

Intermolecular Forces

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(Chemistry Notes)

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Comparing Ionic and Covalent Compounds

Ionic substance with small ions tend to be solids that have high melting points, and covalent substances tend to be gases and liquids or solids that have low melting points.

Oppositely Charged Ions Attract Each Other

Ionic substance generally have much higher forces of attraction than covalent substances. Each ion is attracted to all the ions of opposite charges. Small ions are hold tightly in a rigid crystal lattice that can be distrusted only by heating the crystals to very high temperature.

Strength of ionic forces

The strength of ionic forces depends on the size of the ions the the amount of charges.

Size

Within the same group, the smaller the ions, the stronger the ionic force holding them. Potassium chloride (KCl) has lower melting point than sodium chloride (NaCl).

Charge

If the ions have larger charges, then the ionic force is larger than the ionic forces of ions with smaller charger. This effect explains why calcium fluoride, CaF_2 (Ca^{2+} , 2F^-) melts at a higher temperature than NaCl (Na^+ , Cl^-)

Intermolecular Forces Attract Molecules to Each Other

Intermolecular forces attract molecules to each other in covalent substances. They can be dipole-dipole forces or London dispersion forces. Both forces are short-range and decrease rapidly as molecules get farther apart. Therefore, these forces act only between neighboring molecules.

Intermolecular forces do not have much of an impact on gases because the molecules are far apart from each other.

Table 1 Comparing Ionic and Molecular Substances

Type of substance	Common use	State at room temperature	Melting point (°C)	Boiling point (°C)
Ionic substances				
Potassium chloride, KCl	salt substitute	solid	770	sublimes at 1500
Sodium chloride, NaCl	table salt	solid	801	1413
Calcium fluoride, CaF ₂	water fluoridation	solid	1423	2500
Covalent substances				
Methane, CH ₄	natural gas	gas	-182	-164
Ethyl acetate, CH ₃ COOCH ₂ CH ₃	fingernail polish	liquid	-84	77
Water, H ₂ O	(many)	liquid	0	100
Heptadecane, C ₁₇ H ₃₆	wax candles	solid	22	302

Dipole-Dipole Forces (Polar Compounds)

Dipole-dipole forces are interactions between polar molecules. The positive end of one molecule attracts the negative end of a neighboring molecule.

Dipole-Dipole Forces Affect Melting and Boiling Points

The more polar the molecules are, the stronger the dipole-dipole forces between them, and thus, the higher the boiling point.

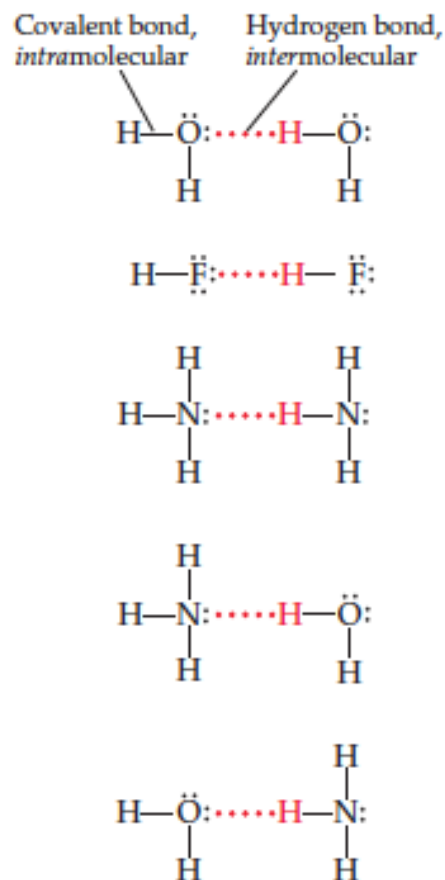
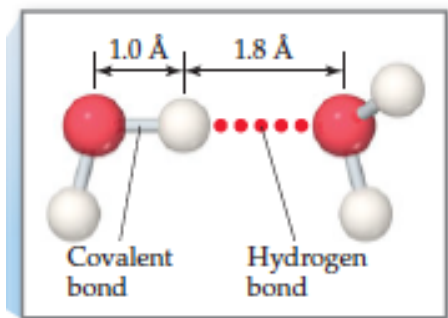
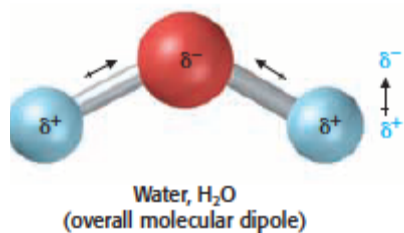
Remember, The greater the difference of electronegativity in a diatomic molecule, the greater the polarity is.

Table 3 below shows that boiling point increases when the difference in electronegativity increases. Fluorine is the most electronegative element in the periodic table. This accounts for the high jump in boiling point for HF.

Substance	HF	HCl	HBr	HI
Boiling point (°C)	20	-85	-67	-35
Electronegativity difference	1.8	1.0	0.8	0.5

Hydrogen Bonds

Hydrogen bond is the intermolecular force occurring when a hydrogen atom that is bonded to a highly electronegative atom (N, O, or F) of one molecule is attracted to two unshared electrons of another molecule. Hydrogen bond is another form of dipole-dipole forces.

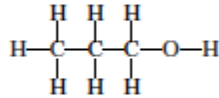
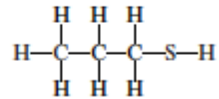
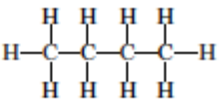






The greater the polarity of the molecule, the higher the boiling point is. When hydrogen atoms are bonded to very electronegative molecule, the effect is even more noticeable.

Compare the boiling points of H_2O (100 °C) and H_2S (-60.7 °C). These two molecules have similar sizes and shapes. Oxygen is more electronegative than sulfur. Therefore, H_2O is more polar than H_2S .

The polar compound 1-propanol $\text{C}_3\text{H}_7\text{OH}$, boils at 97.4 °C. The less polar compound of similar size, 1-propane-thiol boils at 67.8 °C. However, the non polar compound butane C_4H_{10} also to similar size boils at -0.5 °C. (Table 2 below)

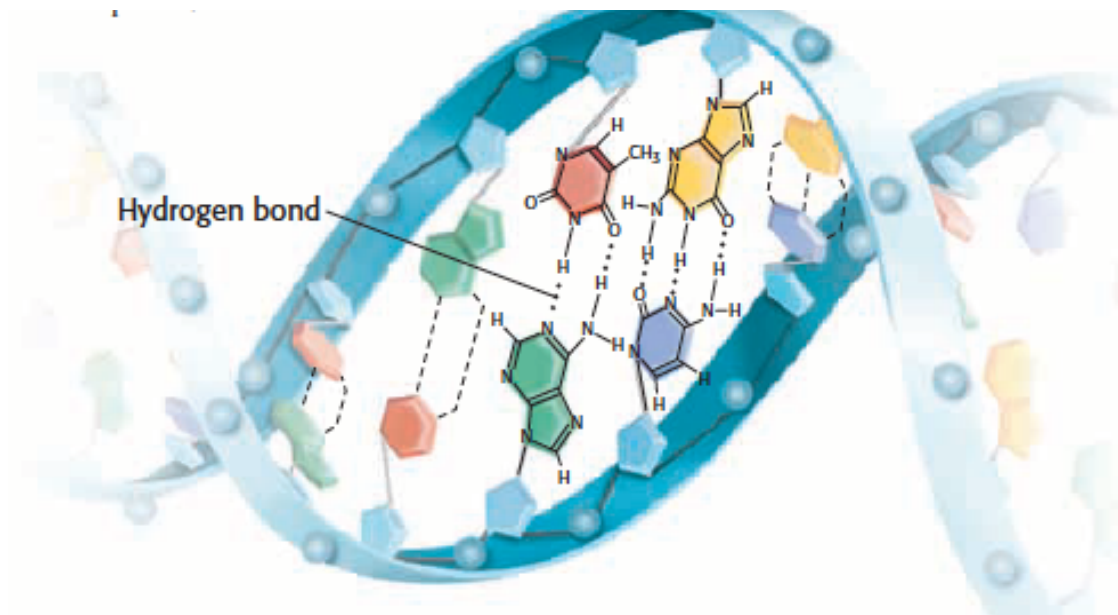
Table 2 Comparing Dipole-Dipole Forces

Substance	Boiling point (°C)	Polarity	State at room temperature	Structure
1-propanol, $\text{C}_3\text{H}_7\text{OH}$	97.4	polar	liquid	
1-propanethiol, $\text{C}_3\text{H}_7\text{SH}$	67.8	less polar	liquid	
Butane, C_4H_{10}	-0.5	nonpolar	gas	
Water, H_2O	100.0	polar	liquid	
Hydrogen sulfide, H_2S	-60.7	less polar	gas	
Ammonia, NH_3	-33.35	polar	gas	
Phosphine, PH_3	-87.7	less polar	gas	

Hydrogen Bond Form with Electronegative Atoms.

When a hydrogen atom bonds to an atom of N, O or F, the hydrogen atom has a large partially positive charge. The partially positive hydrogen atom of polar molecule can be attracted to the unshared pairs of electrons of neighboring molecules.

Hydrogen bonding between base pairs on adjacent molecules of DNA holds the two strands together. Yet the force is not so strong that the strands cannot be separated.



Hydrogen Bonds are Strong Dipole-Dipole Forces.

The strength of the hydrogen bond depends on two factors:

- 1) The difference in electronegativity between hydrogen and N, O or F.
- 2) The small size of the hydrogen atom that has only one electron.

When hydrogen is attached to N, O or F, its single electron is pulled away from it. Thus, the single proton of the hydrogen nucleus is partially exposed and strongly attracted to the unshared pair of electrons of other molecules.

Hydrogen Bonds Explain Water's Unique Properties.

A) The intermolecular forces in water are strong.

In water H_2O , two hydrogen atoms can form hydrogen bonds with neighboring molecules. Because of the water molecule's ability to form multiple hydrogen bonds at once, the intermolecular forces in water are strong.

B) Crystal structure of ice has large volume and low density.

Unlike most solids, which are denser than liquids, solid water is less dense than liquid water and floats in liquid water.

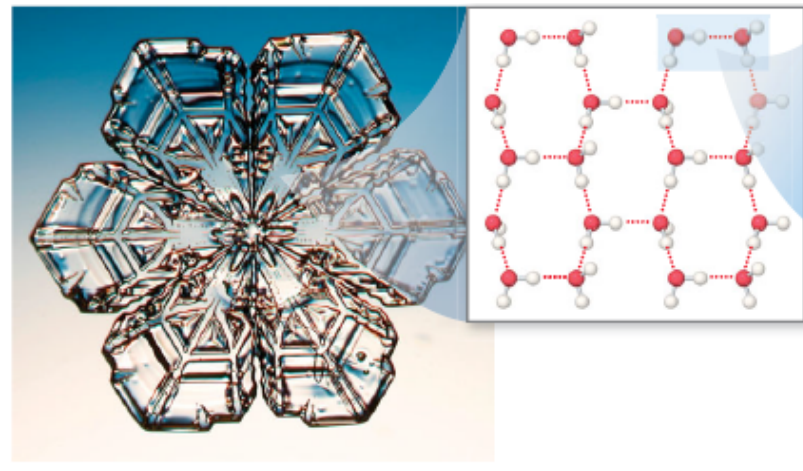
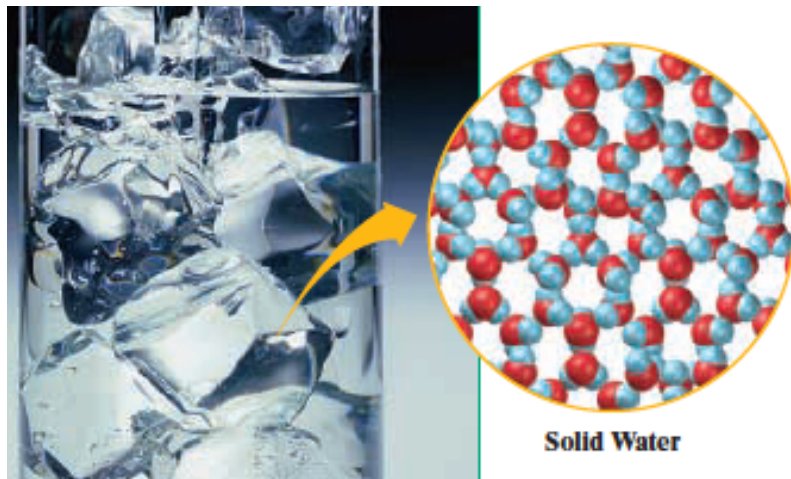
The angle between the two hydrogen atoms in water is 104.5° . This angle is very close to tetrahedral angle of 109.5° . When water forms solid ice, the angle in the molecules causes the special geometry

in the crystal structure. Ice crystals have large amounts of open space with cause ice to have low density.

The unusual density difference between liquid and solid water explains many important phenomena in the natural world.

1- Because ice water has lower density than liquid water, ice floats on water. Ponds freeze from top down and not from bottom up. Thus, fish can survive the winter in water under insulating layer of ice.

2- Because water expands when it freezes, water seeping into the cracks of rock or concrete can cause considerable damage due to fracturing.



London Dispersion Forces (Non-polar Molecules)

Ionic compounds: Force of attraction between ions of opposite charge cause the ions to stick together.

Polar Covalent compounds: dipole-dipole forces holds polar molecules together. The negative part of the molecule attracts the positive region of the neighboring molecules.

What force of attraction hold together no polar molecules and atoms?

No polar molecules experience a special form of dipole-dipole forces called London dispersion force.

In London's dispersion forces, there is not special part of the molecule that is always positive or negative. The intermolecular attraction results from the uneven distribution of electrons and creation of temporary dipole.

London Dispersion Forces Exist Between Non-polar Molecules Increases with Molar Mass.

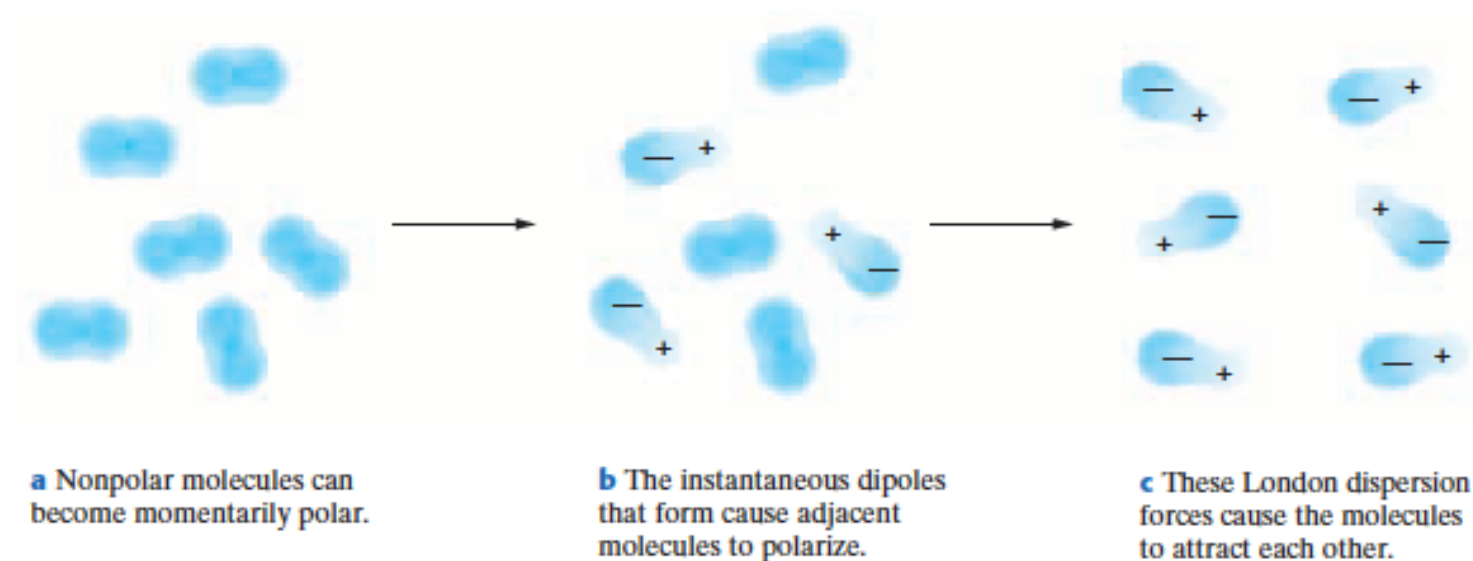
In general, the strength of the London dispersion forces between no polar particles increases as the molar mass of the particles increases. In general, as the molar mass increases, the number of electrons in the molecule increases. Consequently, the London dispersion forces increases leading to an increase in boiling point.

Table 4 Boiling Points of the Noble Gases

Substance	He	Ne	Ar	Kr	Xe	Rn
Boiling point (°C)	-269	-246	-186	-152	-107	-62
Number of electrons	2	10	18	36	54	86

London Dispersion Forces Result from Temporary Dipoles.

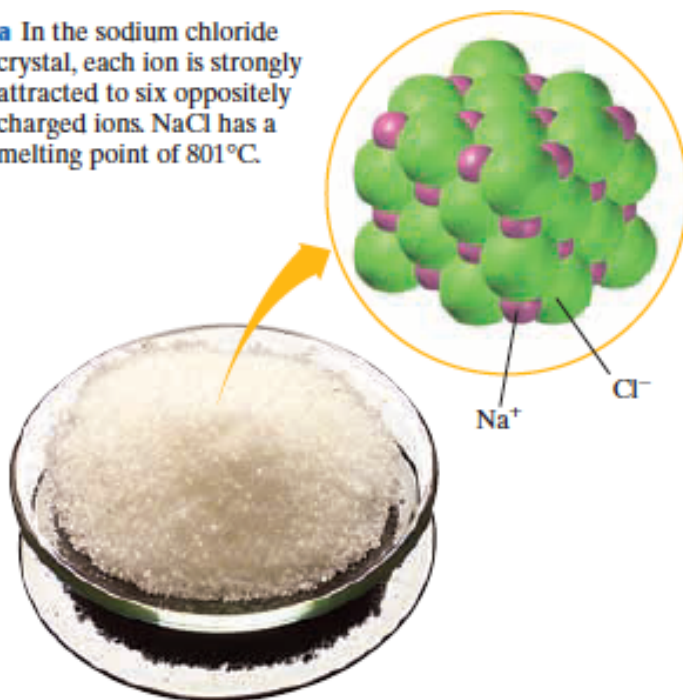
Electron can move from one side of an atom to the other. When the electrons move toward one side of the atom or molecule, that side becomes momentarily negative and the other side becomes momentarily positive. The temporary dipoles that form attract each other and make temporary dipole form in other molecule. When molecules are near each other, they always exert an attractive force because electrons can move.



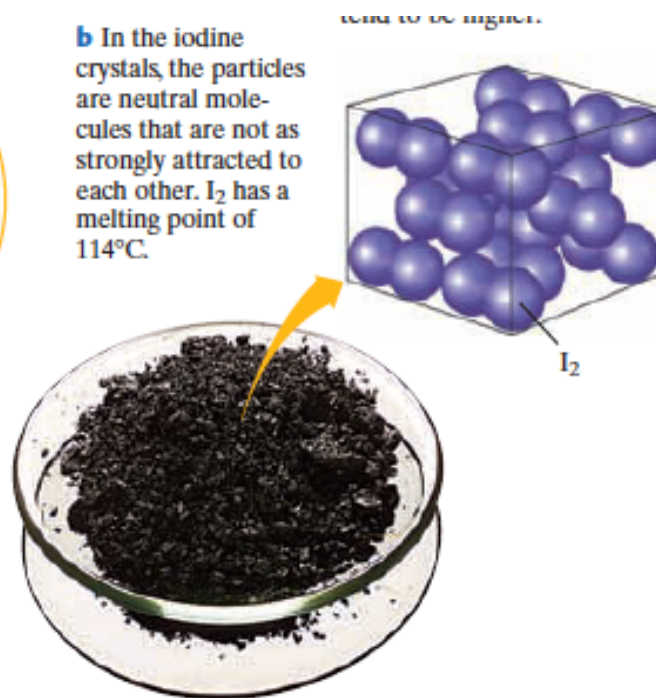
Properties Depend on Types of Intermolecular Force.

Forces between ions are generally much stronger than the forces between molecules, so the melting points of ionic substances tend to be higher. Compare the properties of an ionic substance, NaCl, with those of non-polar substance, I₂.

a In the sodium chloride crystal, each ion is strongly attracted to six oppositely charged ions. NaCl has a melting point of 801°C.



b In the iodine crystals, the particles are neutral molecules that are not as strongly attracted to each other. I₂ has a melting point of 114°C.



Particle Size and Shape Also Play a Role

Strength of intermolecular forces:

Ionic Forces > Dipole-Dipole > London Dispersion Forces

Exception:

Size:

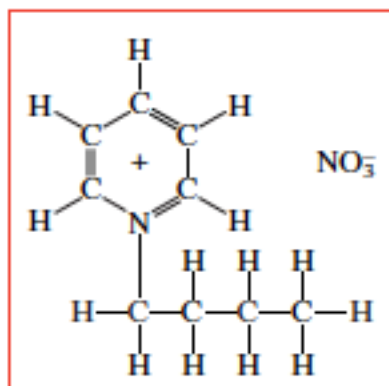
Size of the atoms, molecules or ions. The larger the particles are, the farther apart they are and the smaller the effects of the attraction, the lower the melting point. However, 1-butylpyridinium nitrate is ionic with low melting point due to its large size. (Figure 15)

Shape:

The boiling point of non-polar coronene $C_{24}H_{12}$ is as high as that of some ionic compounds. They are flat, so they can come closer together and the attractive forces have a greater effect.

Figure 15

a The polyatomic ionic compound 1-butylpyridinium nitrate is a liquid solvent at room temperature. The large size of the cations keeps the ionic forces from having a great effect.



b A molecule of coronene, $C_{24}H_{12}$, is very large, yet its flat shape allows it to have relatively strong London dispersion forces.

