Chapter 14 Lecture Outline

A. Properties of liquids

The intermolecular forces in liquids are stronger than those in gases, so although the molecules of a liquid are free to move around, they remain connected to the other molecules. Thus liquids have a fixed volume but no fixed shape. The mobility of the liquid molecules allows them to assume the shape of any container.

There are five important properties of liquids that are determined by the magnitude of these intermolecular forces. These are: ***viscosity***, ***boiling point***, ***surface tension***, ***vapor pressure***, and ***heat of vaporization***. Before we discuss these in detail, it is important to understand the nature of the attractions between molecules.

B. Intermolecular Forces

When atoms of nonmetals bond to form a molecule, the bonds are always covalent, i.e., they involve the sharing of electrons. Of course, nonmetals would prefer to take electrons from another element and form an anion, but this is possible only if the other atom is a metal. But even though the atoms must share electrons, they don't necessarily share equally.

Each element has a property called ***electronegativity***. This is a measure of the ability of an atom to pull a pair of bonding electrons away from another atom to which it is bonded. The electronegativity of an element increases from left to right across a period in the periodic table and as you move up a group of elements. Thus, fluorine, being the farthest up and farthest right of the elements (not including noble gases, which don't bond), has the greatest electronegativity. Think of fluorine as the bully of the periodic table, always taking electrons from other elements.

In molecules such as H_2, N_2, or F_2, the electronegativities are equal for the bonding atoms and they must share the electrons equally. However, in a molecule such as HF, the electrons in the bond are pulled toward the more electronegative fluorine atom. This causes the fluorine to have a small negative charge while the hydrogen has a small positive charge. In the H_2 molecule, there are no

$$^{0}\mathbf{H{-}H}^{0} \qquad\qquad\qquad ^{\delta+}\mathbf{H{-}F}^{\delta-}$$

charges, so it is considered to be a ***nonpolar molecule***. The HF molecule, with its positive and negative poles, is considered to be a ***polar molecule***. We also describe the HF molecule as having a ***permanent dipole*** (dipole meaning having two poles). Because the H_2 molecule has no charges, molecules of H_2 do not attract each other significantly. However, the opposite charges in HF molecules cause them to attract each other. These attractions are the source of intermolecular forces and are known as ***dipole-dipole forces***.

$$^{\delta+}\mathbf{H}\text{—}\mathbf{F}^{\delta-}\text{ - - - }^{\delta+}\mathbf{H}\text{—}\mathbf{F}^{\delta-}\text{ - - - }^{\delta+}\mathbf{H}\text{—}\mathbf{F}^{\delta-}$$

Dipole-Dipole Forces in HF

The strength of dipole-dipole forces depends on the differences in the electronegativities of the two elements. HF has a fairly strong dipole because there is a large difference (1.9) in the electronegativities of H and F. The dipole-dipole forces in H-Cl would be less, since the electronegativity difference is only 0.9.

In certain cases, the dipole-dipole forces are significantly stronger than is observed in most polar molecules. When a molecule has a hydrogen atom directly bonded to either a nitrogen, oxygen, or fluorine atom, this type of permanent dipole attraction is called ***hydrogen bonding***. The strength of these attractions is due to two factors. The large difference in electronegativities between the three atoms and hydrogen produces a large dipole, and the small size of the four atoms allows them to approach more closely and feel the attractions more strongly.

Since all intermolecular attractions are due to dipoles, do nonpolar molecules such as H_2 or O_2 attract each other? Logically, we can deduce that **ALL** molecules exhibit intermolecular attractions. Since all substances become liquids at sufficiently low temperatures, then they must have at least some small amount of attraction for each other. Otherwise they would remain gases even near absolute zero! But what is the nature of these attractions?

Remember that the electrons in a molecule are constantly moving. Although they are equally shared in a nonpolar molecule, their random motion sometimes finds them on one side of a molecule or the other. In the instant that they are on one side of the molecule, that side becomes negative and the other positive. A moment later they may be equally distributed and then find themselves on the other side of the molecule. In these instants where the electrons are unequally distributed, the molecule has a dipole, and there is an attraction to other molecules with a similar unequal distribution. Because these dipole are only temporary, the attractions are not as great as those in molecules with permanent dipoles. Gases are almost all nonpolar substances, which makes sense, as gases must have weak intermolecular forces. These attractions in nonpolar molecules are referred to as London forces or dispersion forces.

London forces can actually be quite strong, even stronger than hydrogen bonding in some cases. The strength of London forces depends on the number of electrons in a molecule. The more electrons moving around, the greater the dipole can be produced. Looking at the elements in Group VIIA, we see that F and Cl are gases, while Br is a liquid and I is a solid. The greater number of electrons in Br and I produce stronger London forces and allow them to exist as a liquid and solid at room temperature.

Oil is a good example of strong London forces. Even though oil is nonpolar, it has a higher boiling point and a greater viscosity than water, indicating its stronger intermolecular attractions. The large number of electrons in the oil molecule are responsible for this. A fairer comparison would be between methane, CH_4, and water. Both have 10 electrons, giving them comparable London forces. However, water also has a permanent dipole and exhibits hydrogen bonding. The large difference in boiling points, -164 °C for methane and 100 °C for water, illustrates the strength of the permanent dipole.

Since most molecules are nonpolar, the easiest way to distinguish between polar and nonpolar is to learn which are nonpolar. There are four cases, which are illustrated below.

1. Any molecule which contains only one type of atom, H_2, P_4, or C_{60} for example, must be nonpolar.

2. A molecule which consists of two identical atoms in a linear arrangement about a central atom will be nonpolar. In CO_2, for example, the two strongly electronegative oxygen atoms balance each other, much like a tug-of-war between two teams of equal strength. The electrons do not move and the molecule is nonpolar.

3. A molecule consisting of three identical atoms in a trigonal planar arrangement around a central atom will be nonpolar as well. In SO_3, the three oxygen atoms balance each other, making the molecule nonpolar.

4. A molecule consisting of four identical atoms in a tetrahedral arrangement around the central will be nonpolar. In CF_4, the four fluorine atoms, although very electronegative, are balanced by the other fluorine atoms.

Keep in mind that not all molecules with two, three, or four identical atoms will be nonpolar. The atoms must be equally spaced around the center. Ammonia, NH_3, and water, H_2O, contain nonbonding electrons on their central atoms, forcing the hydrogen to one side of the molecule. Thus, the molecules are not symmetrical and are polar. Anytime the central atom has even a single nonbonding electron, the molecule must be polar.

C. Properties of Liquids, Revisited

Now that you understand the nature of intermolecular forces, let's return to the five properties of liquids mentioned in Part A.

Viscosity is a measure of the resistance to flow exhibited by a liquid. As the liquid flows, molecules slide past one another. Attractions between the molecules inhibit that flow, so the greater the viscosity of a liquid, the greater its intermolecular forces must be.

For a liquid to boil, the attractions between molecules of liquid must be broken. The greater the forces of attraction, the more energy will be required to break the bonds. Thus, the greater the intermolecular forces, the greater the ***boiling point***.

Surface tension is the tendency of a liquid to minimize its surface area. In simple terms, liquids often tend to bead up rather than spread out. This is easily seen when a droplet of water is placed in a waxed surface, such as a car, or on the surface of a teflon pan. The water beads up in order to become spherical, since a sphere has the largest amount of volume per amount of surface area of any shape. In the case of a waxed car, the polar water molecules have strong attractions to other water molecules. Since wax is nonpolar, the attractions between water and wax are less. It is important to note that water IS NOT repelled by wax, nor do oil and water repel each other. It is simply that water finds itself more attractive than wax or oil. The water beads up in order to reduce the number of water molecules forces to bond with wax and increase the number of water molecules that get to bond with other water molecules. The driving force is always to try and get the strongest bonds possible.

The observation of a meniscus when water is place in a graduated cylinder shows the reverse effect. The water literally climbs the glass in order to spread out over the glass surface. This shows that water is more strongly attracted to glass than it is to itself. This is due to the polar –O-H groups present on glass surfaces, making hydrogen bonding possible between water and glass. Thus, the greater the intermolecular forces, the greater the surface tension.

All liquids have a tendency to evaporate, some slowly and others very rapidly. For a liquid to evaporate, a molecule must have enough energy to overcome the attractions it has with other molecules of the liquid, and must be at the surface of the liquid. Remember from our study of gases, that, while molecules will have an average energy at a particular temperature, some will always have more energy and others less. In a liquid at room temperature, some molecules will have much higher energy and some less. If a high energy molecule makes it to the surface, it can escape and become a gas.

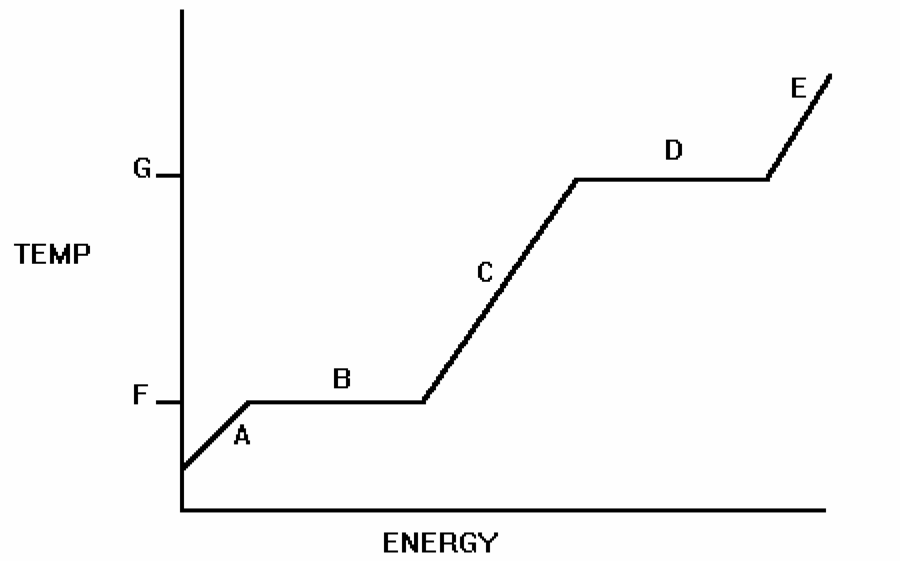
In a sealed container, as liquid molecules evaporate, the additional molecules of gas present cause the pressure to rise in the container. This extra pressure caused by the liquid vapor is called the ***vapor pressure***. Since stronger intermolecular forces will make it more difficult for liquids to evaporate, the stronger the intermolecular forces, the lower the vapor pressure.

You have probably noticed that water in a puddle on the ground will eventually evaporate completely, while water in a sealed container will never disappear. In the container, as more and more molecules enter the vapor, they bounce around the container and some eventually bounce back into the liquid. As more and more liquid molecules become gases, they are more likely to return to the liquid. After enough liquid molecules have evaporated, the rate that they return is as great as the rate of evaporation. At this point it appears that evaporation has ceased. But in fact, the liquid is evaporating just as fast as always. But for every molecule leaving the liquid, another returns. This state of balance is known as ***dynamic equilibrium***. Once dynamic equilibrium has been achieved, the vapor pressure will remain constant. It can only be increased by raising the temperature of the liquid, which will increase the rate at which molecules evaporate from the surface of the liquid.

For a molecule to break free of the bonds holding it to the other molecules, energy is always required. This energy is known as the ***heat of vaporization***, symbolized by ΔH_{vap}. Not surprisingly, the greater the intermolecular forces in a liquid, the greater the energy required to vaporize it. For water, 2260 J of energy are needed to vaporize one gram of liquid. There is a similar measure for the energy required to melt a solid, called the ***heat of fusion***. Because it is easier to melt a solid (weakening the bonds) than it is to vaporize a liquid (breaking the bonds), the heat of fusion is always less. For water it is 335 J/g.

D. Heating-Cooling Curves

A heating-cooling curve is a graph that shows the changes in temperature of a substance as energy is added to removed from it. On the graph below, points F and G represent the melting and boiling points of a substance. If this were water, F would be 0°C and G 100 °C. The most important thing to note is that, during a change in physical state, the temperature remains constant.



On segment 'B' of the graph, solid is melting or liquid is freezing, depending on the direction. In either case, the temperature remains fixed. As ice melts, the temperature remains at 0°C until the solid has completely melted. The same is true on segment 'D'. As a liquid boils the temperature remains constant. No matter how much you heat a pot of boiling water, you can't get it above 100°C. Segments 'A', 'C', and 'E' represent the heating or cooling of the solid, liquid, and gas phases, respectively.

In addition to the term fusion being used for melting, there are a few other terms to know. ***Condensation*** is defined as a gas being converted into either a liquid or solid. ***Sublimation*** is the term for a solid that skips the liquid phase and is converted directly into a gas. This is most commonly seen with dry ice. However, even water sublimes. Have you ever found ice cubes in your freezer which have become small and oddly shaped? Given enough time, the ice cubes in a tray will completely vaporize by sublimation.

E. Boiling vs Evaporation

There are some important differences between boiling and evaporation. First, evaporation occurs at any temperature in which a substance is a liquid. Even ice water will evaporate, although slowly. Boiling, on the other hand, takes place at a specific temperature. Think of evaporation as guerrilla warfare. Liquid molecules sneak out between the air molecules to escape. Boiling, on the other hand, is a full frontal assault. The water vapor literally pushes the air out of the way.

Now, air is not easily moved. At sea level, it pushes down with a pressure of 14.7 psi, or 760 mmHg. In order to boil, the water vapor pressure must be equal to this. At 25 °C, the water vapor pressure is only 24 mmHg. At 50 °C it is 92 mmHg and by 75 °C it reaches 289 mmHg. This is still well below the required level. As you may have guessed, at 100 °C the vapor pressure of water reaches 760.00 mmHg and the water boils.

Does water always boil at 100 °C? No it does not. Only at a pressure of 760 mmHg. In the mountains where the pressure is lower, water boils below 100 °C. At the top of Mt. Everest, water boils at only 70 °C! Below sea level water will boil above 100 °C. Pressure cookers are designed to operate at pressures greater than normal atmospheric pressure. Thus the water inside boils at a temperature above 100 °C and food cooks faster.