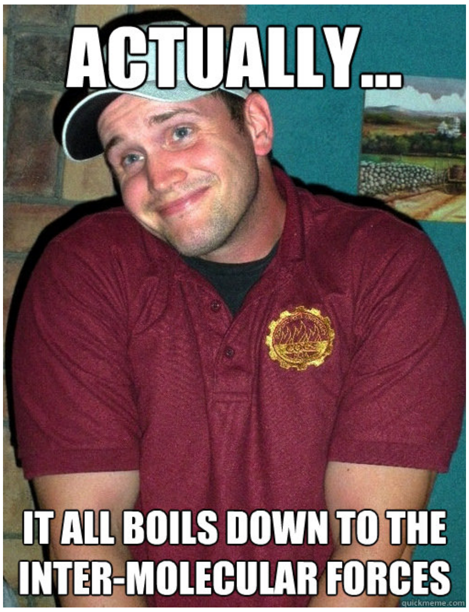
Chapter 10:
Liquids and Solids



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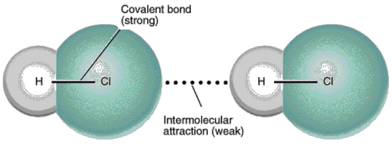
10.1 Intermolecular Forces

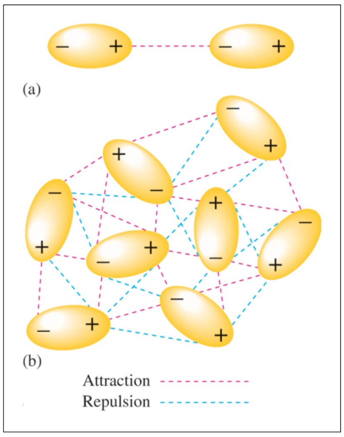
- List intermolecular forces and describe some of the effects on liquids and solids.

- **Intra**molecular forces mean **forces within a molecule.**
- **Inter**molecular forces mean **forces between molecules.** these are the forces that hold molecules together as liquids and solids.



There are three kinds of forces that discussed in this section

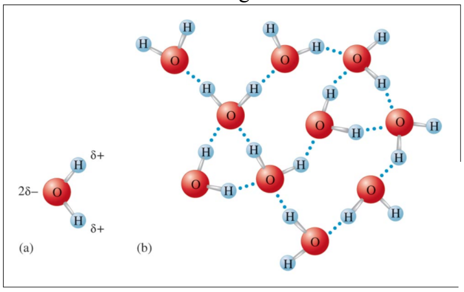
Dipole-dipole forces result when the partial positive and negative charges of neighboring polar covalent molecules attract. These forces are about 1% as strong as intramolecular covalent bonds.



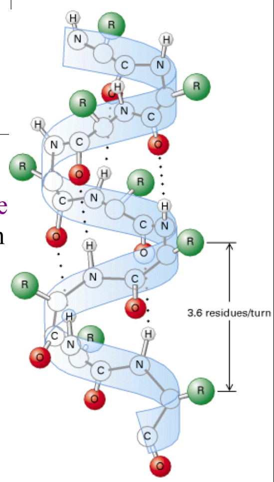
(a) The electrostatic interaction of two Polar molecules
(b) The interaction of many dipoles in a condensed state

Mar 10-12:04 PM

Hydrogen bonds are a special case where dipoles in **small, highly electronegative atoms** (such as fluorine) form a **surprisingly strong** interaction with the small hydrogen, which has a highly positive charge per unit size. Hydrogen bonding leads to substances with unusually high intermolecular bond energies.



(a) The polar water molecule
(b) Hydrogen bonding among water molecules



H bonded directly to a very electronegative atom (N, O, F) interacts with lone electron pairs on N, O, F of another molecule.

- H bond energies are ~ 4-25kJ/mole
- Strong IMF's but weak compared to covalent bonds

Hydrogen Bonding Explains:

- why ice floats on water
- double helix in DNA
- α-helix in proteins

Hydrogen Bonding in Water Tutorial

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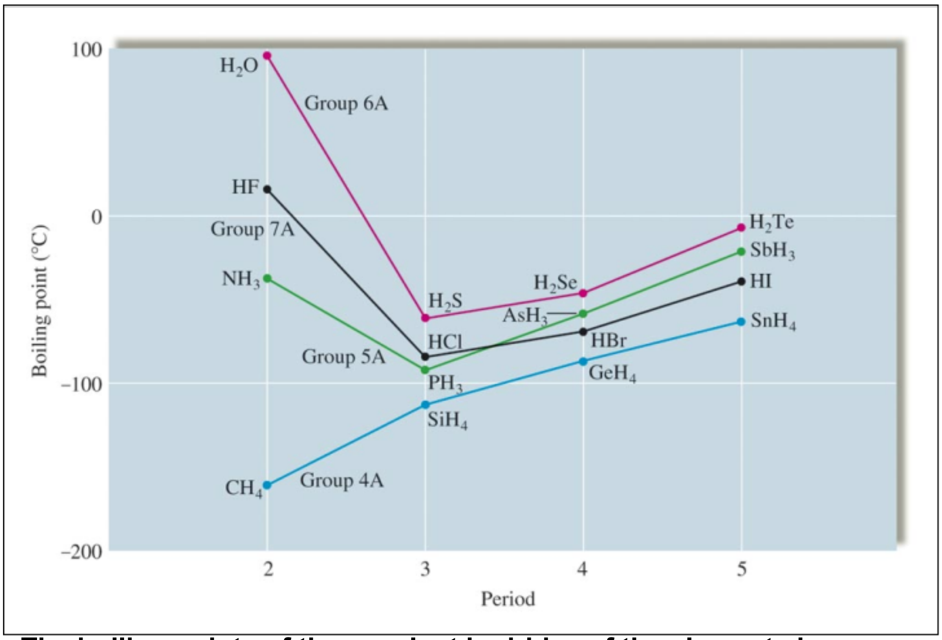

The boiling points of the covalent hydrides of the elements in groups 4A, 5A, 6A, and 7A

Notice:

- Increase in B.P for group 4 nonpolar tetrahedral hydrides with molar mass increase.
- The lighter member of groups 5,6, and 7 have high B.P. (why?)

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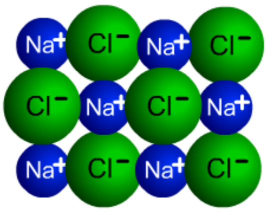
A large sample of sodium chloride is also held together by attractions between opposite charges. These attractions, called **ion-ion** forces, are the strongest king of intermolecular force



The strength of the ion-ion forces for a substance can be estimated using two factors:

- the product of the charges of the atoms involved
- the distance between nuclei

Example: $CaO > CaF_2 > KF$

+2 -2 +2 -1 +1 -1

Reason: (2 x 2 = 4) > (2 x 1 = 2) > (1 x 1 = 1)

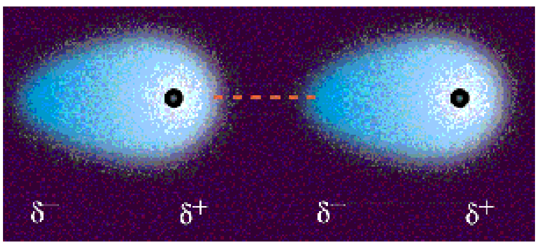
Example: CaO > CaS > SrS

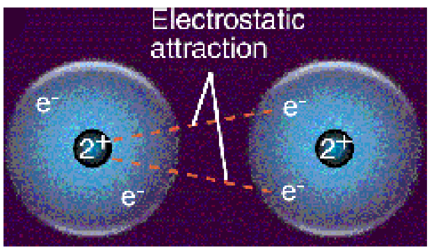
Reason: Ca is smaller than Sr, and O is smaller than S. Smaller atoms mean that the nuclei are closer together.

Mar 30-10:10 PM

London dispersion forces are caused by the instantaneous dipoles that arise in a molecule as a result of momentary imbalances in elector distribution. These are very weak forces that become more important as the size of the atom of interest increases

These forces exist among noble gas atoms and nonpolar molecules





[Intermolecular Forces Tutorial]

Example 10.1 A London Dispersion Forces

The boiling point of argon is -189.4°C.
a. Why is it so low?
b. How does this boiling help prove that London dispersion forces exist?
c. The boiling point of xenon is -119.9°C. Why is it higher than that of argon?

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Trends in the Forces

While the intramolecular forces keep the atoms in a molecule together and are the basis for the chemical properties, the intermolecular forces are those that keep the molecules themselves together and are virtually responsible for all the physical properties of a material.

The relative size of these interactions is important so the relative effects are understood. Relative strengths for the different interactions are listed here:

Hydrogen Bonding> Dipole-Dipole Attractions> London Forces
12-16 kcal > 2-0.5 kcal > Less than 1 kcal

As these forces increase in strength it becomes harder to remove the molecules from each other. Therefore, one would expect the ***melting*** and ***boiling*** points to be ***higher*** for those ***substances that have strong intermolecular forces.***

Example 10.1 B The Effect of Intermolecular Forces

Put the following substances in order from the lowest to the highest boiling point: C_2H_6, NH_3, F_2

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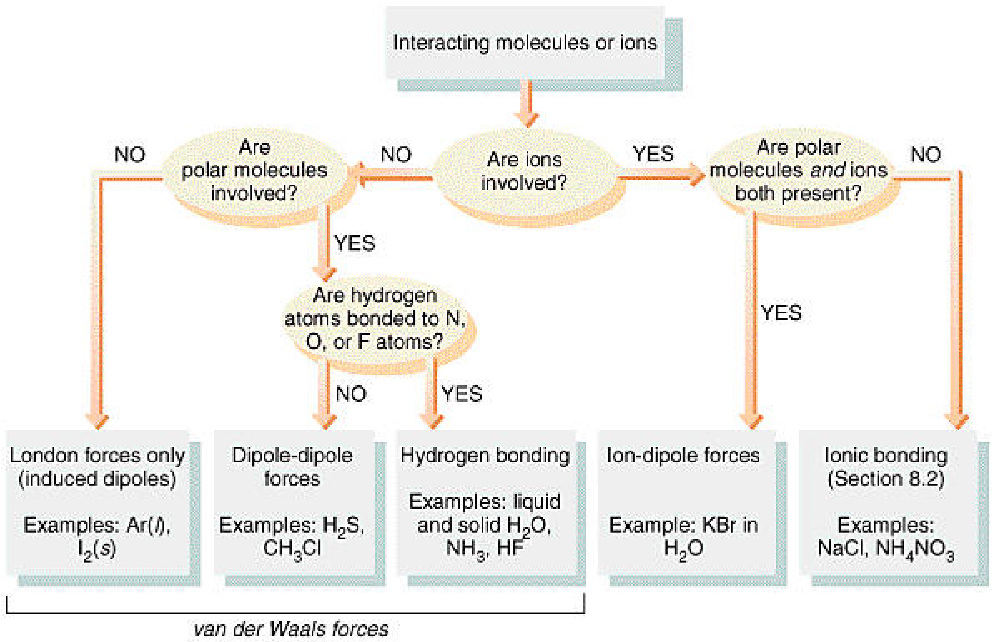
Summary of Types of Intermolecular Forces



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10.2 The Liquid State

The following review questions will serve to test your understanding of the material in this section.

1. Why do liquids tend to bead up when on solid surfaces?
2. What are **cohesive forces**? **Adhesive forces**? What causes these forces?
3. What is surface tension? Why does it occur?
4. Why does water form a concave meniscus when in a thin tube?
Why does mercury form a convex meniscus?
5. What is **viscosity**? What is a requirement for a liquid to be viscous?
6. Why do models of liquids tend to be more complex than those for either solids or gases?

Example 10.2 Properties of Liquids

Which would have a higher surface tension, H_2O or C_6H_{14}? Why?
Would the shape of the H_2O meniscus in a glass tube be the same or different than C_6H_{14}?

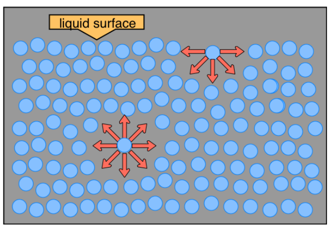
Mar 10-8:13 AM

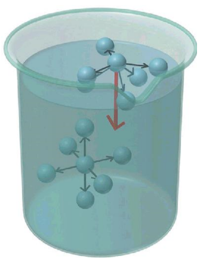
Viscosity ***is the measure of a liquid's resistance to a flow***.
Low viscosity fluids flow easily (water, alcohol);
High viscosity fluids pour slowly (molasses, cold honey).
Liquids with large intermolecular forces tend to be highly viscous.

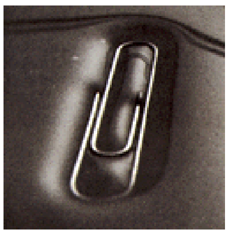
Example:
Rank the following liquids from highest viscosity to lowest viscosity.
Br_2, H_2O, CCl_4, PH_3

Surface Tension: ***The resistance of a liquid to an increase in its surface area.***

- A molecule in the interior of a liquid is attracted by the molecules surrounding it. These attractions average out to zero, there is no net force on the molecule.
- A molecule at the surface is attracted only by molecules below it and on each side. This is what creates the stretched-membrane effect.







The Surface Tension Demo

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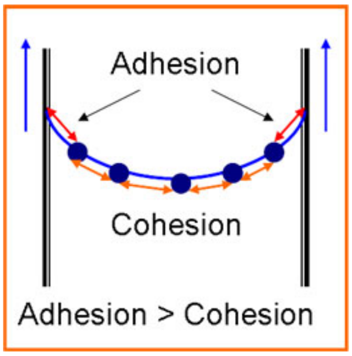
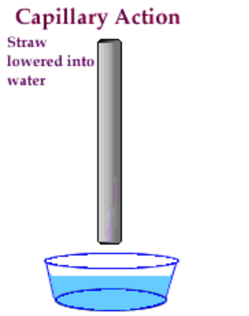
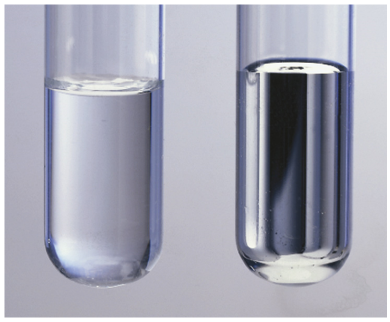
Capillary Action

With capillary action, liquid climbs up capillary tube without external pressure.
Cohesion tends to minimize the area of free surface.
Adhesion tends to pull the surface to the boundaries.







Capillary Action Tutorial

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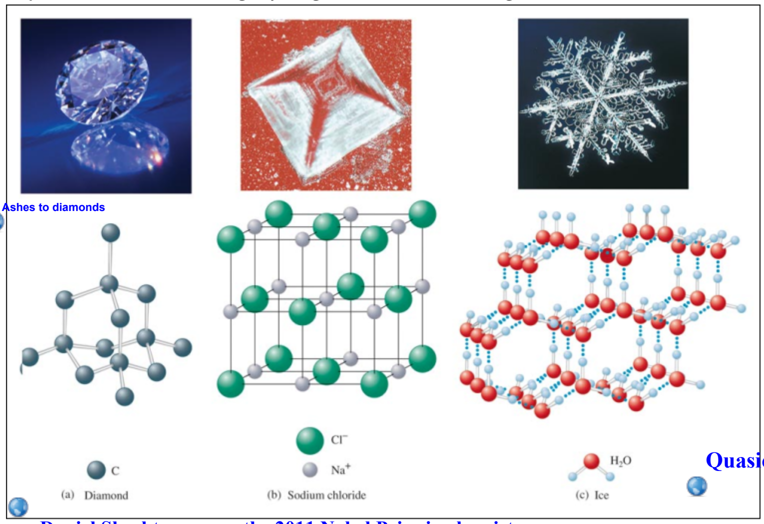
10.3 An Introduction to Structures and Types of Solids

When you finish this study section you will be able to:

- Define the basic terms relating to the structure of solids.

Crystalline solids - highly regular atomic arrangements



Quasicrystal

Daniel Shechtman won the 2011 Nobel Prize in chemistry

Examples of three types of crystalline solids. Only part of the structure is shown in each case. (a) An atomic solid. (b) An ionic solid. (c) A molecular solid. The dotted lines show the hydrogen bonding interactions among the polar water molecules.

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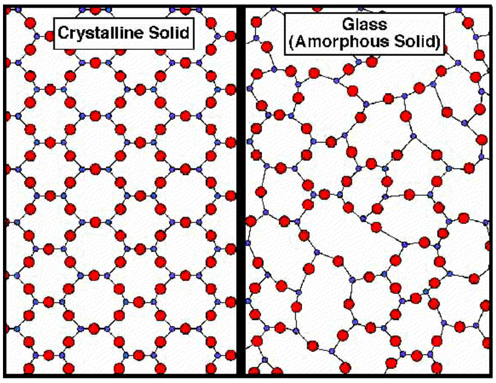
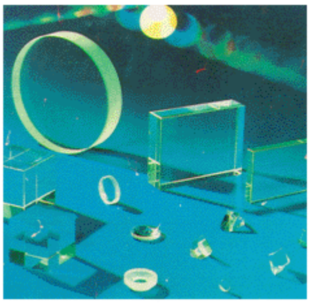
Amorphous solids- disordered atomic arrangements.

The arrangement of atoms (or molecules) is not repeated according to a pre-established order (the unit cell), but randomly.





Glass and ceramics are amorphous solids

Basic Terms

a. Lattice: A three-dimensional system of points designating the centers of the constituent building units in a crystalline solid.

b. Unit cell: the smallest repeating unit of a lattice.

Unit Cell Tutorial

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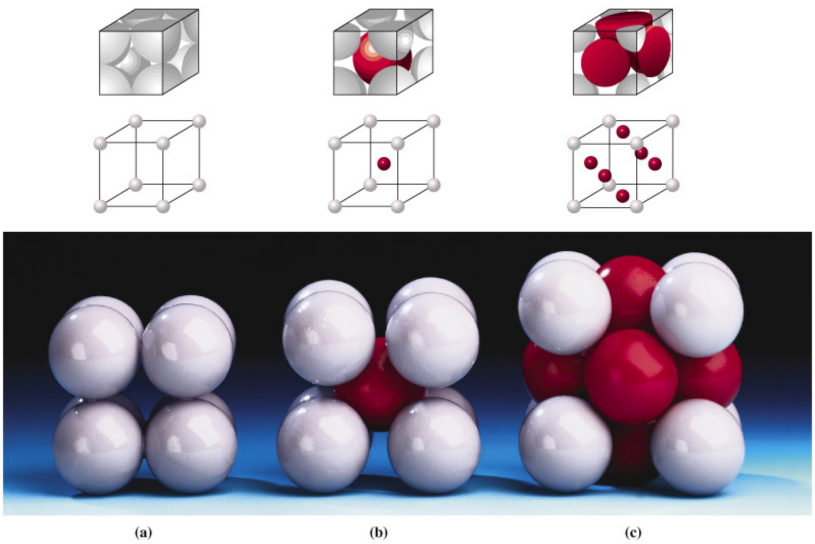
c. As shown in Figure 10.9 of your textbook, the three types of cubic unit cells are **simple cubic, body-centered cubic** and **face-centered cubic**.



d. Ionic solids form electrolytes when dissolved in water.
Molecular solids do not. An **atomic solid** contains atoms of only one element. These atoms are covalently bonded to each other.

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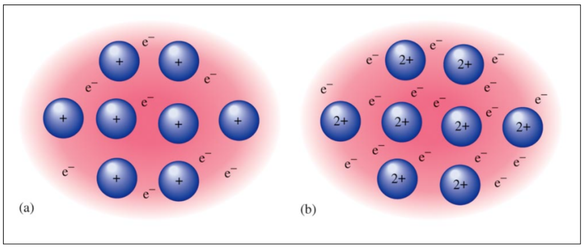
10.4 Bonding Model for Metals: *Electron Sea Model*

A regular array of metal cations in a "sea" of valence electrons.



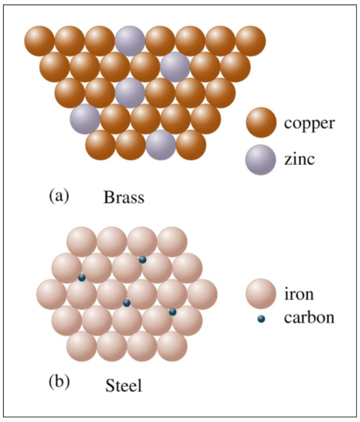
(a) alkali metals
(b) Alkaline earth meals

Metal Alloys

Alloy is ***a substance that contains a mixture of elements and has metallic properties***

A **Substitutional alloy** contains **similar-sized** atoms of more than one element (the holes are not occupied). An example is the combination of copper and zinc to form the brass alloy.

An **Interstitial alloy** is formed when holes in the closet packed metal structure are occupied by **small atoms** (in high carbon steels the iron holes are filled by carbon).



Note that the makeup of the alloy greatly affects its properties

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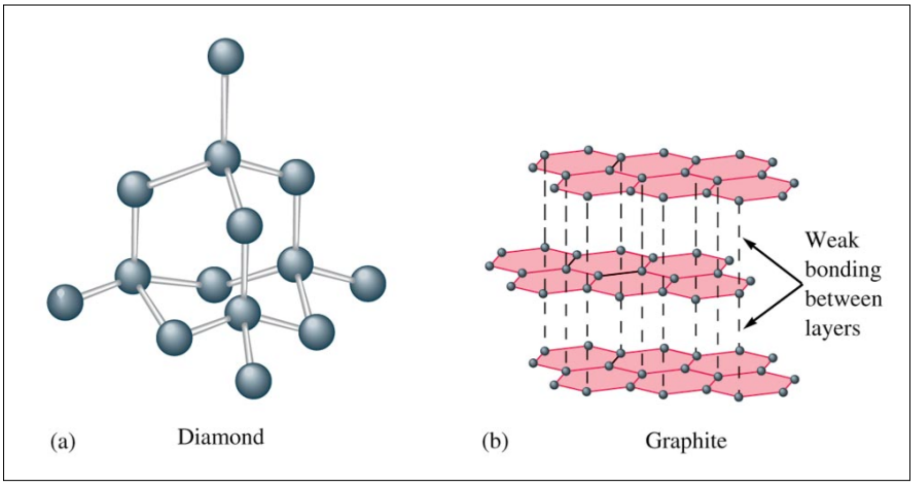
10.5 Carbon and Silicon: Network Atomic Solid

1. Define **network** solid.
2. List the **properties** of network solids.
3. Why does diamond have carbons with sp^3 hybridizations while those in graphite are sp^2 hybridized?



Carbon Nanotubes

Allotropes of Carbon Tutorial

The C_{60} "buckyball" Fullerene

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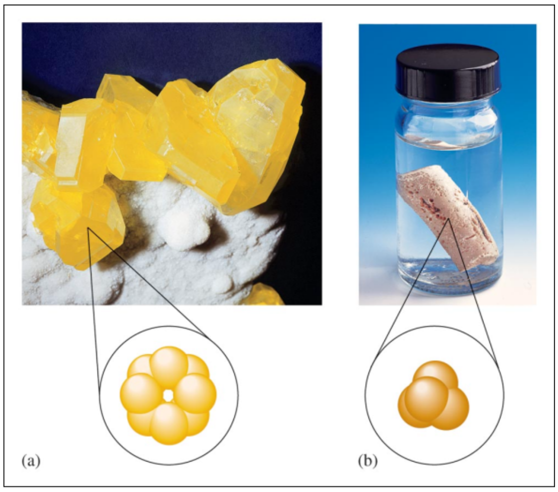
10.6 Molecular Solids

1. Define **molecular solid**
2. Give some **examples** of molecular solids.
3. Describe the relative bonding strength and bond distances **within** and **between** molecules of a molecular solid.
4. Why are some larger nonpolar molecular solids solid at 25°C?

Dry Ice



(a) Sulfur crystals contain S_8 molecules
(b) White phosphorus contain P_4 molecules

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10.7 Ionic Solids

The structure of most binary ionic solids can be explained by the **closest packing of spheres**. Anions, which are usually larger than the cations with which they combine (see <u>Section 8.4 in your textbook</u>). Cations fill the holes within the packed anions.

Key Idea: The packing arrangement is done in such a way as to minimize anion-anion and cation-cation repulsions.

The nature of the holes depends on the ratio of anion to cation size. Trigonal holes are smallest, followed by tetrahedral, and octahedral are the largest.

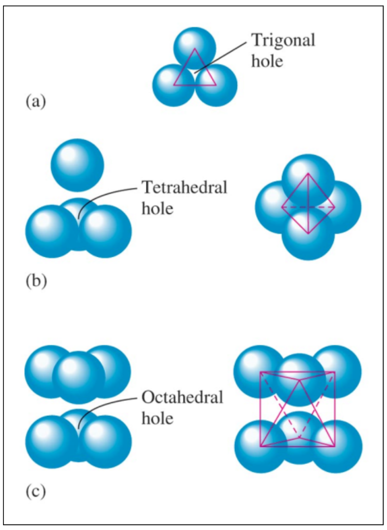

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TABLE 10.9 Types of Crystalline Solids and Their Characteristics

Type of Solid	Intermolecular Forces	Properties	Examples
Ionic	Ion–ion forces	Brittle, hard, high-melting	NaCl, KBr, $MgCl_2$
Molecular	Dispersion forces, dipole–dipole forces, hydrogen bonds	Soft, low-melting, nonconducting	H_2O, Br_2, CO_2, CH_4
Covalent network	Covalent bonds	Hard, high-melting	C (diamond, graphite), SiO_2
Metallic	Metallic bonds	Variable hardness and melting point, conducting	Na, Zn, Cu, Fe

Example 10.7B Types of Solids

Based on their properties, classify each of the following substances as to the **type of solid** it forms:

a. Fe b. C_2H_6 c. $CaCl_2$ d. graphite e. F_2

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10.8 Vapor Pressure and Changes of State

Vapor is the gas phase of a substance that exists as a solid or liquid at 25°C and 1 atm

Vaporization or evaporation the change in state that occurs when a liquid evaporates to form a gas.

Heat of vaporization or the **enthalpy of vaporization, ΔH_{vap},** the energy required to vaporize 1 mole of a liquid at a pressure of 1 atm.

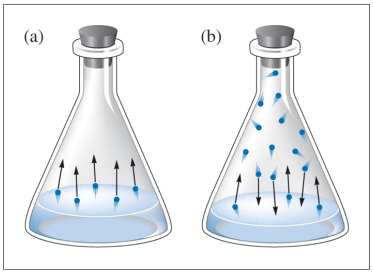
Condensation the process by which vapor molecules re-form a liquid.

Sublimation the process by which a substance goes directly from the solid to the gaseous state without passing through the liquid state.

Vapor Pressure

The pressure of over a liquid at equilibrium.

Equilibrium is the point no further net change occurs in the amount of liquid or vapor because the two opposite processes exactly balance each other, but the system in not static.



The equilibrium vapor pressure means that evaporation and condensation by a liquid are occurring at the same rate. The net effect is to have a **constant** vapor pressure exerted by the liquid.

The vapor pressure of a liquid varies with the molecular weight of the liquid and other molecular properties such as polarity and hydrogen bonding.

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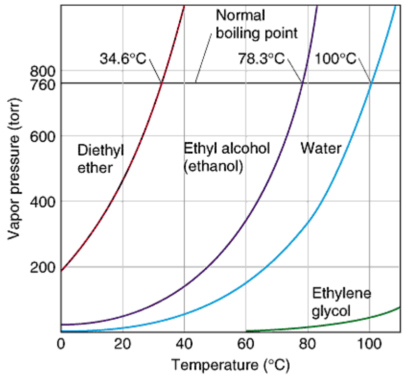
The stronger the attraction between molecules in the solid or liquid, the fewer particles can escape into the vapor phase and the lower the Vapor Pressure of the material; the weaker the attraction between molecules, more molecules can escape into the vapor phase and the higher the Vapor Pressure.

The vapor pressure of a liquid is dependent only upon the nature of the liquid and the temperature.
Different liquids at any temperature have different vapor pressures.
The vapor pressure of every liquid increases as the temperature is raised.



Melting Point the temperature at which the solid and the liquid states have the same vapor pressure under conditions where the total pressure is 1 atmosphere.

Boiling *occurs when the vapor pressure of a liquid is equal to the pressure of its environment.*

Boiling Point is the temperature at which the vapor pressure of the liquid is exactly 1 atmosphere.

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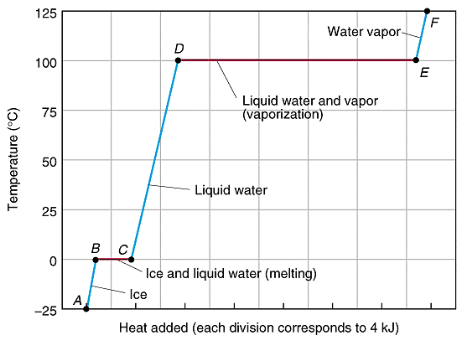
Heating Curve

A plot of temperature versus time for a process where energy is added at constant rate.

The **heat of fusion** is the amount of energy associated with the freezing or the melting of the substance.
The **heat of vaporization** is the amount of energy associated with the vaporizing or the condensing of the substance.



Note two important observations:

- The **temperature** of the substance **remains constant** during a **phase change.**
- The **temperature rises** when heat is input while a substance is in one phase.

You can find the amount of energy required to convert water from ice at T_1 to steam at T_2 by using the following information:

- **specific heat capacity of ice (2.1 J/g°C)**
- **ΔH_{fus} of water (6.0 kJ/mol)**
- **specific heat capacity of liquid water (4.2 J/g°C)**
- **ΔH_{vap} of water (43.9 kJ/mol)**
- **specific heat capacity of steam (1.8 J/g°C)**

Example 10.8 B Heating Curve.

How much energy does it take to convert 130. g of ice at -40°C to steam at 160°C?

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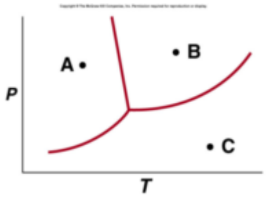
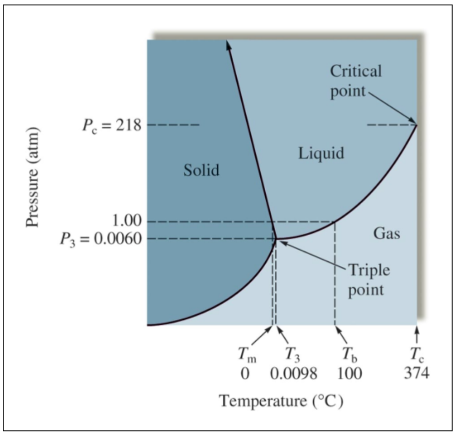
10.9 Phase Diagrams

A phase diagram for a material compiles information about the phases of a substance as a function of pressure and temperature. The general shape of a phase diagram is the same:

Region **A**: the material is solid
Region **B**: the material is liquid
Region **C**: the material is gas



The Phase Diagram for Water



At the **triple point** all three states are present.

The **critical point** is the point at which the temperature and pressure have their critical values and vapor can not be liquefied.

T_m - normal melting point
T_3 & P_3 - triple point
T_b - normal boiling point
T_c - Critical temperature
P_c - Critical pressure

The negative slope of the solid/liquid line reflects the fact that the density of ice is less than that of liquid water.

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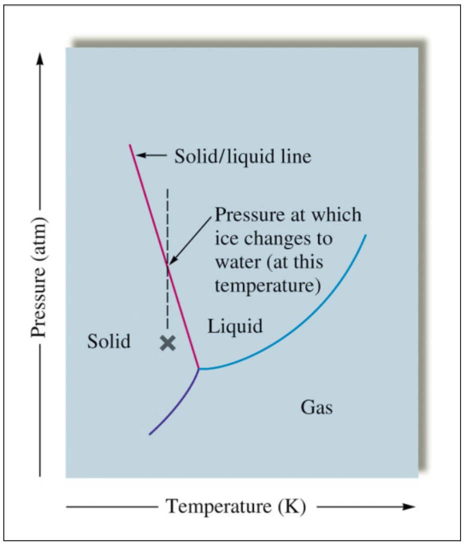

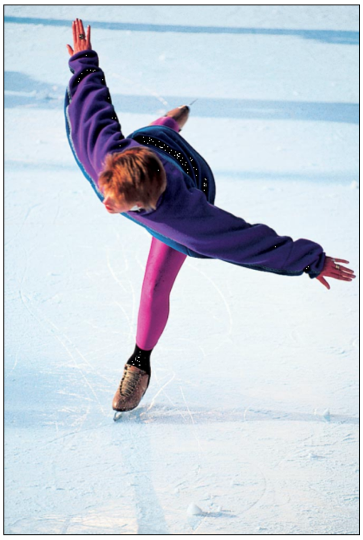

The solid/liquid boundary line has a negative slope. This means that melting point of ice *decreases* as the pressure *increases*. This behavior is opposite to that observed for most substance. It occurs because the density of ice is *less* than that of liquid water at the melting point.

In ice skating the narrow blade exerts a large pressure and the frictional heating contributes to the melting of the ice and the smooth gliding. After the blade passes, the liquid refreezes as normal pressure and temperature returns.

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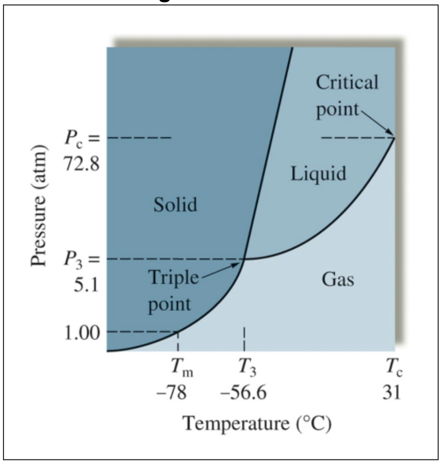
The Phase Diagram for Carbon Dioxide



The solid/liquid slope is positive since solid CO_2 is more dense than its liquid.

CO_2 is often used in fire extinguishers, where it exist as a liquid at 25°C under high pressure. this liquid turns to vapor upon release. Since it is heavier than air it smothers the fire.

You should be able to answer the following general questions regarding material presented in this section.

1. Why does the solid/liquid line in the phase diagram of water have a negative slope? Why is it positive for carbon dioxide?
2. Why does it take longer to cook an egg in the Rocky Mountains than at sea level?
3. How does the phase diagram for water help explain why your blades glide on a liquid layer when you ice skate?
4. How does the phase diagram for carbon dioxide help explain how a CO_2 fire extinguisher works?
5. Snow sometimes sublimes. How can this be so in spite of the phase diagram?

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