

## LIQUIDS / SOLIDS / IMFs

Covalent bond

Hydrogen bond

about 610 Pa

273.15 K (0.01°C)

Pressure

Temperature

Ice (solid)

Water (liquid)

Water vapor (gas)

Triple point

Temporary, fluctuating induced-dipole

## Intermolecular Forces (IMFs)

*Attractions BETWEEN molecules*

- **NOT** within molecules
- **NOT** true bonds... weaker attractions
- Represented by dashed lines
- Physical properties (melting points, boiling points, vapor pressures, etc.) can be attributed to the amount and strength of IMFs

Example: **HIGHER BP = STRONGER IMFs**

Dispersion

Octane (C<sub>8</sub>H<sub>18</sub>)

C<sub>6</sub>H<sub>14</sub>

Dipole-dipole

CH<sub>3</sub>OH

Chloroform (CHCl<sub>3</sub>)

Methanol (CH<sub>3</sub>OH)

H bond

## Intermolecular Forces

*Attractions BETWEEN molecules*

**InTRAmolecular Force** → TRUE BONDS that hold atoms together... **STRONGER!**

**InTERmolecular Force** → attractive force that keeps molecules together... **WEAKER!**

Weak intermolecular

Strong covalent intramolecular

Intermolecular Force

Intramolecular forces (Covalent Bonding)

## London Dispersion Forces (LDFs)

- **INSTANTANEOUS** dipoles due to random movement of e<sup>-</sup> (because of collisions with other molecules)
- Exist in all molecules even **NONPOLAR**
- Creates momentary, short-lived nonsymmetrical distribution of charge (dipole) in neighboring molecule

Instantaneous uneven distribution of electrons in He atom

Nonpolar He atom

Instantaneous dipole

Induced dipole on neighboring He atom. Resultant attractive force

I<sup>δ+</sup> I<sup>δ-</sup> ... I<sup>δ+</sup> I<sup>δ-</sup>

## London Dispersion Forces (LDFs)

- **WEAKEST** of the IMFs
- Overall strength of the LDFs depends on the ease with which the charge distribution in a molecule can be distorted to induce an instantaneous dipole...

Instantaneous dipole here

repel

attract

Causes dipoles here

## London Dispersion Forces (LDFs)

- **POLARIZABILITY**: ease of distortion of the e<sup>-</sup> cloud
- **MORE ELECTRONS** (aka greater mass) = **GREATER POLARIZABILITY** = **STRONGER LDFs** for a substance!!!

**This is ONLY used to explain stronger LDFs between substances!**

Example: F<sub>2</sub> and Cl<sub>2</sub> gases... Br<sub>2</sub> and I<sub>2</sub> are not because they can't overcome the IMFs!

Electrostatic attraction

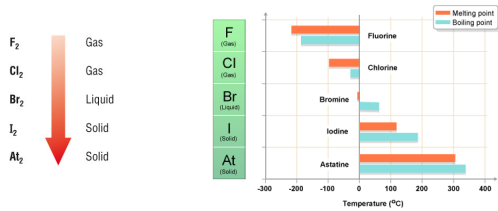
Helium atom 1

Helium atom 2

δ<sup>+</sup> δ<sup>-</sup> δ<sup>+</sup> δ<sup>-</sup>

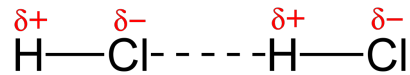
**\*For the AP Exam... It's the ELECTRONS not the mass that is important!**

## London Dispersion Forces (LDFs)



Directly related to the **POLARIZABILITY** of each substance... more electrons as go down the periodic table, so **STRONGER LDFs** lead to solids and higher boiling and melting points!

## Dipole-Dipole Forces

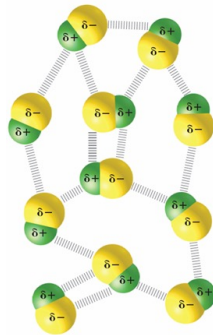


- Attractions between molecules with dipoles (**POLAR**)
- Molecules arrange themselves so opposite poles align
- Larger the dipole, stronger the force of attraction
- **LITTLE STRONGER**... only 1% as strong as ionic bonds

## Dipole-Dipole Forces

Attractive forces **DISSIPATE** with **INCREASED** distances!

Ex: Gases

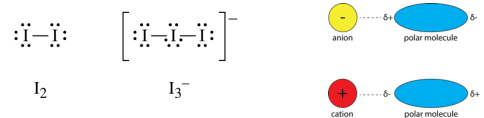


## Ion-Dipole Interaction

Type of IMF that occurs between an **ION** and a **POLAR molecule** (stronger than dipole-dipole)

### EXAMPLE:

The triiodide ion,  $\text{I}_3^-$ , is significantly more soluble in water than elemental iodine,  $\text{I}_2$ , is. Identify an intermolecular force between  $\text{I}_3^-$  and water that is not present between  $\text{I}_2$  and water, which could explain the difference in solubility.



## Hydrogen Bonding

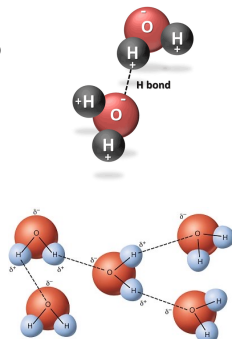
• Special type of dipole-dipole attraction... **Hydrogen** bonded to **N, O, or F**

• Attraction strength is higher because H bonded to highly electronegative elements

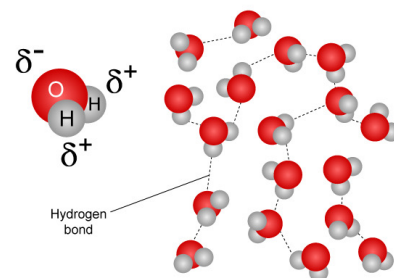
• Opposite poles align

• **STRONGEST** of the IMFs

• Important for bonding and properties of water and DNA

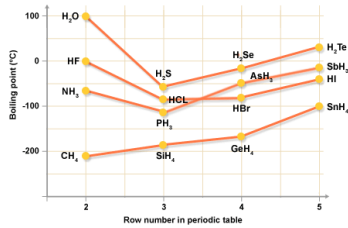


## Hydrogen Bonding



## Hydrogen Bonding

\*Notice that  $\text{H}_2\text{O}$ ,  $\text{HF}$ , and  $\text{NH}_3$  are **HIGHER** than should be!



- Expect that BP would increase with increasing molar mass (more polarizable cloud)... Stronger IMFs mean higher BP
- BUT lighter hydrides have H bonding and stronger IMFs and small size which means closer, stronger dipoles!

## Intermolecular Forces

### • EXAMPLE:

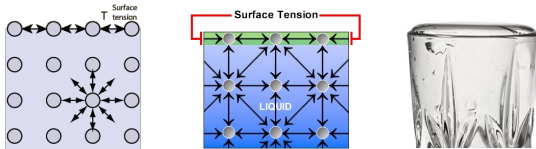
Identify the main / strongest type of IMF in each.

\*Important to understand molecules that have **H-bonding** have **ALL** three IMFs present, while molecules with dipole-dipole have **2 types of IMFs (LDF and D-D)** present!!

## Liquid State Properties

• **SURFACE TENSION:** resistance of a liquid to increase its surface area / beading of liquid droplets

**HIGHER IMFs = GREATER!**



## Liquid State Properties

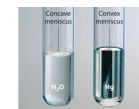
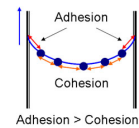
• **CAPILLARY ACTION:** spontaneous rising of a liquid in a narrow tube

**HIGHER IMFs = GREATER!**

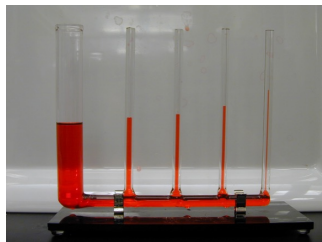
-**COHESIVE FORCES:** between molecules

-**ADHESIVE FORCES:** between molecules and container

-Water... Adhesive **GREATER** than cohesive (concave meniscus)... Hg would be convex!



## Capillary Action

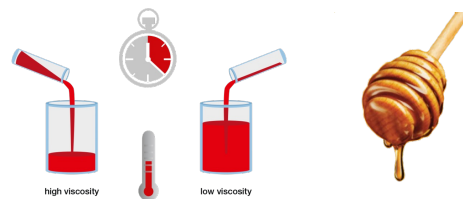


**Narrower the tube... More surface area of glass = HIGHER!**

## Liquid State Properties

• **VISCOSITY:** resistance to flow / increases with greater size and lower temps too

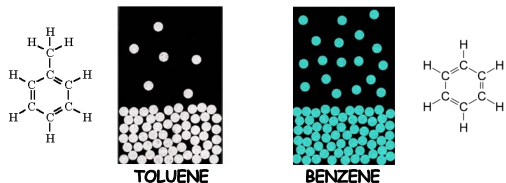
**HIGHER IMFs = GREATER!**



## Liquid State Properties

- **VOLATILITY:** ability to evaporate readily

**HIGHER IMFs = LESS VOLATILE!**



## Solution Formation and IMFs

- In order to dissolve a substance in a solvent:

1) Must overcome (**requires energy**)

- Solute-solute IMFs
- Solvent-solvent IMFs

2) Form solute-solvent attractive forces upon mixing (**releases energy**)

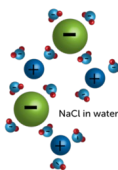


**DO NOT SAY "LIKE DISSOLVES LIKE" ON THE AP EXAM!!**

## Solution Formation and IMFs

**POLAR / IONIC** dissolve in **POLAR:**

- $\Delta H$  required to overcome IMFs in both the polar/ionic solute and the polar water molecules is quite **LARGE**
- $\Delta H$  released due to the interactions between the polar/ionic solute and the polar water molecules is very **LARGE**
- Solute can dissolve because it gets as much energy "back" (and more) from the interactions as was required to overcome the IMFs
- Same goes for nonpolar/nonpolar solutions



## Solution Formation and IMFs

**POLAR / IONIC** do NOT dissolve in **NONPOLAR:**

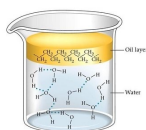
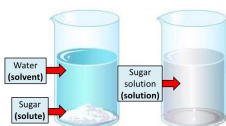
- $\Delta H$  released due to interactions between the polar/ionic solute and the nonpolar solvent is quite **SMALL**
- Solute **CANNOT** dissolve because the energy required to overcome the IMFs is not provided by the solute-solvent interactions



## Solution Formation and IMFs

**SUMMARY:**

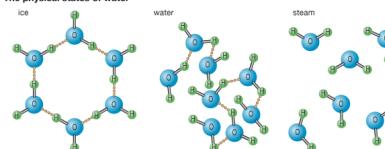
- If energy released when solute-solvent interact is **GREATER** than energy needed to break IMFs in each, then a substance **WILL** dissolve
- If energy released when solute-solvent interact is **LOWER** than the energy needed to break IMFs in each, then a substance will **NOT** dissolve



## Intermolecular Forces

- Gases have **WEAK IMFs** and lots of motion
- Solids have **STRONG IMFs** and no motion
- Liquids have both **STRONG IMFs** and motion

The physical states of water



## IMFs and Properties

- When considering strength of properties, remember:

**Dispersion < Dipole-Dipole < H-Bonding**

More for Organic molecules

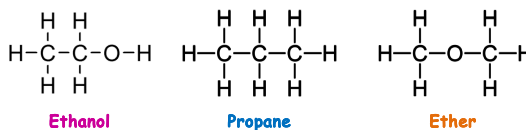
-Linear / Flat molecules = **MORE IMFs**

-Spherical / Branched molecules = **LESS IMFs**

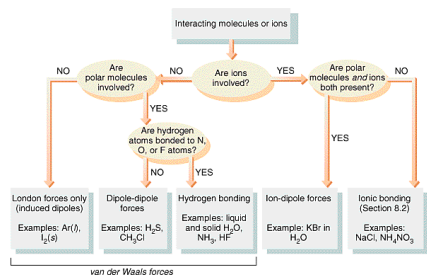
-If molecules have REALLY large e- cloud (or size), dispersion forces could be strongest!

## IMFs and Properties

- EXAMPLE:** Arrange the following in order of increasing boiling point.



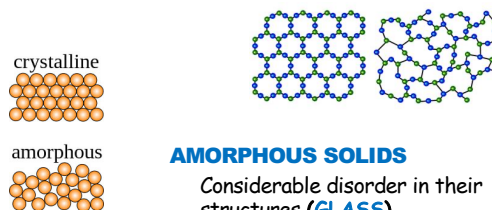
## Intermolecular Forces



## Types of Solids

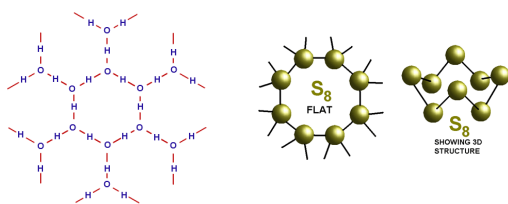
### CRYSTALLINE SOLIDS

Highly regular arrangement of their components (**IONIC**)



## Main Types of Solids

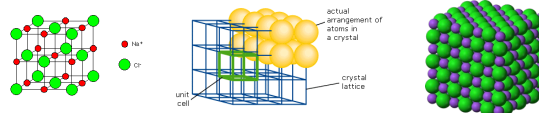
- MOLECULAR:** orderly 3D structure with discretely bonded **molecules** at each of its lattice points / Low MP (Ex: water, dry ice, P<sub>4</sub>, S<sub>8</sub>)



## Main Types of Solids

- IONIC:** orderly pattern of anions and cations; **ions** occupy lattice points / Very high MP (Ex: NaCl, CaCl<sub>2</sub>)

-**Closest Packing** → Large particles (anions) get arranged in a way that they are all packed tightly together; Small particles (cations) fit into the holes... Maximizes +/- attraction and minimizes +/+ or -/- repulsions

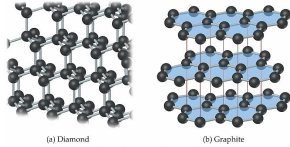


## Main Types of Solids

• **COVALENT NETWORK:** large networks of strong covalent (C or S) bonds (Ex: Quartz, Graphite, Diamond)

-**Diamond** → All C are  $sp^3$  hybridized making it strong and hard (must break ALL the bonds)

-**Graphite** → Forms layers of C atoms arranged in fused  $sp^2$  hybridized rings (delocalized e- allow it to conduct)

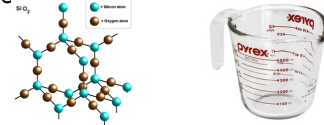


## Main Types of Solids

• **COVALENT NETWORK:** large networks of strong covalent (C or S) bonds (Ex: Quartz, Graphite, Diamond)

-**Quartz / Silica ( $SiO_2$ )** → Structure is actually based on a interconnected  $SiO_4$  tetrahedral

-**Glass** → Formed by quickly cooling melted silica, giving an amorphous solid / Other compounds added before cooling to give different types

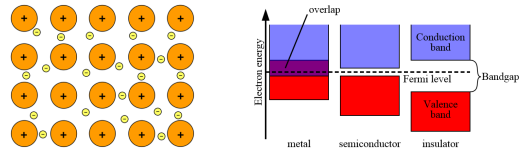


## Main Types of Solids

• **ATOMIC:** includes atoms held together by LDF (Ex: Noble gases) and atoms with free-moving e- (Ex: Metals)



## Bonding Models of Metals



• **Electron Sea Model:** regular array of metals in a "sea of electrons" that conduct heat and electricity

• **Band (Molecular Orbital) Model:** e- travel within molecular orbitals formed by the valence orbitals of the metal cations

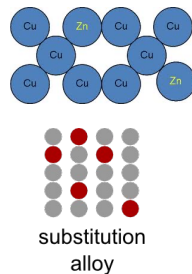
## Metal Alloys

*Mixtures of two or more elements with at least one being a metal*

### SUBSTITUTIONAL

Most metal atoms are replaced in the lattice by other atoms of **SIMILAR SIZE** (radii are close)

- Still remains somewhat malleable and ductile with a similar density to the original metal
- Ex: Brass, sterling silver, etc.



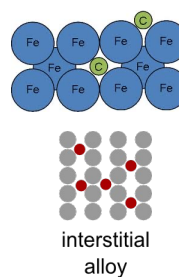
## Metal Alloys

*Mixtures of two or more elements with at least one being a metal*

### INTERSTITIAL

Holes in the closest packed metal structure filled by small atoms, typically nonmetals

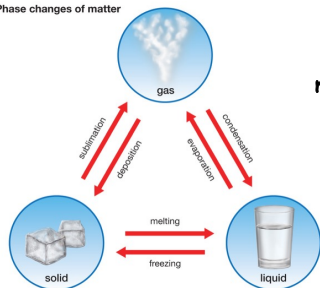
- Becomes more rigid, less malleable and ductile with a higher density
- Ex: Steel



## Phase Changes

*Change in state*

Phase changes of matter



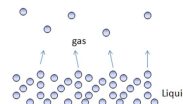
To change phase, enough energy is needed to allow the molecules to overcome the IMFs!

**MORE IMFs = MORE energy needed!**

## Vaporization (Evaporation)

*Molecules of a liquid escaping from the surface to form a gas*

- Always **ENDOTHERMIC**... energy absorbed in order to overcome the IMFs in the liquid
- **Enthalpy of Vaporization ( $\Delta H_{\text{vap}}$ )**: energy required to vaporize **ONE** mole of a liquid at 1 atm (heat of vaporization)
- $\text{H}_2\text{O}$  has a **HIGH** heat of vaporization (40.7 kJ/mol)... lots of energy needed to evaporate!



## Vapor Pressure

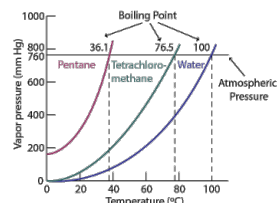
*Pressure of vapor present at equilibrium (rate of condensation equals rate of evaporation)*



- **NONVOLATILE**: liquids with low VPs and high IMFs
- **VOLATILE**: liquids with high VPs and low IMFs
- VP **INCREASES** as temperature **INCREASES**... more energy to escape
- VP **DECREASES** as MM **INCREASES**... more e- mean more polarizable, causing more IMFs! H-bonding is an exception... gives more IMFs so lower VP

## Vapor Pressure

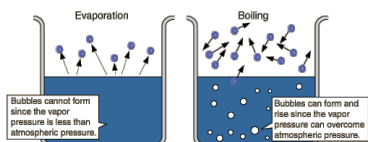
*Pressure of vapor present at equilibrium (rate of condensation equals rate of evaporation)*



## Boiling Point

*Temperature at which the VP of a liquid equals the atmospheric pressure*

- **NORMAL Boiling Point**: temperature at which VP of the liquid equals 1 atm



## Sublimation

*Substance goes directly from solid to gas*



- Solids have VP, but it's usually very low
- Solids with few IMFs can have high VP and sublime at room temp

## Melting Point

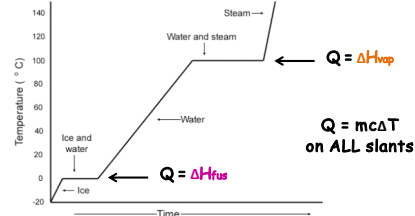
Molecules break loose from the lattice points in a solid, changing to a liquid

- **Enthalpy of Fusion ( $\Delta H_{fus}$ ):** energy required to convert one mole of a solid to one mole of a liquid
- **Normal melting point:** temperature at which solid and liquid states have same VP where total pressure is 1 atm



## Heating Curve

$\Delta H_{fus}$  always less than  $\Delta H_{vap}$  for substance because vaporizing has to overcome ALL IMFs not just some!



- Temperature remains **CONSTANT** during a phase change (PE changes... adding energy = INCR., removing energy = DECR., while KE remains same)
- Chemical bonds are **NOT** being broken during phase changes

## Exceptions

- Changes of state do not always form at the exact MP and BPs

### SUPERCOOLING

Rapid cooling allows liquid to remain a liquid at temperature below its FP... Quick temp change does not allow molecules to organize properly (solid will form readily once it happens)



## Exceptions

- Changes of state do not always form at the exact MP and BPs

### SUPERHEATING

Rapid heating allows liquid to remain a liquid at temperature above its BP... Quick temp change does not allow enough high energy molecules to accumulate in one place (bubbles very large when form... add boiling chips!)



## Phase Diagrams

Represent phases of matter as a function of temperature (x) and pressure (y)... closed systems NOT outdoors!

- Lines represent when two phases are in equilibrium
- **TRIPLE POINT:** all three phases exist in equilibrium
- **CRITICAL TEMP ( $T_c$ ):** temp above which the vapor cannot be liquified
- **CRITICAL PRESSURE ( $P_c$ ):** pressure required to liquefy AT  $T_c$
- **CRITICAL POINT:** point defined by  $T_c$  and  $P_c$

Gas and liquid no longer distinguishable!

## Phase Diagrams

### SOLIDS

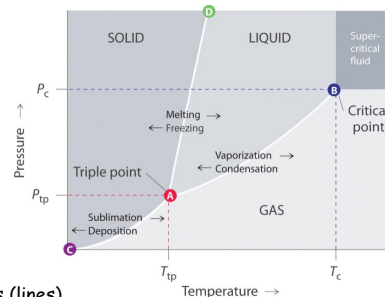
Low temp  
High pres

### LIQUIDS

In between

### GASES

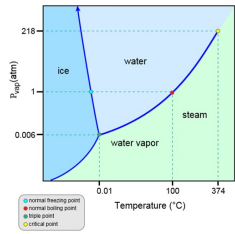
High temp  
Low pres



\*Phase boundaries (lines) represent **EQUILIBRIUM** set of conditions for temp and pressure!!

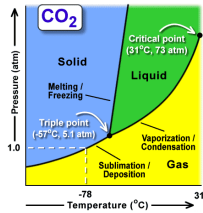
# Phase Diagrams

**WATER**



Notice how the solid-liquid line tilts to the left (- slope) since solid is **LESS DENSE** than liquid form

**CARBON DIOXIDE**



Notice how the solid-liquid line tilts to the right (+ slope) since solid is **MORE DENSE** than liquid form