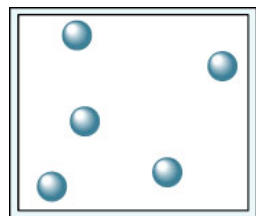
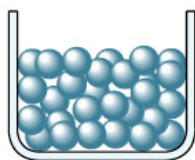


AP Chemistry Chapter 10 Liquids and Solids

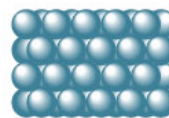
Now it is time to consider the forces that condense matter. These can be due to ionic or covalent bonding [intramolecular forces—ionic stronger than covalent] or much weaker attractive forces we call intermolecular forces. These are the forces *between* (rather than within) molecules. We briefly visited the IMF's earlier when discussing the nonideal behavior of gases. These forces cause changes of state by causing changes among the molecules NOT within them.



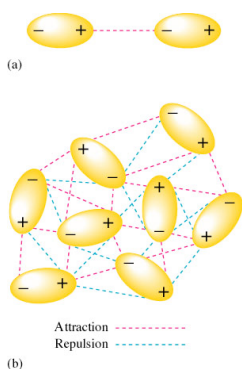
Gas



Liquid



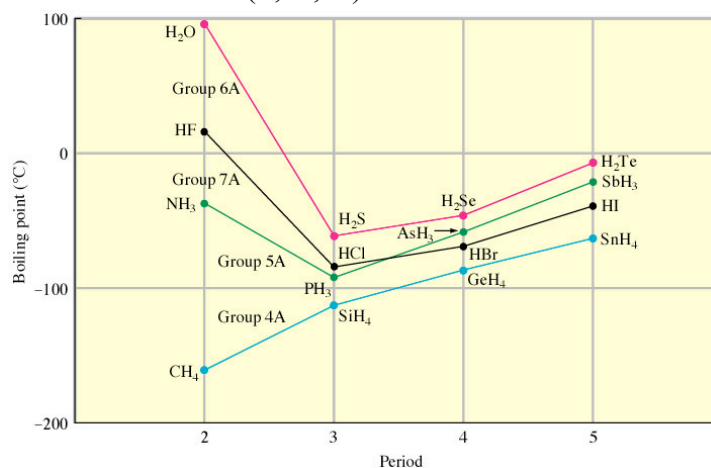
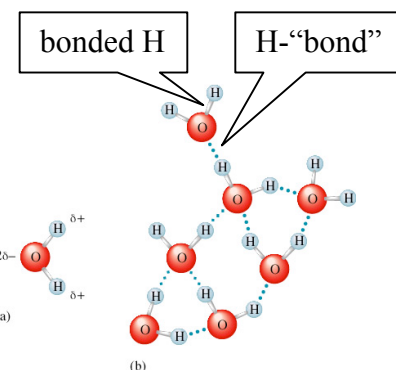
Solid



Dipole-Dipole—strongest IMF's

! dipole-dipole attraction: molecules with dipoles orient themselves so that “+” and “-” ends of the dipoles are close to each other.

! hydrogen bonds: dipole-dipole attraction in which hydrogen on one molecule is attracted to a highly electronegative atom on an adjacent molecule. (F, O, N)

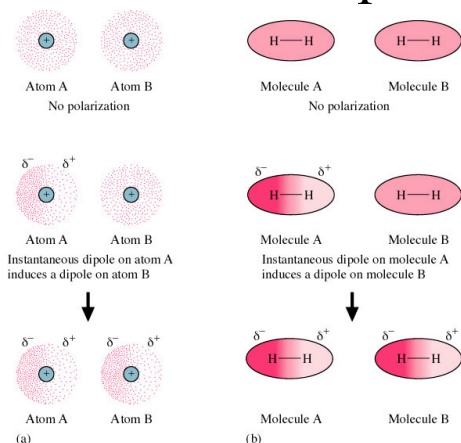


! **WHY** is there such variation among the covalent hydrides of groups IV through VII? One would expect that BP would increase with increasing molecular mass [since the more electrons in a molecule, the more polarizable the cloud {more about that in the next section}, the stronger the IMF's, the more E needed to overcome these attractions and vaporize]. Hydrogen bonding, that's why!

! TWO reasons: both enhance the IMF we refer to as hydrogen bonding.

1. The lighter hydrides have the highest En values which leads to especially polar H-X bonds.
2. The small size of each dipole allows for a closer approach of the dipoles, further strengthening the attractions.

London Dispersion Forces—weakest IMF's



- relatively weak forces that exist among noble gas atoms and **nonpolar** molecules. (Ar, C₈H₁₈). (the only IMF that exists) (LDF exist between polar molecules also)

- caused by instantaneous dipole formation, in which electron distribution becomes asymmetrical. The newly formed dipoles now find each other FAR more attractive than before! (a.k.a. dipole-induced dipole if an *ion or polar molecule* causes the distortion OR induced dipole-induced dipole if a *nonpolar molecule* sets off the chain reaction of induction like in iodine.)

- the ease with which electron “cloud” of an atom can be distorted is called **polarizability**. You’ll want to write about polarizability

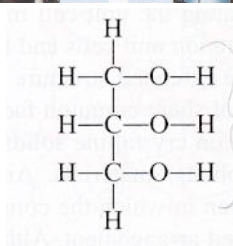
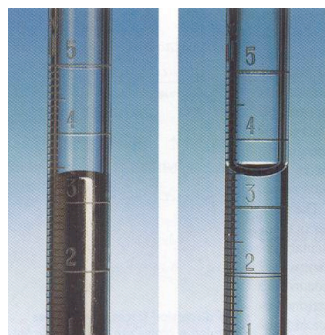
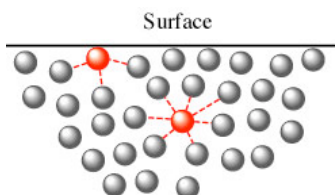
when EXPLAINING these concepts.

Without these forces, we could not liquefy covalent gases or solidify covalent liquids.

Consider the halogens, these forces INCREASE as we go down the family since the electron cloud becomes more polarizable with increasing FW [more principle E levels added, more electrons present, more shielding, valence farther from the nucleus, etc.]. It explains WHY F₂ and Cl₂ are gases, Br₂ is a liquid [moderate dispersion forces a.k.a. London forces, a.k.a. dipole-induced dipole forces] and ultimately I₂ is a solid! What does that tell us about boiling points??

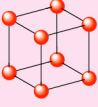
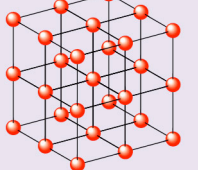
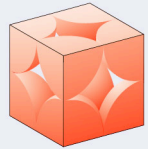
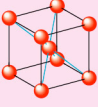
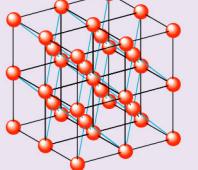
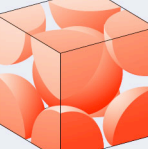
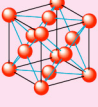
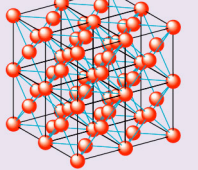
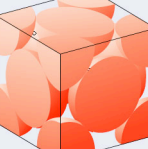
Some Properties of a Liquid

All of the following are greater for polar molecules since their IMF's are greater than nonpolar molecules.



- **Surface Tension**: The resistance to an increase in its surface area (polar molecules). High ST indicates strong IMF's. 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.
- **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 just the opposite. 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.
- **Viscosity**: Resistance to flow (molecules with large intermolecular forces). Increases with molecular complexity [long C chains get tangled] and increased with increasing IMF's. Glycerol [left] has 3 OH groups which have a high capacity for H-bonding so this molecule is small, but very viscous.

- Liquids with large IMF tend to be highly viscous.
- Modeling a liquid is difficult. Gases have VERY SMALL IMFs and lots of motion. Solids have VERY HIGH IMFs and next to no motion. Liquids have both strong IMFs and quite a bit of motion.

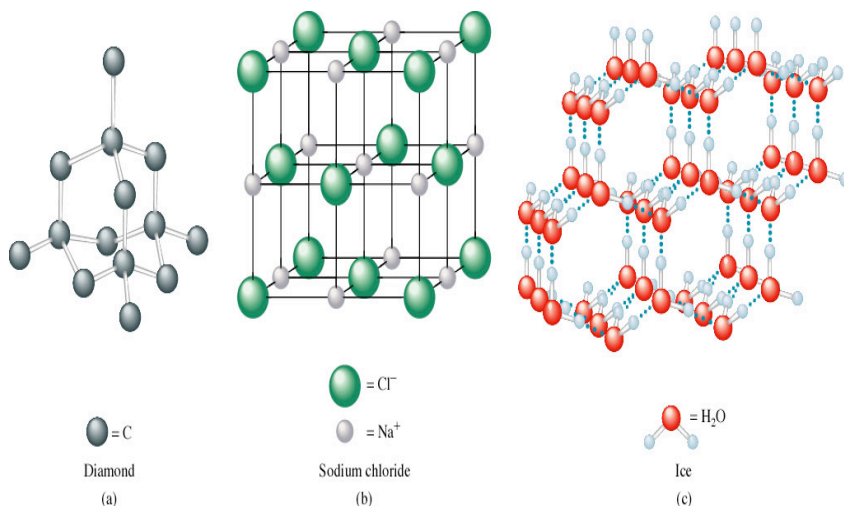
Unit cell	Lattice	Space-filling unit cell	Example
(a)  Simple cubic			Polonium metal
(b)  Body-centered cubic			Uranium metal
(c)  Face-centered cubic			Gold metal

Types of Solids

- **Crystalline Solids:** highly regular arrangement of their components [often ionic, table salt (NaCl), pyrite (FeS₂)].
- **Amorphous solids:** considerable disorder in their structures (glass). Glass is made from sand, silicon dioxide that has been melted and super-cooled, or solidified without order to the atoms.

Representation of Components in a Crystalline Solid

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



(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, make sheets that slide and is MUCH softer! (pictured later)

(b) **ionic salt crystal lattice**

(c) **ice**—notice the “hole” in the hexagonal structure and all the H-bonds. The “hole” is why ice floats—it makes it less dense than the liquid!

X-RAY Analysis of Solids

- **X-ray diffraction**—A bending or scattering of light. The beams of light are scattered from a regular array of points in which the spacings 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.

Types of Crystalline Solids – based on particles located at the lattice points

- 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.
- 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. Dramatically different properties are illustrated below.
 - (i) Metallic solids – delocalized, nondirectional covalent bonds occur
Example: copper, mp = 1083°C conductor, malleable, ductile
 - (ii) Network solids – strong directional covalent bonds occur
Example: diamond, mp = 3500 °C, hardest substance known
 - (iii) Group 8A (18) solids (Noble Gases) LDF (IMF)
Example: Argon, mp = -189°C, insulator
- Know this chart well:

Table 10.3 Classification of Solids

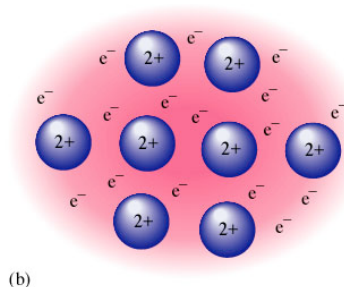
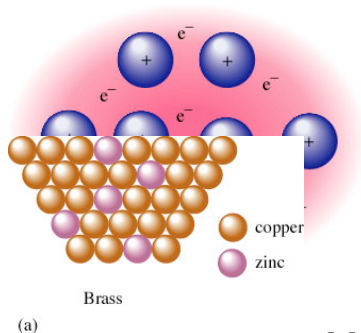
	<i>Atomic Solids</i>			<i>Molecular Solids</i>	<i>Ionic Solids</i>
	<i>Metallic</i>	<i>Network</i>	<i>Group 8A</i>		
Components that occupy the lattice points:	Metal atoms	Nonmetal atoms	Group 8A atoms	Discrete molecules	Ions
Bonding:	Delocalized covalent	Directional covalent (leading to giant molecules)	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.

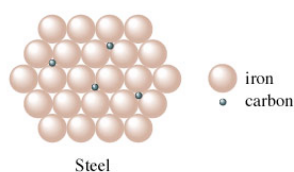
Bonding Models for Metals

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!



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.

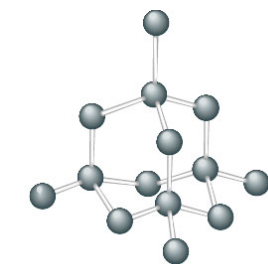


Metal alloys: a substance that has a mixture of elements and has metallic properties

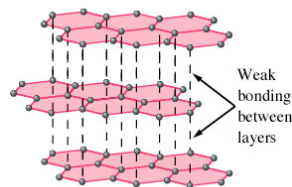
Network Atomic Solids—a.k.a. Network Covalent

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:

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

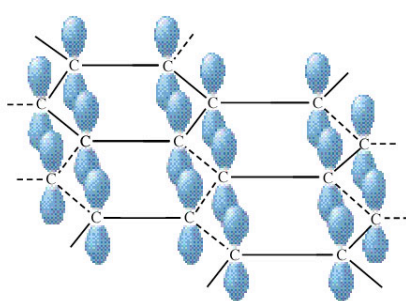


(a) Diamond

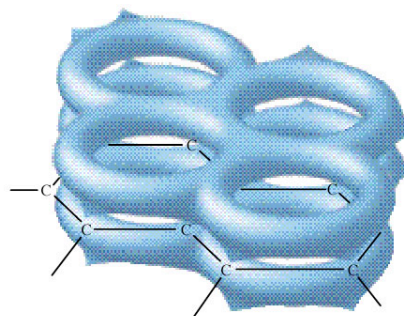


(b) Graphite

- Graphite is slippery, black and a conductor. Graphite is bonded so that it forms layers



(a)



(b)

of carbon atoms arranged in fused six-membered rings. This indicates sp^2 hybridization and 120° 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.

Molecular Solids

Simply where 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 IMF's **London dispersion forces**.

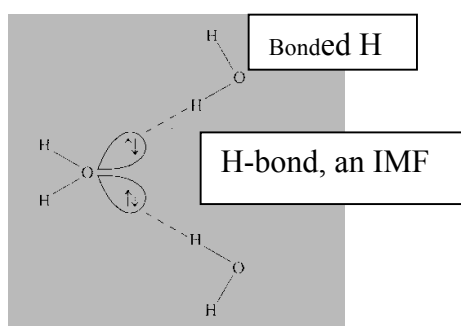
- As the size of the molecule increases [often reported in a Chem I book as “increased MM”], the London dispersion forces increase ***because the larger the molecule the more electrons, the more polarizable its electron cloud***. If it is more polarizable, temporary dipoles can easily form which shifts the IMF’s from weak London dispersion to a weak form of induced dipole-induced dipole.

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.



- When molecules DO have dipole moments their IMF’s are greater, especially if H-bonding is present—it’s like an added bonus.

Ionic Solids

Stable, high-melting substances held together by **STRONG** electrostatic forces that exist between oppositely charged ions

Table 10.7 Types and Properties of Solids

Type of solid:	Atomic			Molecular	Ionic
Structural unit:	Network Atom	Metallic Atom	Group 8A 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	Wide range of hardness	Very low melting	Soft	Hard
	High melting point Insulator	Wide range of melting points Conductor		Low melting point Insulator	High melting point Insulator
Examples:	Diamond	Silver Iron Brass	Argon(s)	Ice (solid H ₂ O) 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.

- Gold
- Carbon dioxide
- Lithium fluoride
- Krypton

A: atomic solid w/metallic properties

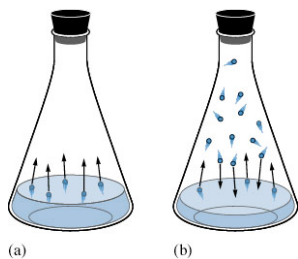
B: molecular solid

C: binary ionic solid

D: atomic solid w/ properties characteristic of molecular solid w/nonpolar molecules

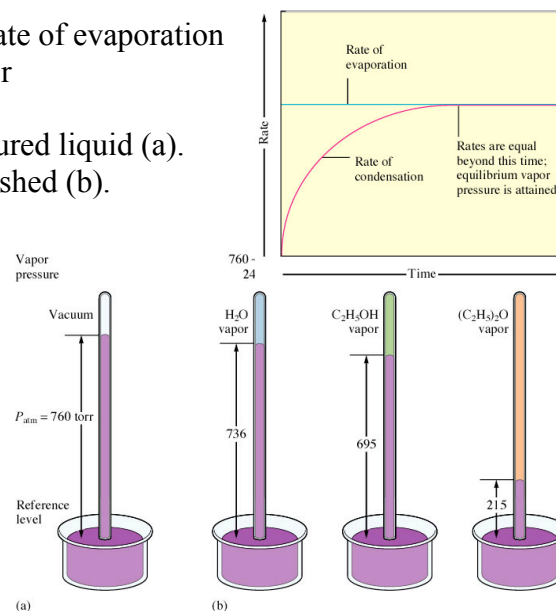
Vapor Pressure and Changes of State

- 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 it's ΔH_{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 solution 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).

Molecules leave and enter the liquid phase @ the SAME RATE.

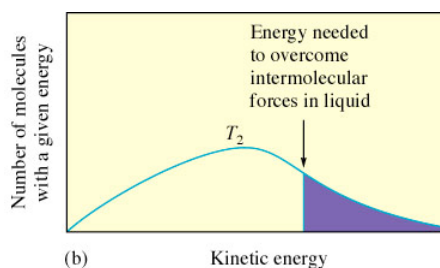
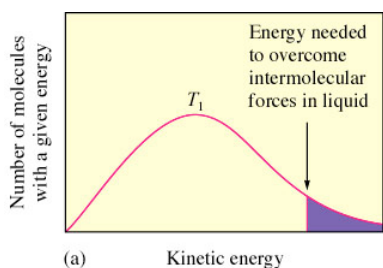


- The VP of a liquid can be measured easily using a simple barometer. (b) The three liquids water, ethanol, and diethyl ether have quite different vapor pressures. Ether is by far the most volatile of the three [escapes easiest]. Note that in each case a little liquid remains (floating on the mercury).

- **volatile**—have high VP, thus low 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

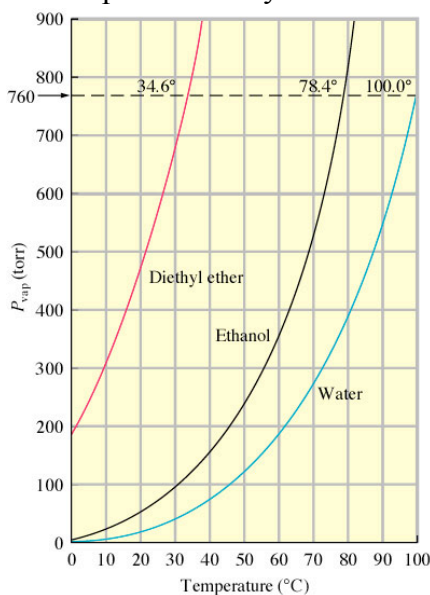
Table 10.8 The Vapor Pressure of Water as a Function of Temperature

$T (^{\circ}\text{C})$	$P (\text{torr})$
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

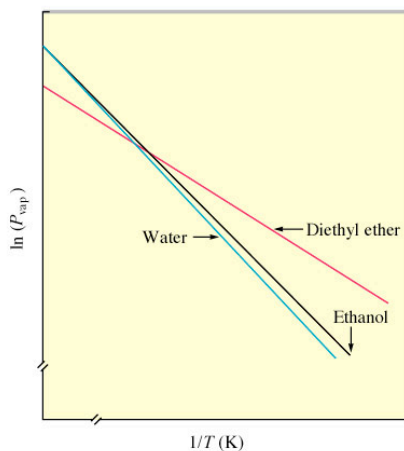


In general, as MM \uparrow VP \downarrow

- 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 $\ln VP$ 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/K.

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

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

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:

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

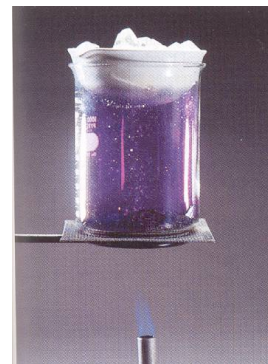
This form is called the **Clausius- Clapeyron equation**.

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.

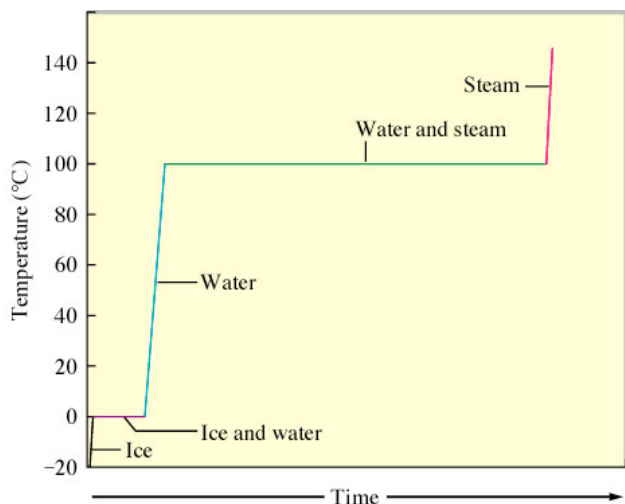
= 93.7 torr

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 is constant as melting occurs.) PE is changing like crazy while KE remains constant!



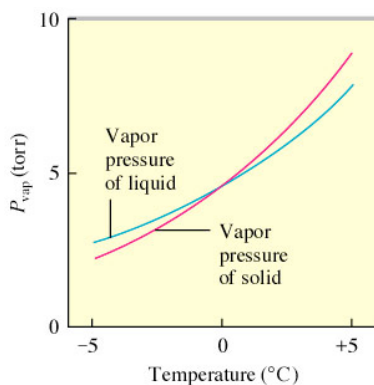
- **ΔH_{fus} , enthalpy of fusion**—the enthalpy change that occurs at the melting point [which is the freezing point, by the way]. This energy is clearly going into increasing the PE of the molecules since the temperature or ave KE of the molecules is plateaued or staying the same.
- vapor pressure of solid = vapor pressure of liquid [equil. is established]

On the plateaus, calculate the E change using $q = \Delta H_{[\text{vap or fus}]}m$

On the slants, calculate the E change using
 $q = mc\Delta T$

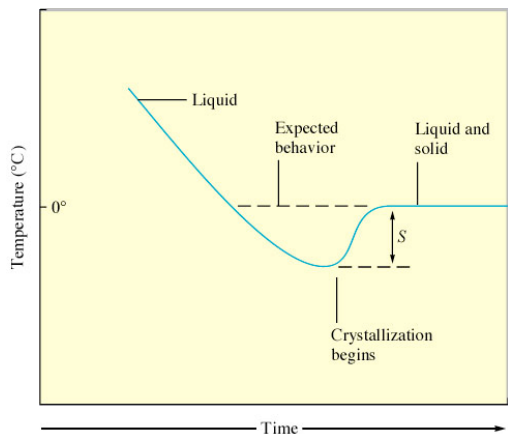
Table 10.9 Melting Points and Enthalpies of Fusion for Several Representative Solids

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 ₂ O	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 = 1 atm
- **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.

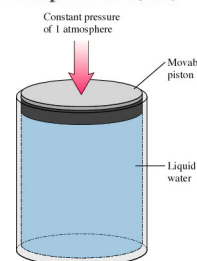
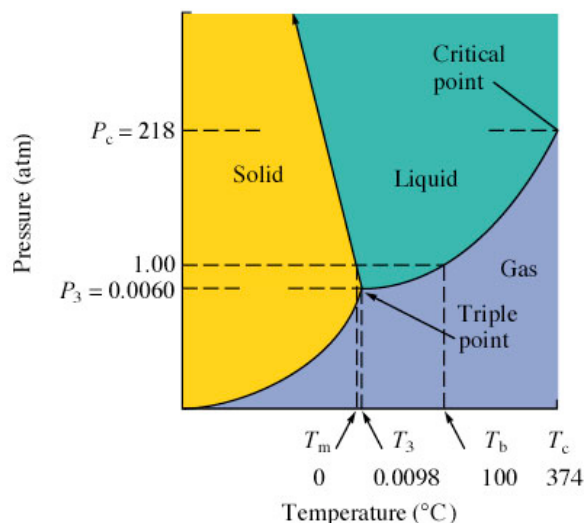
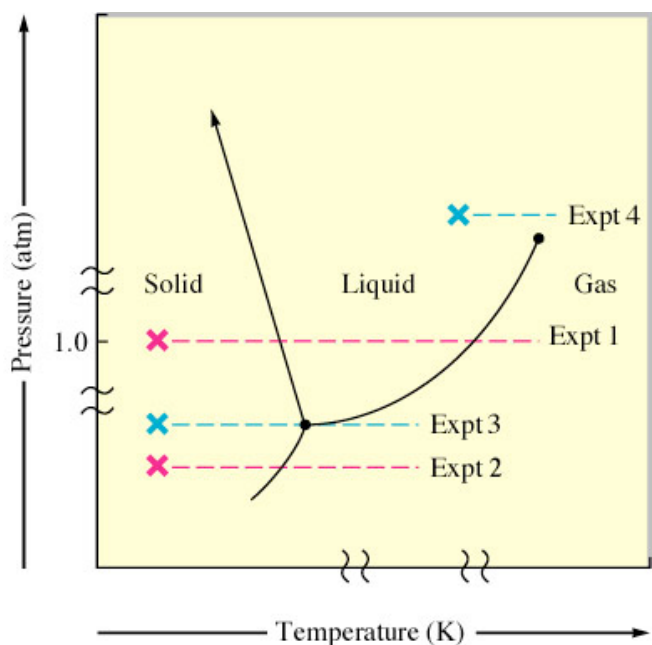
- **superheated**—another oxymoron—the substance is at a temperature above its BP, yet it remains a liquid. Usually happens when heated very rapidly [microwave oven] and bubbles form in the interior with high internal pressures. They often burst before reaching the surface making quite a mess of things! 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

- Represents phases 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 (for water, $T_c = 374^\circ\text{C}$ 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: $P = 1 \text{ atm}$. Completely filled with ONLY ice at -20°C . Heat... $-20 \rightarrow 0$ 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 1 atm, vaporization occurs and steam is formed.

Experiment 2: $P = 2.0 \text{ torr}$ Start again with only ice at -20°C . Heat... As heating proceeds, -10 is reached where ice changed directly to vapor. It sublimates. 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: $P = 4.588 \text{ torr}$

Start again with only ice at -20EC. Heat...

No new phase results until the temperature reaches 0.0098EC. This is the triple point of water and all THREE phases exist in equilibrium at this set of P & T conditions.

Experiment 4: $P = 225 \text{ atm}$

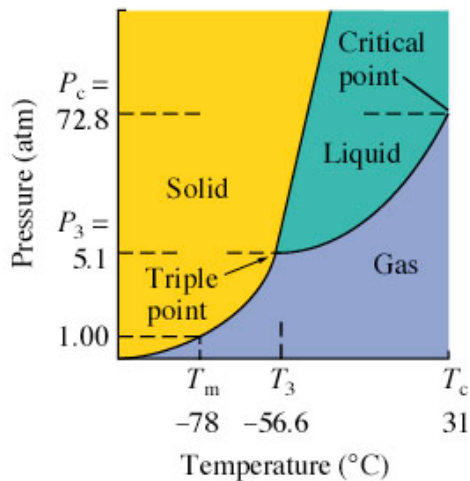
Start this time with only liquid water in the cylinder at 300EC. Heat....

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.

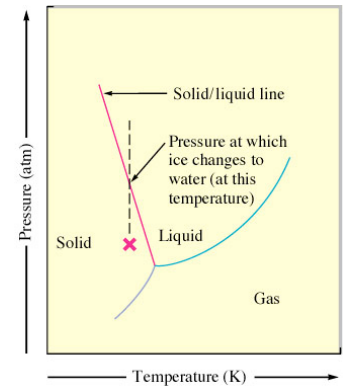
This occurs when the critical point has been exceeded. For water $CT = 374EC$ and $CP = 218 \text{ atm}$.

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!!