# AP* Chemistry
INTERMOLECULAR FORCES
LIQUIDS & SOLIDS

Now it is time to consider the forces that condense matter. The forces that hold one molecule to another molecule are referred to as *intermolecular forces (IMFs)*. These forces arise from unequal distribution of the electrons in the molecule and the electrostatic attraction between oppositely charged portions of molecules. We briefly visited the IMFs earlier when discussing the nonideal behavior of gases. These forces cause changes of state by causing changes among the molecules NOT within them.
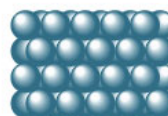
Physical properties such as melting points, boiling points, vapor pressures, etc. can be attributed to the
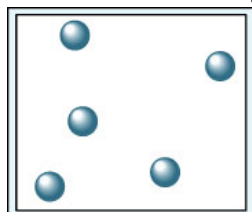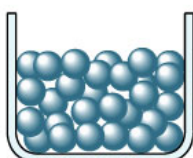

Gas   Liquid   Solid

strength of the intermolecular attractions present between molecules. It works like this: the lower the boiling point (or vapor pressure or melting point), the weaker the intermolecular attractions; the higher the boiling point, the stronger the intermolecular attractions. For example, gasoline evaporates much more quickly than water. Therefore, the intermolecular attractive forces that hold one gasoline molecule to another are much weaker than the forces of attraction that hold one water molecule to another water molecule. In fact, water molecules are held together by the strongest of the intermolecular attractive forces, hydrogen bonds. Hydrogen bonds are not true bonds—they are just forces of attraction that exist between a hydrogen atom on one molecule and the unshared electron pair on fluorine, oxygen or nitrogen atoms of a neighboring molecule. The strands of DNA that make up our genetic code are held together by this type of intermolecular attraction.

THE TYPES OF INTERMOLECULAR FORCES IN ORDER OF DECREASING STRENGTH:

- **Dipole-dipole**—the force of attraction that enables two polar molecules to attract one another. Polar *molecules* are those which have an uneven charge distribution since their dipole moments do not cancel. Compounds exhibiting this type of IMF have higher melting and boiling points than those exhibiting weaker IMFs.
    - Hydrochloric acid molecules are held to each other by this type of force. HCl—the chlorine pulls the electrons in the bond with greater force than hydrogen so the molecule is polar in terms of electron distribution. Two neighboring HCl molecules will align their oppositely charged ends and attract one another.
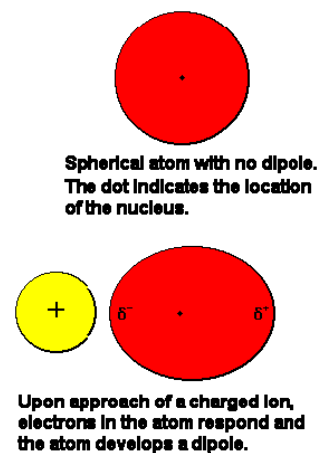

Covalent bond (strong)

Intermolecular attraction (weak)
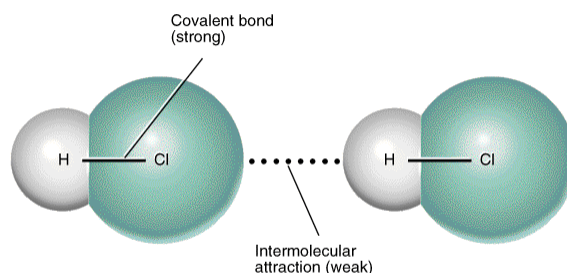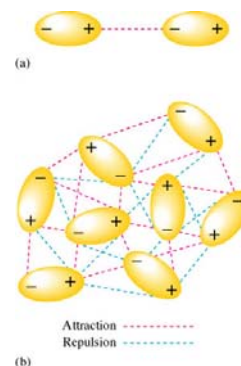
o **Hydrogen bonding**—the force of attraction between the hydrogen atom of one molecule and an unshared electron pair on F, O, or N of a neighboring molecule (a special case of dipole-dipole). *This is the strongest IMF*. Never confuse hydrogen bonding with a bonded hydrogen. The unique physical properties of water are due to the fact that it exhibits hydrogen bonding. As a result of these attractions, water has a high boiling point, high specific heat, and many other unusual properties.
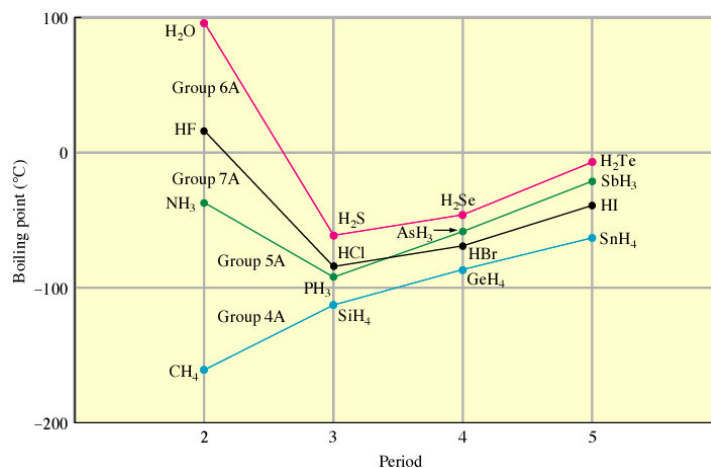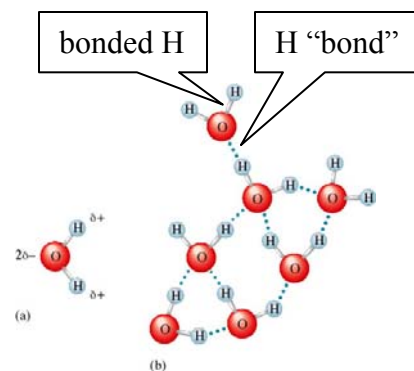

o **WHY** is there such variation in the boiling point among the covalent hydrides of groups IV through VII? One would expect that BP would increase with increasing molecular mass [since the more electrons in a molecule, the more polarizable the cloud {more about that in the next section}, the stronger the IMFs, therefore the more E needed to overcome those increased attractions and vaporize, thus the higher the boiling point. That's how it is supposed to work!]. Hydrogen bonding, that's why!

o TWO reasons: both enhance the IMF we refer to as hydrogen bonding.
  1. The lighter hydrides have the highest En values which lead to especially polar H–X bonds. Increased polarity means increased attraction which makes for a stronger attraction.
  2. The small size of each dipole allows for a closer approach of the dipoles, further strengthening the attractions. Remember, attractive forces dissipate with increased distance.

- **Ion-induced dipole**—the force of attraction between a charged ion and a nonpolar molecule. The ion greatly perturbs the electron cloud of the nonpolar molecule and polarizes it transforming it into a temporary dipole which enhances the ion's attraction for it.

Spherical atom with no dipole. The dot indicates the location of the nucleus.

Upon approach of a charged ion, electrons in the atom respond and the atom develops a dipole.

- **Dipole-induced dipole**—the force of attraction between a polar molecule and a nonpolar molecule. The polar molecule induces a temporary dipole in the nonpolar molecule. Larger molecules are more polarizable than smaller molecules since they contain more electrons. Larger molecules are more likely to form induced dipoles.
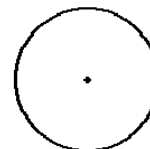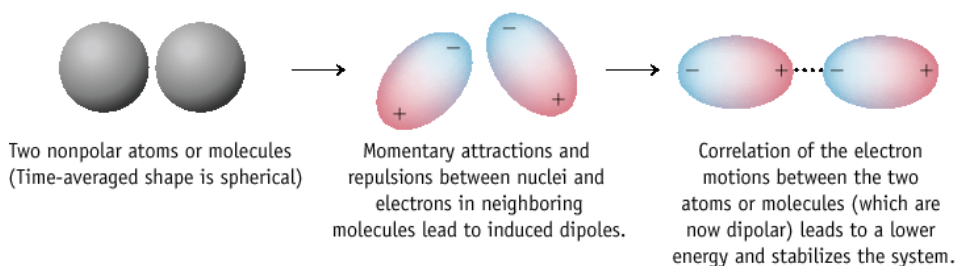
Spherical atom with no dipole. The dot indicates the location of the nucleus.

- **Induced dipole-induced dipole or London dispersion force**—the force of attraction between two non polar molecules due to the fact that they can form temporary dipoles. Nonpolar molecules have no natural attraction for each other. This IMF is known by both names! Without these forces, we could not liquefy covalent gases or solidify covalent liquids.
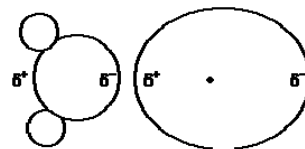
Upon approach of a molecule with a dipole, electrons in the atom respond and the atom develops a dipole.

Two nonpolar atoms or molecules (Time-averaged shape is spherical)

Momentary attractions and repulsions between nuclei and electrons in neighboring molecules lead to induced dipoles.

Correlation of the electron motions between the two atoms or molecules (which are now dipolar) leads to a lower energy and stabilizes the system.

- o These forces are a function of the number of electrons in a given molecule and how tightly those electrons are held.
- o Let us assume that the molecule involved is nonpolar. A good example would be H_2. Pretend that the molecule is all alone in the universe. If that were the case, the electrons in the molecule would be perfectly symmetrical. However, the molecule is not really alone. It is surrounded by other molecules that are constantly colliding with it. When these collisions occur, the electron cloud around the molecule is distorted. This produces a momentary induced dipole within the molecule. The amount of distortion of the electron cloud is referred to as *polarizability*. Since the molecule now has a positive side and a negative side, it can be attracted to other molecules. You'll want to write about polarizability when explaining these concepts.

Atom A   Atom B
No polarization

Molecule A   Molecule B
No polarization

Atom A   Atom B
Instantaneous dipole on atom A induces a dipole on atom B

Molecule A   Molecule B
Instantaneous dipole on molecule A induces a dipole on molecule B

Atom A   Atom B
(a)

Molecule A   Molecule B
(b)

- o Since all molecules have electrons, all molecules have these forces. These forces range from 5—40 kJ/mol. The strength of this force increases as the number of electrons increases due to increasing polarizability.
- o To better understand the induced dipole-induced dipole IMF, examine the halogens. Halogens exist as diatomic molecules at room temperature and atmospheric conditions. F_2 and Cl_2 are gases, Br_2 is a liquid and I_2 is a solid. Why?
    - All of these molecules are completely nonpolar and according to theory, not attracted to each other, so one might predict they would all be gases at room temperature.
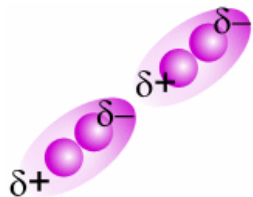
- Bromine exists as a liquid at room temperature simply because there is a greater attractive force between its molecules than between those of fluorine or chlorine. Why?
- Bromine is larger than fluorine or chlorine; it has more electrons and is thus more polarizable. Electrons are in constant motion so it is reasonable that they may occasionally "pile up" on one side of the molecule making a temporary negative pole on that end, leaving a temporary positive pole on the other end.
- This sets off a chain-reaction of sorts and this temporary dipole *induces* a dipole in its neighbors which induces a dipole in its neighbors and so on.
- Iodine is a solid since it is larger still, has even more electrons, is thus even more polarizable and the attractive forces are thus even greater. Note the two spheres representing I_2 the diagram at right. Each iodine *atom* experiences a nonpolar covalent bond within the molecule. Be very clear that the IMF is between molecules of iodine, NOT atoms of iodine!

Clear as mud? This flow chart is worth studying. NOTE that dipole-dipole (and its special case of Hydrogen bonding), dipole-induced dipole, induced dipole-induced dipole (a.k.a. London dispersion forces) are collectively called *van der Waals* forces. It's a simple conspiracy designed to keep you confused—much like the scoring scheme in tennis!
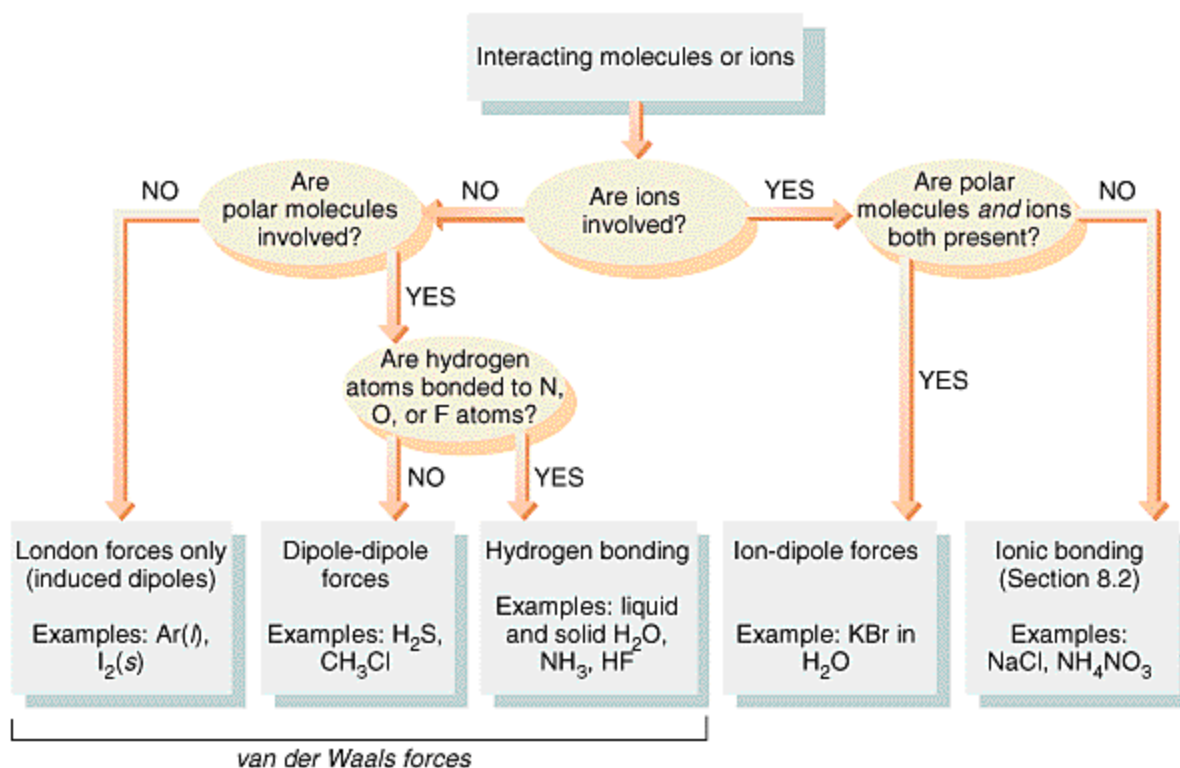
The Liquid State

All of the following are greater for liquids composed of polar molecules since their IMFs are greater than nonpolar molecules.
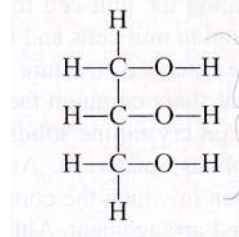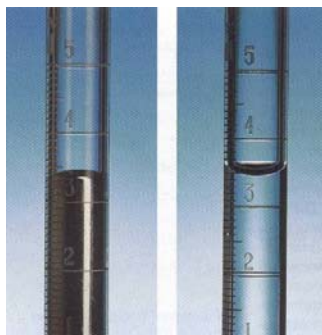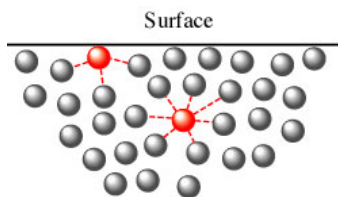
o Surface Tension: The resistance to an increase in its surface area (polar molecules). High ST indicates strong IMFs. Molecules are attracted to each OTHER. A molecule in the interior of a liquid is attracted by the molecules surrounding it, whereas a molecule at the surface of a liquid is attracted only by the molecules below it and on each side.

o Capillary Action: Spontaneous rising of a liquid in a narrow tube. Adhesive forces between molecule and glass overcome cohesive forces between molecules themselves. The narrower the tube, the more surface area of glass, the higher the column of water climbs! The weight of the column sets the limit for the height achieved. Hg liquid behaves opposite to water. Water has a higher attraction for glass than itself so its meniscus is inverted or concave, while Hg has a higher attraction for other Hg molecules! Its meniscus is convex.

o Viscosity: Resistance to flow (molecules with strong intermolecular forces). Increases with molecular complexity [long C chains get tangled and larger electron clouds are more polarizable due to the presence of additional electrons] and increased with increasing IMFs. Glycerol [left] has 3 OH groups which have a high capacity for H-bonding so this molecule is small, but very viscous.

o Modeling a liquid is difficult. Gases have VERY WEAK IMFs and lots of motion. Solids have VERY STRONG IMFs and next to no motion. Liquids have both strong IMFs _and_ quite a bit of motion.

Types of Solids

- Crystalline Solids: highly regular arrangement of their components [often ionic, table salt (NaCl), pyrite (FeS$_2$)].
- Amorphous solids: considerable disorder in their structures (glass).

Representation of Components in a Crystalline Solid

<u>Lattice</u>: A 3-dimensional system of points designating the centers of components (atoms, ions, or molecules) that makes up the substance.

= Cl⁻

= C

= Na⁺

= H₂O

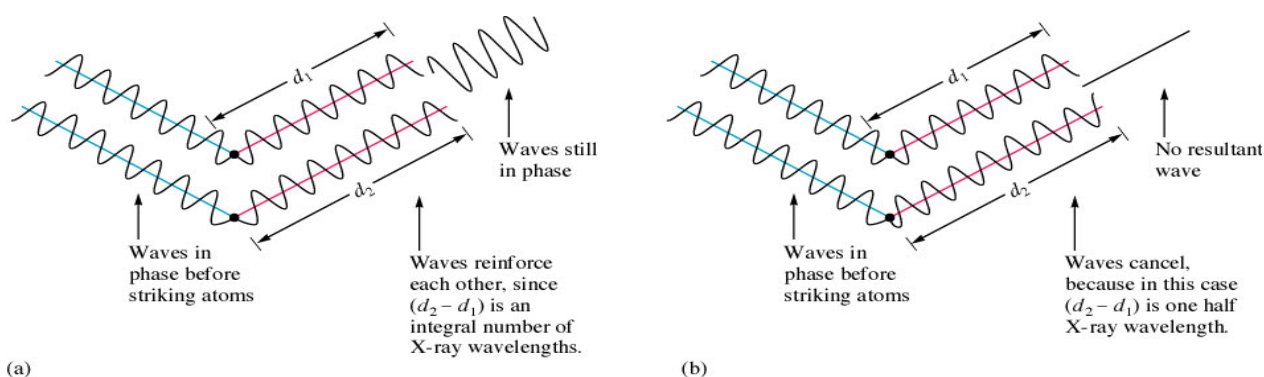Diamond
(a)

Sodium chloride
(b)

Ice
(c)
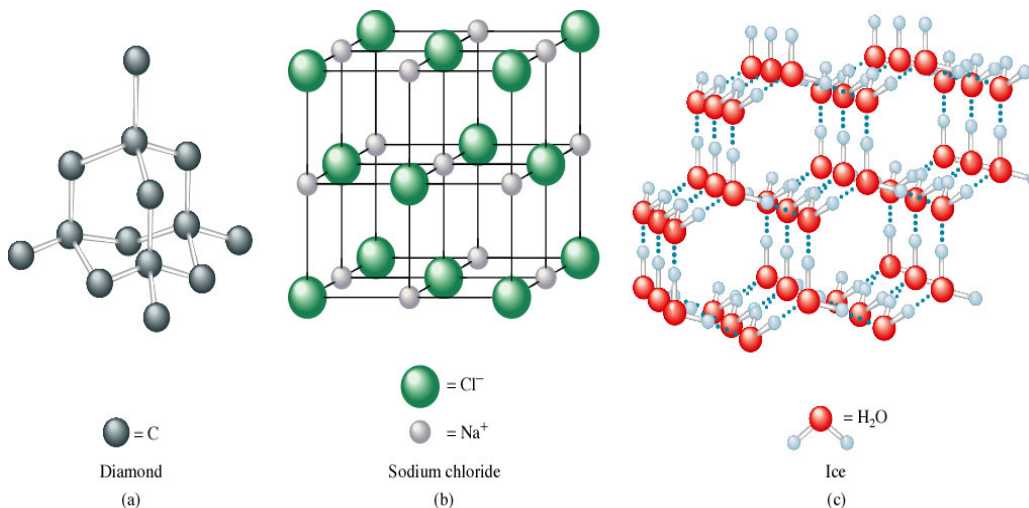
(a) **network covalent**—carbon in diamond form—here each molecule is covalently bonded to each neighboring C with a tetrahedral arrangement. Graphite on the other hand, exists as sheets that slide and is MUCH softer! (pictured later)

(b) ionic salt crystal lattice; Coulomb's Law dictates the strength of the lattice

(c) ice—notice the "hole" in the hexagonal structure and all the H-bonds. The "hole" is why ice floats—it is less dense in the solid state than in the liquid state!

X-RAY Analysis of Solids

- <u>X-ray diffraction</u>—A bending or scattering of light. The beams of light are scattered from a regular array of points in which the spacing between the components are comparable with the λ of the light. It is due to constructive interference when the waves of parallel beams are in phase and to destructive interference when the waves are out of phase.

- **The waves are in phase before they strike the crystal. IF the difference traveled after reflection is an *integral number of λ*, the waves will still be in phase.**

- Since the distance traveled after reflection depends on the distance between the atoms, the diffraction pattern can be used to determine the interatomic spacing.

d_1

d_2

Waves still
in phase

Waves in
phase before
striking atoms

Waves reinforce
each other, since
$(d_2 - d_1)$ is an
integral number of
X-ray wavelengths.

(a)

d_1

d_2

No resultant
wave

Waves in
phase before
striking atoms

Waves cancel,
because in this case
$(d_2 - d_1)$ is one half
X-ray wavelength.

(b)

The diagram below shows two in-phase waves being reflected by atoms in two different layers in a crystal. The extra distance traveled *y* the lower wave is the sum of the distances *xy* and *yz* and the waves will be in phase after reflection if $xy + yz = n\lambda$.

Incident rays   Reflected rays
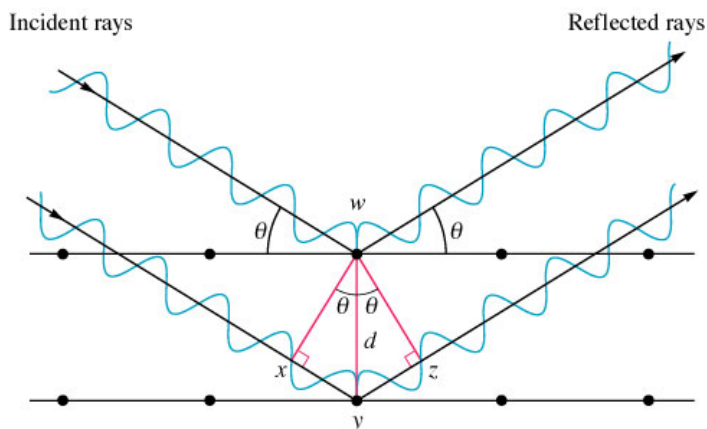
Trig time! If $\sin\theta = \dfrac{opposite}{hypotenuse} = \dfrac{xy = yz}{d_{for\ each}}$

then, $2d \sin\theta = xy + yz = n\lambda$ [from above]

where *d* is the distance between the atoms and θ is the angle of incidence and reflection.

Combine all of this and you get the Bragg equation named after William Henry Bragg and his son William Lawrence Bragg who shared the Nobel Prize in physics in 1915 for their pioneering work in x-ray crystallography. Do you know of any other famous x-ray crystallographers? Why didn't she win a Nobel Prize?

Bragg Equation $n\lambda = 2d \sin\theta$

Exercise 1   **Using the Bragg Equation**
X rays of wavelength 1.54 Å were used to analyze an aluminum crystal. A reflection was produced at θ = 19.3 degrees. Assuming *n* = 1, calculate the distance d between the planes of atoms producing this reflection.

d = 2.33 Å = 233 pm

Types of Crystalline Solids
- Ionic Solid: contains ions at the points of the lattice that describe the structure of the solid (NaCl). VERY high MP's. Hard. Ion-Ion Coulombic forces are the strongest of all attractive forces. "IMF" usually implies covalently bonded substances, but can apply to both types.

- Molecular Solid: discrete covalently bonded molecules at each of its lattice points (sucrose, ice).

- Atomic Solid: atoms of the substance are located at the lattice points. Carbon—diamond, graphite and the fullerenes. Boron, and silicon as well.

Know this chart well:

Table 10.3 Classification of Solids

|	Atomic Solids			Molecular Solids	Ionic Solids
	Metallic	Network	Group 8A		
Components that occupy the lattice points:	Metal atoms	Nonmetal atoms	Group 8A atoms	Discrete molecules	Ions
Bonding:	Delocalized covalent	Directional covalent (leading to giant molecules)	London dispersion forces	Dipole–dipole and/or London dispersion forces	Ionic

Structure and Bonding in Metals

Metals are characterized by high thermal and electrical conductivity, malleability, and ductility. These properties are explained by the nondirectional covalent bonding found in metallic crystals.
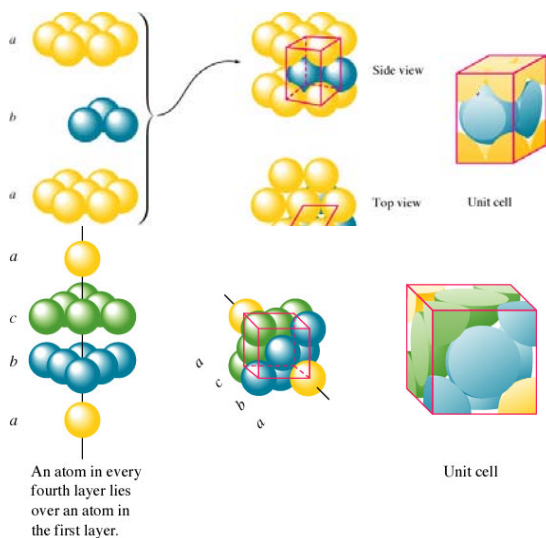

(a) abab — Closest packing
Top view   Top view   Side view

(b) abca — Closest packing
Top view   Top view   Top view   Side view
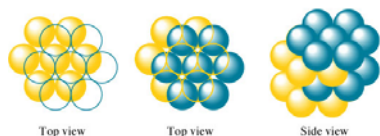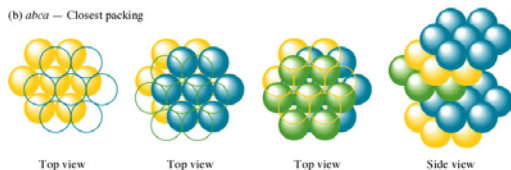
- <u>closest packing</u>—a model that uses hard spheres to represent the atoms of a metal. These atoms are packed together and bonded to each other equally *in all directions*. It will be easiest for you to understand if you can imagine taking a cubic box and pouring in golf balls. The balls will layer, perhaps directly on top of one another, but perhaps one layer slides into the "dimple" [pun intended] made by the first layer so that the two layers are offset a bit. Next, remove the golf balls and place tennis balls into the box. They will fill the box differently since they are of a different size.

- In the diagram above, in each layer, a given sphere is surrounded by six others.

  o a) above exhibits aba packing—the second layer is like the first, but it is displaced so that each sphere in the second layer occupies a dimple in the first layer. The spheres in the third layer occupy dimples in the second layer so that the spheres in the third layer lie directly over those in the first layer hence aba.
  o b) above exhibits abc packing—the spheres in the third layer occupy dimples in the second layer so that no spheres in the third layer lie above any in the first layer. The fourth layer is like the first.

An atom in every fourth layer lies over an atom in the first layer.

Side view
Top view   Unit cell
Unit cell

- aba has the hexagonal unit cell shown below and the resulting structure is **hexagonal closest packed (hcp) structure.** ababab….
- abc has a face-centered cubic unit cell and the resulting structure is **cubic closest packed (ccp) structure.** abcabc…
- The red sphere on the right, the one in the center of row a that is not numbered, has 12 nearest neighbors. This one is hcp, but this is true for both types of packing.

hcp
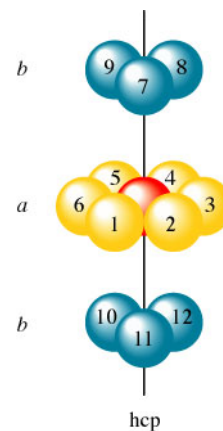
Let's consider a face-centered cubic cell:


(a)   (b)   (c)
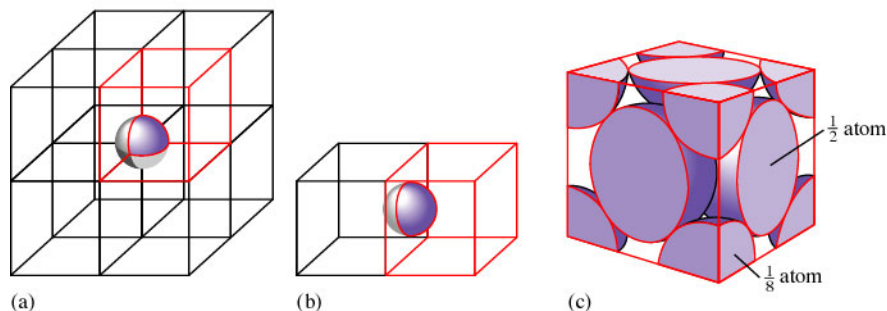
A cubic cell is defined by the *centers* of the spheres [atoms] on the cube's corners. How many corners are in a cube? How many faces are in a cube? Note that face centered means an atom is stuck smack dab in the middle of the face of one cube and consequently, the adjacent cube—1/2 in each! How many spheres [atoms] are in one cube that is face-centered? $\left(8 \times \dfrac{1}{8}\right) + \left(6 \times \dfrac{1}{2}\right) = 4$

**Exercise 2**   **Calculating the Density of a Closest Packed Solid**

Silver crystallizes in a cubic closest packed structure. The radius of a silver atom is 144 pm. Calculate the density of solid silver.
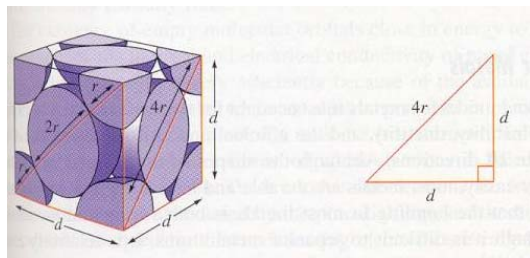

density = 10.6 g/cm^3

Bonding Models for Metals

Remember, metals conduct heat and electricity, are malleable and ductile, and have high melting points. These facts indicate that the bonding in most metals is both strong and nondirectional. Difficult to separate atoms, but easy to move them provided they stay in contact with each other!


(a)   (b)
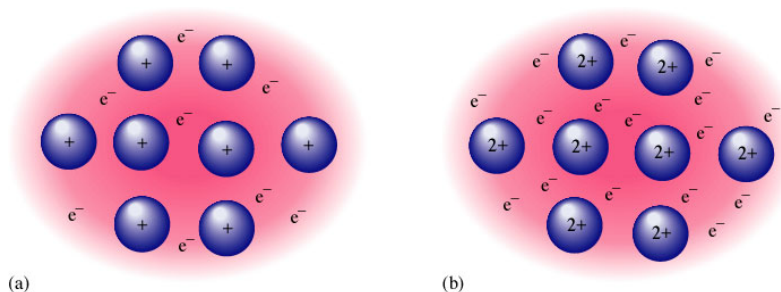
Electron Sea Model: A regular array of metals in a "sea" of electrons. I A & II A metals pictured at left.

Band (Molecular Orbital) Model: Electrons assumed to travel around metal crystal in MOs formed from valence atomic orbitals of metal atoms.

Brass
(a)

Steel
(b)
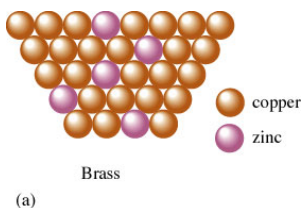
Metal alloys: a substance that has a mixture of elements and has metallic properties

- **substitution alloys**—in brass 1/3 of the atoms in the host copper metal have been replaced by zinc atoms. Sterling silver—93% silver and 7% copper. Pewter—85% tin, 7% copper, 6% bismuth and 2% antimony. Plumber's solder—95% tin and 5% antimony.
- **interstitial alloy**—formed when some of the interstices [fancy word for holes] in the closest packed metal structure are occupied by small atoms. Steel—carbon is in the holes of an iron crystal. There are many different types of steels, all depend on the percentage of carbon in the iron crystal.
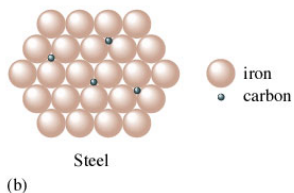
Network Atomic Solids—a.k.a. Network Covalent

(a)   Diamond

(b)   Graphite

Composed of strong directional covalent bonds that are best viewed as a "giant molecule". Both diamond and graphite are network solids. The difference is that diamond bonds with neighbors in a tetrahedral 3-D fashion, while graphite only has weak bonding in the 3rd dimension. Network solids are often:

- o brittle—diamond is the hardest substance on the planet, but when a diamond is "cut" it is actually fractured to make the facets
- o do not conduct heat or electricity
- o carbon or silicon-based
- o Diamond is hard, colorless and an insulator. It consists of carbon atoms ALL bonded tetrahedrally, therefore sp^3 hybridization and 109.5E bond angles.
- o Graphite is slippery, black and a conductor. Graphite is bonded so


(a)

(b)
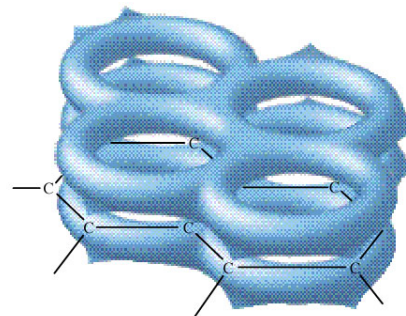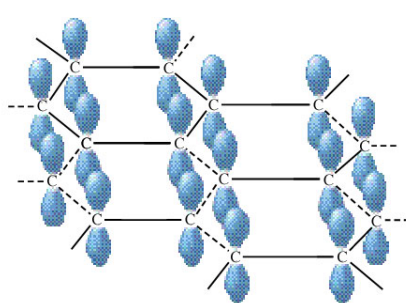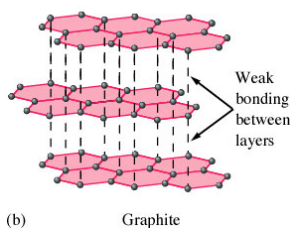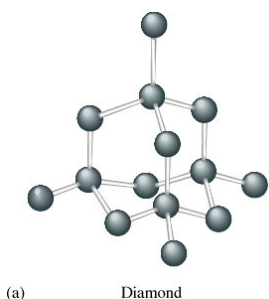
that it forms layers of carbon atoms arranged in fused six-member rings. This indicates sp^2 hybridization and 120E bond angles within the fused rings. The unhybridized p orbitals are perpendicular to the layers and form π bonds. The delocalized electrons in the π bonds account for the electrical conductivity while also contributing to the mechanical stability of the layers. It is often used as a lubricant in locks—grease or oil collects dirt, graphite does not.

- Silicon is to geology what carbon is to biology! The most significant silicon compounds involve chains with silicon-oxygen bonds.
- silica—empirical formula SiO_2—not at all like its cousin CO_2! Quartz and some types of sand are silicon dioxide as opposed to a clear colorless gas such as carbon dioxide. Why such drastic differences? Bonding.

Draw the Lewis Structure for CO_2:

What is carbon's hybridization?
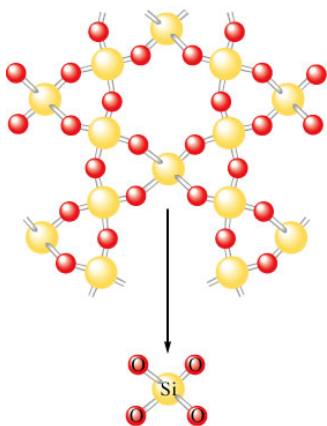
- Silicon cannot use its valence 3p orbitals to form strong π bonds with oxygen, mainly due to the larger size of the silicon atom and its orbitals—you get inefficient overlap.
- INSTEAD of forming π bonds, the silicon atom satisfies the octet rule by forming single σ bonds with FOUR OXYGEN atoms.
- Each silicon is in the center of a tetrahedral arrangement of oxygen atoms. This means that although the empirical formula is SiO_2, the structure is based on a network of SiO_4 tetrahedra with *shared* oxygen atoms.

- Silicates are the compounds found in most rocks, soils and clays. Silicates contain a O/Si ratio greater than 2:1 and contain silicon-oxygen *anions*.   That means silicates are salts containing metallic cations that are needed to make neutral arrangements.
- Common silicate anions are pictured on the right.
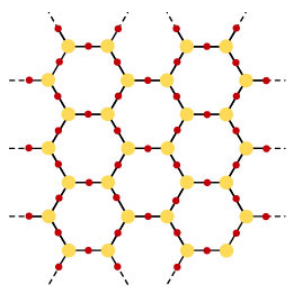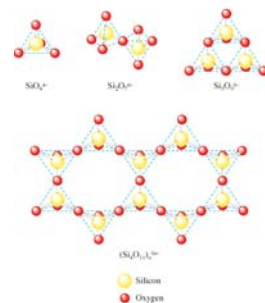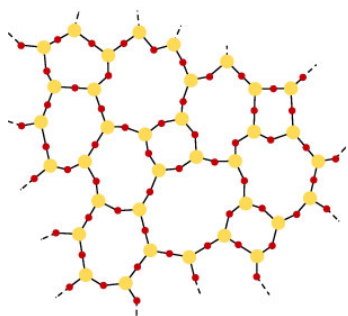
- When silica is heated above its MP of about 1600EC and cooled rapidly, an amorphous ["without shape"—not a crystal] solid forms.
  We call it glass—it's really a supercooled, ultra viscous liquid with a great deal of disorder.

- At left, a) is quartz while b) is quartz glass. These pictures are 2-D, not 3-D.

- Common glass results when Na_2CO_3 is added to the silica melt.

- Pyrex®, a borosilicate glass [lab ware] is made when B_2O_3 is added to the silica melt.

- Eyeglasses are made from glass that is especially hard so it can be ground into precise shapes. K_2O has been added.

(a)

(b)

Table 10.5 Compositions of Some Common Types of Glass

Type of Glass	Percentages of Various Components						
	SiO_2	CaO	Na_2O	B_2O_3	Al_2O_3	K_2O	MgO
Window (soda-lime glass)	72	11	13	—	0.3	3.8	—
Cookware (aluminosilicate glass)	55	15	—	—	20	—	10
Heat-resistant (borosilicate glass)	76	3	5	13	2	0.5	—
Optical	69	12	6	0.3	—	12	—

Molecular Solids

These solids differ in that a molecule occupies the lattice position rather than an atom. Ice & dry ice, [solid carbon dioxide] are examples. Allotropes of sulfur and phosphorous are included. S_8 or P_4 occupy the lattice positions in these allotropes [many forms] of these elements.

- Characterized by strong covalent bonding *within* the molecule yet weak forces *between* the molecules.
- It takes 6 kJ of energy to melt one mole of solid water since you only have to overcome H-bonding while it takes 470 kJ of energy to break one mole of O—H bonds.
- Molecules such as CO_2, I_2, P_4, and S_8 have no dipole moment.
- We call their IMFs **induced dipole—induced dipole or London dispersion forces.**
- As the size of the molecule increases [often reported in a Chem I book as "increased MM"], the London dispersion forces increase *because the larger the molecule the more electrons, the more polarizable its electron cloud*. If it is more polarizable, temporary dipoles can easily form.

Table 10.6 Comparison of Atomic Separations Within Molecules (Covalent Bonds) and Between Molecules (Intermolecular Interactions)		
Solid	Distance Between Atoms in Molecule*	Closest Distance Between Molecules in the Solid
P_4	220 pm	380 pm
S_8	206 pm	370 pm
Cl_2	199 pm	360 pm
*The shorter distances within the molecules indicate stronger bonding.		

- So what? The MP and BP increase since the molecules are MORE attracted to each other as a result of this polarizing of the electron cloud.

Ionic Solids

Stable, high-melting substances held together by STRONG electrostatic forces that exist between oppositely charged ions. Coulomb's Law dictates the strength of the electrostatic force.

Table 10.7 Types and Properties of Solids					
Type of solid:	Atomic			Molecular	Ionic
	Network	Metallic	Group 8A		
Structural unit:	Atom	Atom	Atom	Molecule	Ion
Type of bonding:	Directional covalent bonds	Nondirectional covalent bonds involving electrons that are delocalized throughout the crystal	London dispersion forces	Polar molecules: dipole–dipole interactions Nonpolar molecules: London dispersion forces	Ionic
Typical properties:	Hard High melting point Insulator	Wide range of hardness Wide range of melting points Conductor	Very low melting	Soft Low melting point Insulator	Hard High melting point Insulator
Examples:	Diamond	Silver Iron Brass	Argon(s)	Ice (solid H_2O) Dry ice (solid CO_2)	Sodium chloride Calcium fluoride

Exercise 4   **Types of Solids**

Using Table 10.7, classify each of the following substances according to the type of solid it forms.

a. Gold
b. Carbon dioxide
c. Lithium fluoride
d. Krypton

A: **atomic solid w/metallic properties**
B: **molecular solid**
C: **binary ionic solid**
D: **atomic solid w/ properties characteristic of molecular solid w/nonpolar molecules**

Vapor Pressure and Changes of State

- **vaporization or evaporation**—when molecules of a liquid can escape the liquid's surface and form a gas. ENDOTHERMIC since energy must be absorbed so that the liquid molecules gain enough energy to escape the surface and thus overcome the liquid's IMFs.
- **ΔH_{vap}—enthalpy of vaporization**—the energy required to vaporize ONE mole of a liquid at 1 atm pressure
- Water's heat of vaporization is 40.7 kJ/mol. This is huge! Water makes life on this planet possible since it acts as a coolant. The reason its)H_{vap} is so large has everything to do with hydrogen bonding. The IMFs in water are huge, thus a great deal of the sun's energy is needed to evaporate the rivers, lakes, oceans, etc. of Earth. Perspiration is a coolant for animals possessing sweat glands. Energy from your hot body is absorbed by the water sol'n to evaporate.
- **condensation**—opposite of vaporization. When the energetic steam molecules generated by your morning shower hurl themselves across the bathroom and collide with the cold mirror, they lose energy and return to the liquid phase.
- **equilibrium vapor pressure**—reached when the rate of evaporation equals the rate of condensation in a closed container
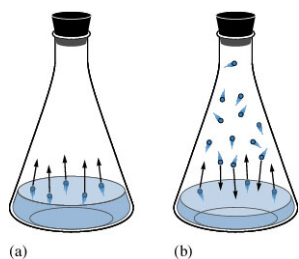
Stopper a flask of a freshly poured liquid (a). Equilibrium VP will be established (b).

Moleucles leave and enter the liquid phase @ the SAME RATE.
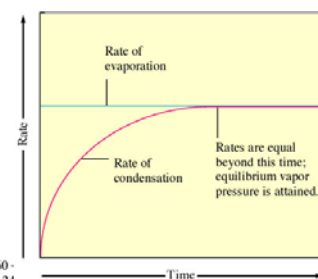
(a) The VP of a liquid can be measured easily using a simple barometer. (b) The three liquids water, ethanol, and diethyl ether have quite different vapor pressures. Ether is by far the most volatile of the three [weakest IMFs thus escapes easiest]. Note that in each case a little liquid remains (floating on the mercury).
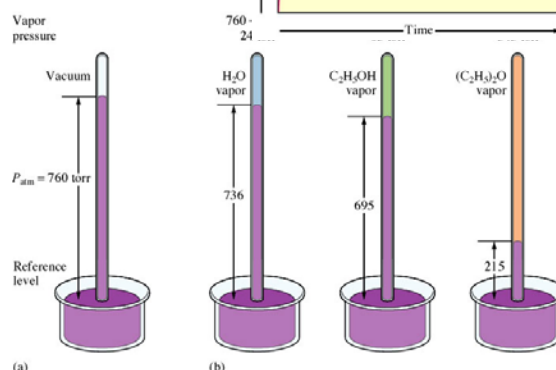
- **volatile**—have high VP, thus weak IMFs. These liquids evaporate readily from open containers since they have so little attraction for each other. It takes very little energy being absorbed in order for them to escape the surface of the liquid. The heat energy absorbed from a warm room is usually enough to make these substances evaporate quickly. If there is an odor to the substance, these are the liquids you smell almost as soon as you open the bottle! The molecules have been banging against the lid wanting out!

- VP increases significantly with temperature! Heat 'em up, speed 'em up, move 'em out! Increasing the temperature increases the KE which facilitates escape AND the speed of the escapees! They bang into the sides of the container with more frequency [more of them escaped] and more energy [more momentum].

- More molecules can attain the energy needed to overcome the IMFs in a liquid at a higher T since the KE increases

Table 10.8 The Vapor Pressure of Water as a Function of Temperature

T (°C)	P (torr)
0.0	4.579
10.0	9.209
20.0	17.535
25.0	23.756
30.0	31.824
40.0	55.324
60.0	149.4
70.0	233.7
90.0	525.8

(a) Kinetic energy   (b) Kinetic energy
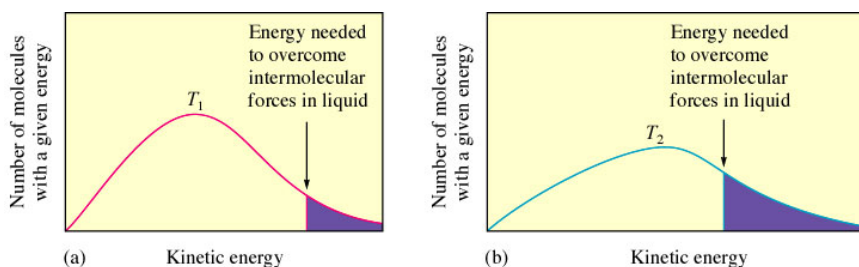
In general, as MM ↑ VP ↓

- BECAUSE as molecules increase in molar mass, they also increase in the number of electrons. As the number of electrons increase, the polarizability of the molecule increases so more induced dipole-induced dipole or dispersion forces exist, causing stronger attractions to form *between* molecules. This decreases the number of molecules that escape and thus lowers the VP.
- H-bonding causes a major exception! It's presence greatly increases the IMFs of the liquid. Water has an incredibly low VP for such a light [*MM* = 18.02] molecule.
- We can put the math to this. Plot lnVP vs. 1/*T* [in Kelvins] and we get a straight line. Next, put this into *y* = *mx* + *b* format:
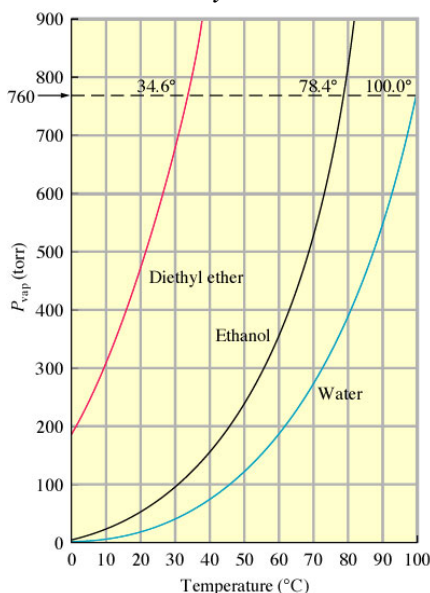
$$\ln VP = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C$$
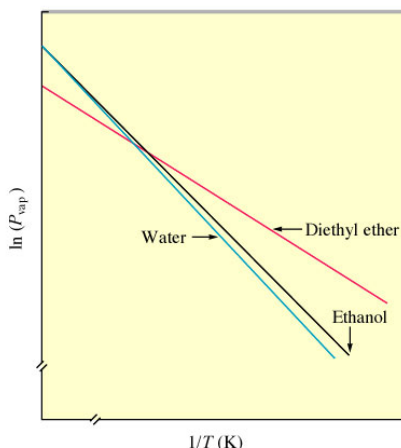
R is the universal gas constant—since this is all about energy, use the "energy" *R*, 8.31 J/mol•K.

C is a constant characteristic of the liquid [*y*-intercept].

slope, $m = \dfrac{\Delta H_{vap}}{R}$

Exercise 5	Determining Enthalpies of Vaporization

Using the plots in (b) above, determine whether water or diethyl ether has the larger enthalpy of vaporization.

water

If we know the values of ΔH_{vap} and VP at one temperature we can solve the above expression for the constant, C and set a second expression for T_2 equal to the first since the value of C is NOT dependent upon temperature:

$$\ln VP_1 + \frac{\Delta H_{vap}}{RT_1} = C = \ln VP_2 + \frac{\Delta H_{vap}}{RT_2} \quad \text{which can be rearranged into} \quad \ln\left(\frac{VP_1}{VP_2}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

This form is called the **Clausius- Clapeyron equation.**

Exercise 6	Calculating Vapor Pressure

The vapor pressure of water at 25°C is 23.8 torr, and the heat of vaporization of water at 25°C is 43.9 kJ/mol. Calculate the vapor pressure of water at 50°C.

93.7 torr

sublimation—solids also have vapor pressures. Some solids go directly to the vapor phase at 1atm, skipping the liquid phase all together! Iodine and dry ice [solid carbon dioxide] both do this.

Melting Point
- A heating curve is pictured below:
- Molecules break loose from lattice points and solid changes to liquid. Temperature remains constant during ANY phase change. PE is changing like crazy while KE remains constant!
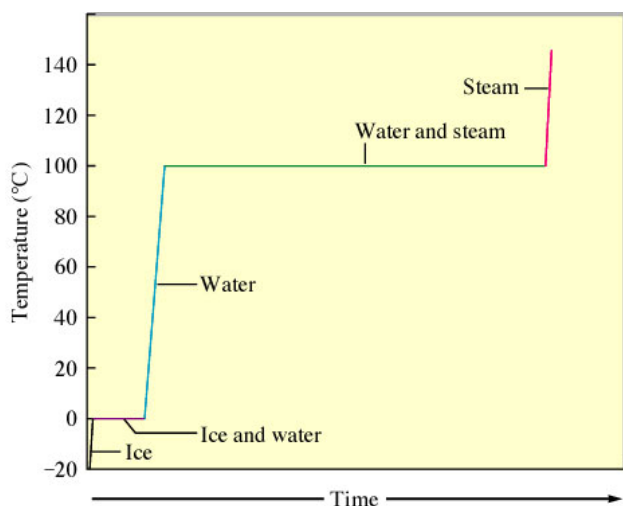
- **ΔH_{fus}, enthalpy of fusion**—the enthalpy change that occurs at the melting point [which is the freezing point, by the way]. This energy is clearly going into increasing the PE of the molecules since the temperature or ave KE of the molecules is plateaued or staying the same.
- vapor pressure of solid = vapor pressure of liquid [equil. is established]

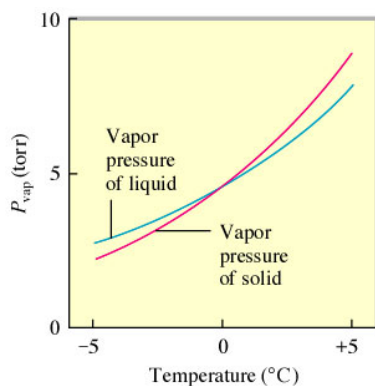On the plateaus, calculate the E change using
$$q = \Delta H_{[vap\ or\ fus]}m$$
On the slants, calculate the E change using
$$q = mc_{[solid,\ liquid\ or\ gas]}\Delta T$$

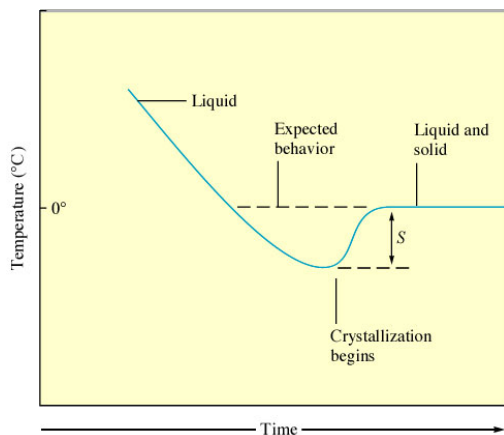**Table 10.9** Melting Points and Enthalpies of Fusion for Several Representative Solids

Compound	Melting Point (°C)	Enthalpy of Fusion (kJ/mol)
O_2	−218	0.45
HCl	−114	1.99
HI	−51	2.87
CCl_4	−23	2.51
$CHCl_3$	−64	9.20
H_2O	0	6.02
NaF	992	29.3
NaCl	801	30.2

The melting and boiling points of water are determined by the vapor pressures of the solid and liquid states. This figure shows VP of solid and liquid water as a function of temperatures near zero.

- Below zero—VP of ice has a larger T-dependence
- This means the VP of ice increases more rapidly than the liquid's VP for each increase in temperature.
- A point is eventually reached where the VP solid = VP liquid.
- We call this temperature the MP!

- **normal melting point**—the temperature at which the VP solid = VP liquid AND P total = 1atm
- **normal boiling point**—the temperature at which the VP liquid = exactly 1 atm
- FREAKS—changes of state do not always form at the exact MP and BP's.
  - **supercooled**—oxymoron—the substance is at a temperature below its FP, yet it remains a liquid. Usually happens when the cooling has been gradual and the degree of organization needed to form crystals hasn't happened. At some point, organization happens and the solid is readily formed, the temperature rises back to the MP as the heat of crystallization is released.
  - **superheated**—another oxymoron—the substance is at a temperature above its BP, yet it remains a liquid. Usually happens when heated very rapidly [microwave oven] and bubbles form in the interior with high internal pressures. They often burst before reaching the surface making quite a mess of things! Really ruins an experiment. This is called bumping in the lab. Prevent it by adding boiling chips to the flask. These chips are porous and have air trapped in them, upon heating tiny air bubbles form and act as "starters" for vapor bubble formation.

Phase Diagrams—closed systems

- Represent phases of matter as a function of temperature and pressure.
- critical temperature: temperature above which the vapor cannot be liquefied.
- critical pressure: pressure required to liquefy AT the critical temperature.
- critical point: critical temperature and pressure coordinates (for water, $T_c = 374°C$ and 218 atm).

Water is a freak! The solid-liquid line tilts to the left [negative slope] since its solid is *less* dense than its liquid phase—ice floats. Usually the solid sinks as it is more dense.

Consider the cylinder pictured right.
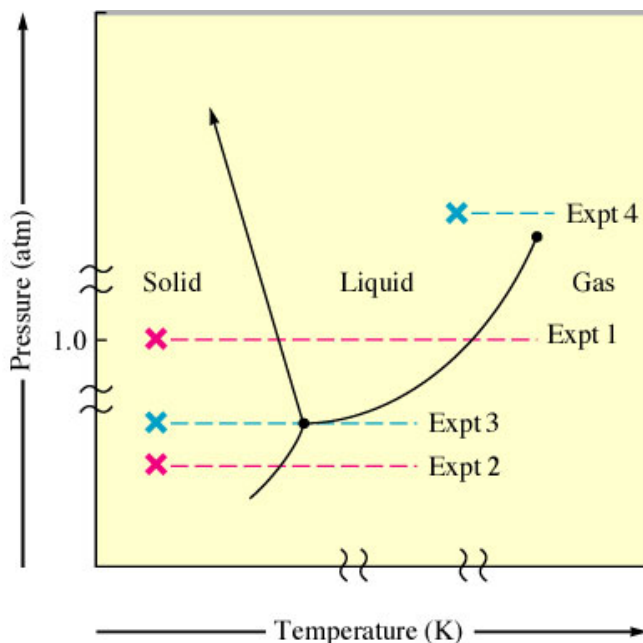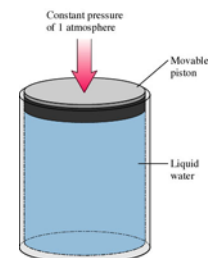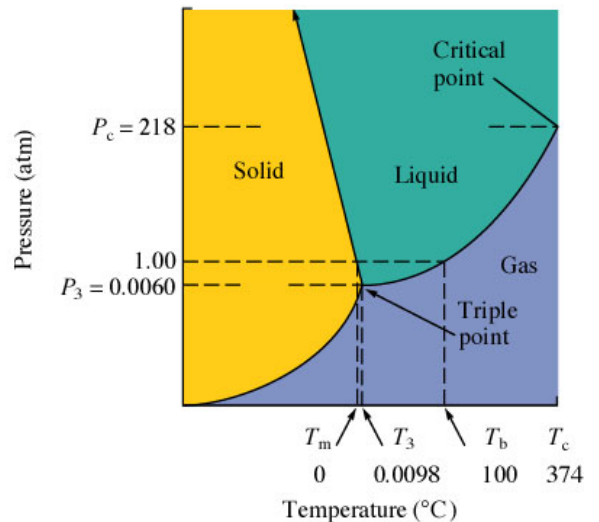
Experiment 1: $P = 1$ atm.
Completely filled with ONLY ice at −20°C. Heat…
−20 →0 only ice present
at 0, ice melts [no vapor]
past 0 liquid water begins to exert a VP. When the VP of the liquid reaches 1atm, vaporization occurs and steam is formed.

Experiment 2: $P = 2.0$ torr
Start again with only ice at −20°C. Heat…
As heating proceeds, −10 is reached where ice changed directly to vapor. It sublimes. No liquid water forms *because* the VP of water is always greater than 2.0 torr. If water were placed into the cylinder at these conditions, it would freeze if less than −10 or vaporize if greater than −10. Water cannot exist at these conditions!

Experiment 3: $P = 4.588$ torr
Start again with only ice at −20°C. Heat…
No new phase results until the temperature reaches 0.0098°C. This is the triple point of water and all THREE phases exist in equilibrium at this set of P & T conditions.

Experiment 4: $P = 225$ atm
Start this time with only liquid water in the cylinder at 300°C. Heat….
The liquid water gradually changes to vapor, but it goes through a fluid state that was not present at any of the other pressures and temperatures. This fluid region, is neither true liquid nor true vapor.
This occurs when the critical point has been exceeded. For water CT = 374°C and CP = 218 atm.

What is the effect of pressure on ice? It melts it.

You can take a block of ice, connect a wire to two heavy weights and drape it across the block. The wire will exert pressure on the block, melt it and begin a journey downward through the block due to the force of gravity acting on the weights. The "cool" thing [pun intended] is that after the wire has left the surface, the block refreezes!
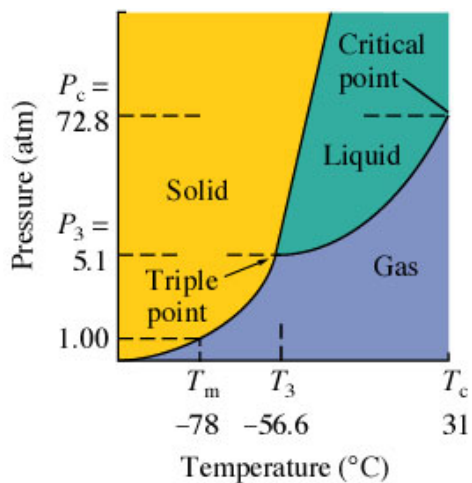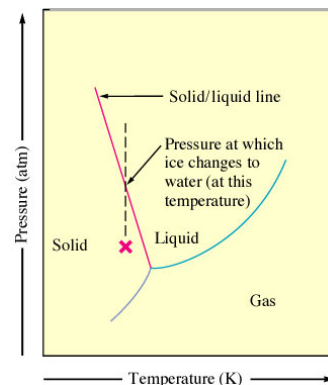
Most substances have a solid-liquid line that has a positive slope since their solid phase is more dense than the liquid. This one is for carbon dioxide.

EACH PHASE BOUNDARY REPRESENTS AN EQUILIBRIUM SET OF PRESSURE AND TEMPERATURE CONDITIONS!! Be sure and use the word equilibrium in your writing as you explain phase diagrams.