Chapter 12: Liquids, Solids, and Intermolecular Forces

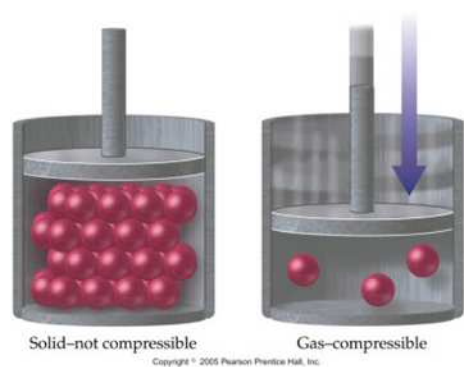
Why are some substances solids, while others are liquids or gases at room temperature and pressure (25°C, 1 atm)?

The different physical states of matter (SOLID, LIQUID, GAS) exist primarily because of differences in **INTERMOLECULAR FORCES** that act between particles of these substances.

Substances that are GASES at room temp. and pressure:

Gas

- Have very weak intermolecular interactions
- Have particles that are far apart
  - The particles have complete freedom from each other
- Have low density compared to liquids and solids
- Expand to fill their container
  - The particles are constantly flying around, bumping into each other and their container
- Can be easily compressed into a smaller volume



- Are fluid - exhibits a smooth, continuous flow as it moves
- Are either monoatomic atoms (He, Ne) or are molecules with covalent bonding

Liquids and Solids

Substances that are LIQUIDS at room temp. and pressure:

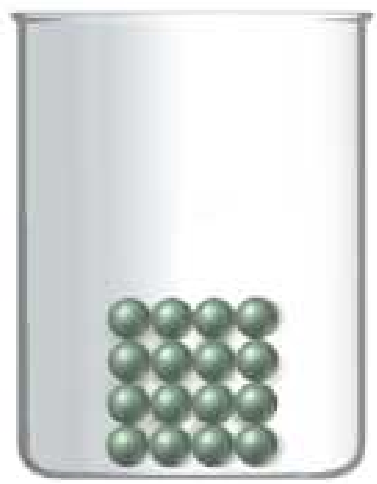
- Have stronger intermolecular interactions than gases
- Have particles that are much closer together compared to gases, **but they have some ability to move around**
- Have a high density compared to gases

Liquid

- Take the shape of their container, but keep their volume
- Cannot be easily compressed into a smaller volume
- Are fluid - exhibits a smooth, continuous flow as it moves
- Are composed of molecules with covalent bonding (exception: Hg)

Substances that are SOLIDS at room temp. and pressure:

- Have much stronger intermolecular interactions than gases
- Have particles that are packed close together and **are fixed in position (though they vibrate)**
  - Close packing results in solids being incompressible
- Have high densities compared to gases



Solid

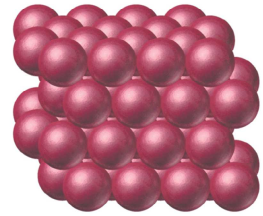
- Are nonfluid - they move as an entire "block" rather than with a smooth, continuous flow
- Can be pure metals, ionic compounds, or molecular compounds

Solids

Types of Solids

Crystalline solids - particles arranged in an orderly geometric fashion

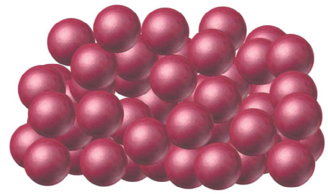
- Examples - salt and diamond



(a) Crystalline solid

Amorphous solids - particles DO NOT exhibit a regular geometric pattern over a long range

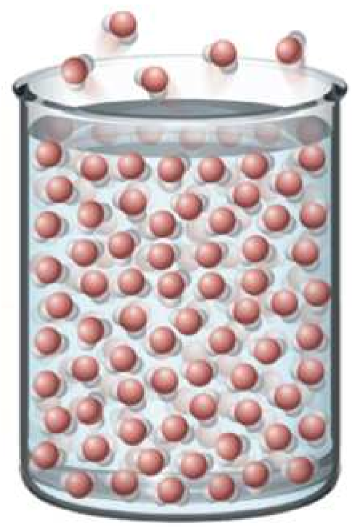
- Examples - plastic and glass



(b) Amorphous solid

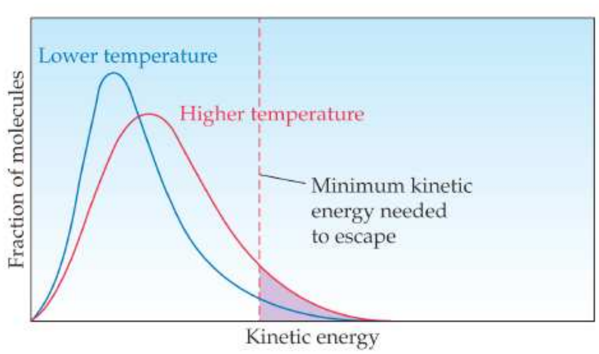
Evaporation

The process where molecules break free from the surface of a liquid and go into the gas phase (aka vaporization)



Molecules are in constant motion. When a molecule on the surface of a liquid has enough energy to break away from the intermolecular interactions that keep it in the liquid state, the molecule goes into the gas state (a physical change).

If the container is open, eventually all the molecules in the liquid state will go into the gas state.



Raising the temperature increases the number of molecules with sufficient energy to escape.

Evaporation and Condensation

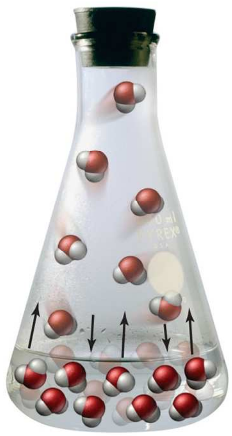
Condensation

The process in which molecules in the gas phase go into the liquid phase

- When a liquid evaporates in a closed container, the vapor molecules are trapped. The vapor molecules will eventually bump into to the surface of the liquid **and get recaptured by the liquid.**

If a container is closed, a **DYNAMIC EQUILIBRIUM** is established, where the rate of evaporation **<u>is equal to</u>** the rate of condensation.

When water is just added to the flask and it is capped, all the water molecules are in the liquid.



Soon, the water starts to evaporate. Initially the rate of evaporation is much faster than rate of condensation.

Eventually, condensation and evaporation reach the same speed - the system has reached dynamic equilibrium

Once dynamic equilibrium is attained the amount of vapor in the container will remain the same.

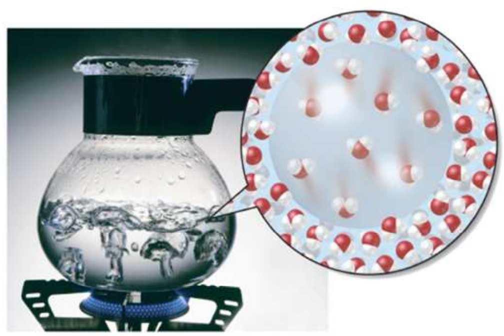
Boiling Point of a Liquid

Vapor Pressure - the partial pressure of a gas in dynamic equilibrium with it's liquid.

- ➢ The vapor pressure of a liquid depends on the temperature and strength of intermolecular attractions

- If a liquid is heated its molecules will move around faster and will have more energy. Consequently, it will be easier for them to break away from the intermolecular forces that keep them in the liquid state → **the liquid will evaporate more quickly**

- When the amount of heat is high enough to allow the vapor pressure (the pressure due to the molecules in the gas phase above a liquid) to be **EQUAL TO** the pressure exerted by the air molecules above the liquid, the liquid will reach its **BOILING POINT**

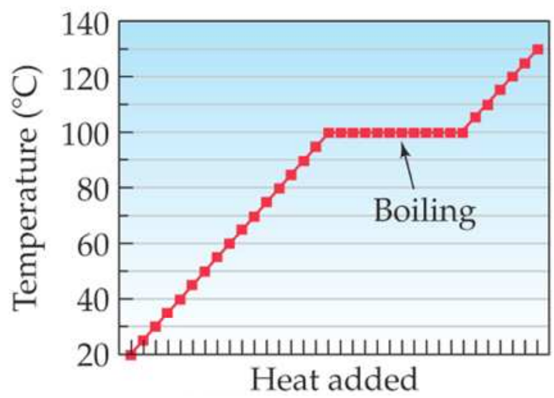


At the boiling point, the temperature is high enough for molecules in the interior of the liquid to escape. (The bubbles of gas you observe in a boiling liquid are pockets of gaseous water that have formed within the liquid water.)

- The boiling point depends on what the atmospheric pressure is.
  - ➢ The temperature of boiling water on the top of a mountain will be lower than boiling water at sea level

Energetics of Boiling, Evaporation and Condensation

As you heat a liquid, its temperature increases until it reaches its boiling point. Once the liquid starts to boil, **<u>the temperature remains the same</u>** until it all turns to a gas. (All the energy from the heat source is being used to overcome all of the attractive forces in the liquid).



<u>Energetics of Evaporation and Condensation</u>

During evaporation, since the higher energy molecules from the liquid are leaving, the total kinetic energy of the liquid decreases, and the liquid cools.

The remaining molecules <u>redistribute their energy</u>, generating more high energy molecules. Since the liquid is now cooler than the surroundings, heat energy is transferred from the surroundings into the liquid.

Hence, evaporation is an **ENDOTHERMIC PROCESS**

(As heat flows *out of the surroundings*, it causes the surroundings to cool)

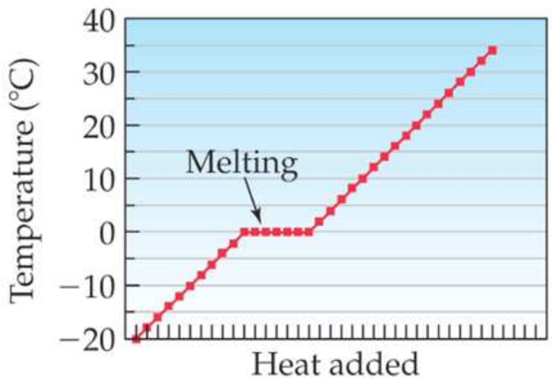
During condensation, <u>energy is given off</u> because the gas molecules slow down when they are recaptured by the surface of the liquid and go back into the liquid phase.

Hence, condensation is an EXOTHERMIC PROCESS

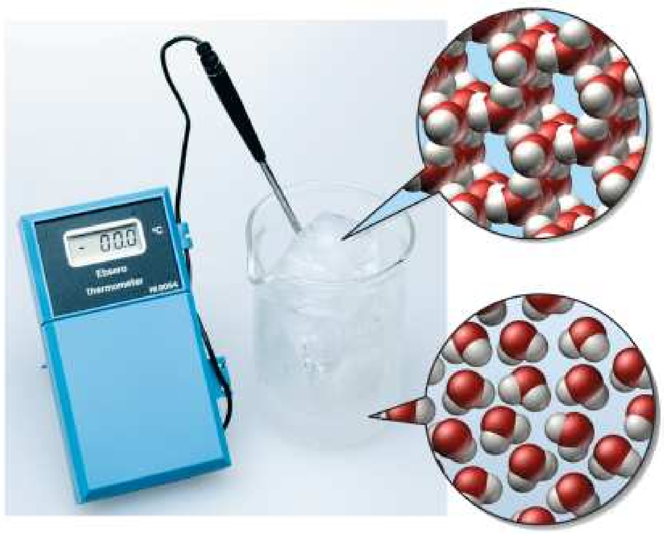
Melting and Freezing

When heat is added to a solid, its molecules or particles move around <u>more rapidly</u>. This added energy allows the attractive forces holding the particles together in a more rigid state to be overcome and for <u>the solid to be converted into a liquid</u>: **TO MELT**

Melting- an **endothermic** process



Once the solid starts to melt, the temperature remains the same until it all turns to a liquid.



Ex: Melting of Ice
As ice melts the temp. of the ice-water mixture remains at 0°C - the melting point of ice (or freezing point of water)

When a liquid <u>loses energy</u> (an **exothermic** process), the molecules move around less rapidly and the particles begin to arrange themselves in a more orderly fashion due to the intermolecular forces that attract the molecules to one another - <u>the liquid turns into a solid</u> - **IT FREEZES**

Melting Point of a Substance = Freezing Point of a Substance

- We use 'melting point' if the substance is a solid at room temp and pressure; we use 'freezing point' if the substance is a liquid at room temp. and pressure (Freezing pt of water = 0°C, Mpt of ice = 0°C)

Sublimation

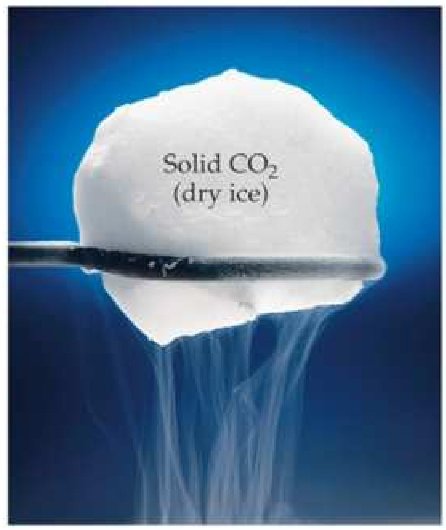
Melting Point and Intermolecular Forces Relationship

- Substances with STRONGER intermolecular forces will have HIGHER melting points.
- Substances with WEAKER intermolecular forces will have LOWER melting points

SUBLIMATION

Sublimation is a physical change in which the solid state of a substance changes directly to the gaseous state **without** going through the liquid state.

Like melting, sublimation is an endothermic process (energy absorbed from the surroundings)



Ex: Sublimation of Dry Ice

We will not cover "Heat of Vaporization" nor "Heat of Fusion" calculations in Section 12.4 pp 416 - 418 and Section 12.5 pp 420 - 421. **You do not need to know how to do these types of calculations.**

Intermolecular Forces:

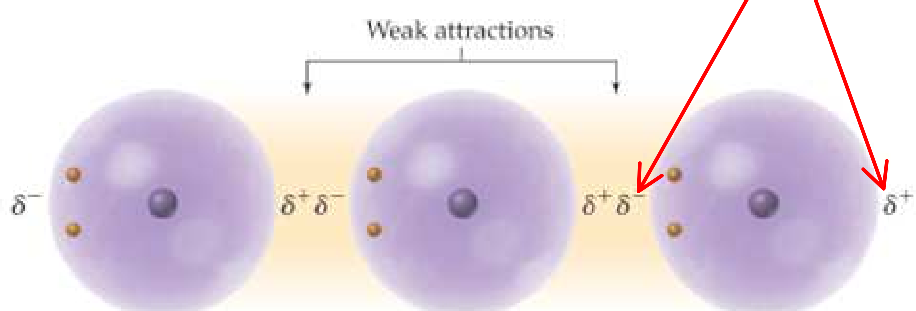
Attractive forces that exist **BETWEEN** molecules

Three Types of Intermolecular Forces

1) Disperson Forces
2) Dipole-Dipole Forces
3) Hydrogen Bonding

<u>Dispersion Forces</u> (aka London or Van der Waal Forces)

- Caused by distortions in the electron cloud of one molecule **inducing distortion** in the electron cloud on another
- Distortions in the electron cloud lead to a **<u>temporary dipole.</u>**



- The temporary dipoles lead to a weak attraction between neighboring molecules—**dispersion forces**
- **All molecules** have attractions caused by dispersion forces.
- **Strength of the dispersion force gets greater with larger molecules because larger molecules have electron clouds that are more easily distorted.**
- **WEAKEST OF THE INTERMOLECULAR FORCES**
- **Nonpolar molecules interact <u>ONLY</u> by Dispersion Forces**

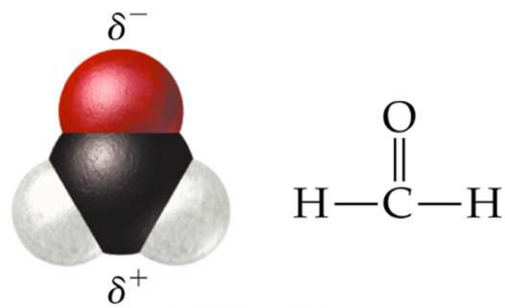
Dipole-Dipole Forces

Polar Molecules

Molecules with one or more **POLAR BONDS**, but are not symmetrical (*their bond dipoles don't cancel out*)

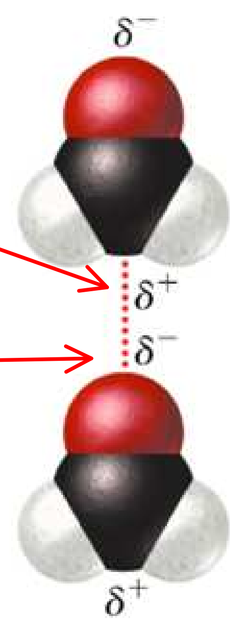
- They have a <u>PERMANENT net dipole moment</u>

Ex: Methanal (Formaldehyde)



Methanal is a polar molecule- it has a permanent dipole moment

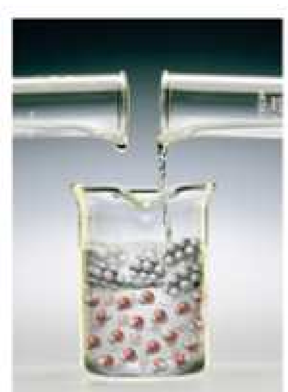
The partial positive (δ+) end of one polar molecule is attracted to the partial negative (δ-) end of another polar molecule: **a DIPOLE-DIPOLE attraction**



Dipole-Dipole forces are a stronger intermolecular interaction than Dispersion forces

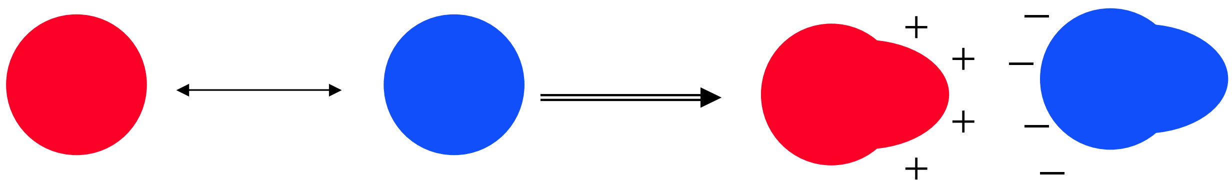
Polarity determines <u>**miscibility**</u> - whether or not two liquids will mix.

Only substances with similar polarities will mix.

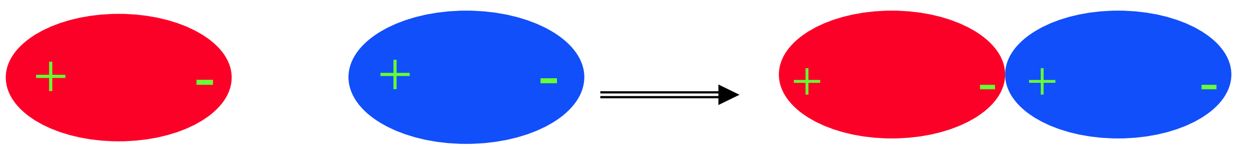


Intermolecular Attraction and Properties

Dispersion forces—All molecules



Dipole-dipole forces—Polar molecules



All molecules are attracted by dispersion forces.

Polar molecules are also attracted by dipole-dipole attractions.

Therefore, the strength of attraction is **stronger between polar molecules** than between nonpolar molecules of the same size.

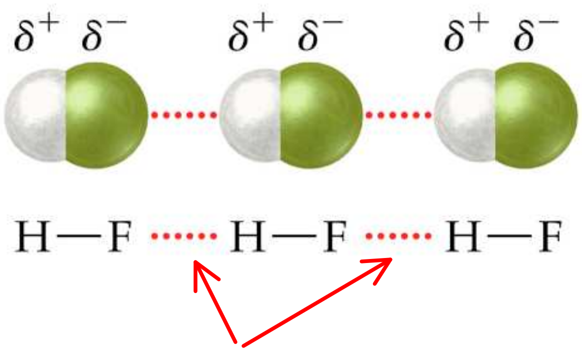
	Molar Mass (g/mol)	Boiling Point, °C	Dipole size, D
$CH_3CH_2CH_3$	44	-42	0
CH_3-O-CH_3	46	-24	1.3
CH_3 - CH=O	44	20.2	2.7
CH_3-C≡N	41	81.6	3.9

For molecules with a similar molecular weight, as the *dipole moment increases*, the *boiling point increases* (the molecules stick together more)

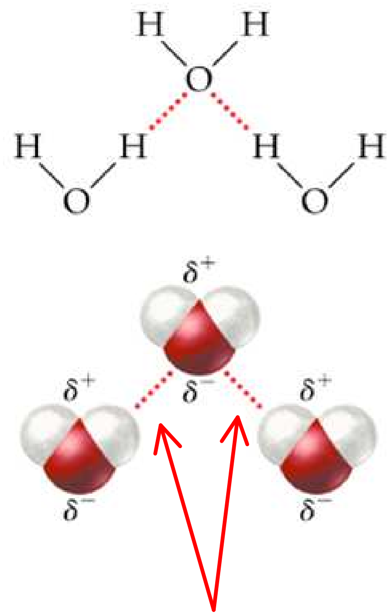
Hydrogen Bonding

HF, or molecules that have **OH** or **NH** groups can produce a **particularly strong dipole-dipole attraction** called

HYDROGEN BONDING



Hydrogen bonding between HF molecules

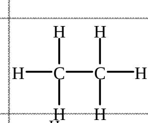
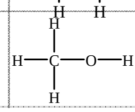


Hydrogen bonding between H_2O molecules

- When a very electronegative atom (like O, F or N) is bonded to hydrogen, it strongly pulls the bonding electrons toward it.
- Since hydrogen has no other electrons, when it loses much of it's electron density due to the electronegative atom, the nucleus becomes greatly deshielded.
- The partially exposed proton acts as a very strong center of positive charge, attracting the electron clouds from neighboring molecules.

Hydrogen Bonding

Properties and Hydrogen Bonding

Name	Formula	Molar mass (g/mol)	Structure	Boiling point, ℃	Melting point, ℃	Solubility in water
Ethane	C_2H_6	30.0		-88	-172	Immiscible
Methanol	CH_4O	32.0		64.7	-97.8	Miscible

For molecules with similar molecular weight, those that interact by hydrogen bonding have MUCH HIGHER melting and boiling points compared to molecules that are only attracted by Dispersion Forces (nonpolar molecules).

NOTE: Hydrogen bonds are ***not*** chemical bonds. Hydrogen bonds are attractive forces ***between*** molecules.

Types of Intermolecular Forces

Type of force	Relative strength	Present in	Example
Dispersion force	Weak, but increases with molar mass	All atoms and molecules	H_2
Dipole–Dipole force	Moderate	Only polar molecules	HCl
Hydrogen Bond	Strong	Molecules having H bonded to F, O, or N	HF

Ranking Boiling Point

To rank compounds in order of boiling point:

1. Find compounds with **H-bonding** - they will have higher bp's than compounds without H-bonding
2. Use molar mass to determine **dispersion forces** (a difference of less than 10 g/mol is not significant)
3. Use polarity to determine **dipole-dipole forces**

The compound with the <u>strongest</u> intermolecular forces will have the ________ boiling point.

Which has a higher boiling point, dimethyl ether (CH_3OCH_3) or ethanol (CH_3CH_2OH)?

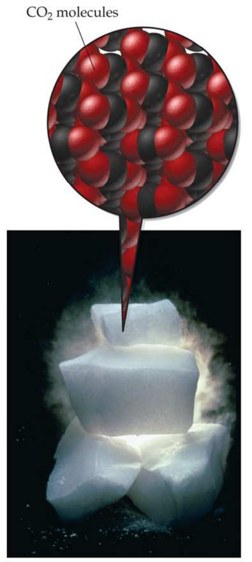
Rank these in order of increasing boiling point, with 1 as the lowest and 3 as the highest:
CH_3Cl, CH_3OH, CH_3CH_3

Rank these in order of increasing boiling point, with 1 as the lowest and 4 as the highest:
CH_2F_2, CH_3OH, CH_3CH_2OH, N_2.

Three Types of Crystalline Solids
Molecular, Ionic and Atomic

Molecular solids - solids whose **composite units are molecules**

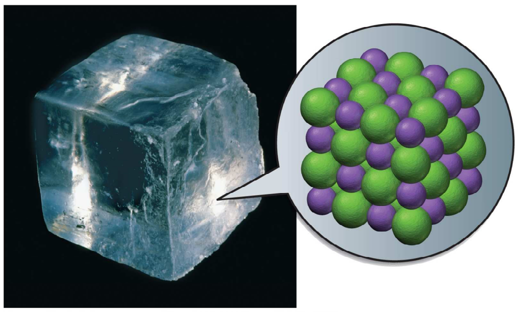
- Held together by intermolecular attractive forces (dispersion, dipole-dipole, or H-bonding)
- Generally have low melting points



Ex: solid CO_2 (dry ice)

Ionic solids - solids whose composite units are formula units

- Solid held together by *electrostatic attractive forces between cations and anions*
- Cations and anions arranged in a geometric pattern called a **crystal lattice** to maximize attractions
- Generally higher melting points than molecular solids (because ionic bonds are stronger than intermolecular forces)

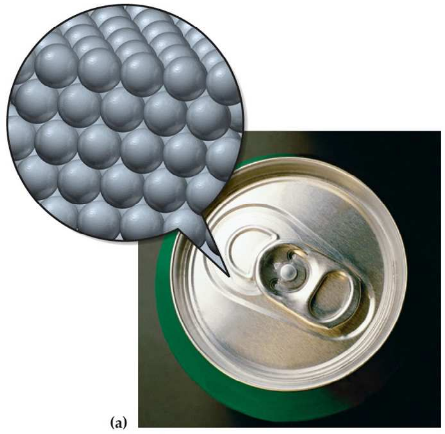


Ex: sodium chloride (NaCl)

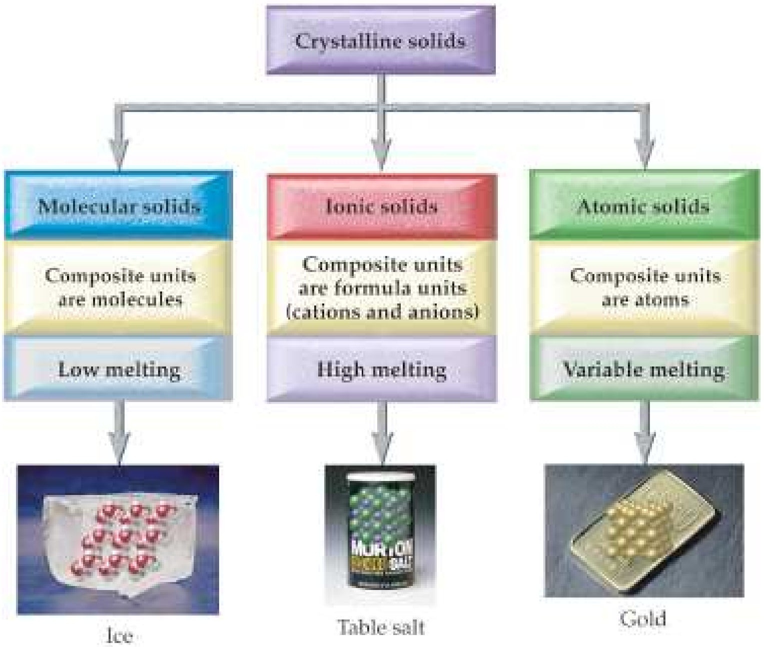
Atomic Solids

Atomic solids - solids whose composite units are individual atoms

- Solids held together by either covalent bonds, dispersion forces, or metallic bonds
- Melting points vary depending on the attractive forces between the atoms



Ex: Aluminum (Al)

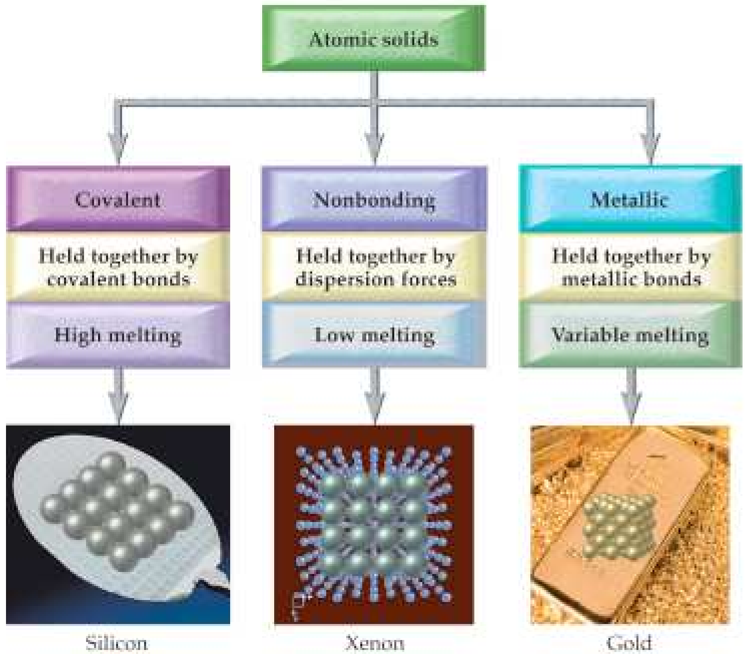


Classify the following solids as molecular, ionic or atomic:

$H_2O(s)$ $Al(NO_3)_3(s)$ $Si(s)$ $C_{12}H_{22}O_{11}(s)$ $CaF_2(s)$

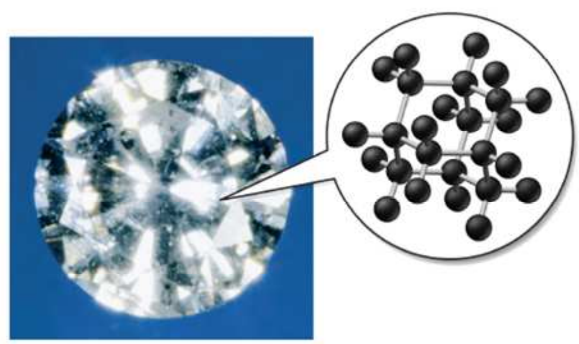
Types of Atomic Solids:

Covalent, Nonbonding and Metallic



Covalent atomic solids have their atoms attached by covalent bonds

- Effectively, the entire solid is one giant molecule
- Because covalent bonds are strong, these solids have <u>very high melting points.</u>
- These substances <u>tend to be very hard</u>
- Elements found as covalent atomic solids are C, Si, and B.

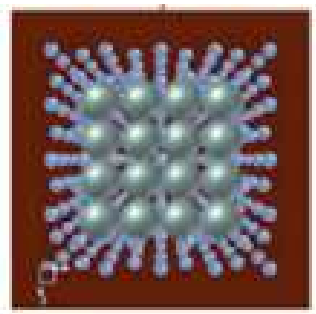


Ex: Diamond (a form of carbon)

Nonbonding and Metallic Solids

Nonbonding atomic solids are held together by dispersion forces.

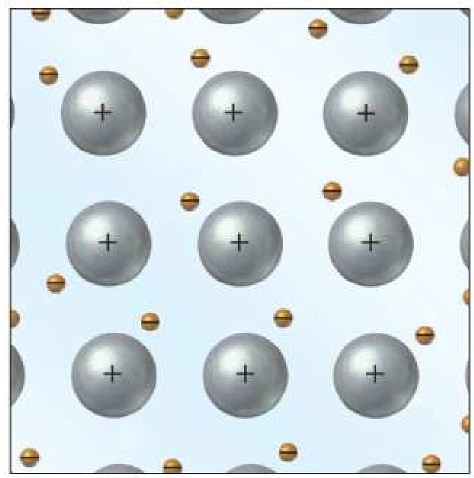
- Because dispersion forces are relatively weak, these solids have <u>very low melting points</u>
- All the noble gases form nonbonding atomic solids



Ex: Xenon(Xe)

Metallic solids are held together by metallic bonds

- Metal atoms **release some of their electrons to be <u>shared by all the other atoms in the solid</u>** **(**often described as islands of cations in a **sea of electrons**)
- The metallic bond is the attraction of the metal cations for the mobile electrons



Metallic Bonding Model and Properties of Metals

The luster, malleability, ductility, and electrical and thermal conductivity of metals are **ALL** related to the **mobility of the electrons in the metallic solid**

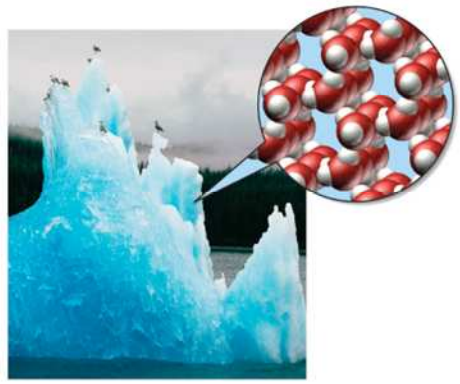
The strength of the metallic bond varies, depending on the charge and size of the cations, so the melting points of metals vary as well

Water: A Most Unusual Liquid

Why is water unusual?

1st - It's solid state is LESS DENSE than it's liquid state

- ice floats on water



For almost all other compounds, the reverse is true - the solid state is MORE DENSE than the liquid state and the solid sinks in the liquid

Consequence of this property of H_2O:

- Lakes don't freeze solid in winter (fish live)
- Living cells can be killed as the temp. drops and ice crystals form. (The cells can rupture because ice takes up more space than liquid H_2O).

2nd - Water molecules have a particularly strong intermolecular force holding them together - HYDROGEN BONDING

Consequence:

- Liquid H_2O molecules need **A LOT** of heat to disrupt these forces and convert them to the vapor state - **much more than most other liquids**.
- Water can "hold" or absorb a lot of heat before it vaporizes, a property that allows the oceans to moderate the temp. of the earth more readily than most other liquids would

Water: A Most Unusual Liquid

3rd - Water molecules are HIGHLY POLAR. Other polar molecules and many ionic compounds are VERY SOLUBLE in it. Water molecules solvate cations and anions of ionic compounds and allow them to dissolve (solvation overcomes binding energy of ionic bonds).

Consequence:

- Many important ions for life (Na^+, K^+, etc.) and polar biological molecules are soluble in H_2O
- Life as we know it would not exist without H_2O!