

# Chapter 11: Forces Between Molecules and the Liquid State

## Introduction

Why is the mineral quartz a solid? Why is water a liquid? Why does it freeze? Why does salt dissolve readily in water, but not sand? Why is one plastic hard, while another is flexible and soft?

### CHAPTER INTRODUCTORY MODULE

*Video introductory module with things in different phases, and maybe some animations on the molecular scale?*

The answers to these questions rest on the interactions between individual molecules and ions: generally referred to as intermolecular forces, or IMFs for short.

Through this point, we have described the structures of individual atoms and individual molecules in great detail. For atoms, we have centered on the structure the electrons take about the nucleus and for molecules, we have centered on the arrangement of terminal atoms about a central atom. We are now ready to move to the next level of complexity in chemical systems: how collections of molecules interact and how those interactions control the physical properties of matter. Indeed, our understanding of the physical properties of matter arises from our understanding of the nature of smaller and smaller objects. The flow of thought is shown in Figure 11.1

atomic structure → molecular structure → polarity and polarizability → IMFs → physical properties

Figure 11.1 Flow of ideas relating to our understanding of physical properties.

### Relevance

Why is this important? Why do we care? Oh, let us count some of the many ways. Consider the refrigerator. It works using a coil containing a liquid that vaporizes readily under low pressure. The vaporization process absorbs energy, which makes the inside of the fridge cold. The amount of energy absorbed is directly related to how well adjacent molecules in the liquid adhere to one another. The more tightly they bind, the more energy absorbed in order to vaporize them. However, if the molecules bind too tightly to one another, the liquid simply will not vaporize under useful conditions. So, to be a useful refrigerant, a liquid must not have IMFs that are too weak and must not have IMFs that are too strong. They must be just right. This is not called the Goldilocks principle, but it could be.

Throughout the 1960s and 1970s, chlorofluorocarbons (CFCs) were used as refrigerants in refrigerators and air conditioners. Since then, as everyone knows, they were found to cause damage to the ozone layer in the upper atmosphere. The ozone layer absorbs UV radiation from the Sun that causes damage to humans, animals, and plants. When that was found out, everyone decided to not use them anymore

and the hunt for replacements was on. The molecules now in use are HCFCs (hydrofluorocholorocarbons) or HFCs (hydrofluorocarbons), which are similar in physical properties to CFCs, but more reactive. Ironically, CFCs turn out to be harmful to the ozone layer in part due to their chemical inertness. Because they are very unreactive, they do not break down in the lower atmosphere and can rise to the upper layers. HCFCs and HFCs are more reactive (though certainly not highly reactive by chemical standards) and break down well before being able to reach near the ozone layer.

## I. States of Matter

What is the difference, on the molecular scale, between a solid, a liquid, and a gas? Gaseous molecules are all separate and move about independently. Moreover, the distance between them is large compared to their size. Liquids and solids are called **condensed phases** because in both molecules are packed in close proximity to one another. This is easily observed by examining the densities of a substance in each of its three states. For water, the densities measured at 0 °C and 1 atm pressure are:

$$\text{H}_2\text{O}(\text{g}) \quad 0.000804 \text{ g/cm}^3$$

$$\text{H}_2\text{O}(\text{l}) \quad 0.9999 \text{ g/cm}^3$$

$$\text{H}_2\text{O}(\text{s}) \quad 0.9150 \text{ g/cm}^3$$

It appears from the densities that the liquid and solid states involve packing of water molecules that are within a few percent of each other. The gaseous state is about 1/1200 as dense as either of the condensed phases. This means that water molecules in the gaseous state are spaced about 11 times farther apart than in the liquid or solid states. A 2-dimensional view of how the solid, liquid and gaseous states appear on the molecular scale is shown in Figure 11.2.

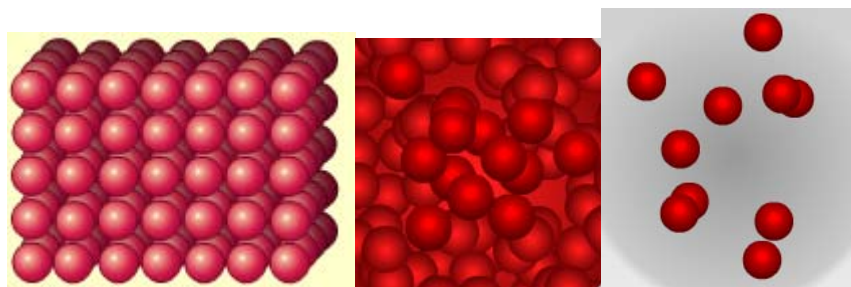


Figure 11.2: Solids have molecules close together and held in place. Liquids have molecules close together but in a random network. The molecules of the liquid can move past one another. Gases have molecules far apart from one another.

If the liquid and solid states are so similar to each other on the molecular scale, in what way do they differ? The main point of difference is the relative movement of molecules in relation to neighboring

molecules. In a solid, each molecule can vibrate and rotate in place, but cannot change places or move past other molecules. That is, they can wiggle around, but they can't go anywhere. In a liquid, by contrast, molecules stay close to each other but they readily move past each other.

A human analogy is helpful here. Imagine that each student on your campus is a molecule. When you are sitting in a large lecture hall, you and the other students are collectively acting as a solid. You can move about in your seat, turn around and the like. But, you do not readily change seats with other students during the class period. The students are solid.

Now imagine a crowded, really crowded, dance floor (if that's what it's even called anymore). You are just as close to your neighbors as you were in lecture, if not closer, but now you are free to move about and change who you are near. (The analogy, of course, breaks down when talking about forces of attraction. For molecules, those in the solid state are experiencing stronger forces of attraction to one another than in the liquid state. Students probably experience stronger attractions at the dance place than in lecture.)

The gaseous state is represented by the students moving about between classes. Each goes his or her own way, briefly interacting but mainly moving independently of one another.

*Imagine photos of three states represented by students.*

This ability of liquid molecules to move past one another is the reason a liquid flows. When you pour a glass of water, the molecules are all tumbling over one another as they move due to the force of gravity. A solid does not do this. In a solid, the force of gravity is resisted by the forces holding the molecules in place. When you first take an ice cube out of the freezer, it does not flow down to the lowest point but instead holds its shape- the water molecules are each holding those around it in place. As it melts, though, the molecules in the newly formed liquid state can move past one another and, in a word, drip.

## II. Properties of Liquids

The forces that hold molecules in the liquid and solids states near one another are called **intermolecular forces**, or IMFs for short. These forces are different than chemical bonds: they do not account for atoms staying near each other in a molecule; instead, they account for one molecule staying near another molecule.

Another human analogy: a chemical bond is like that bond that holds your arms to the rest of your body. An intermolecular force is like the force that leads you to hang out with another person.

All liquids share some basic properties:

They flow.

They fit the shape of their container.

They have the potential to boil or evaporate over time, depending on temperature.

These similarities come from all liquids having IMFs of intermediate strength. Were the IMFs much weaker, the compound would be a gas. If they were much stronger, it would be a solid.

So, all liquids share certain properties but they clearly have many differences. Antifreeze, for example, has a lower freezing point than water. It also has a higher boiling point. Ethanol evaporates more readily than does water, as is seen with warm alcoholic drinks. Some liquids, like honey, are very viscous (they are “thick”) while others, like gasoline, have low viscosity (they are “thin”).



Wine is a solution of ethanol in water, along with some other hopefully good tasting flavor molecules. Although difficult to see in the glass, the reflection on the background clearly shows evaporated “legs.” This comes about from the ethanol, which has a lower boiling point, evaporating from the solution and recondensing on the cool glass surface.

These differences come mostly from the strength by which the IMFs hold the molecules near one another, and to some extent, by the shapes of the molecules and how they entangle. The stronger the IMFs, the harder to break the molecules apart; the weaker the IMFs, the easier molecules in a liquid can be pulled separated.

There are four properties of liquids we will explore here: enthalpy of vaporization, vapor pressure, boiling point, and surface tension. Each is described below in general terms of intermolecular force strength. The following section examines the detailed relationship between molecular structure and IMF strength.

## II a. Enthalpy of Vaporization

Enthalpy of vaporization is the energy needed to vaporize a given amount of a liquid to yield the corresponding gas. Enthalpy of vaporization values are generally given in units of energy per gram or energy per mole. The enthalpy of vaporization for water at XX oC is YYY kJ/mol. Some other values are given in Table 11.1. Enthalpy of vaporization depends strongly on molecular structure, but is nearly independent of temperature.

**Table 11.1 Enthalpy of Vaporization Values**

| Compound                        | Molar Mass  | Enthalpy of Vaporization |
|---------------------------------|-------------|--------------------------|
| He                              | 4.00 g/mol  | 0.0828 kJ/mol            |
| Ar                              | 39.9 g/mol  | 6.43 kJ/mol              |
| CH <sub>4</sub>                 | 16.01 g/mol | 8.17 kJ/mol              |
| CH <sub>3</sub> CH <sub>3</sub> | 30.06 g/mol | 14.7 kJ/mol              |
| CH <sub>3</sub> OH              | 32.04 g/mol | 35.4 kJ/mol              |
| H <sub>2</sub> O                | 18.02 g/mol | 40.7 kJ/mol              |

A liquid's enthalpy of vaporization is a direct indication of the strength of its IMFs. From Table 11.1 we can infer that Ar has greater IMF strength than does He and that H<sub>2</sub>O has stronger IMFs than CH<sub>3</sub>OH.

Enthalpy of vaporization values tend to be much smaller than the energies of chemical bonds. This is why when a liquid is heated, it generally will boil (a physical change where intact molecules are separated from one another) before it decomposes (a chemical change where bonds between atoms within molecules are broken, resulting in a new compound). For example, the enthalpy of vaporization of H<sub>2</sub>O is 40.7 kJ/mol. This is much smaller than the O-H bond energy of 463 kJ/mol. So, when water is heated, the energy is first used to vaporize the water by separating the molecules. In order to break the O-H bonds, the temperature would need to be increased to a very high value.

## II b. Vapor Pressure

*BBQ introduction video. Showing that propane C<sub>3</sub>H<sub>8</sub> is stored in a steel container, while the larger hydrocarbon butane, C<sub>4</sub>H<sub>10</sub>, can be stored in a plastic container.*

All liquids (and solids for that matter) exhibit a vapor pressure. Consider a liquid in an evacuated, sealed flask. Some of the molecules at the surface of the liquid can escape into the gas phase. These molecules in the gas phase exert a pressure. This pressure is like any other gas pressure, but is called a vapor pressure because it arises from the formation of a vapor from a liquid. At first this pressure increases as more molecules in the liquid evaporate but as more and more molecules are present in the gas phase, some of those will recondense, reentering the liquid phase. Eventually (actually in a few seconds in most cases) the rates of vaporization and recondensation will become equal and an equilibrium will be established. In this equilibrium state, vaporization and condensation both continue to occur but because

they do so at the same rate, the total amount of compound in the gaseous state will become constant. The pressure therefore also becomes constant, and is termed the equilibrium vapor pressure.

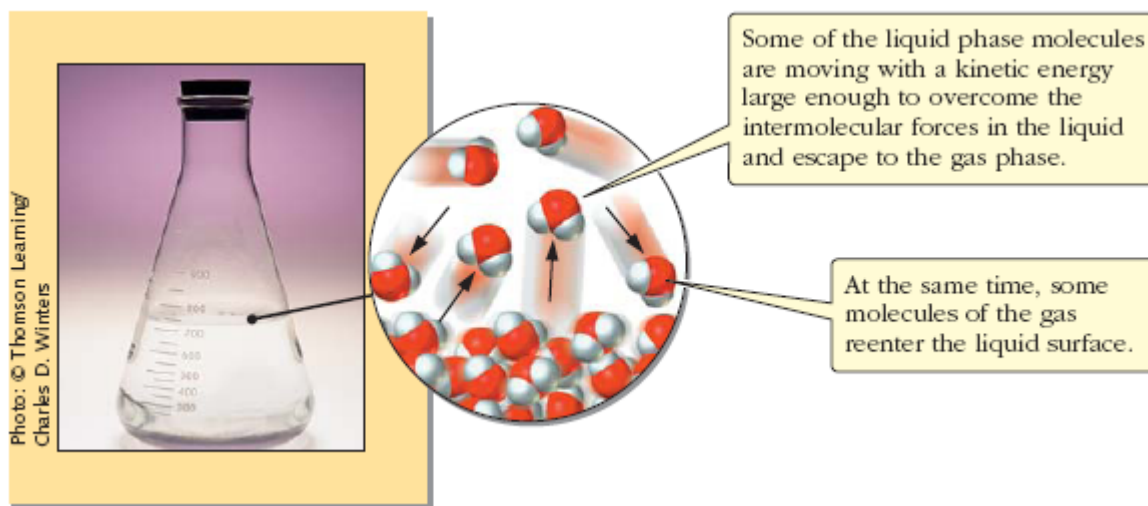


Figure 11.3. Molecular scale view of evaporation.

Vapor pressure values for some liquids measured at 25 °C are given in Table 11.2.

Table 11.2 Vapor Pressures of Liquids at 25 °C

| Compound                           | Molar Mass  | Vapor Pressure |
|------------------------------------|-------------|----------------|
| C <sub>5</sub> H <sub>12</sub>     | 72.15 g/mol | 514 mm Hg      |
| C <sub>6</sub> H <sub>14</sub>     | 86.18 g/mol | 152 mm Hg      |
| CH <sub>3</sub> OH                 | 32.04 g/mol | 143 mm Hg      |
| CH <sub>3</sub> CH <sub>2</sub> OH | 46.07 g/mol | 68 mm Hg       |
| H <sub>2</sub> O                   | 18.02 g/mol | 28 mm Hg       |

The vapor pressure of a liquid depends strongly on molecular structure and on temperature.

### **Vapor pressure and intermolecular force strength**

At any particular temperature, the energies of the molecules in a liquid are present at a range of energies. Like gases, this distribution of energies follows a Boltzmann distribution. Figure 11.4 shows such a distribution for water and methanol. We saw earlier that water has a larger enthalpy of vaporization than does methanol, and therefore has stronger IMFs. The two curves are identical because kinetic energy depends only on temperature, not on the nature of the molecules at that temperature.

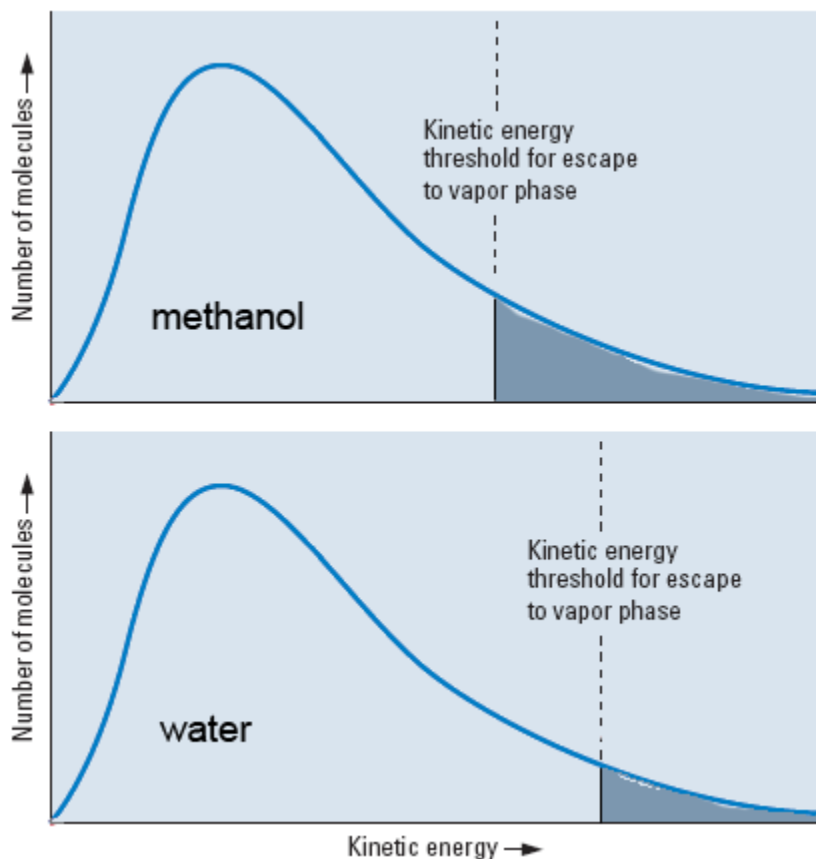


Figure 11.4 need to show two identical curves, but one with a low cutoff and a large fraction of molecules above the cutoff (low IMF liquid) and the other with a high cutoff and a small fraction of molecules above it (high IMF liquid)

However, an energy “threshold” is shown for the two liquids, indicating the energy above which a molecule needs to be in order to overcome its IMFs and break away from the other molecules in the liquid. Water has stronger IMFs, and therefore has a higher energy threshold. The fraction of molecules exceeding the energy needed to overcome their IMFs is represented by the area of the curve to higher energy (to the right) of the energy threshold. Because methanol has weaker IMFs than water, its energy threshold is lower, and a greater fraction of its molecules can overcome their IMFs. Therefore, at any given temperature, methanol will have more molecules in the gas phase and higher vapor pressure than water.

### **Vapor pressure and temperature**

Unlike a compound’s enthalpy of vaporization, vapor pressure is highly dependent on temperature. Figure 11.5 shows Boltzmann distribution curves for water at 25 °C and 50 °C.

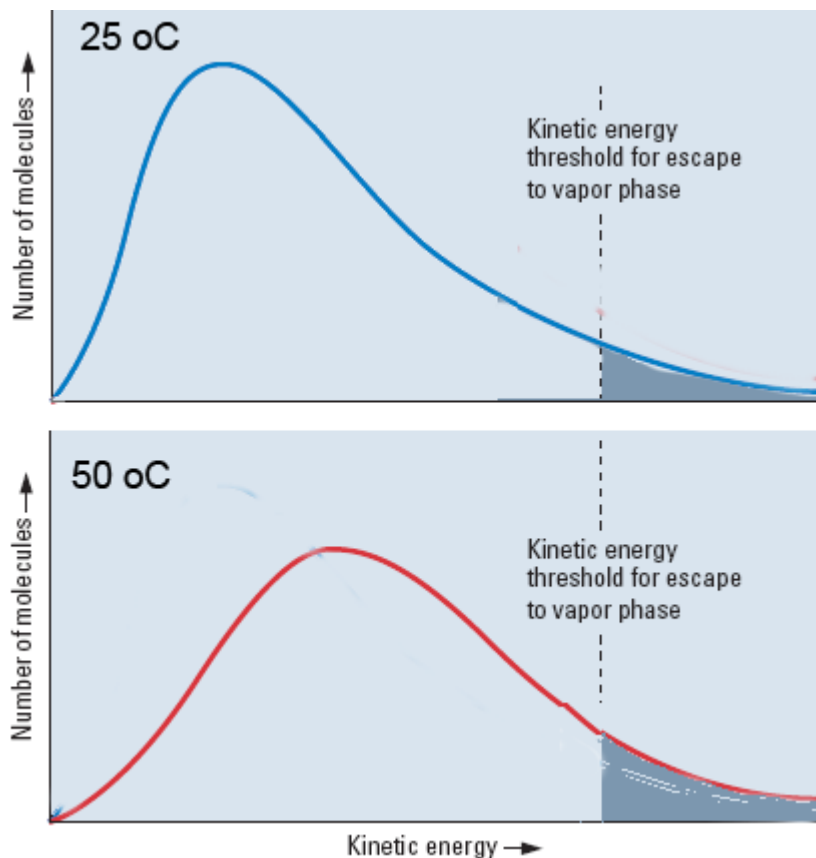


Figure 11.5. Boltzmann plots of a liquid sample at 25 °C and at 50 °C.

Because the molecules, on average, have greater kinetic energy at a higher temperature, the curve at 50 °C is shifted to the higher energy (to the right) from the 25 °C curve. The energy threshold for a water molecule is not a function of temperature, so the energy threshold is the same for both cases. A greater fraction of water molecules exceed the energy threshold needed to overcome their IMFs at 50 °C than at 25 °C. Therefore, at 50 °C more water molecules are in the gas phase and the vapor pressure is greater.

Figure 11.6 shows vapor pressure-temperature curves for carbon disulfide, methanol, ethanol, and heptane.



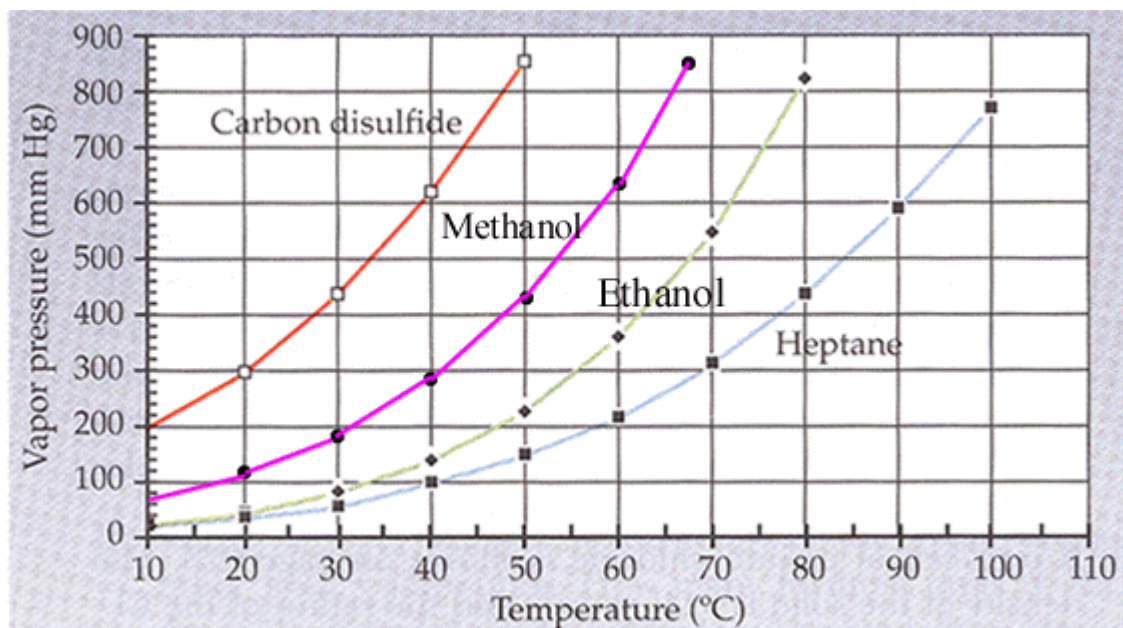


Figure 11.6. Vapor pressure vs. temperature plots for four compounds.

For each liquid, the vapor pressure increases with increasing temperature. This reflects the increasing fraction of molecules above the escape threshold as temperature increases. At any given temperature, however, the different liquids have different vapor pressures. This is a reflection of the different IMF strengths experienced by the different liquids. Of the four, carbon disulfide has the highest vapor pressure and therefore we know it has the weakest IMFs. Heptane has the lowest vapor pressure, so we know it has the strongest IMFs of the four.

### **Mathematical Treatment: The Clausius-Clapeyron Equation**

The equation governing vapor pressure must be a function of both IMF strength and temperature, and so it is. The Clausius-Clapeyron equation is given here. The IMF strength is accounted for in terms of the enthalpy of vaporization. The temperature,  $T$ , is in Kelvins, and  $R$  is the gas constant,  $8.314 \times 10^{-3}$  kJ/K·mol. In this form of the equation,  $C$ , is a constant of integration and is unimportant.

$$\ln P = \frac{-\Delta H_{\text{vap}}^{\circ}}{RT} + C$$

As expected, this equation predicts that large values of  $\Delta H_{\text{vap}}^{\circ}$  will lead to small values of pressure, whereas large values of  $T$  will lead to large values of  $\Delta H_{\text{vap}}^{\circ}$ .

### **Using the CC Equation 1: Predicting Vapor Pressure**

The CC equation can be used to predict the vapor pressure of a liquid if the both the enthalpy of vaporization and the vapor pressure at another temperature are known. To do this, the two-point version of the CC equation is used.

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{vap}^{\circ}}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

In this form, two temperature/vapor pressure pairs are compared. There are five variables:  $P_1$ ,  $P_2$ ,  $T_1$ ,  $T_2$ , and  $\Delta H_{vap}^{\circ}$ .

### Example: 11.1

#### Problem:

The vapor pressure of liquid **aluminum** is 400 mm Hg at **2.59E+3** K. Assuming that its molar heat of vaporization is constant at **296** kJ/mol, what will the vapor pressure of liquid **Al** be at a temperature of **2.56E+3** K?

#### Solution:

The Clausius-Clapeyron equation gives the variation of vapor pressure with temperature, assuming the value of the heat of vaporization to be constant over the temperature range in question. The two-point form of this equation is:

$$\ln \left( \frac{p_2}{p_1} \right) = - \left( \frac{\Delta H_{vap}}{R} \right) \times \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

where  $p_1$  and  $p_2$  are the vapor pressures of the substance at the Kelvin temperatures  $T_1$  and  $T_2$ , respectively,  $\Delta H_{vap}$  is the molar heat of vaporization of the substance, and  $R$  is the ideal gas constant.

The vapor pressures may be expressed in any self-consistent set of pressure units. The energy units for both  $\Delta H_{vap}$  and  $R$  must also be consistent.

In this case:

$$p_1 = 400 \text{ mm Hg}$$

$$T_1 = \mathbf{2.59E+3} \text{ K}$$

$$p_2 = ? \text{ mm Hg}$$

$$T_2 = \mathbf{2.56E+3} \text{ K}$$

$$\Delta H_{vap} = \mathbf{296} \text{ kJ/mol}$$

Using the value of 0.008314 kJ/mol K for  $R$  and substituting into the above equation gives:

$$\ln\left(\frac{p_2}{400 \text{ mm}}\right) = \frac{-296 \text{ kJ}}{\text{mol}} \times \frac{\text{mol K}}{0.008314 \text{ kJ}} \times \left(\frac{1}{2.56\text{E}+3 \text{ K}} - \frac{1}{2.59\text{E}+3 \text{ K}}\right)$$

Keeping extra significant digits in the intermediate values to avoid roundoff errors:

$$\ln(p_2 / 400 \text{ mm}) = \mathbf{-0.16109}$$

$$p_2 / 400 \text{ mm} = e^{-0.16109} = \mathbf{0.85122}$$

$$p_2 = \mathbf{0.85122} \times 400 \text{ mm} = \mathbf{340} \text{ mm Hg}$$

Note that  $T_2$  is **lower** than  $T_1$  and that the vapor pressure **decreases** as the temperature **decreases**.

### Using the CC Equation, Part 2: Determination of Enthalpy of Vaporization

Tabulated enthalpy of vaporization values are determined by measuring the vapor pressure of a liquid at various temperatures, employing the CC equation.

The general form of the CC equation can be slightly rewritten in the form of a straight-line equation.

$$\ln P = \frac{-\Delta H_{vap}^{\circ}}{R} \frac{1}{T} + C$$

$$y = m x + b$$

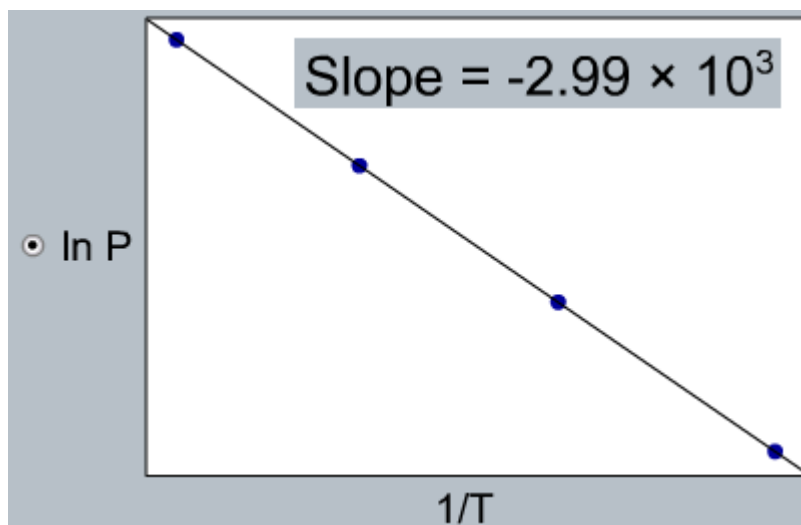
In order to determine a liquid's enthalpy of vaporization, the vapor pressure is measured over a range of temperatures. The natural log of the measured pressures ( $\ln P$ ) are plotted against their inverse temperatures ( $1/T$ ). The resulting linear plot has a slope of  $-\Delta H_{vap}^{\circ}/R$ .

#### Example 11.2

Consider the case of sulfur dioxide,  $\text{SO}_2$ . Its vapor pressure is measured at four temperatures with the following results.

| T, K | Pressure, mm Hg |
|------|-----------------|
| 220  | 81.6            |
| 230  | 147.4           |
| 240  | 253.6           |
| 250  | 417.7           |

These are plotted as  $\ln P$  vs.  $1/T$ .



*This needs units and tick marks and numbers. Just what any axis deserves.*

The slope can be used to determine the enthalpy of vaporization.

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

$$\Delta H_{\text{vap}} = -\text{slope} \times R = -(-2.99 \times 10^3)(8.314 \times 10^{-3} \text{ kJ} / \text{K} \cdot \text{mol}) = 24.8 \text{ kJ} / \text{mol}$$

### **Using Vapor Pressure**

Let's say your bedroom has the dimensions 4 m x 3 m x 3 m. You are leaving for break and want the air to stay moist so as to pamper your plants. So, you put out a large pan containing 8 L of water and completely seal the room airtight. Assuming there was no water vapor in the room to begin, would all the water in the pan evaporate? Assume the room is at, appropriately, room temperature (298 K). The vapor pressure of water at 298 K is 23.7 mm Hg.

Using the vapor pressure of water and the amount in the pan, we can solve this puzzle. The key is that the vapor pressure of water at this temperature is the maximum pressure of water that can exist. After you leave, the water will start to evaporate, raising the pressure of water vapor in the air. If excess water is present and the pressure reaches the equilibrium vapor pressure, then the excess will remain in the liquid state. If not enough water is present to reach the equilibrium vapor pressure, then it will all evaporate.

#### **Example 11.3**

Let's say your bedroom has the dimensions 4 m x 3 m x 3 m. You are leaving for break and want the air to stay moist so as to pamper your plants. So, you put out a large pan containing 8 L of water and completely seal the room airtight. Assuming there was no water vapor in the room to

begin, would all the water in the pan evaporate? Assume the room is at, appropriately, room temperature (298 K). The vapor pressure of water at 298 K is 23.7 mm Hg.

Solution

$$8 \text{ L} = 8000 \text{ g} = 444 \text{ mol}$$

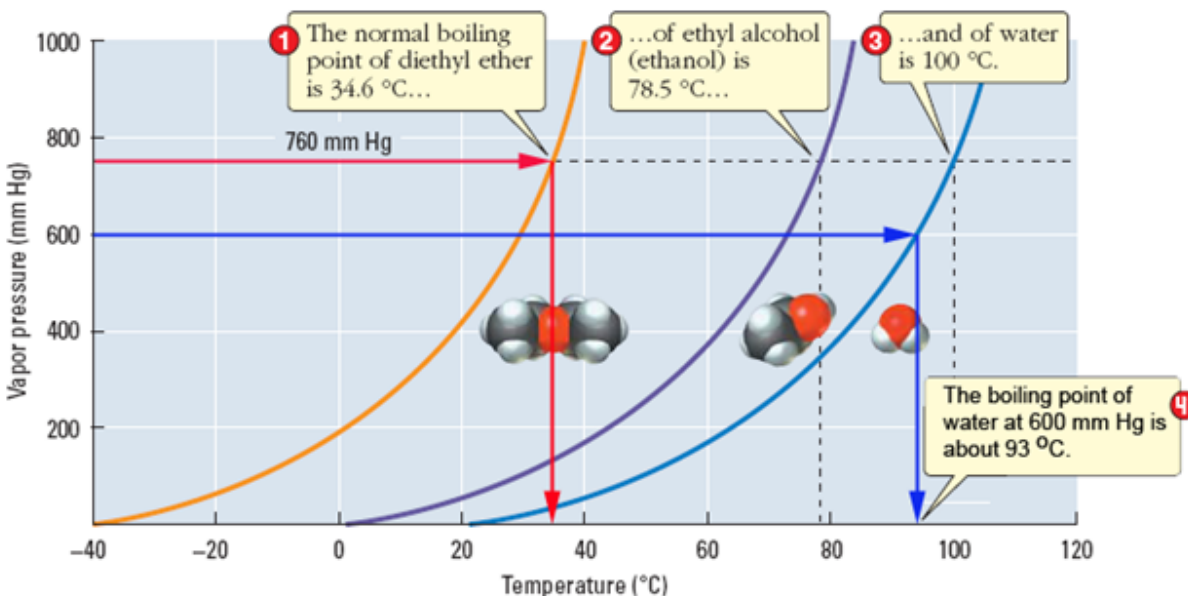
$$P = nRT/V = 444 \times 0.0821 \times 298/36000 \text{ L} = 0.302 \text{ atm} = 229 \text{ mm Hg}$$

This is much greater than the equilibrium vapor pressure of water, so the majority of the water remains in the liquid state.

## II c. Boiling Point

One of the most familiar properties of liquids is that they boil. But what is boiling, anyway? Boiling happens when the vapor of a liquid equals or exceeds the atmospheric pressure pressing down on that liquid. As we have been describing, at any temperature some molecules of liquid can break their IMFs and escape to the vapor phase. When the vapor pressure of the liquid is lower than the atmospheric pressure, this vaporization occurs only on the surface of the liquid. As a liquid is heated and the vapor pressure reaches the atmosphere pressure, the liquid can vaporize inside the liquid and just push the rest of the liquid out of the way. Bubbles in boiling water are composed principally of water vapor. A bubble in boiling water is essentially water evaporating inside the liquid. Because the gaseous state has molecules that are spread apart so much more, the newly evaporated water molecules take up more room- forming a bubble. Or whatever.

Because the temperature at which a liquid boils is that temperature at which its vapor pressure reaches the external atmospheric pressure, the boiling point must depend on that atmospheric pressure. Consider the curves in Figure CC. Each shows the vapor pressure as a function of temperature for a different liquid: diethyl ether, ethyl alcohol, and water.



**Figure 11.7.** Vapor pressure curves for diethyl ether ( $C_2H_5OC_2H_5$ ), ethyl alcohol ( $C_2H_5OH$ ), and water.

Figure 11.7. Vapor pressure vs. temperature plots of four compounds showing boiling points.

The temperature at which a liquid boils under an atmospheric pressure of exactly 1 atm is called the **normal boiling point**. The temperature at which each liquid passes through this pressure is its normal boiling point. For diethyl ether, the normal boiling point is shown by the red arrows moving across the graph until reaching the vapor pressure curve and then down to give the temperature: 34.6 °C. For ethyl alcohol this is 78.5 °C, and, of course, for water it is 100 °C.

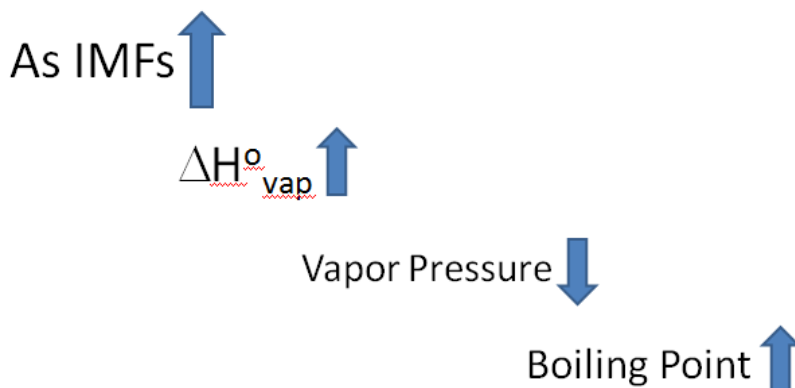
We can see that of the three liquids, diethyl ether has the highest vapor pressure and therefore the lowest boiling point. This indicates diethyl ether to have the weakest IMFs of the three compounds.

### Boiling Under Reduced Pressure

On a typical high altitude jet airplane, the cabin pressure is reduced to approximately 80% of an atmosphere; about 600 mm Hg. Therefore, the boiling point for water under these conditions is the temperature at which the vapor pressure reaches 600 mm Hg. This is shown in Figure 11.7 using the line moving across at 600 mm Hg till it hits the water vapor pressure curve, and then down to give the temperature. This is about 93 °C, significantly lower than at atmospheric pressure. This same effect is seen at high altitude, where cooking directions often recommend heating foods for a longer time due to the lower temperature of boiling water and the corresponding slower rates of the chemical reactions constituting the cooking process.

## Relating Enthalpy of Vaporization, Vapor Pressure and Boiling Point

It is clear that IMFs control the enthalpy of vaporization, vapor pressure and boiling point of liquids. For a series of liquids, as IMF strength increases, the energy needed to vaporize the liquid increases. As IMF strength increases, the liquid's vapor pressure decreases, and consequently, its boiling point increases.



## II d. Viscosity and Surface Tension

The last properties of liquids are surface tension and viscosity. These properties involve **cohesive forces**, which are the bulk-scale manifestations of how molecules in the liquid state interact. Surface tension is the tendency of the surface of a liquid to resist being “broken.” This is visualized in Figure 11.8,



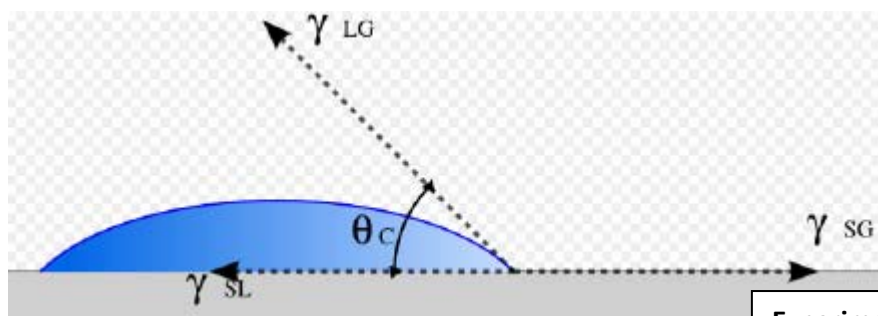
Figure 11.8.

which shows an insect sitting on top of a water surface. Surface tension is thought to arise from the difference in IMFs for water molecules within and on the surface. Molecules inside the liquid have interactions with other water molecules in all directions. Molecules on the surface can only have interactions with others to the side and below. The molecules on the surface are therefore less stable, and the liquid avoids creating more surface. Another manifestation of surface tension is that droplets of

liquid attempt to form a spherical shape, which is the shape with the smallest surface area for any given volume. Figure 11.HH shows a sample of liquid water on the space shuttle in nearly zero gravity. The water takes a spherical shape.

This can also be seen in droplets of different liquids sitting on a horizontal surface. The stronger any liquid's surface tension, the better job it does of fighting against the force of gravity and attain a spherical shape. This is called the liquid's **contact angle** and serves as an easy, visible measure of surface tension.

Figure 11.9 shows photographs of droplets of pure mercury, water, and octane. Notice that the mercury forms the most spherical droplets and the octane the flattest. Figure 11.JJ also shows a diagrammatic view of how contact angle is measured.



*need to add photograph part of this*

Figure 11.9. Diagram of a droplet on a surface, illustrating contact angle.

**Experiments you can do:**

Contact angle depends on the liquid, but also on whether anything is dissolved in it, and what the surface is. Try placing droplets of water on glass, ceramic, and plastic. Then try adding soap to the water.

Surface tension is related to IMF strength, but not it is less well tied to other properties such as boiling point. Table 11.2 gives some typical surface tension values.



| Substance  | Formula                            | Surface Tension<br>(J/m <sup>2</sup> at 20 °C) | Normal<br>Boiling Point, oC |
|------------|------------------------------------|--|-----------------------------|
| Octane     | C <sub>8</sub> H <sub>18</sub>     | 2.16 × 10 <sup>-2</sup>                        | 125.52                      |
| Ethanol    | CH <sub>3</sub> CH <sub>2</sub> OH | 2.23 × 10 <sup>-2</sup>                        | 78.4                        |
| Chloroform | CHCl <sub>3</sub>                  | 2.68 × 10 <sup>-2</sup>                        | 61.2                        |
| Benzene    | C <sub>6</sub> H <sub>6</sub>      | 2.85 × 10 <sup>-2</sup>                        | 80.1                        |
| Water      | H <sub>2</sub> O                   | 7.29 × 10 <sup>-2</sup>                        | 100.0                       |
| Mercury    | Hg                                 | 46 × 10 <sup>-2</sup>                          | 356.73                      |

These values generally increase with increases IMF strength, as measured in terms of boiling point. However, the trends are not clean. While mercury, with very strong IMFs and a high boiling point also has a large surface tension, octane has a lower surface tension than does chloroform, even though octane has a much higher boiling point. Because of this, we find that trends in surface tension are less amenable to prediction than are the other properties discussed.

**Viscosity** is a measure of a liquids resistance to flow: its “thickness.” The thicker the liquid, the more viscous. Like surface tension, viscosity is not highly predictable based on other properties. Viscosity does depend on IMF strength but also has a strong dependence on molecular structure, and in particular molecular length. Long, flexible molecules tend to become entangled and have trouble moving past one another as they tumble downhill while the liquid flows. This leads to a liquid like mercury, with very strong IMFs, having a very low viscosity—the individual mercury atoms can move past one another with little effort. A long molecule, like stearic acid has a much higher viscosity, even though it has weaker overall IMFs.

*Photo of liquids with different  
viscosity, or better, an experiment  
using different motor oils.*

Thickening agents used in cooking, such as corn starch, are made of long molecules that get stuck as they move and hold up water molecules from moving as well.

### III. The Nature of Intermolecular Forces

We have seen that various properties of liquids depend on the strength of their IMFs. But controls the strength of those IMFs? Why does water have stronger IMFs than methane, even though they have

about the same mass? Forces between molecules all arise from the same source: differing charges on adjacent molecules that lead to electrostatic attractions. These attractions follow Coulomb's Law,

$$Force \propto \frac{\text{Charge}_1 \times \text{Charge}_2}{\text{distance}^2}$$

As the size of the charges leading to the attractions increase, so does the force between the molecules. As the distance between those charges decreases, the force increases.

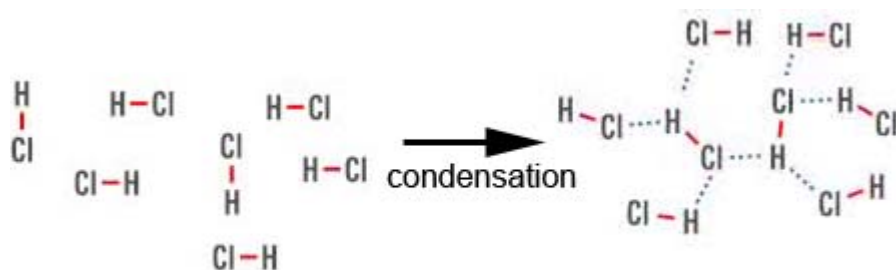
All IMFs arise due to partial charges on molecules, and IMFs are categorized by the origin of those charges. We will see that the origins of these charges differ for polar and nonpolar molecules.

### III a. Dipole-Dipole Forces

A polar molecule has a permanent dipole, meaning it has a positive end and a negative end. Each of these ends represents an area of permanent, partial positive or negative charge. Take for example hydrogen chloride, which is a gas at room temperature but condenses to form a liquid at colder temperatures. Each HCl molecule is polar, with a partially positive H end and the partially negative Cl end. When two HCl molecules approach each other, there is an electrostatic force of attraction that arises between the H on one molecule and the Cl on the other.



This attraction between two polar molecules is called a dipole-dipole force. The term "dipole" represents the source of the charges is the permanent molecular dipole. Consider what happens when gaseous HCl condenses. When a large number of polar molecules are present, they form a weakly bound network of molecules joined by one or more dipole-dipole forces.



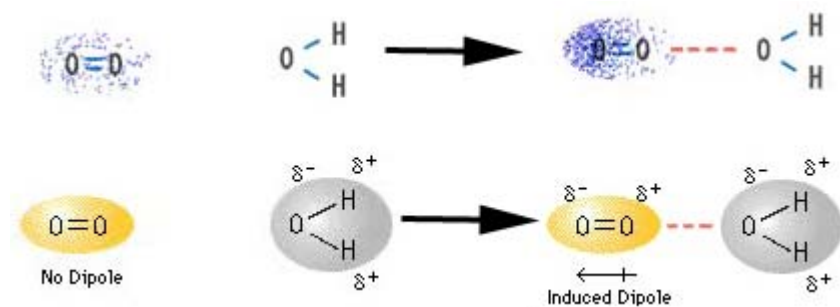
Dipole-dipole forces become stronger as the size of the partial charges increase. So,

Consider the examples of HCl and HF. HCl has the greater molar mass (36.5 g/mol vs. 20.0 g/mol) but a smaller enthalpy of vaporization (16.2 kJ/mol vs. 25.2 kJ/mol). This means that HF has stronger IMFs,

which are due to the greater polarity of the H-F bond compared to the H-Cl bond. This results in larger partial charges on H and F, compared to H and Cl.

### III b. Dipole-Induced Dipole Forces

Consider the case of a dioxygen molecule dissolved in water. Water is polar and permanent dipoles serve to hold one water molecules near other water molecules. But what force causes an  $O_2$  molecule to be attracted to the water molecules? While a water molecule is polar and has positively and negatively charged ends, an  $O_2$  molecule is nonpolar and possesses no permanent partial charges that can be attracted to the charges on the water molecules. The answer is that when an  $O_2$  molecule approaches a water molecule, the charges on the water molecule induce temporary charges on the  $O_2$  molecule. As illustrated in Figure 11.11, if an  $O_2$  molecule approaches the O end (which is negatively charged) of a water molecule, the electron cloud on the  $O_2$  molecule will be repelled. This forms an electron deficiency on the side near the water molecule, and a partial positive charge on that side of the  $O_2$  molecule and negative charge on the far side. The  $O_2$  molecule has therefore had a dipole induced by its proximity to the water molecule.



The now temporarily polar  $O_2$  molecule experiences a force of attraction to the permanently polar water molecule. This type of force is called a dipole-induced dipole force because the attracting charges come from one permanent dipole and one induced dipole.

The ability of a nonpolar molecule to have a dipole induced is directly dependent on how easy it is to perturb the molecule's electron cloud. This is known as polarizability, and generally increases as the number of electrons in the molecule increases. Data for different diatomic nonpolar gases showing solubility in water, number of electrons and polarizability are given in Table 11.3. As the number of electrons increase, so does the polarizability and the solubility (which indicates the formation of stronger dipole-induced dipole forces with water).

| Compound                                | Molar Mass (g/mol) | $\Delta H_{\text{vap}}^{\circ}$ (kJ/mol) † | Boiling Point (°C) (Vapor pressure = 760 mm Hg) |
|---|--------------------|--|---|
| <i>Nonpolar Compounds</i>               |                    |  |   |
| CH <sub>4</sub> (methane)               | 16.0               | 8.2  | -161.5  |
| C <sub>2</sub> H <sub>6</sub> (ethane)  | 30.1               | 14.7                                       | -88.6   |
| C <sub>3</sub> H <sub>8</sub> (propane) | 44.1               | 19.0                                       | -42.1   |
| C <sub>4</sub> H <sub>10</sub> (butane) | 58.1               | 22.4                                       | -0.5  |
| <i>Monatomic Elements</i>               |                    |  |   |
| He                                      | 4.0                | 0.08                                       | -268.9  |
| Ne                                      | 20.2               | 1.7  | -246.1  |
| Ar                                      | 39.9               | 6.4  | -185.9  |
| Xe                                      | 131.3              | 12.6                                       | -108.0  |
| <i>Diatomic Elements</i>                |                    |  |   |
| H <sub>2</sub>                          | 2.0                | 0.90                                       | -252.9  |
| N <sub>2</sub>                          | 28.0               | 5.6  | -195.8  |
| O <sub>2</sub>                          | 32.0               | 6.8  | -183.0  |
| F <sub>2</sub>                          | 38.0               | 6.6  | -188.1  |
| Cl <sub>2</sub>                         | 70.9               | 20.4                                       | -34.0   |
| Br <sub>2</sub>                         | 159.8              | 30.0                                       | 58.8  |

IMFs for Nonpolar Substances. As the substance increases in size and number of electrons, the IMF force strength also increases. This is seen as an increase in the enthalpy of vaporization and the boiling point.

### III c. Hydrogen Bonding *(it might make sense to move this to section III e.)*

We find that certain polar molecules exhibit much stronger dipole-dipole forces than others. These compounds invariably contain bonds between a H atom and a highly electronegative atom such as N, O, or F. These compounds exhibit what is called hydrogen bonding. Consider the plot of boiling points of simple Group 6A hydrogen compounds of the type H<sub>2</sub>A, where A = Te, Se, S, and O.

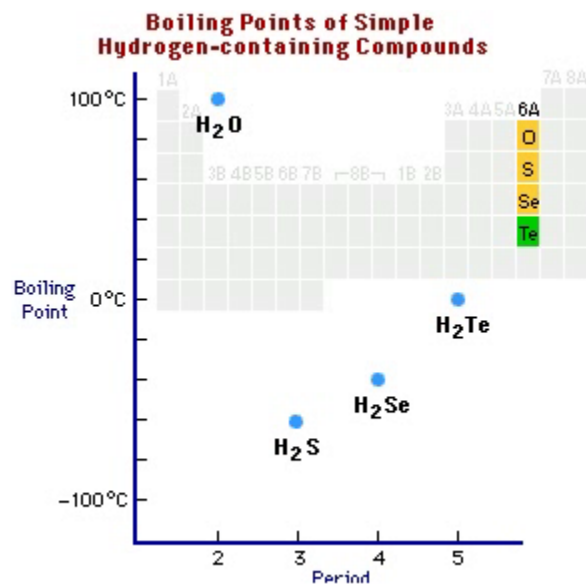


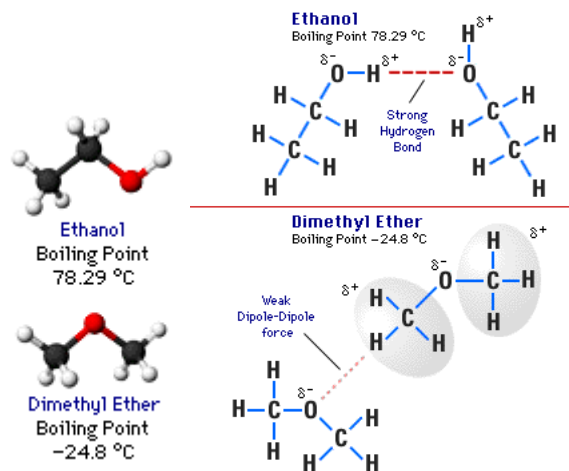
Figure 11.9. A plot of boiling point vs. group number for  $H_2X$ , where X is a Group 6A element.

Moving up the periodic table from Te to Se to S, the compounds  $H_2Te$ ,  $H_2Se$ , and  $H_2S$  experience weaker and weaker IMF as the molar mass of the compound decreases. Considering this trend, the boiling point of  $H_2O$  would be expected to be about  $-100\text{ }^\circ\text{C}$ . However, as we know, water's boiling point is about  $200\text{ }^\circ\text{C}$  greater than this. This discrepancy is a reflection of the fact that water experiences hydrogen bonding while the other compounds in the series do not.

Hydrogen bonds are especially strong IMFs because of two combining effects:

1. H has a very low electronegativity and makes particularly polar bonds.
2. H is very small and allows for a very close approach of neighboring molecules. Moreover, the elements that form H bonds (N, O, and F) are also very small, increasing the strength of the dipole-dipole interaction.

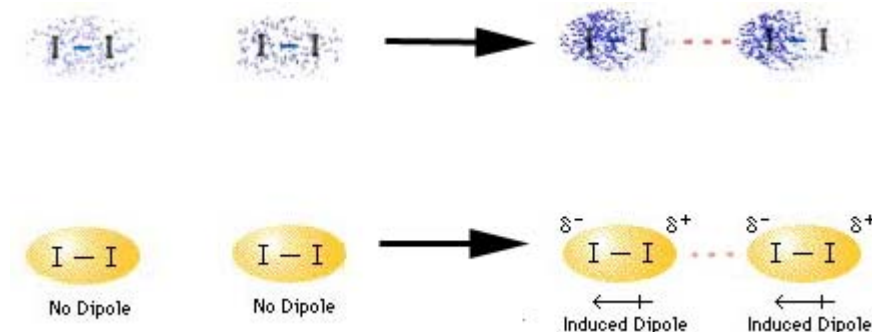
Another example of hydrogen bonding is the pair of isomers ethanol and dimethyl ether.



The two compounds are made of identical elements but where ethanol contains an O-H bond, dimethyl ether does not. Ethanol's boiling point is about 100 °C greater than the corresponding non-hydrogen bonding compound. This illustrates an important point: it is not enough to have N, O, or F along with a H atom in a molecule; there must be an N-H, O-H, or F-H bond.

### III d. Induced Dipole-Induced Dipole Forces

Many pure liquids and solids are composed completely of non-polar molecules. Consider the case of iodine, I<sub>2</sub>, which is a solid at room temperature. I<sub>2</sub> is a nonpolar molecule and has no permanent charges. But, when two I<sub>2</sub> molecules approach each other they induce temporary dipoles in each other. These temporary, induced dipoles on adjacent molecules lead to an attraction.



These forces between nonpolar molecules are called induced dipole-induced dipole forces, reflecting the origin of the attraction coming from two nonpolar molecules inducing dipoles in each other. These forces are also commonly termed **London dispersion** or just **dispersion** forces.

Dispersion forces depend on the strength of the ease with which a dipole can be induced in a molecule. This again is a measure of the molecule's polarizability and generally increases with increasing number of electrons, or basically, molar mass. Table 11.4 shows the data for a series of straight-chain

hydrocarbons. Each is nonpolar and they all have the same molecular structure except that for the length of the carbon chain.

| Molecular Formula               | Name        | Boiling Point | State at Room Temp |
|---------------------------------|-------------|---------------|--------------------|
| CH <sub>4</sub>                 | Methane     | -161 °C       | Gas                |
| C <sub>2</sub> H <sub>6</sub>   | Ethane      | -88 °C        |                    |
| C <sub>3</sub> H <sub>8</sub>   | Propane     | -42 °C        |                    |
| C <sub>4</sub> H <sub>10</sub>  | Butane      | -0.5 °C       |                    |
| C <sub>5</sub> H <sub>12</sub>  | Pentane     | 36 °C         | Liquid             |
| C <sub>6</sub> H <sub>14</sub>  | Hexane      | 69 °C         |                    |
| C <sub>7</sub> H <sub>16</sub>  | Heptane     | 98 °C         |                    |
| C <sub>8</sub> H <sub>18</sub>  | Octane      | 126 °C        |                    |
| C <sub>9</sub> H <sub>20</sub>  | Nonane      | 150 °C        |                    |
| C <sub>10</sub> H <sub>22</sub> | Decane      | 174 °C        |                    |
| C <sub>11</sub> H <sub>24</sub> | Undecane    | 194.5 °C      |                    |
| C <sub>17</sub> H <sub>36</sub> | Heptadecane | 303 °C        | Solid              |
| C <sub>18</sub> H <sub>38</sub> | Octadecane  | 317 °C        |                    |
| C <sub>19</sub> H <sub>40</sub> | Nonadecane  | 330 °C        |                    |

*Need to add molar mass and  $\Delta H_{vap}$  and polarizability.*

Notice that as molecular size increases, so do IMFs strengths as indicated by increasing enthalpy of vaporization and boiling point. In general, for dispersion forces, IMF strength increases with increases molar mass.

## IV. Predicting the Properties of Liquids

We have seen that three properties of liquids all relate closely to IMF strength: enthalpy of vaporization, vapor pressure, and normal boiling point. We also understand the trends that govern relative strengths of each type of IMF. In this section we put together these different aspects in order to give a more complete picture of the predictions that can be made based solely on what we know about molecular structure. We will do this first in general and then in a series of side-by-side comparisons.

### IV a. Quantitative Comparison of Different IMF Trends

Because IMF strength depends on the sizes of the charges that are present on molecules, it is reasonable to predict that polar molecules will lead to stronger IMFs than would comparably sized nonpolar molecules. We can see this holds true in Table 11.P.

| Molar Masses and Boiling Points of Nonpolar and Polar Substances |           |         |                  |                  |
|--|-----------|---------|------------------|------------------|
| Nonpolar   |           |         | Polar            |                  |
|  | M         | b.p.    |                  |                  |
|  | M         | b.p.    | M                | b.p.             |
| N <sub>2</sub>   | 28 g/mol  | -196 °C | CO               | 28 g/mol -192 °C |
| SiH <sub>4</sub>   | 32 g/mol  | -112 °C | PH <sub>3</sub>  | 34 g/mol -88 °C  |
| GeH <sub>4</sub>   | 77 g/mol  | -90 °C  | AsH <sub>3</sub> | 78 g/mol -62 °C  |
| Br <sub>2</sub>  | 160 g/mol | 59 °C   | ICl              | 162 g/mol 97 °C  |

For each pair of molecules with similar molar mass, the polar case has a higher boiling point. But, how much of a difference is this? Consider the plot of boiling point vs. molar mass for four series of compounds. These are based on six alkyl groups, which can be collectively represented by the letter R.

Methyl CH<sub>3</sub>-

Ethyl CH<sub>3</sub>CH<sub>2</sub>-

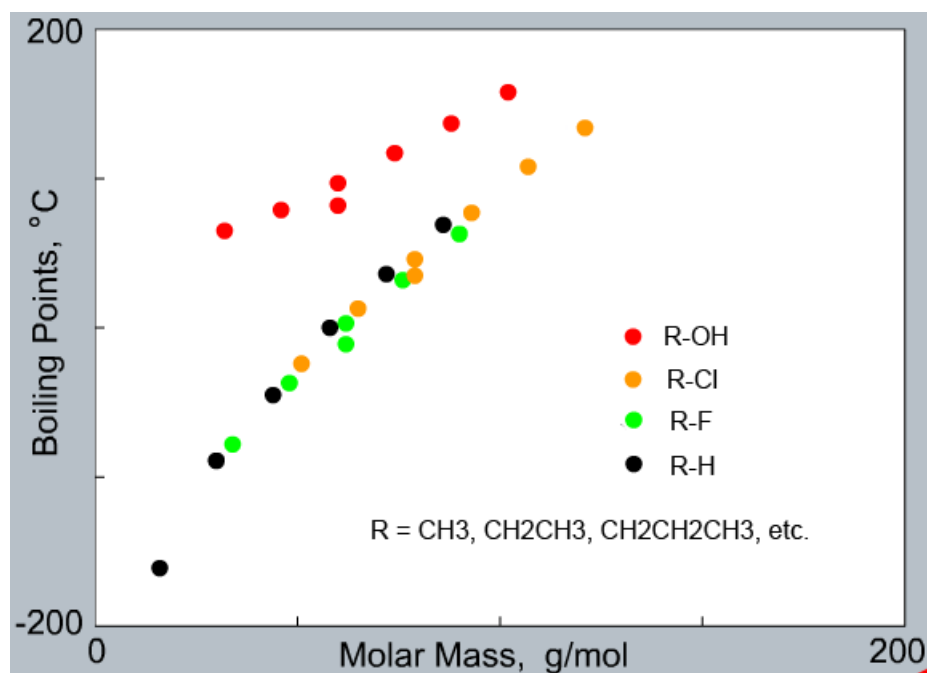
Propyl CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>-

Butyl CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-

Pentyl CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-

Hexyl CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-

To each alkyl group is attached one of four "end groups." These are the atoms H, F, and Cl, and the group OH.

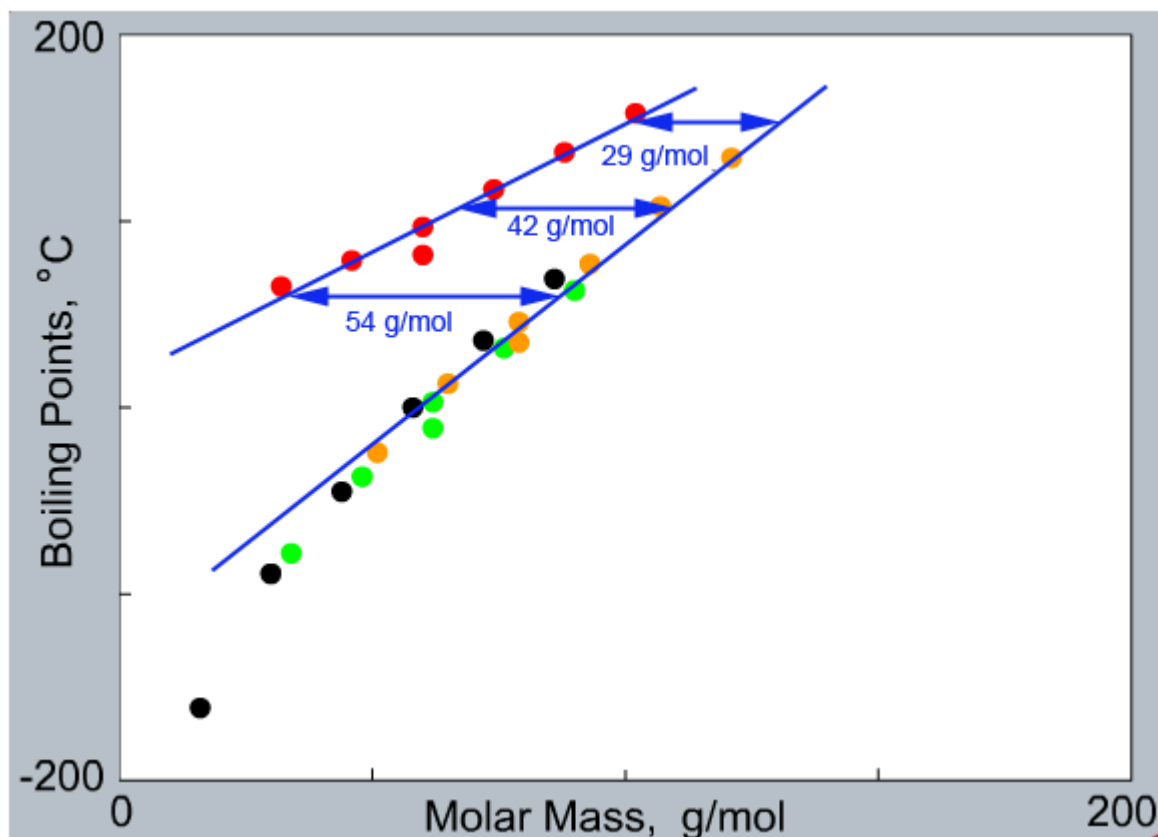




The plot shows a fairly linear relationship for R-H, R-F, and R-Cl. This is striking because where R-H is a nonpolar hydrocarbon, R-F and R-Cl are polar molecules. The linear plot implies that the strength of the induced dipole dispersion forces in these series are the controlling factors and polarity plays a relatively small role.

The data for the alcohols, R-OH, differ greatly from the rest. These compounds have much higher boiling points for the same molar mass than the others. The reason for this difference is that the R-OH compounds can form hydrogen bonds while the others cannot. So, the conclusion is that polarity can influence IMF strengths and the properties of liquids, but this influence is mostly seen in hydrogen bonding compounds.

So, what's a hydrogen bond worth, anyway? If greater molar mass leads to stronger dispersion forces, but hydrogen bonds make a big difference, how do we compare hydrogen bonding compounds to non-hydrogen bonding ones. To decide this, we use the same plot but examine the differences in molar mass needed to obtain the same boiling point.



For small molecules, a nonpolar molecule needs to have a molar mass of about 50 g/mol greater than a corresponding hydrogen bonding molecule. This is about the same as a 3-4 carbon long alkyl group. For larger molecules the difference is smaller, and a 2-carbon alkyl group can make up the difference.