonds, ionic bonds or metallic bonds)
- dispersion forces are the weakest intermolecular force (one hundredth-one thousandth the strength of a covalent bond), hydrogen bonds are the strongest intermolecular force (about one-tenth the strength of a covalent bond).
- dispersion forces < dipole-dipole interactions < hydrogen bonds

London Dispersion Forces - Weakest weak bond (London Forces, Dispersion Forces, Weak Intermolecular Forces, van der Waals' Forces)

- are very weak forces of attraction between molecules resulting from:
 - momentary dipoles occurring due to uneven electron distributions in neighbouring molecules as they approach one another
 - the weak residual attraction of the nuclei in one molecule for the electrons in a neighbouring molecule.
- The more electrons that are present in the molecule, the stronger the dispersion forces will be.
- Dispersion forces are the only type of intermolecular force operating between non-polar molecules, for example, dispersion forces operate between hydrogen (H₂) molecules, chlorine (Cl₂) molecules, carbon dioxide (CO₂) molecules, dinitrogen tetroxide (N₂O₄) molecules and methane (CH₄) molecules.

Dipole-Dipole Forces - Medium weak bond

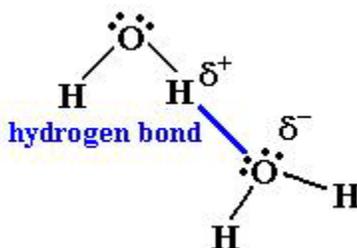
- Dipole-dipole forces exist between **neutral, polar** molecules where the positive end of one molecule is attracted to the negative end of another molecule.



- The greater the polarity (difference in electronegativity of the atoms in the molecule), the stronger the dipole-dipole attraction.
- Dipole-dipole attractions are very weak and substances held together by these forces have low melting and boiling point temperatures. Generally, substances held together by dipole-dipole attractions are gases at room temperature.

Hydrogen Bonding - Strongest weak bond

- In hydrogen bonds, the positively charged hydrogen end of one molecule is attracted to the negatively charged end of another molecule which must be an extremely electronegative element (fluorine, oxygen, or nitrogen - FON)
 - e.g. H₂O, HF, and NH₃.
 - [Alcohols](#) can also form hydrogen bonds with water in which the O in the OH group of the alcohol bonds to the positively charged H end of the water molecule and the H in the OH group of the alcohol bonds to the negatively charged O of the water molecule.



- Hydrogen bonds are the strongest weak bond because the H atom essentially gives its single electron to form a bond and is therefore left unshielded. The relatively strength of hydrogen bonds results in higher melting and boiling point temperatures than those in molecules with other van der Waals forces of attraction.
- Hydrogen bonding can explain why water is less dense in the solid phase than it is in the liquid phase (contrary to most other substances). The hydrogen bonds between water molecules in ice to form a crystal structure, keeping them further apart than they are in the liquid phase.

Effect of Intermolecular forces on melting and boiling points of molecular covalent substances:

Since melting or boiling result from a progressive weakening of the attractive forces between the covalent molecules, the stronger the intermolecular force is, the more energy is required to melt the solid or boil the liquid.

If only dispersion forces are present, then the more electrons the molecule has (and consequently the more mass it has) the stronger the dispersion forces will be, so the higher the melting and boiling points will be.

Consider the hydrides of Group IV, all of which are non-polar molecules, so only dispersion forces act between the molecules.

CH_4 (molecular mass ~ 16), SiH_4 (molecular mass ~ 32), GeH_4 (molecular mass ~ 77) and SnH_4 (molecular mass ~ 123) can all be considered non-polar covalent molecules.

As the mass of the molecules increases, so does the strength of the dispersion force acting between the molecules, so more energy is required to weaken the attraction between the molecules resulting in higher boiling points.

If a covalent molecule has a permanent net dipole then the force of attraction between these molecules will be stronger than if only dispersion forces were present between the molecules. As a consequence, this substance will have a higher melting or boiling point than similar molecules that are non-polar in nature.

Consider the boiling points of the hydrides of Group VII elements.

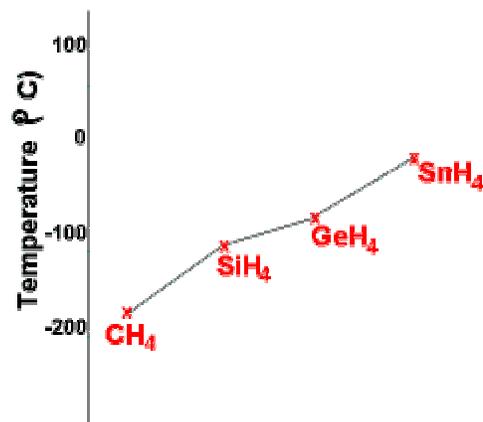
All of the molecules HF (molecular mass ~ 20), HCl (molecular mass ~ 37), HBr (molecular mass ~ 81) and HI (molecular mass ~ 128) are polar, the hydrogen atom having a partial positive charge ($\text{H}^{\delta+}$) and the halogen atom having a partial negative charge ($\text{F}^{\delta-}$, $\text{Cl}^{\delta-}$, $\text{Br}^{\delta-}$, $\text{I}^{\delta-}$).

As a consequence, the stronger dipole-interactions acting between the hydride molecules of Group VII elements results in higher boiling points than for the hydrides of Group IV elements as seen above.

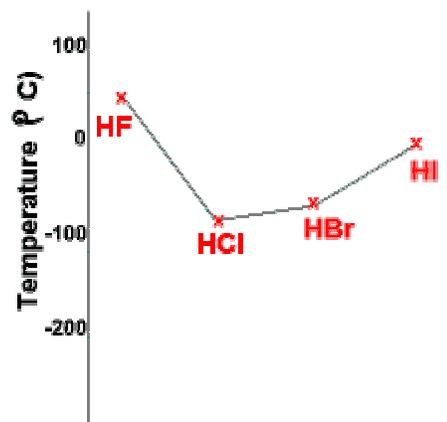
With the exception of HF , as the molecular mass increases, the boiling point of the hydrides increase.

HF is an exception because of the stronger force of attraction between HF molecules resulting from hydrogen bonds acting between the HF molecules.

Weaker dipole-dipole interactions act between the molecules of HCl , HBr and HI . So HF has a higher boiling point than the other molecules in this series.



Boiling Points of Group IV Hydrides



Boiling Points of Group VII hydrides

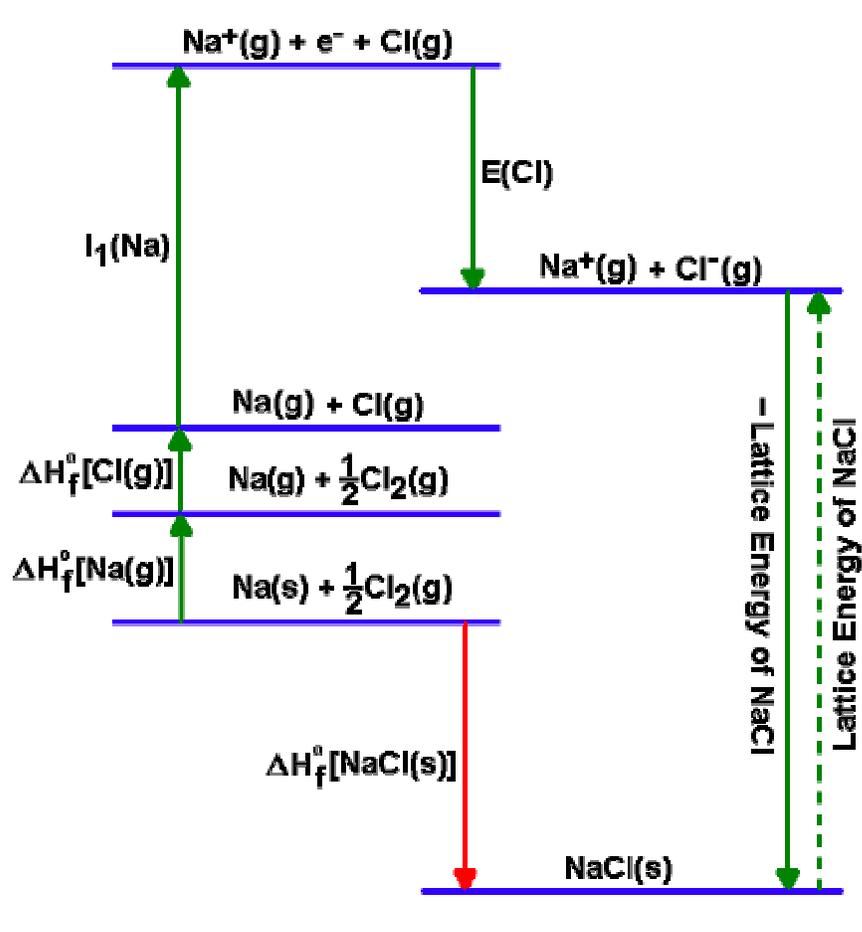
Effect of Intermolecular Forces on Solubility

In general like dissolves like:

- non-polar solutes dissolve in non-polar solvents
Paraffin wax ($C_{30}H_{62}$) is a non-polar solute that will dissolve in non-polar solvents like oil, hexane (C_6H_{14}) or carbon tetrachloride (CCl_4).
Paraffin wax will NOT dissolve in polar solvents such as water (H_2O) or ethanol (ethyl alcohol, C_2H_5OH).
- polar solutes such as glucose ($C_6H_{12}O_6$) will dissolve in polar solvents such as water (H_2O) or ethanol (ethyl alcohol, C_2H_5OH) as the partially positively charged atom of the solute molecule is attracted to the partially negatively charged atom of the solvent molecule, and the partially negatively charged atom of the solute molecule is attracted to the partially positively charged atom of the solvent molecule.
Glucose will NOT dissolve in non-polar solvents such as oil, hexane (C_6H_{14}) or carbon tetrachloride (CCl_4).
- Ionic solutes such as sodium chloride ($NaCl$) will generally dissolve in polar solvents but not in non-polar solvents, since the positive ion is attracted the partially negatively charged atom in the polar solvent molecule,

Born-Haber Cycle

The Lattice energy can be calculated with Hess's law and the following steps:



The Born-Haber Cycle