

## Intermolecular forces

Recall the following:

1) While **intramolecular** forces hold atoms together to form molecules, **intermolecular** forces make one molecule or ion attract another.

2) As intermolecular forces increase, these physical properties are affected:

- melting point (MP) increases
- boiling point (BP) increases
- vapor pressure (VP) decreases
- enthalpy of vaporization  $\Delta H_{\text{vap}}$  increases
- capillary action may increase
- surface tension may increase

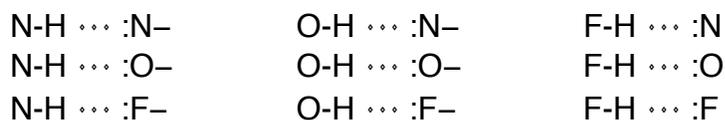
3) Strength of intermolecular forces (strongest force / highest polarity on top)

- ion-ion
- ion-dipole
- hydrogen bonding
- dipole dipole
- dipole-induced dipole
- induced-dipole induced dipole (London forces, Van der Waals forces)

4) Ion-ion forces increase with increasing charge and decreasing size of ions.

5) Dipole-dipole forces increase between molecules having larger permanent dipoles as caused by larger electronegativity differences between atoms and less symmetry.

6) Hydrogen bonding is a special case of the dipole-dipole force that occurs when one of the nine patterns below occurs between two molecules (the pattern involves nitrogen, oxygen, or fluorine bonded to hydrogen and another nitrogen, oxygen or fluorine atom with a lone pair):



**Induced-dipole induced-dipole forces** (also called London forces, London dispersion forces, Van der Waals forces, and nonpolar forces) are dominant among nonpolar molecules and increase with increasing molar mass. The trend of increasing strength is explained as follows: as molar mass increases, the induced dipole increases because the electrons in larger species are less tightly held allowing the electrons to be more easily polarized. Polarizability increases with increased molar mass.

Here is an explanation of polarizability:

- Induced-dipole induced-dipole forces result from momentary distortion of electron clouds which cause momentary attractions between molecules.

- Induced-dipole induced-dipole forces are present between all molecules (even if another intermolecular force dominates in strength).
- Induced-dipole induced-dipole forces dominate in species that are nonpolar (or with polar bonds and symmetrical), such as  $\text{CH}_4$ ,  $\text{SF}_6$ , Ne,  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ , and  $\text{H}_2$ . Unless you mastered the skill in Chem I, draw the Lewis structure of a molecule and apply VSEPR theory to see if the molecule is symmetrical. Try this example: <http://www.youtube.com/watch?v=3lcD43aUhtA&NR=1>

**London dispersion** (induced-dipole induced dipole) forces explain why  $\text{I}_2$  is a solid,  $\text{Br}_2$  is a liquid, and  $\text{Cl}_2$  is a gas at room temperature.

- London forces are the dominant force because these molecules are all nonpolar. London forces increase with increasing molar mass causing the melting and boiling points to increase with increasing molar mass.

Because **Van der Waals** (induced-dipole induced dipole) forces are so weak, nonpolar molecules are more likely to sublime than to melt. For example, iodine sublimates,  $\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g})$ , at room temperature and pressure. (You should have done this experiment in lab.) Mothballs also sublime.

As molar mass increases, induced-dipole induced-dipole forces increase, and boiling point increases. For example, this series of nonpolar molecules shows that relationship:  $\text{CH}_4$  (methane, MM 16, BP  $-164^\circ\text{C}$ ),  $\text{C}_2\text{H}_6$  (ethane, MM 30, BP  $-89^\circ\text{C}$ ),  $\text{C}_3\text{H}_8$  (propane, MM 44, BP  $-42^\circ\text{C}$ ), and  $\text{C}_4\text{H}_{10}$  (butane, MM 58, BP  $0^\circ\text{C}$ ).

**Dipole-induced dipole forces** occur between a nonpolar molecule and a polar one.

- Dipole-induced dipole forces increase with increasing molar mass and increasing dipole strength. Stronger dipoles are better able to induce dipoles in nonpolar substances.
- Dipole-induced dipole forces enable a nonpolar molecule, such as  $\text{O}_2$ , to dissolve appreciably in a polar substance, such as water. This data shows the trend of increasing molar mass increasing the solubility of gases in water:  $\text{H}_2$  (MM 2, solubility 0.00016g/100g  $\text{H}_2\text{O}$ ),  $\text{N}_2$  (MM 28, solubility 0.0019g/100g  $\text{H}_2\text{O}$ ), and  $\text{O}_2$  (MM 32, solubility 0.0043g/100g  $\text{H}_2\text{O}$ ).

Real molecules often have a combination of intermolecular forces. However, a dominant intermolecular force may be sufficient to describe or rank physical properties such as melting point, boiling point, vapor pressure, and enthalpy of vaporization.

**'Like dissolves like' rule:** substances with a given polarity (intermolecular force) tend to dissolve other substances with a similar polarity. Using this rule, we predict correctly that methanol ( $\text{CH}_3\text{OH}$ ) dissolves in water. We predict correctly that butane ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ ) dissolves in hexane ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ). We predict correctly that silver metal dissolves in mercury metal. This is a very helpful rule to predict solubility of substances in other substances. Note that a limited amount of dissolving may occur, as explained above, when the intermolecular forces do not match.

The following paragraphs **describe liquids and their properties (condensing, evaporating) using intermolecular forces**:

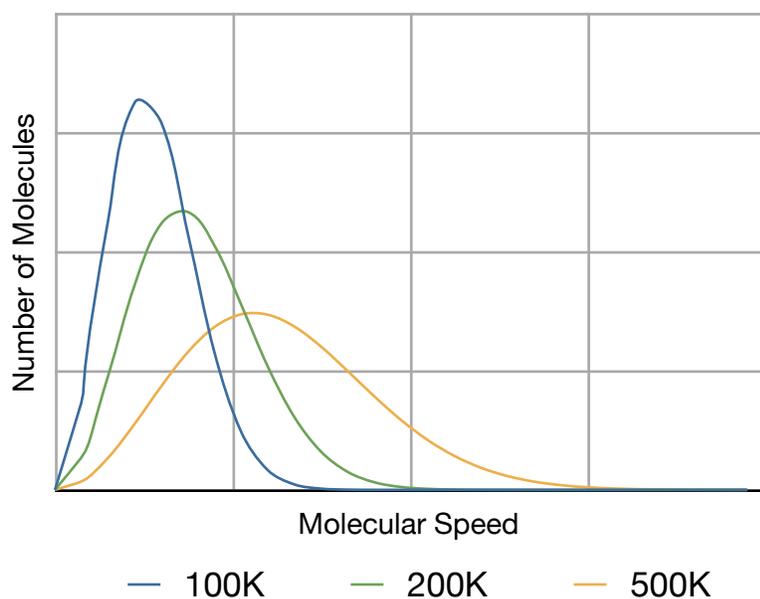
- molecules and/or atoms are in constant motion
- intermolecular forces are larger than for gases but smaller than for solids
- molecules and/or atoms are close together
- incompressible
- do not completely fill containers (only the portion that they occupy)

Liquids evaporate and can be condensed from gases. Evaporating requires **kinetic energy** (heat) to break intermolecular forces, so evaporation is an **endothermic process**. Opening the valve of a lighter causes gas to evaporate, which requires energy to break intermolecular forces (an endothermic process), so the temperature of the lighter goes down making it feel cold to the touch.

**Condensing** makes/releases the energy stored by intermolecular forces. Condensing releases kinetic energy (heat), so condensation is an **exothermic process**.

Liquids have a distribution (or range) of kinetic energies (given by Maxwell's distribution). A certain (or target) kinetic energy is needed for a molecule or atom to escape a liquid, where the kinetic energy is related to the speed of a molecule. Raising the temperature of a liquid increases the speed and the kinetic energy, which increases the fraction of species that have the required energy to escape. In the yellow curve (500K), a greater fraction of molecules has the kinetic energy (based on having a particular molecular speed) to escape the liquid, as compared to the green (200K) and blue (100K) curves.

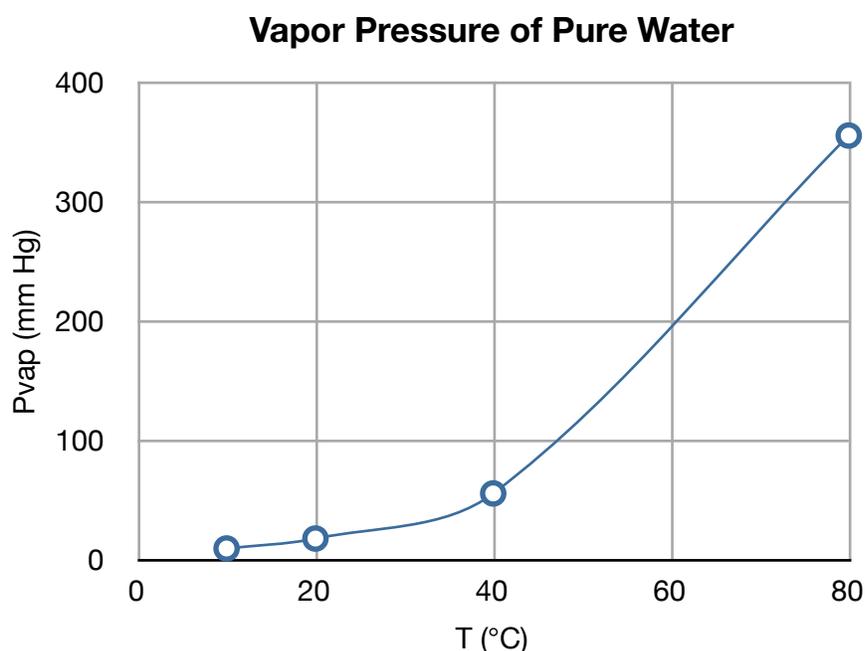
### Distribution of Molecular Speeds



### Vapor Pressure ( $P_{\text{vap}}$ )

Gases above liquids have a vapor pressure that arises from particles escaping the liquid. The equilibrium vapor pressure is the pressure exerted by a vapor over a liquid when the evaporation rate equals the condensation rate (note that solids and gases also have equilibrium vapor pressures). When we compare two different substances with different intermolecular forces, as the strength of intermolecular forces increases, the vapor pressure decreases. If substance 2 has stronger intermolecular forces than substance 1, it will have a lower vapor pressure than substance 1. Stronger intermolecular forces mean decreased equilibrium vapor pressure. As temperature increases, a greater fraction of molecules have the energy to escape.

The graph below shows the equilibrium vapor pressure ( $P_{\text{vap}}$  in mmHg) for pure water under one atmosphere of pressure as the temperature ( $^{\circ}\text{C}$ ) increases. Applying the previous discussion, the expectation is that the vapor pressure would increase as the temperature increases. In fact, the vapor pressure does increase with increasing temperature, but not in a linear fashion.



### Relationship between $P_{\text{vap}}$ , $T$ , and $\Delta H_{\text{vap}}$

For a given substance, such as pure water, a plot of the natural log of the equilibrium vapor pressure versus the reciprocal of the absolute temperature (in Kelvin) gives a linear relationship with a slope of  $-\Delta H_{\text{vap}}/R$ , where  $R$  is the gas constant ( $8.314 \text{ J/mol K}$ ). This is the most important point to remember. Mathematically this relationship is:  $\ln(P_{\text{vap}}) = -\Delta H_{\text{vap}}/R (1/T) + C$ , which is known as the Clausius Clapeyron equation. An example appears below. If you measured the vapor pressure of pure water at different temperatures in lab, you could collect these data and make these graphs.

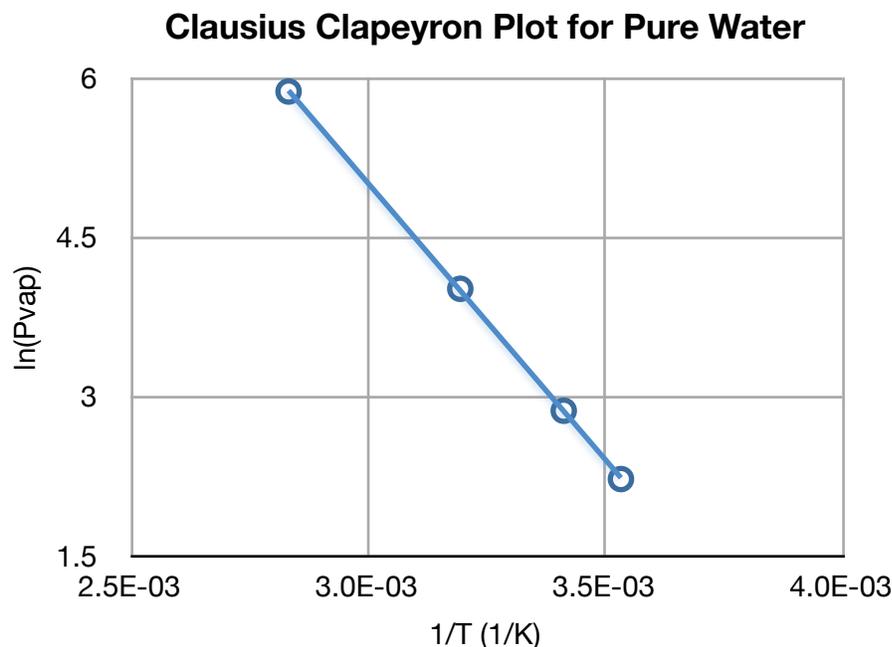
The data below for the vapor pressure of pure water and temperature are from Perry's Chemical Engineers' Handbook, 6th ed. McGraw Hill, 1984, p3-45.

Temperature (°C)	Vapor Pressure (mmHg)
10.	9.209
20.	17.535
40.	55.324
80.	355.1

When graphed, these data give the curved relationship shown in the previous figure, titled "Vapor Pressure of Pure Water." To get a linear relationship from these data using the Clausius Clapeyron equation, calculate  $1/T$  and  $\ln(P_{\text{vap}})$  as shown in the table below.

$1/T$ (1/K)	$\ln(\text{Vapor Pressure})$
$3.53 \times 10^{-3}$	2.22
$3.41 \times 10^{-3}$	2.86
$3.19 \times 10^{-3}$	4.01
$2.83 \times 10^{-3}$	5.87

A plot of the data in the table above appears in the figure below, "Clausius Clapeyron Plot for Pure Water." The slope of this line is  $-5200$  K. According to the Clausius Clapeyron equation, the slope is equal to  $-\Delta H_{\text{vap}}/R$ . Solving for  $\Delta H_{\text{vap}}$ , gives:  
 $\Delta H_{\text{vap}} = (-5200 \text{ K}) \cdot (8.314 \text{ J/mol K}) = 43000 \text{ J/mol} = 43 \text{ kJ/mol}$ .



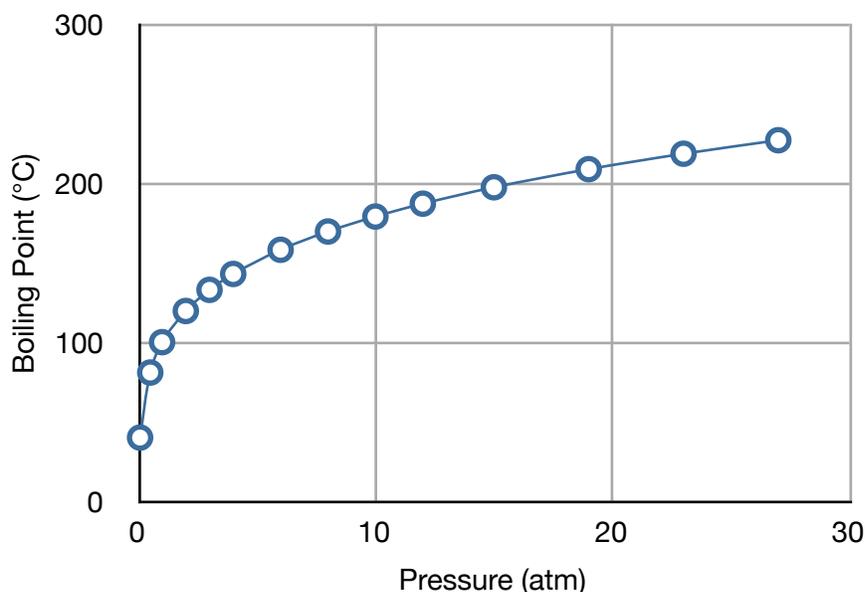
Again, the most important point is that a plot of the natural log of the equilibrium vapor pressure,  $\ln(P_{\text{vap}})$ , against the reciprocal of the Kelvin temperature ( $1/T$ ) gives a line with slope  $-\Delta H_{\text{vap}}/R$ . The above example shows how the analysis to calculate  $\Delta H_{\text{vap}}$  would be done.

**Relationship Between Enthalpy of Vaporization ( $\Delta H_{\text{vap}}$ ) and Equilibrium Vapor Pressure ( $P_{\text{vap}}$ ) when comparing two different substances at a given temperature**  
 $\Delta H_{\text{vap}}$  is related to the equilibrium vapor pressure of a given substance. When comparing two different substances at a given temperature, a higher  $\Delta H_{\text{vap}}$  for the first substance means to expect a lower vapor pressure for that substance as compared to the second one. Likewise, a higher equilibrium vapor pressure ( $P_{\text{vap}}$ ) for the second substance at a given temperature means that the first substance will have a higher  $\Delta H_{\text{vap}}$ .

### Effect of External Pressure on Boiling Point

Liquids boil when their vapor pressure equals atmospheric pressure. The boiling points of substances goes down as altitude increases because the pressure of the atmosphere decreases as altitude increases. Water boils at a lower temperature on top of a mountain than at sea level because the pressure of the atmosphere is greater at sea level. The **normal boiling point** of a substance is the temperature at which the liquid exerts a vapor pressure of 1 atmosphere (atm) = 760mmHg. Water has a normal boiling point of 100°C. Substances can boil at lower temperatures if we decrease the external pressure by applying a vacuum. (This trick is used commonly in organic synthesis.) To make water boil at a higher temperature, increase the pressure (such as in a pressure cooker). The graph below shows the expected boiling point of water (in °C) at different applied pressures (atm). Data for the graph came from Lange's Handbook of Chemistry, thirteenth edition, McGraw Hill, 1985, p10-54. When the applied pressure is 1atm, the boiling point is 100°C. When the applied pressure is 10 atm, the boiling point is 179°C. when the applied pressure is 0.072atm, the boiling point is 40°C.

**Boiling Point of Water**



**Using Trends in Intermolecular Forces to Predict Relative Boiling Points, Equilibrium Vapor Pressures, and Enthalpies of Vaporization.**

Predict the relative boiling points of these molecules:

- ethyl alcohol (ethanol):  $C_2H_5-OH$
- diethyl ether (ethoxyethane):  $C_2H_5-O-C_2H_5$
- Water:  $H_2O$

First (draw the Lewis structure) rank the dominant intermolecular force. Water and ethanol have hydrogen bonds and diethyl ether has dipole-dipole forces as the strongest intermolecular force (note that they all have London forces, but we are considering the dominant intermolecular force - number and type).

At this point ethoxyethane is expected to have the lowest boiling point. This is true: BP=35°C, MM=74. Water can extensively hydrogen bond (2 OH bonds per molecule and 2 lone pairs on each oxygen, whereas ethanol cannot, 1 OH bond per molecule). Using this data we predict BP (water > ethanol > ethoxyethane). This is true: BP (ethanol)=78°C and MM=46, and BP(water)=100°C, MM=18. Note that the boiling point depends less on molar mass because London forces are substantially weaker than dipole-dipole forces and hydrogen bonding. Conversely, if London forces were dominant, then the boiling points would have increased with increasing molar mass (not observed for the previous series).

As the intermolecular forces in liquids increases,  $\Delta H_{vap}$  increases. The heat of vaporization ( $\Delta H_{vap}$ ) is the heat required to vaporize a liquid at constant pressure. Stronger intermolecular forces means more heat energy needed to vaporize which means a higher  $\Delta H_{vap}$ .

Predict the relative melting points, boiling points, vapor pressures, and  $\Delta H_{vap}$  of these molecules:

- hexane:  $C_6H_{14}$
- heptane:  $C_7H_{16}$
- pentane:  $C_5H_{12}$

You should have learned in CHEM I that hydrocarbons (exclusively contain carbon and hydrogen) are considered nonpolar. Using the table below, the bond electronegativity difference between carbon and hydrogen is 0.5 (see electronegativity table); however most of the bond polarity cancels because of symmetry (draw the Lewis structure and apply VSEPR theory). Hexane, heptane, and pentane are nonpolar.

Electronegativity																	
H																	He
2.1																	--
Li	Be											B	C	N	O	F	Ne
1.0	1.6											2.0	2.6	3.0	3.4	4.0	--
Na	Mg											Al	Si	P	S	Cl	Ar
0.9	1.3											1.6	1.9	2.2	2.6	3.2	--
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.8	1.0	1.4	1.5	1.6	1.7	1.6	1.8	1.9	1.9	1.9	1.7	1.8	2.0	2.2	2.6	3.0	--
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
0.8	1.0	1.2	1.3	1.6	2.16	1.9	2.2	2.3	2.2	1.9	1.7	1.8	2.0	2.1	2.1	2.7	--
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
0.79	0.89		1.3	1.5	2.4	1.9	2.2	2.2	2.3	2.5	2.0	2.0	2.3	2.0	2.0	2.2	--
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Uun								
0.7	0.89		--	--	--	--	--	--	--								
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
1.10	1.12	1.13	1.14	1.13	1.17	1.2	1.20	1.1	1.22	1.23	1.24	1.25	1.1	1.27			
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			
1.1	1.3	1.5	1.38	1.38	1.36	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3			

Therefore, the dominant intermolecular forces in hexane, heptane, and pentane are induced-dipole induced dipole forces. Relative melting point (MP), boiling point (BP), and vapor pressure (VP) can be predicted by comparing molar mass (MM). Because the  $MM(\text{heptane}) > MM(\text{hexane}) > MM(\text{pentane})$ , we expect that  $BP(\text{heptane}) > BP(\text{hexane}) > BP(\text{pentane})$ ,  $MP(\text{heptane}) > MP(\text{hexane}) > MP(\text{pentane})$ ,  $VP(\text{heptane}) < VP(\text{hexane}) < VP(\text{pentane})$ , and  $\Delta H_{\text{vap}}(\text{heptane}) > \Delta H_{\text{vap}}(\text{hexane}) > \Delta H_{\text{vap}}(\text{pentane})$ . Pentane has the highest vapor pressure, the lowest boiling point, the lowest melting point, and the lowest  $\Delta H_{\text{vap}}$ , which can be confirmed by looking up these quantities in the correct tables. Try using your textbook or an online search engine to find the information.

Which of these substances has the strongest intermolecular forces: Xe  $\Delta H_{\text{vap}}(13\text{kJ/mol})$ ,  $\text{H}_2\text{O}$   $\Delta H_{\text{vap}}(41\text{kJ/mol})$ , and  $\text{SO}_2$   $\Delta H_{\text{vap}}(27\text{kJ/mol})$ ?

A larger  $\Delta H_{\text{vap}}$  means stronger intermolecular forces, so water has the strongest intermolecular forces (hydrogen bonds), followed by  $\text{SO}_2$  (dipole-dipole forces), followed by Xe induced-dipole induced-dipole forces). (As indicated previously, draw the Lewis structures and apply VSEPR theory to determine molecular polarity as you learned in CHEM I.) Note that we expect other physical properties, such as boiling point, to follow the trends in  $\Delta H_{\text{vap}}$ , giving  $BP(\text{H}_2\text{O})=100^\circ\text{C} > BP(\text{SO}_2)=-10^\circ\text{C} > BP(\text{Xe})=-108^\circ\text{C}$ .

**Surface tension** is the energy required to break the surface of a liquid. Surface molecules experience a net force toward the inside of a liquid, which leads to the

formation of spherical droplets. Surface tension may increase with increasing intermolecular forces. Surface tension is the physical property that allows some insects to walk on water. Surface tension can be broken by adding soap or a solvent to water.

**Capillary action** is related to intermolecular forces that allow liquid species to climb the sides of a glass or up a paper towel (or inside a plant). Intermolecular forces (as well as bonds) may hold the liquids and solids together; however, the liquid must be more attracted to the solid support than to itself for capillary action to occur.

The following paragraphs **describe physical properties of solids in terms of intermolecular forces**.

Silicon (and diamond) are network solid because atoms of silicon have chemical bonds to other atoms of silicon. The chemical bonds are located between the silicon atom centers. Silicon is a hard substance that does not readily conduct electricity (it is a semiconductor). Diamond does not readily conduct heat or electricity.

Aluminum, and other metals, are metallic solids, where electrons are fairly equally shared among all other atoms, rather than just between atom centers as in the case of silicon. The bonding gets a special class, metallic bonding, because the sharing of electrons is different than for network solids. Aluminum, and other metals, are good conductors of heat and electricity because of the ease of electron movement. Metals are often ductile (can draw into wires) and malleable (hammer out a shape) for similar reasons of electrons being communally shared.

Potassium bromide is an ionic solid (salt) that is held together by strong ion-ion intermolecular forces. Electrons have been exchanged, so they are not free to easily move about to conduct heat or electricity. Salts are hard, brittle, and can often be cleaved along crystal boundaries. (Melting the salt allows the ions to move and conduct electricity).

Plastics (such as polyethylene) are amorphous solids. The molecules in plastic are held together by covalent bonds, but one polyethylene molecule is held to another by induced-dipole induced-dipole forces. This gives rise to flexibility. Plastic containers are often flexible.

The type of solid that forms for a substance depends on the intermolecular and intramolecular forces that exist. Ice and iodine form molecular solids that relate to hydrogen bonding and induced-dipole induced-dipole forces respectively.

Ionic solids (strong ion-ion intermolecular forces) often arrange in crystal lattices that are closely packed, highly order, and almost incompressible. The **unit cell** is the smallest repeating unit of a solid that has a symmetry that is characteristic of the solid. Crystal lattices are made of unit cells. Metals also arrange in unit cells (see the periodic table in the lab for the unit cell structure of metals).

The composition of three cubic unit cells for metallic solids are discussed here: simple cubic (SC), body-centered cubic (BCC), and face-centered cubic (FCC). A **simple cubic** unit cell has eight atoms located on the corners of a cube. The corners of the cube are shared with eight other surrounding cubes, so the corners of a unit cell are  $1/8$ th contained by the unit cell. As a result, a simple cubic unit cell contains 8 corner atoms  $(1/8) = 1$  atom. A simple cubic unit cell contains 1 atom. A **body-centered cubic** unit cell is like a simple cubic unit cell with an extra atom located in the center (completely contained in the unit cell). The number of atoms in a body-centered cubic unit cell is given by 8 corners  $(1/8) + 1 = 2$  atoms. A body-centered cubic unit cell contains two atoms. A **face-centered cubic** unit cell is like a simple-cubic unit cell with 6 extra atoms that are located on each face of the cube. Faces of a cube are shared with one other unit cell, so atoms on a face are half contained in a unit cell. A face-centered cubic unit cell of a metal contains 8 corners  $(1/8) + 6$  faces  $(1/2) = 4$  atoms.

Some **ionic compounds form using the SC or FCC unit cell**. When they do form, ions of the opposite charge occupy the holes in the lattice. For example, certain 1:1 salts form with the cation in the center of a SC unit cell and the anions on each corner. The one center atom is 100% contained in the unit cell, while the eight corners are  $1/8$ th contained. This gives a 1:1 salt. (An equivalent view of the unit cell for this salt would be to have the anion in the center and the eight cations at the corner). Both ions would need to be +1, +2, or +3 to form with this unit cell.

The FCC unit cell has two types of holes (the SC unit cell had only one type of hole). The first type of hole is an octahedral hole with six nearest neighbors. The center of an FCC unit cell has one octahedral hole. The 12 edges of the FCC unit cell have the remaining octahedral holes. An edge is  $1/4$ th contained in the unit cell. Counting octahedral holes gives  $1 + 12$  edges  $(1/4) = 4$ . Recall that FCC unit cells also contained 4 metal atoms. A 4:4 ratio also makes 1:1 salts. As with ionic compounds with SC unit cells, the cation and anion would each need to be +1, +2, or +3 to form using the octahedral holes in this unit cell. A second type of hole exists in the FCC lattice, a tetrahedral holes. There are 8 tetrahedral holes completely contained in the FCC unit cell. When half of the tetrahedral holes are occupied, 1:1 salts form. When all of the tetrahedral holes are occupied, 1:2 or 2:1 salts form. More complicated salts require other unit cells than those that are covered here.