

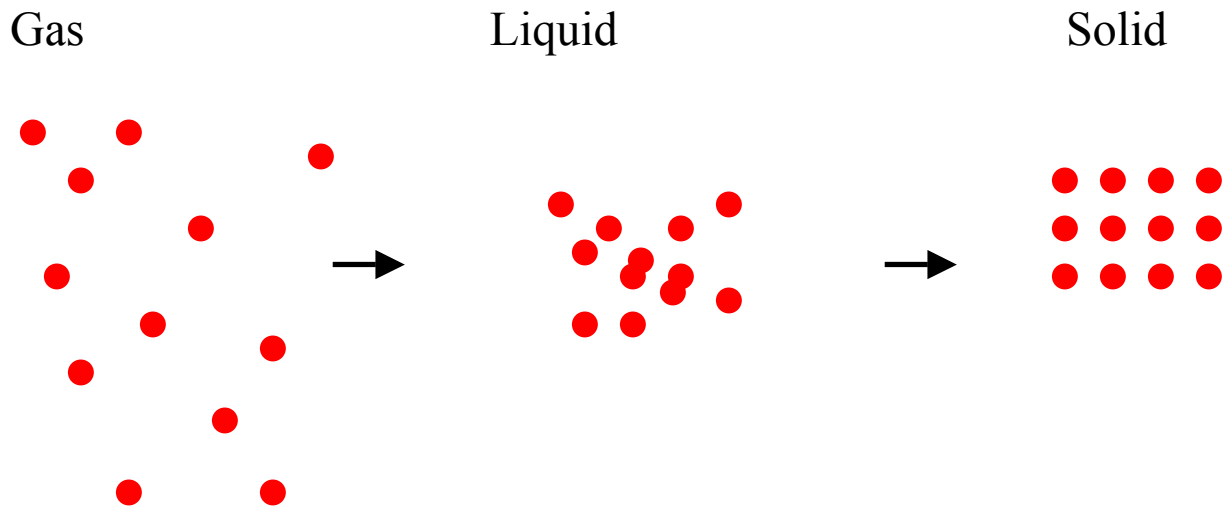
13 Liquids and Solids (the Condensed Phase)

Kinetic Theory and the Condensed State. As you learned in Chapter 1, when it comes to dividing matter into different categories, one approach is to define various “states” of matter: gas, liquid and solid. You have developed your own definitions based upon appearance, but shown below are some of the physical properties that distinguish the three states of matter. Of particular interest here is the last category, which attempts to characterize the states of matter on the basis of how they behave as individual particles (what you have learned to be atoms, molecules or ions in CH301). In Chapter 12 the properties of gases were developed theoretically from something called the **kinetic molecular theory**. **KMT proposes** that in the gas phase, **individual particles move about in a random motion** at high velocity, in a way you might associate with billiard balls. In the ideal case these gas molecules have no distinctive chemical properties. As we saw in Chapter 12, under certain conditions this model works pretty well. The **ideal gas law was derived from it** and the ability to calculate gas velocity, collision frequency and diffusion rates was possible.

KMT after Cooling Things Down

Well that same kinetic molecular theory can be applied to particles when they happen to slow down at cold temperature or high pressure. Under these conditions, the molecules enter a condensed state (become either a liquid or a solid.) You see a nice demonstration of this when liquid nitrogen is poured over an air balloon at room temperature. The **particles tend to become very closely spaced** and form clusters that are always touching each other. Very little volume is taken up by these particles. Only the particles on the surface of the liquid can easily return to the gas phase without significant input of energy to the system.

If either the pressure of the system increases or **the temperature decreases further, the liquid can become a solid.** The **primary distinction between a liquid and a solid is that a well ordered arrangement of the particles** has occurred and a very stable low energy form of matter has been created. The particles have no particular desire to leave this well-ordered environment or even to diffuse to other sites in the solid state.



P increases or V decreases or T decreases

Random motion decreases and molecules become more organized as intermolecular interactions increase.

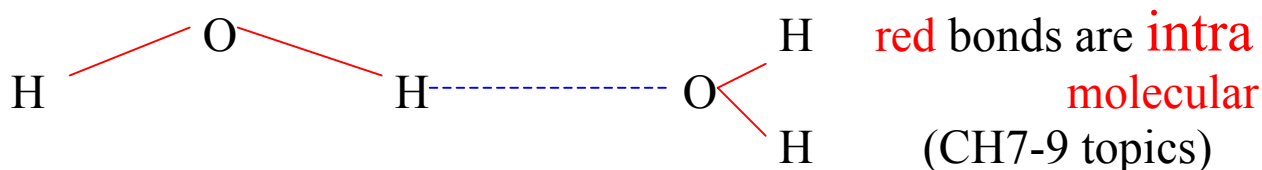
KMT Falls Apart Due to Intermolecular Attractions

(Hint: Pull out that worksheet on intermolecular attractions and go back and read about electronegativity in Chapter 6)

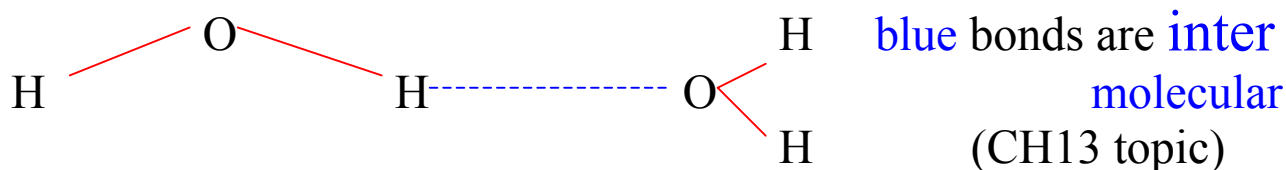
In developing the kinetic molecular theory, it was suggested that for some reason the condensed molecules would prefer to stay in proximity to each other rather than separate. There are a collection of reasons why they stay together and they all share a common theme: charged particles of opposite sign attract and charged particles of the same sign repel. Where do these charged particles come from? They are the fundamental particles, the negatively charge electron and the positively charged proton, in the nucleus. Now we spent the entire first half of general chemistry discussing the attraction that electrons have for protons in atoms and molecules. This attraction formed the basis for both atomic theory and for theories describing the chemical bond.

Time out for two important definitions. We can distinguish two kinds of forces at work that hold matter together: *intermolecular* attraction and *intramolecular* attraction.

Intramolecular attraction: Coulombic interaction between electrons of one atom and nuclei of another atom within a molecule. This is a fancy way of describing a chemical bond.



Intermolecular attraction: Coulombic interaction between electrons of one atom in a molecule with the nucleus of an atom in a separate molecule.



Note that **intra** means one molecule is involved and **inter** means multiple molecules are involved.

It all comes down to Coulomb's Law.

Now you might ask why molecules would be attracted to one another. Simply, charged particles aren't all that particular when it comes to creating an attractive force. Coulomb's Law

$$F \propto \frac{q^+ q^-}{d^2}$$

indicates that an attractive force is created by two charges of opposite sign, for example an e^- and a proton.

An important paragraph on why CH₁₃ exists. Read and comprehend.

Obviously within a molecule the electrons of one atom will be really close to the nucleus of another atom, (d will be small), hence a strong force and a strong bond. But this doesn't mean that there will be no attraction between the charged particles in molecules that are adjacent to each other. Now the kinetic molecular theory says that particles have no interaction with each other. But we know better from Coulomb's Law. We know that in adjacent water molecules, for example, one of those electrons in an oxygen will be attracted to the positively charged nucleus of the hydrogen in another molecule. The attractions aren't all that great because the distance is larger, but they are often enough to make one molecule want to hang out in the vicinity of another.

Four Important Intermolecular Attractions

I am about to introduce you to **four kinds of intermolecular interactions**. The details of the interactions may start to blur after a while, and the reason is that they are really all the same: they are all Coulombic interactions between negatively charged electrons and positively charged nuclei. The **distinction** between the types of intermolecular attractions **is in the relative strength of the attraction**. **All intermolecular attractions are much less than a covalent bond**, but all are responsible for why liquids and solids exist.

attractive force	covalent bonds	ion-ion interaction	hydrogen bonding	permanent dipoles	London forces
chapter	CH 7-9	CH 7-9	CH13	CH13	CH13
magnitude	400 kJ/mole	200 kJ/mole	20 kJ/mole	5 kJ/mole	<1 kJ/mole
	intra	intra	inter	inter	inter
example	C-C	Na ⁺ -Cl ⁻	HCl...H ⁺	δ ⁺ ...δ ⁻	δ ⁺ ...δ ⁻

Covalent bonds. You spent all of CH301 learning about covalent bonds. They are formed through a sharing of electrons between nuclei. Molecular orbital theory is used to explain this very strong intramolecular bond. It is how atoms become molecules, not how gases become condensed phase liquids and solids. Note that they are **one to two orders of magnitude more stable than the intermolecular interactions of Chapter 13.**

Ion-Ion Interactions. Recall from CH301 that elements at the far right and far left hand side of the periodic table gain or lose electrons to form cations or anions to satisfy the octet rule. So Na becomes Na^+ and Cl becomes Cl^- . Now obviously as oppositely charged particles, Na^+ and Cl^- are strongly attracted to each other in the process of donating and accepting electrons. The **magnitude of an ion-ion interaction, then, while not equal to a covalent bond, is still quite large.**

Recall also from CH301 that a single NaCl doesn't exist but rather combines with multiple Na^+ and Cl^- ions to form a highly ordered crystalline solid. The single entity, NaCl is simply the formula unit. Ion-ion interactions are responsible for formation of the crystal lattice.

Understanding melting point rankings.

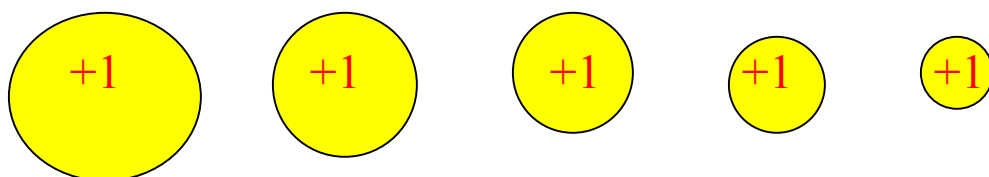
In trying to generalize the magnitude of an ion-ion interaction, for ions of like charge, the smaller the ion, the higher the melting point. For example, in the following series of singly charged ions:

Compound	NaF	NaCl	NaBr	KCl
Melting point	993 °C	801 °C	747 °C	770 °C

All are singly charged ions. The highest melting point, indicating the strongest attraction, is for the smallest ions.

An important concept: Charge Density

The ranking of melting points we just saw are based on more than just the concept of charge. Obviously a triply charged ion will take more energy to melt than a singly charged ion. But what about ranking the singly-charged ions. With the charge the same, how do you do the ranking? The answer is **density of charge**. In general, the amount of charge per unit volume is what determines the ranking—in this case, **the higher the charge density, the higher the melting point**.



Which is why NaF has a higher melting point than NaCl.

You will see charge density rearing it's head a lot in science.

Dipole-Dipole interactions.

Recall again from CH301 that every element has a different desire for electrons. **Halogens would love an electron.** **Alkali metals would love to lose one.** A qualitative approach to determining this relative desire for an electron, **the electronegativity scale, was devised to give a rough measure of this attraction for electrons.** We learned to use it to determine where in a molecule the electron density would be more likely located. We found that even when an electron is not completely donated as in an ion-ion interaction, it often has a propensity for certain regions of the molecule. We designate the high and low regions of electron density in a molecule with:

δ^+ : high electron density and δ^- : low electron density

For example: in water the δ^- is around the O and the δ^+ is around the H.

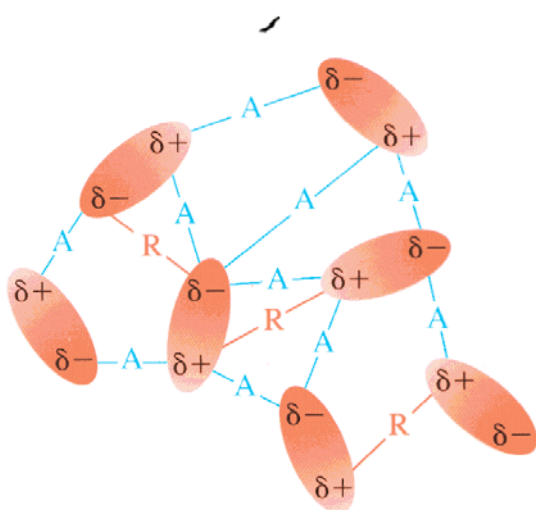
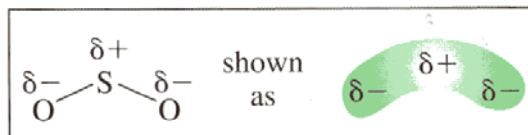
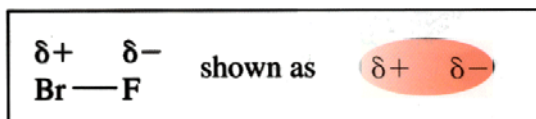
This difference in electron density is responsible for the formation of a dipole moment in a molecule, a vector that gives directionality to the change in electron density in a molecule.

Forming INTERMOLECULAR DIPOLES.

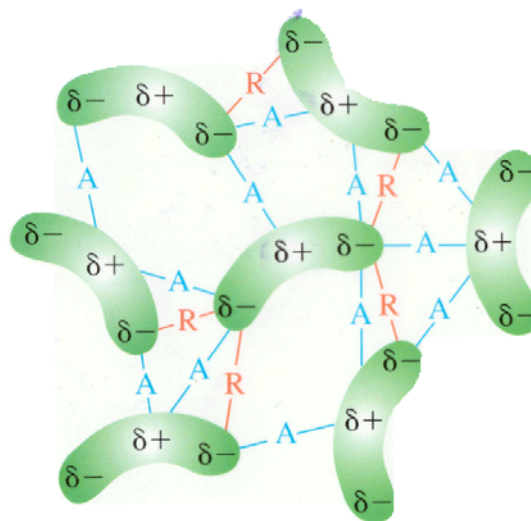
If a molecule has a permanent dipole, as in water, it is possible for the δ^+ of one molecule to be attracted to the δ^- of another molecule. This is shown below in the figure for condensed phase BrF and SO₂ which both have permanent dipoles (asymmetric molecules with non-zero ΔEN .)

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Text Figure 13.3, page 445



(a)



(b)

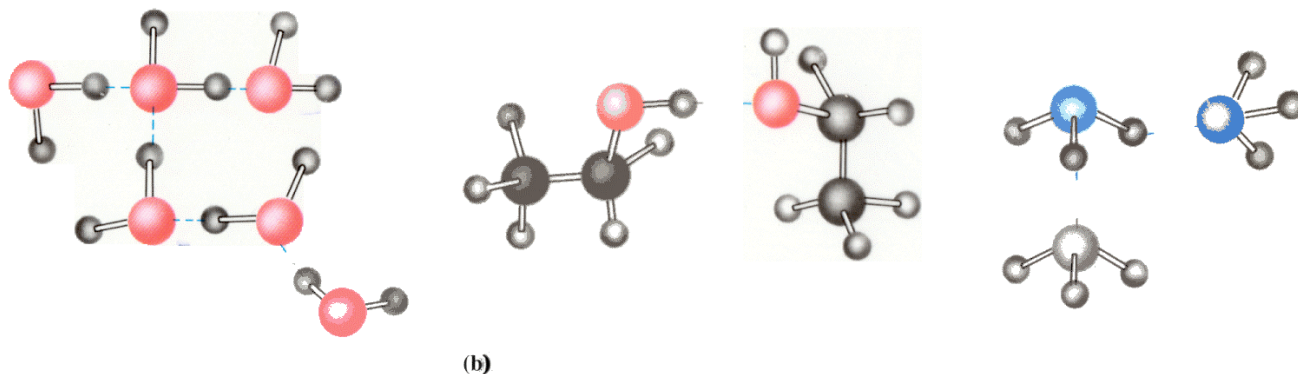
Whitten/Davis/Peck, *General Chemistry and General Chemistry with Qualitative Analysis*, 5/e

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The magnitude of this intermolecular interaction varies significantly, but never approaches that for intramolecular bonds. Typical values are in the 3 to 5 kJ/mole range for permanent dipoles.

Hydrogen bonding. There is a special case of dipole-dipole interactions in which one of the atoms involved is hydrogen. Hydrogen bonding when the following two features of molecules are present in a chemical system:

- Presence of a hydrogen atom
- Presence of a highly electronegative atom like a halogen, O or N.



Whitten/Davis/Peck, *General Chemistry and General Chemistry with Qualitative Analysis 5/*

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The combination of the small size of the H and the high electron density of the electronegative atom contribute to much higher intermolecular bond energies—as much as 20 kJ/mole—than you see in a typical dipole. Examples are shown in the figure above. The red and blue electronegative atoms are attracted to the little hydrogen atoms.

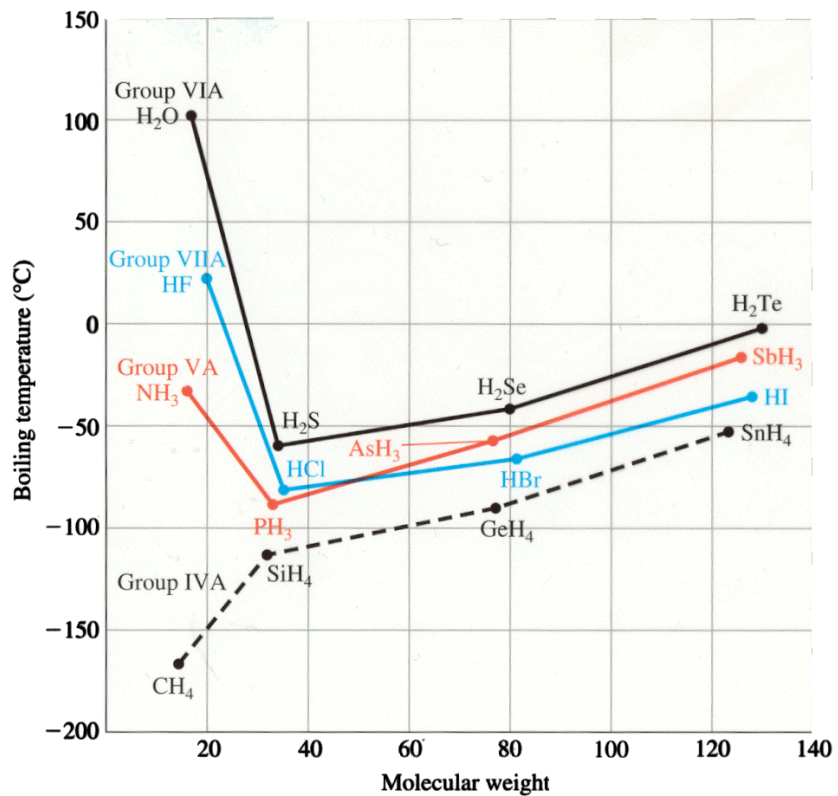
Relative H bonding strength.

In comparing the relative strengths of hydrogen bonding, it is instructive to look at what happens as you move down and across the periodic table. This is shown in the accompanying graph through a comparison of boiling points for families of hydrides. In general, **as you move toward more electronegative elements across a row, the hydrogen bonding strength increases** because the electronegative atom has a stronger attraction to the hydrogen.

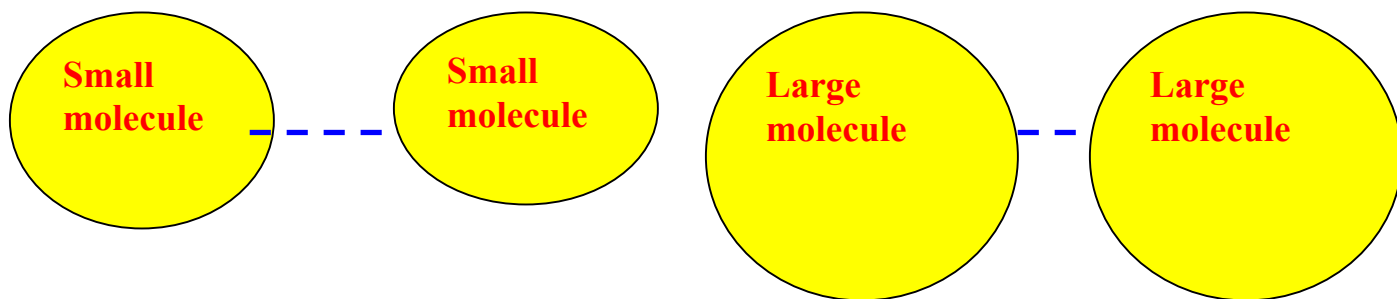
The graph also shows that once you move away from the second row, boiling point tends to increase with size of the molecule. For example, boiling point increases in the sequence



as you move down column VIA. The explanation for this trend can be attributed to a phenomenon known as polarizability.



Polarizability: An effect that results because large diffuse electron clouds in larger atoms are less strongly attracted to their nuclei. They are thus more easily distorted by neighboring nuclei. One consequence is increased intermolecular attraction between adjacent molecules. Thus the larger atoms in a molecule exhibit a higher boiling point within a series. Note that H bonding in the second row is a special exception to this rule.



The large molecule has a larger intermolecular interaction, stronger H bond (shorter blue dashes means stronger H bonds.)

London Forces. There are a collection of names used to describe the fact that even molecules and atoms without permanent dipoles are capable of being attracted to adjacent molecules or atoms. Terms used to describe this are London forces or van der Waals forces or dispersion forces. We will use London forces in a general sense to describe this phenomenon which results in weak intermolecular attractions.

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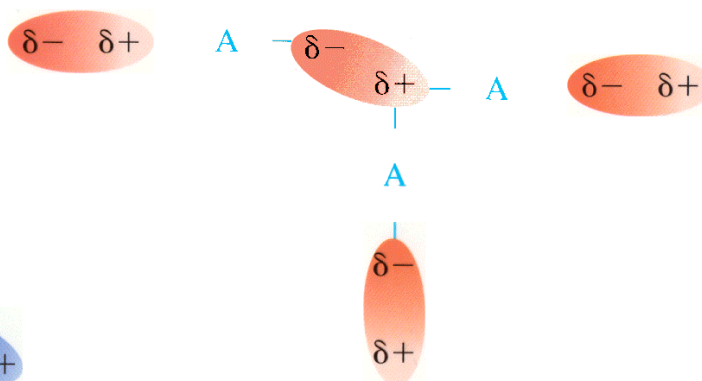
Text Figure 13.6, page 447



(a)



(b)



d

(e)

Explaining why symmetrical molecules like N₂ can form liquids and solids.

To understand the instantaneous dipole, it is important to remember that electrons don't just sit still within a molecule. They are in constant motion and although on average they might be symmetrically distributed around the molecule, at any given instant a dipole might be formed. Shown in the figure above is the symmetrically distributed charge around argon. However when a passing molecule, ion or atom with a permanent or momentary δ^+ and δ^- , is seen by the electrons surrounding the argon atom, attraction occurs. This attraction immediately disappears when the instantaneous dipole changes, but it is enough to create weak intermolecular attractions among the oddest fellows. It is the reason, for example, that a symmetrical molecule like methane forms a liquid at low temperature. Even argon has weak attractions so that at very cold temperatures liquid argon forms.

Ranking the Properties of Liquids (Or, why we learned all that intermolecular interaction stuff.)

Quick, name some of the ways to characterize a liquid. For example, contrast liquids like water, pentane, glycerin. Each of these compounds is a liquid at room temperature, but each possess very different properties, properties which depend primarily on differences in the intermolecular forces we just discussed. What are these properties?

Viscosity,
 surface tension,
 capillary action,
 evaporation,
 vapor pressure
 boiling point.

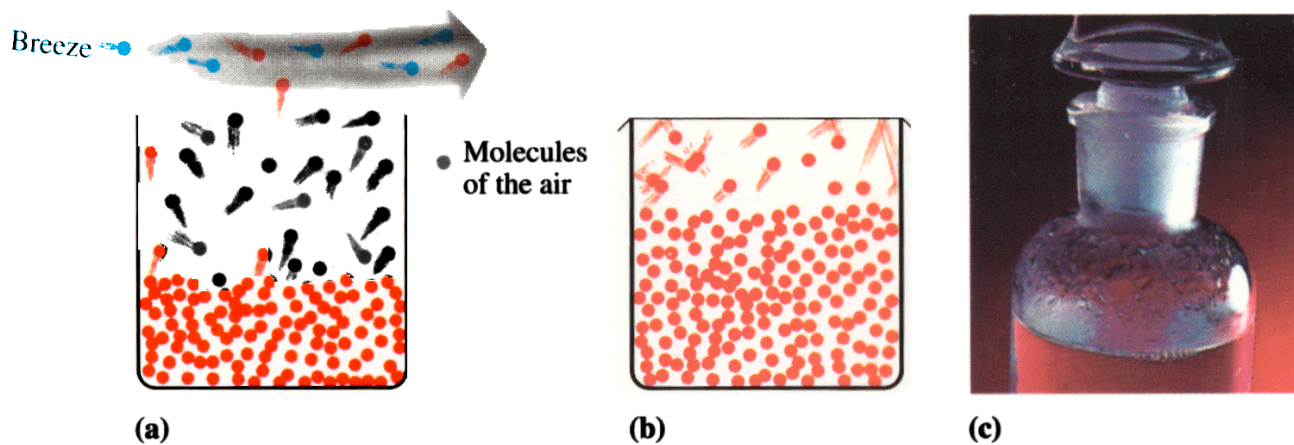
Many of these properties are interrelated, precisely because they depend in large measure on the intermolecular forces that are in turn a consequence of molecular structure and size. So as you learn trends associated with properties, look at how they interrelate to each other.

Viscosity. Viscosity is simply a resistance to flow and is measured with a viscometer that measures in units of centipoise. For the most part, viscosity is dependent on the strength of the intermolecular forces. Thus compounds that have a lot of hydrogen bonding like glycerin (due to lots of exposed OH group), are highly viscous. Compounds like pentane, which has only London forces holding it together is less viscous. And in general, the larger the molecule, the more viscous it is because of the increased London forces.

Surface Tension. It might not seem all that significant to you on the surface, but surfaces are incredibly interesting and complicated. There are whole fields of study having to do with what takes place at a surface. After all, the surface of anything (whether a liquid or a person), is a boundary separating two different things. In a homogeneous environment, for example in the middle of a solution, everything experiences a uniform collection of forces pulling in every direction. Everything averages out. In contrast, at a surface, the forces pulling from one side of a surface are very different from the forces at work on the other side of the surface. You can see this in the figure below.

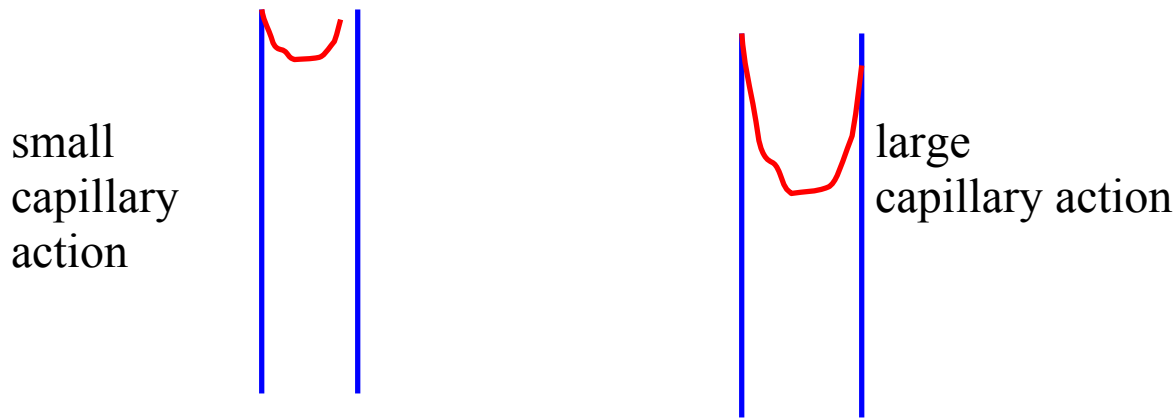
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Text Figure 13.11, page 451



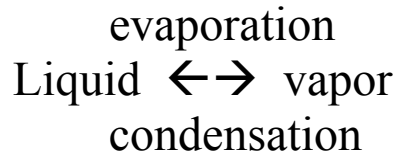
In a liquid, the intermolecular attractions that pull on molecules at the surface tend to attract the molecule toward the center of the liquid. This tendency to want to minimize the area of the surface is called surface tension. It is why lots of liquids bead up into spheres—these liquids have relatively high surface tension. In contrast, some liquids have low surface tension and tend to spread out in sheets. Contrast the difference between water with a high surface tension due to intermolecular hydrogen bonding, which tends to bead up, and a non-hydrogen bonding liquid like acetone which does not.

Capillary Action. Capillary action occurs due to a property known as adhesion in which the solvent exhibits an attraction for the surface. You are most commonly aware of this with water which is said to wet a surface because the hydrogen atoms in the water express an attraction to the electron rich oxygen atoms in glass. This process causes a creeping up of the water along the sides of the glass and result in the formation of a meniscus. The creeping up the sides of a capillary tube that results, continues until gravity rears its ugly head.



Evaporation. Everyone's first science experiment involves watching water evaporate (vaporize) from a pie tin. And I am sure it remains an ongoing tradition that students believe that during the night, the teacher actually removes some of the water so that she can claim evaporation has occurred. I also think this is probably the place where the initial distrust between student and teacher develops. But anyway, we are now smart enough to develop a theory, which explains that the teacher went home along with everybody else. Evaporation is the process whereby heat is added to a chemical system in sufficient amounts to allow particles on the surface of the liquid to overcome the surface tension that held the liquid together in the first place. Kinetic molecular theory states that there is a distribution of energies in the molecules. Some fraction of those molecules at the surface with the highest energy can break away from the surface—vaporize. The interesting thing that happens is that heat is removed from the system, causing the system to cool down. It is why you feel chilled when you perspire. Now at the same time that molecules leave a surface, gas molecules collide with the surface. Suddenly the gas molecule feels the attraction of the intermolecular forces. If the molecule is cool enough, the attractive forces win out and the molecule becomes part of the condensed phase.

Now in a closed system (for example, a bottle of Diet Coke with the cap on, there is an on-going exchange of water molecules that are evaporate and condense. An equilibrium has been established and the total quantity of the condensed phase and the gas phase above it remain constant.



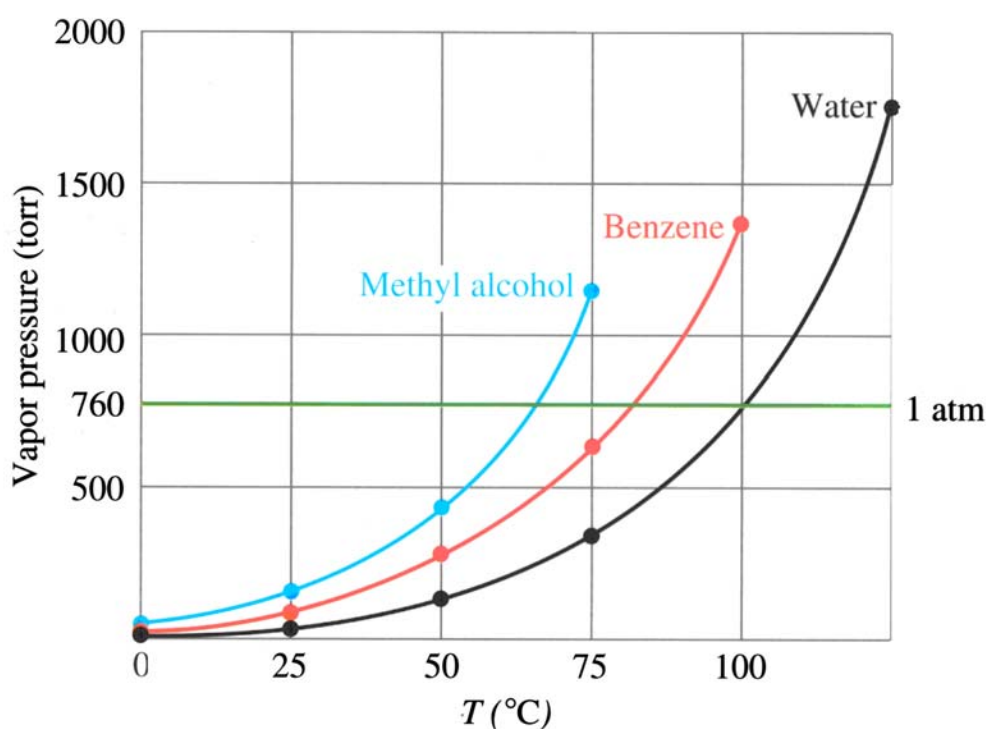
In an open system (one in which the top is removed from the bottle) it is possible for the vaporized water molecule to be carried away from the surface of the liquid. There is no longer an equilibrium exchange of gas and liquid molecules. Over time the amount of liquid decreases. You show up for school the next day and the pie tin is empty, and I promise you, your teacher didn't pout it out (well maybe she did if it wasn't evaporating fast enough.)

Vapor Pressure

We can become a little more quantitative about this evaporation thing by asking about concentration of condensed phase molecules that enter the gas phase. In the area above the solution surface it is possible to count the number of gas phase molecules per unit volume. We can give these numbers in units of concentration, but since we are talking about a gas now, perhaps pressure would be a better unit of measure.

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Vapor pressure is a measure of the gas phase concentration of a substance above its solution surface. As you can imagine, substances that evaporate readily have high vapor pressure and those that take forever (like water) have lower vapor pressures. Not surprisingly, the stronger the intermolecular forces, the lower the vapor pressure when comparing compounds.

Of course there is also a common sense relationship involving temperature. **The high the temperature, the higher the vapor pressure.** Again, if you consider the kinetic molecular model, by increasing the temperature of a solution, you increase the internal energy of a molecule. Once that internal energy is high enough, the molecule is able to break free of the surface tension caused by the intermolecular forces.

Tabulated below are some vapor pressures at different temperatures. The vapor pressures are in units of torr. Look for the correlation to what you know about intermolecular forces.

	Kind of inter-molecular interaction	0°C	25 °C	60 °C	75 °C	100 °C
Water	Asymmetric, polar, H bond	5	24	93	300	760
Diethyl ether	Symmetric Non-polar London forces	185	470	1325	2680	4859

Note the red vapor pressure values is the last one before the onset of boiling.

Boiling point. When addressing evaporation, we have talked about a surface phenomenon—gas molecules ripping free of intermolecular forces felt the surface. In contrast, boiling is the process by which gas molecules are formed below the surface. You recognize this as the formation of bubbles. Now in order for a gas bubble to escape the solution, the pressure exerted externally (atmospheric pressure) has to be overcome. This is in fact the definition of boiling:

*The **boiling point** of a liquid is the point when the vapor pressure of the bubbles which are formed is greater than atmospheric pressure.*

If this occurs, the bubbles can escape the liquid. Under normal conditions the solution remains at the boiling point because additional energy added to the solution is used to overcome the intermolecular forces and increase the boiling process.

An interesting topic of conversation at your next party.

As a side point, those of you into cooking at high altitude know that it takes longer to make dinner. This is because if the external pressure (atmospheric pressure) that must be overcome is less than atm, then the amount of work necessary for vapor to escape the liquid is decreased. Consequently the boiling point is reduced which means you can't dump as much energy into cooking your pasta as you could at 100°C. Thus you have to cook longer.

Heat of Vaporization: ΔH_{vap}

The material to be covered in Chapter 15 is the study of thermodynamics, the quantitative process of following the transfer of energy in chemical and physical processes. The first effort to understand thermodynamics comes right now with the definition of a heat of vaporization, ΔH_{vap} .

The heat of vaporization is the amount of energy necessary to convert a liquid to a gas at the boiling point. In other words, put one mole of water on the stove and heat it to 100°C . Now, how much energy will be required to make it all boil away—what is the ΔH_{vap} . Obviously the stronger the intermolecular bonds that hold a solution together (like hydrogen bonding), the larger ΔH_{vap} . Not surprisingly, water has a large heat of vaporization as do other compounds with lots of OH groups. For example, water has a heat of vaporization of 22.6kJ/g in contrast with compounds that exhibit only London forces and have ΔH_{vap} an order of magnitude smaller.

Another interesting topic of conversation at your next party.

So it is time to fill your radiator with a coolant. What should you use, a compound with a high ΔH_{vap} or a low ΔH_{vap} ? Now the idea is that your car engine is generating a lot of heat and you want somehow to dissipate all that heat energy by running a solution in and around it to carry off the heat. Your preference is something that isn't instantly going to vaporize, creating a high pressure in the cooling system. So you want a compound that has a lot of intermolecular forces that would have to be overcome to convert a liquid into a gas. Thus we choose water, or even better, ethylene glycol, which has an even higher molar ΔH_{vap} .

Note the strong relationship between intermolecular interactions and properties of liquids!!

Listed below is another table that summarizes the role intermolecular forces have in determining the magnitude of solution properties. Once you understand the concepts behind each property, you can use common sense to make a relative comparison of two solutions when comparing properties.

property	Weak attractive forces (like pentane)	Strong attractive forces (like water)
Cohesive forces	Low	High
Viscosity	Low	High
Surface tension	Low	High
Specific heat	Low	High
Vapor pressure	High	Low
Evaporation rate	High	Low
Boiling point	Low	High
ΔH_{vap}	Low	High

Expect to be given a list of chemicals and have to rank their liquid properties based upon their intermolecular interactions. The best thing is that once you figure out the ranking, it is always the same!!

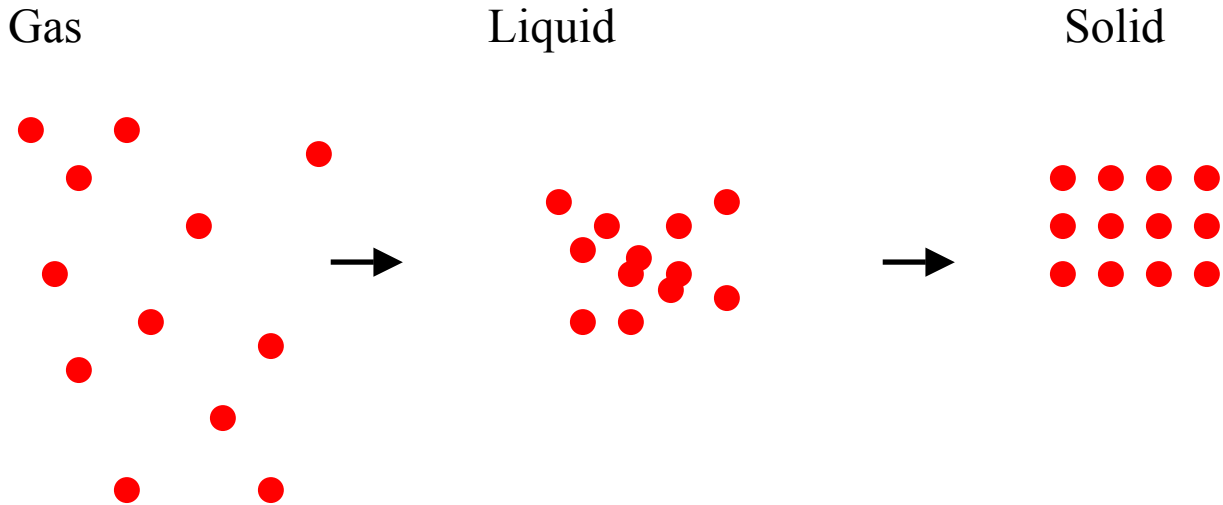
Example: rank any property for water, methane, BCl_3 , NaCl

Highest intermolecular interaction:

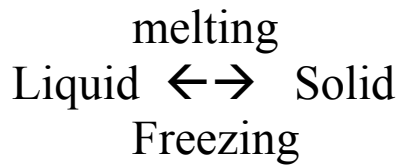
NaCl with ionic bonds	is > than
water with two H bonding sites	is > than
BCl_3 with permanent dipole	is > than
methane with instantaneous dipole	

The Solid Phase

Freezing and melting. If we continue to lower the temperature of a solution, we observe a new phase transition as the liquid becomes a solid. Properties of a solid are clearly distinct from a liquid in that a definite shape is achieved and the molecules diffuse or flow much more slowly (to the casual observer, not at all.)



In the same way that we described the energy associated with the phase transition from liquid to gas, we can identify the amount of energy associated with the freezing or melting process that transitions between a liquid and a solid.



As with the evaporation or condensation process, during the period that melting or freezing occurs, the temperature of the sample remains fixed at what is called the melting point or freezing point. The molar heat of fusion, ΔH_{fus} , and heat of solidification, ΔH_{solid} are of equal value but opposite sign. They describe quantitatively the amount of energy required to completely deliver one mole of a sample through a phase change.

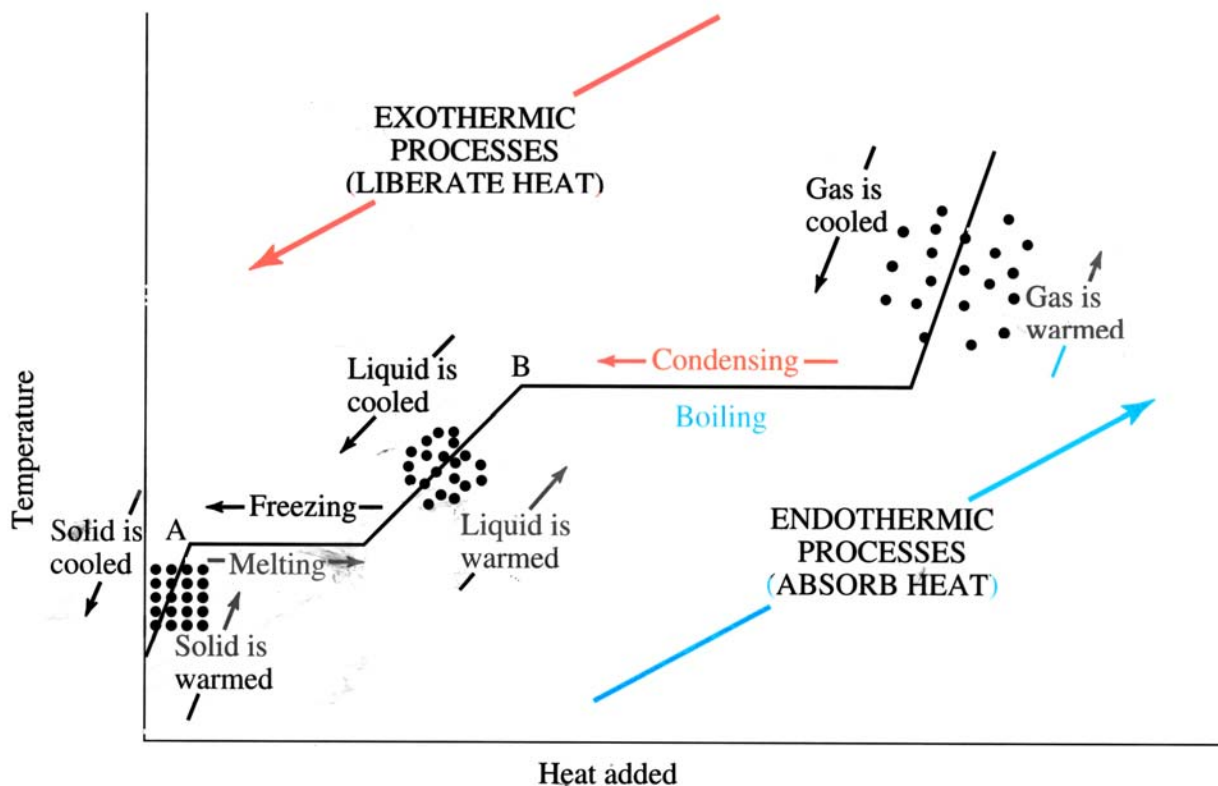
As might be expected, the greater the intermolecular forces, the larger ΔH_{fus} or ΔH_{fus} . Thus ΔH_{fus} for methane is 58.6 J/g and 334 J/g for water.

A big picture picture—be able to explain it to a friend (out loud.)

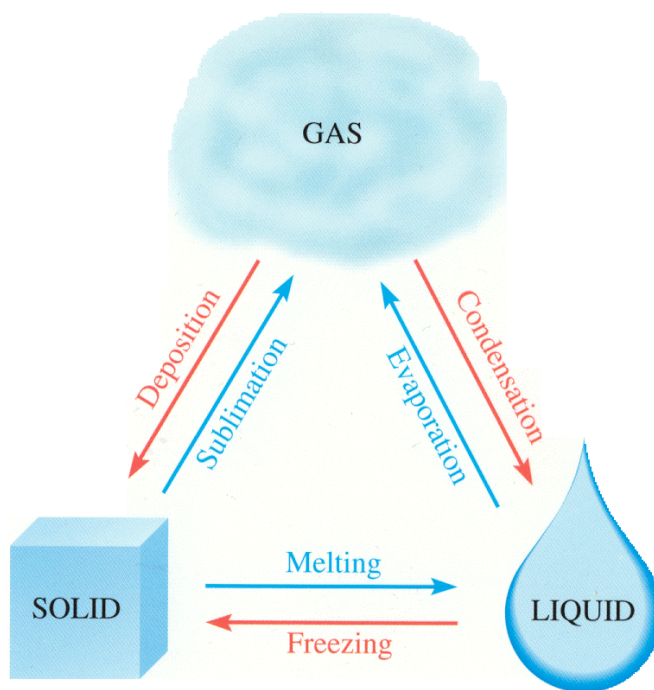
With what we have learned about the energetics of transition from solid to liquid to gas, we can create a temperature/energy diagram that indicates what occurs as energy is added to a frozen sample and is warmed to the point that a gas is formed. This is shown in the accompanying figure. Note the plateaus in the process corresponding to isothermal points where ΔH_{evap} and ΔH_{fus} occur.

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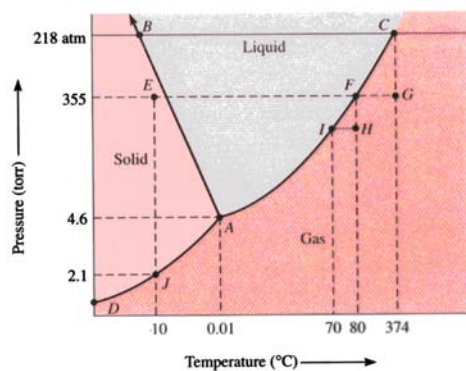


Sublimation and Deposition. Some materials are precocious and want to skip a phase in the same way a bright child skips a grade. For example, carbon dioxide and mothballs (naphthalene) are solids that do not have a ΔH_{fus} . Rather than melt to form a liquid, they transition directly from the solid state to the gas phase through a process called sublimation. The reverse process, transitioning from a gas to a solid is called deposition. Of course, in the same way we have heats of fusion and evaporation, we have heats of sublimation and heats of deposition. The accompanying figure summarizes the possible transitions between the three phases.

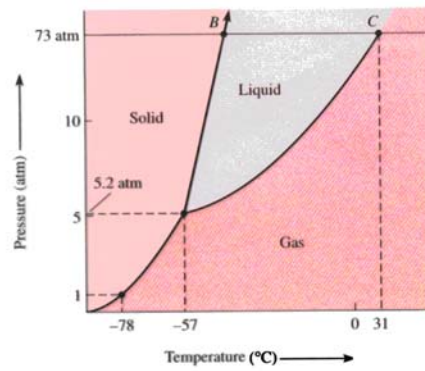


Phase Diagrams: A Plot of Pressure vs. Temperature

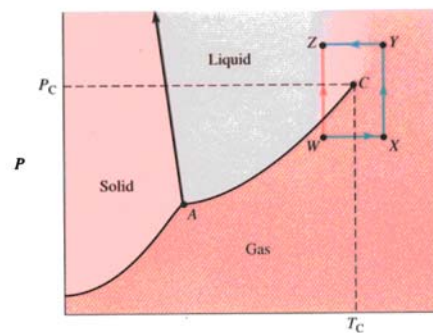
Just for fun, we can play the game of asking what the phase (gas, liquid, solid) is **for every single choice of a pressure and a temperature**. This allows us to construct what is called a phase diagram. Examples are shown below.



(a)



(b)



(c)

Simple things to know about phase diagrams.

Without going into much detail (because I could spend an entire lecture on the above figures), here are some things about phase diagram you should know:

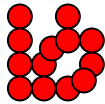
1. The different phases on the graph make sense based on common sense. For example, at really low pressure, we see the gas phase. At really low temperature, we see solids.
2. **The lines represent the interface between phases** and are the location at which the transition—evaporation, sublimation, melting, occurs. By definition, along these lines, you see two phases simultaneously.
3. There is an interesting location **(point) on the plot where all three phases exist at the critical point.**
4. It is possible to walk all around the phase diagram experimentally just by changing P and T. You should do so and ask yourself what is actually happening physically. Note it will be an exercise similar to the earlier figure which is more cumbersome than a PT diagram.

Finally, another interesting piece of party conversation.

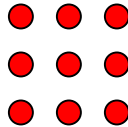
5. The phase diagram is famous for one thing specifically, explaining why it is that H_2O is really a special compound. It is the one common material for which increasing the pressure results in the compound turning from solid to liquid. All of you have had the cool experience of putting a nice piece of ice between your teeth and pressing down. What happens? The ice melts!! Think about it. Nothing else you chew on turns from solid to liquid under pressure.

Descriptions of solids: Amorphous and crystalline solids.

As we cool liquids, they have the choice to become well order or a mess in solid form. Solids that become a mess, in other words, they have **irregularly packed structures, are said to be amorphous.** Example of amorphous solids include rubber and glasses and probably most breakfast cereals. Amorphous solids typically form rapidly from heterogeneous solutions.



Amorphous, formed quickly



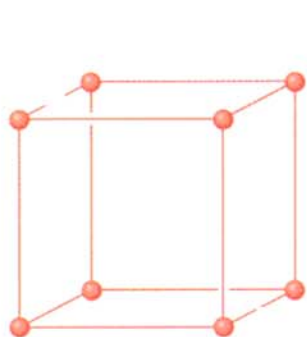
Crystalline, formed slowly

In contrast, some solids are formed slowly from homogeneous solutions, they have the opportunity to become very well ordered. You have all attempted this at some point in the kindergarten years by sticking a string into a solution of sugar water to make rock candy. These kinds of well-ordered samples are called crystalline solids. Count among crystalline solids such ordinary solids as rock salt and ice, and some more exotic materials like rare gems. You always know you have a crystalline solid because if you shatter it, the fragments retain the same ordered structure as the original crystal.

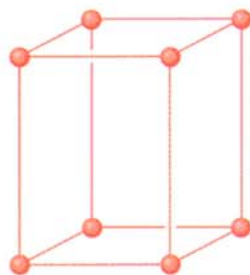
Crystal structures.

(Time out: I make no bones about the fact that this is the area of chemistry, no wait, science, I hate the most. I think it is because this is 3-D stuff and I am very much a 2-D kind of kind. Actually, now that I think about it, I think I am pretty much one-dimensional.)

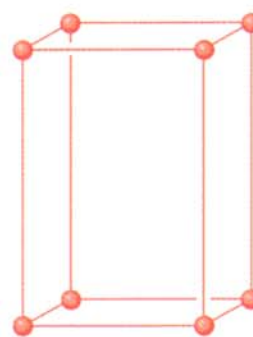
It is now time to pull out the Styrofoam balls and try to pack them together neatly in a confined space like a shoe box. Now some of you are good at this and can instantly visualize all the ways you can put the balls together. Others, like me, always think the different packings look the same. But I am told, and must believe, that there are seven possible crystal systems. The accompanying table and figure present them. Note that the angles and lengths vary between the seven systems, so they must be different. The smallest repeating unit of these crystal structures is called a unit cell. No doubt at some point in your life you were asked to make these units cells with Styrofoam and toothpicks.



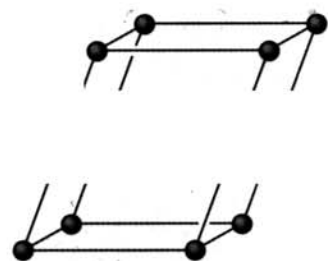
Cubic, simple



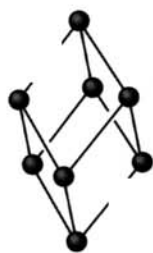
Tetragonal, simple



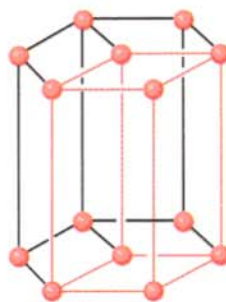
Orthorhombic, simple



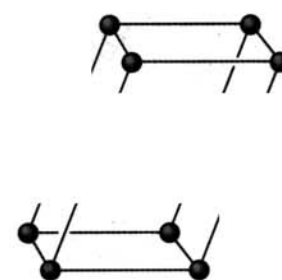
Monoclinic, simple



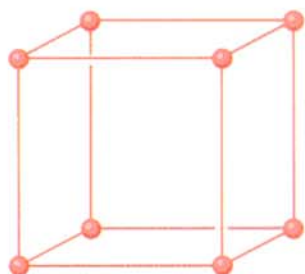
Rhombohedral



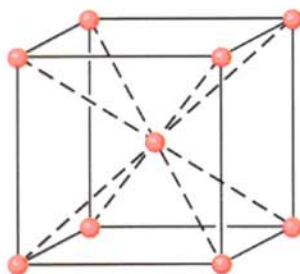
Hexagonal



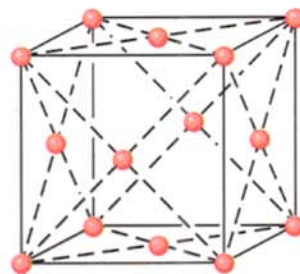
Triclinic



Simple cubic



Body-centered cubic

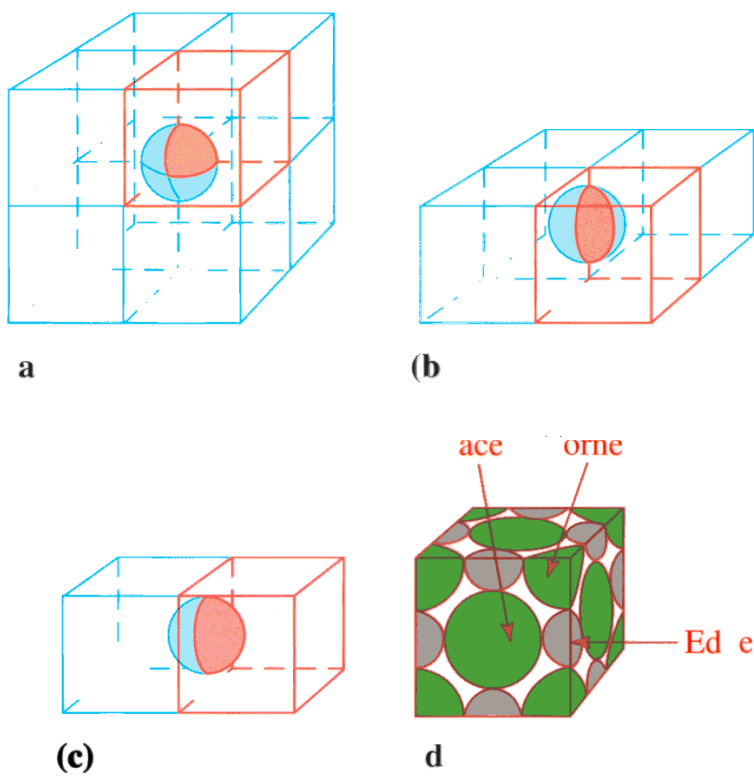


Face-centered cubic

(b)

Face and body-centered cubic cells.

In addition to the seven primitive cells just listed in part a of the figure, it is possible to overlay the primitive cells to create more sophisticated structures that share atoms. This is shown in part b of the figure, and more clearly, in the next figure. These include the body-centered cubic lattice and the face-centered cubic lattice that have additional atoms stuck into the simple cubic unit cell. In distinguishing these lattices, it is necessary to identify the sharing of atoms between unit cells. Atoms can either be in the center of a lattice, on the face or side of a lattice, or on the corner of a lattice. In examining a large crystal, it is important to identify the simplest structure that defines the crystal.



And now for some very good news:

You are responsible for knowing the nomenclature (definitions) for the material on solids. You are not responsible for learning the various types of crystal structures or their common examples. Just be aware the very few geometric shapes just described can be used to identify all crystalline structures. These can be verified experimentally by using a process called X-ray diffraction, which shoots X-rays at a rotating crystal sample and detects the direction in which the X-rays bounce off of the atoms in the crystal. Each unit cell yields a distinctly different pattern.

Bonding in Solids. The final subject of this chapter is bonding in solids. Again, a detailed discussion of bonding is outside the bounds of this course. However you have learned enough about chemical bonding to be able to distinguish four categories of bonds formed in solids. You will be given various solids and asked to place them into each of the categories below.

- Metallic: bonds between metals like sodium: Na-Na-Na-Na
- Ionic: Bonds between anions and cations: Na^+ and Cl^-
- Molecular: Intermolecular bonds between molecules:
sugar-sugar-sugar
- Covalent: bonds between non metallic atoms: C-C-C-C

Some hints for categorizing.

Ionic solids: It is pretty obvious when you have an ionic compound. These are the salts with which you are familiar like CaCl_2 or AgNO_3 .

Metallic solids: These are pretty obvious too. If it is a metal, then it is a metallic bond. Remember the metals are found to the left side of the periodic table.

Covalent solids: This is the tricky part. Compounds on the far right of the periodic table that form solid materials through covalent bonds are covalent solids. Example include graphite or sand (SiO_2 .)

Molecular solids: These are compounds that also are formed by covalent bonds, **BUT ARE NOT SOLIDS AS INDIVIDUAL MOLECULES**. Compounds like H_2O are formed first by covalent **intramolecular** bonds, but form solids through **intermolecular** interactions.

So in a nutshell, the latter two categories are distinguished this way:

If the solid is formed through **intermolecular** interactions, then it is a **molecular** solid.

If the solid is formed through **intramolecular** bonds, then it is a **covalent** solid.