



## Chapter 10: Intermolecular Forces and Liquid Properties

### Section 10.1: Introduction to Intermolecular Forces

Matter exists in one of three physical states: Solid, Liquid or Gas.

Molecules are much closer to one another in solids and liquids than in gases. In solids and liquids, molecules touch one another, whereas in gases they are farther apart. This is the reason why solids and liquids have much larger densities than gases and intermolecular forces are negligible in gases, but play a significant role in solids and liquids. The properties of liquids lie between these of solids and gases. We begin the study of properties of solids and liquids by considering their intermolecular forces.

We all know that atoms can be combined to form molecules by sharing electrons. This is called **intramolecular** bonding. Intramolecular means within the molecule.

**Consider H<sub>2</sub>O:** It changes from solid to liquid to gas as the temperature is raised. However, while changing state, the H<sub>2</sub>O molecules remain intact. The change in physical state is due to a change in the forces between the molecules rather than within the molecules.

The forces between the molecules are called **intermolecular** forces. There are three main types of intermolecular forces:

- London dispersion forces
- Dipole-dipole forces
- Hydrogen bonds

In general, intermolecular forces are weak forces.

### Section 10.2: London Dispersion Forces

London dispersion forces are the most common type of intermolecular force and are found in all molecular compounds. They are the only intermolecular forces found in noble gases and non-polar molecules. Basically, these forces are electrical in nature. Hence, they result in both attractive and repulsive interactions between atoms or molecules.

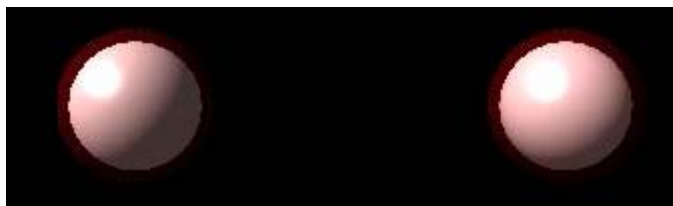
Why and How?

Non-polar gases can be liquefied.

**For example:** Noble elements such as He, Ar, etc... can exist as liquids. These gases are made of atoms which are electrically neutral. How can gaseous neutral atoms attract each other to form a liquid? Since these substances can exist as liquids, there must be some kind of attractive force holding atoms together.

These attractive forces were first studied in 1930 by a physicist named London, hence, the name **London dispersion forces**.

**Consider a pair of noble gas atoms:**



Usually it is assumed that the electrons of an atom are uniformly distributed about the nucleus. This assumption is not true at every instant. As the electrons move about the nucleus, a momentary non-symmetrical electron distribution can develop producing a temporary dipole. This temporary dipole in turn affects the electron distribution of the neighboring atom. This leads to an interatomic attraction called the London dispersion force.



Remember! The London dispersion force is a very weak force and is significant only when molecules or atoms are very close together. These forces are actually sufficiently strong to promote the formation of solids, when the temperature is so low that the motions of atoms are significantly reduced.

**Examine the freezing points of some noble elements:**

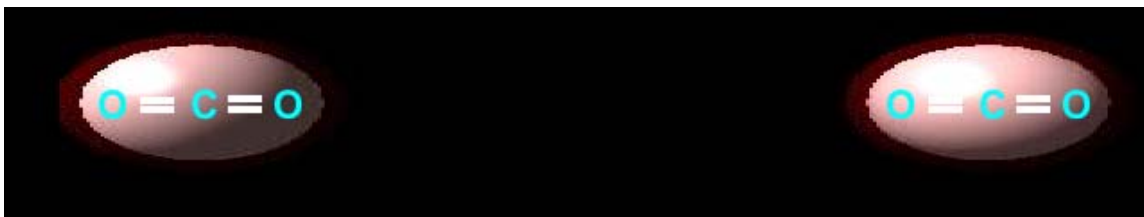
He	-269.7 °C
Ne	-248.6 °C
Ar	-189.4 °C

The freezing point rises going down the group. This is because the atomic number increases as we go down the group. The higher the atomic number, the greater the

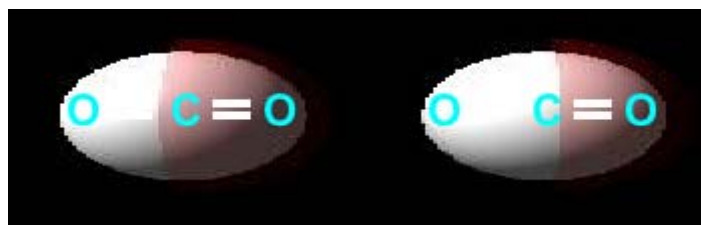
number of electrons and therefore the higher the probability of momentary dipole interactions. The same concept can be applied to non-polar molecules.

### Consider CO<sub>2</sub>:

We know CO<sub>2</sub> exists as a gas. However, CO<sub>2</sub> can also exist as a solid commonly called “dry ice.” Consider a pair of CO<sub>2</sub> molecules:



In the first step, assume that the electrons are uniformly distributed about the respective nuclei. In this case, there is no dipole moment. As the electrons move about the nucleus, a momentary non-symmetrical electron distribution can develop. This produces a temporary dipole moment.



This temporary dipole moment in turn affects the electron distribution of the neighboring molecule. This leads to London dispersion forces between these two CO<sub>2</sub> molecules.

The charge distribution in a molecule can be distorted by the electric field created by neighboring molecules. The ease with which the charge distribution in a molecule is distorted is called “**polarizability**”. Thus, more polarizable molecules have stronger London dispersion forces. Larger molecules have greater polarizability, because they have a greater number of electrons.

In general, the strength of London dispersion forces increases with increasing molar mass.

## Section 10.3: Dipole-Dipole Forces

Polar molecules are attracted to one another by London dispersion forces. In addition, they also interact by **dipole-dipole** forces. Polar molecules attract each other when the positive end of one molecule is near the negative end of another molecule.

**Consider HCl molecules** in the solid state. They are organized either side-by-side or end-to-end.



Adjacent HCl molecules line up so that the more electronegative Cl atom is as close as possible to the less electronegative H atom of its neighbor. This results in an attractive force called the “**dipole-dipole force**”. The dipole-dipole forces are effective only when the polar molecules are very close together.

In polar molecules, dipole-dipole forces are stronger than London dispersion forces. In liquids, polar molecules are free to move with respect to one another. Sometimes they will be in an orientation that is attractive, and sometimes repulsive. Molecules will spend more time near each other in the attractive orientation than in the repulsive orientation. Thus, the overall effect is “net attraction.”

In general, for molecules having approximately the same mass and size, the dipole-dipole forces increase with increasing polarity. The boiling points, as well as the melting points of polar compounds, are higher than those of non-polar compounds of similar molar mass.

## Section 10.4: Hydrogen Bonds

In liquids, polarity alone has a relatively small effect on boiling point.

**For example:** Consider HCl, HBr and HI. The boiling point increases with increasing molar mass even though the polarity decreases.

When hydrogen is bonded to a small, highly electronegative atom in a polar molecule, polarity has a greater effect on the boiling point. The highly electronegative atoms are **N**, **O** and **F**, respectively.

Among HF, HCl and HBr, HF has the highest boiling point despite its lower molar mass. Similarly, H<sub>2</sub>O (molar mass = 18.0 g/mol) and NH<sub>3</sub> (molar mass = 17.0 g/mol) have abnormally high boiling points. The unusually high boiling points of HF, H<sub>2</sub>O and NH<sub>3</sub> result from the strong dipole-dipole force called a **hydrogen bond**.

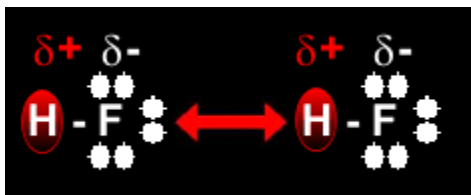
**For example:** Consider a pair of HF molecules. Their Lewis dot structure is:



Once the H-atom is bonded to the F-atom, its electron becomes localized near the fluorine atom because fluorine is very electronegative. Hence, the positive side of the bond is primarily due to the proton in the hydrogen nucleus.



This exposes the positive charge of the H-atom.

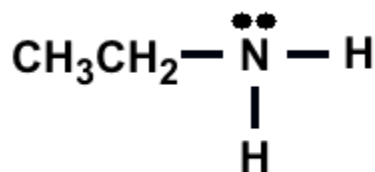


This positive charge is attracted to the electrons of an electronegative atom of the nearby HF molecule. Because the H-atom is very small in size, it can very closely approach the electronegative F-atom, resulting in a very strong attraction called a **hydrogen bond**.

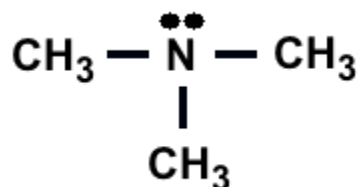
Hydrogen bonds can exist in many molecules other than HF, H<sub>2</sub>O and NH<sub>3</sub>. The basic requirement is that the H-atom is bonded to a F, O or N atom with at least one unshared electron pair.

**For example: Consider two molecules CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> and (CH<sub>3</sub>)<sub>3</sub>N**

Their Lewis structures are:



Molecule A

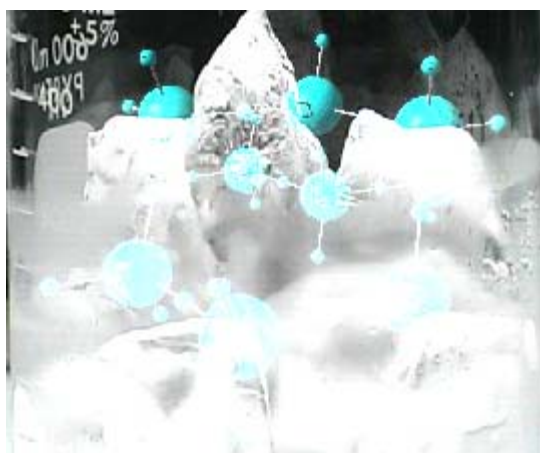


Molecule B

While substance A can form hydrogen bonds, substance B cannot. If we compare these compounds in the liquid state, then  $\text{CH}_3\text{CH}_2\text{NH}_2$  would have a higher boiling point than  $(\text{CH}_3)_3\text{N}$ .

### Hydrogen bonding in ice and in water:

Another consequence of hydrogen bonding is the remarkable difference in the densities of ice and liquid water. Ice is a solid. In most substances, the molecules are more densely packed in the solid state than in the liquid state. However, we know that ice floats on water and thus it must have a lower density than water. This contrast in density between ice and water can be understood in terms of hydrogen bonding. In liquid water,  $\text{H}_2\text{O}$  molecules are close together. When liquid water freezes, the molecules have an open ordered arrangement.



This arrangement optimizes the hydrogen bonding interactions between the molecules. In doing so, it results in the less dense structure of ice compared to water.

Remember: A given mass of ice occupies a greater volume than the same mass of water.

## Section 10.5: Examples of Intermolecular Forces (Interactive)

Practice Interactive Problems to master the concept of intermolecular forces.

## Section 10.6: Viscosity

Liquids such as motor oil flow slowly compared to water. The resistance to flow of a liquid is called the “**viscosity**”. The greater the viscosity, the slower the liquid flows. At

the molecular level, the flow of a liquid can be described as the sliding of molecules past one another.

The higher the viscosity, the more difficult the sliding of molecules past one another or the greater the friction between molecules. Viscosity is therefore controlled by the nature and strength of intermolecular forces. As the temperature of a liquid is increased, its molecules can more easily overcome intermolecular forces. This results in a lower viscosity.

## Section 10.7 Surface Tension

In general, liquids form droplets. This behavior is due to the intermolecular forces at the surface of the liquid. Molecules in the interior of a liquid are attracted equally in all directions. In contrast, molecules at the surface experience a net inward force. This inward force pulls the molecules from the surface into the interior and reduces the surface area. For a given volume, spheres have the smallest surface area. The inward force also makes the molecules at the surface pack closely together. A measure of the inward force is called **surface tension**.

Surface tension is the amount of energy required to increase the surface area of a liquid by a unit amount.

Intermolecular forces that bind similar molecules to one another are called **cohesive forces**. Intermolecular forces that bind liquid molecules to a surface are called **adhesive forces**.

Water placed in a glass beaker exhibits a **concave meniscus** because the adhesive forces between the water molecules and the glass surface are greater than the cohesive forces between the water molecules.

Mercury placed in a glass beaker exhibits a **convex meniscus** because the adhesive forces between the mercury atoms and the glass surface are weaker than the cohesive forces between the mercury atoms.

## Sections 10.8 - 10.9: Vapor Pressure

Consider a liquid placed in a closed container. Initially, molecules are transferred from the liquid to the vapor phase. This process is called **evaporation**. As the number of vapor molecules increases, so does the rate of return of these molecules to the liquid phase. This process is called **condensation**. Eventually, the rate of evaporation becomes equal to the rate of condensation. At this point the system is at equilibrium, and no further changes occur in the amount of liquid or vapor.

The equilibrium is expressed as: Liquid  $\rightleftharpoons$  Vapor

The vapor like any gas can be assumed to obey the ideal gas law. Once the system reaches equilibrium, the pressure exerted by the vapor is called the **vapor pressure**. As long as both liquid and vapor are present in the container, the pressure exerted by the vapor is independent of the volume of the container.

The vapor pressures of liquids vary. Liquids with large vapor pressures are called “**volatile**” liquids. Volatile liquids evaporate rapidly from an open container. Examples: gasoline, acetone, etc...

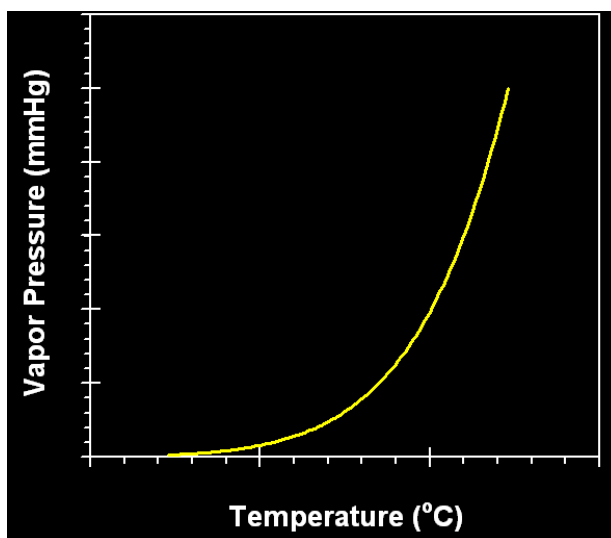
**The vapor pressure of a liquid is lower when the intermolecular forces in the liquid are stronger.**

In general, liquids with large molar masses have relatively low vapor pressures. This is because molecules with large molar masses have greater London dispersion forces.

Substances with “hydrogen bonds” have lower vapor pressure than substances of similar molar masses that do not have “hydrogen bonds”.

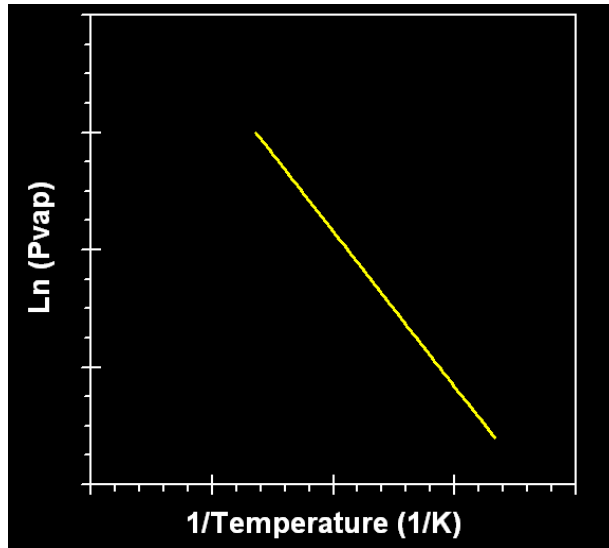
**The vapor pressure of a liquid increases with temperature.**

A plot of vapor pressure as a function of temperature is shown below for water:



The temperature on the x-axis is in deg.C. and the vapor pressure,  $p$ , on the y-axis is in mm Hg. This plot exhibits curvature. In order to obtain a straight line, we must plot  $\ln(p)$  vs.  $1/T$ .





Note: The temperature is now in kelvin (K).

The straight line has a negative slope of magnitude  $= -\frac{\Delta H_{\text{vap}}}{R}$   
 where  $\Delta H_{\text{vap}}$  is the standard enthalpy of vaporization of the substance.

The general equation for the straight line is:  $y = mx + b$

$$\text{or } \ln p = -\frac{\Delta H_{\text{vap}}}{RT} + b$$

If we define  $p_1$  and  $p_2$ , the vapor pressures at temperature  $T_1$  and  $T_2$ , respectively, then,

$$\ln p_1 = \frac{-\Delta H_{\text{vap}}}{RT_1} + b \quad \text{and} \quad \ln p_2 = \frac{-\Delta H_{\text{vap}}}{RT_2} + b$$

Subtracting the second equation from the first, we get:

$$\ln p_2 - \ln p_1 = \frac{-\Delta H_{\text{vap}}}{RT_2} - \left( \frac{-\Delta H_{\text{vap}}}{RT_1} \right) \quad \text{or} \quad \ln \frac{p_2}{p_1} = \frac{\Delta H_{\text{vap}}}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

This equation is called the “**Clausius-Clapeyron**” equation.

The Clausius-Clapeyron equation can be used to calculate any one of the following  $p_1$ ,  $p_2$ ,  $\Delta H_{\text{vap}}$ ,  $T_1$ , or  $T_2$  in terms of the other quantities in the equation. Note: The value of  $R$  to be used here is  $R = 8.31 \text{ J/mol.K}$  and the value of  $\Delta H_{\text{vap}}$  should be expressed in  $\text{J/mol}$ .

**Example: A liquid has a vapor pressure of 283 mm Hg at 50.00 deg.C. Its heat of vaporization is equal to 30.8 kJ/mol. Calculate pressure in mm Hg at 25.00 deg.C.**

$$\Delta H_{\text{vap}} = 30.8 \times 10^3 \text{ J/mol}$$

$$p_2 = 283 \text{ mm Hg}$$

$$p_1 = \text{To be calculated}$$

$$T_1 = 298.15 \text{ K}$$

$$T_2 = 323.15 \text{ K}$$

$$\ln p_2 - \ln p_1 = \frac{\Delta H_{\text{vap}}}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\ln [283 \text{ mm Hg}] - \ln [p_1] = \frac{30.8 \times 10^3 \text{ J/mol}}{8.31 \text{ J/mol K}} \left[ \frac{1}{298.15 \text{ K}} - \frac{1}{323.15 \text{ K}} \right] = 0.963$$

$$\ln [283 \text{ mm Hg}] - \ln [p_1] = 0.963$$

$$\ln [p_1] = \ln [283 \text{ mm Hg}] - 0.963$$

$$= 5.645 - 0.963 = 4.68$$

$$p_1 = e^{4.68} = 108 \text{ mm Hg}$$

In Section 10.9, practice the Interactive Problems.

## Section 10.10: Boiling Point

Place a liquid in an open container and apply heat. Initially small bubbles form, usually at the bottom of the container. These small bubbles are air bubbles. Eventually at a certain temperature, large bubbles form throughout the liquid. This is when we say “the liquid begins to boil.”

The boiling point is defined as the temperature at which the vapor pressure of the liquid is equal to the pressure above its surface. Thus, the temperature at which the liquid boils depends on the pressure above it. In an open container it is the atmospheric pressure. The pressure inside the large bubble is due to the vapor pressure of the liquid. When the vapor pressure of the liquid becomes equal to the atmospheric pressure, the bubble rises to the top and bursts.

The boiling point is defined as the temperature at which the vapor pressure of the liquid is equal to the pressure above its surface. The boiling point of a liquid is constant at a given pressure. At higher altitudes, where the pressure is lower, the liquid boils at a lower temperature.

The **normal boiling point** is defined as the temperature at which the liquid boils when the atmospheric pressure is 1 atm.

Liquids that have “hydrogen bonds” have higher boiling points compared to liquids of similar molar masses that do not have “hydrogen bonds.” Boiling points of polar molecules are greater than boiling points of non-polar molecules of similar size because London dispersion forces are weaker than dipole-dipole interactions.

## Section 10.11: Critical Temperature and Critical Pressure

In principle, there are two techniques to convert a gas into liquid:

1. Decreasing the Temperature: By cooling a gas, the kinetic energy of its molecules can be decreased. Eventually the molecules aggregate to form small droplets of liquid (condensation).
2. Increasing the Pressure: By increasing pressure on a gas, the volume decreases. Hence, the average distance between the molecules decreases. As the molecules approach each other, they start to “feel” the weak intermolecular attractive forces and aggregate to form droplets.

Industrial gases are liquefied by the combination of these two techniques.

In every substance, there is a temperature above which the liquid phase of a pure substance cannot exist no matter how much pressure is applied. This is called the **critical temperature**. The critical temperature is expressed as  $T_c$ .

In every substance, there is a minimum pressure that must be applied to liquefy that substance at  $T_c$ . This is called the **critical pressure**. The critical pressure is expressed as  $P_c$ .

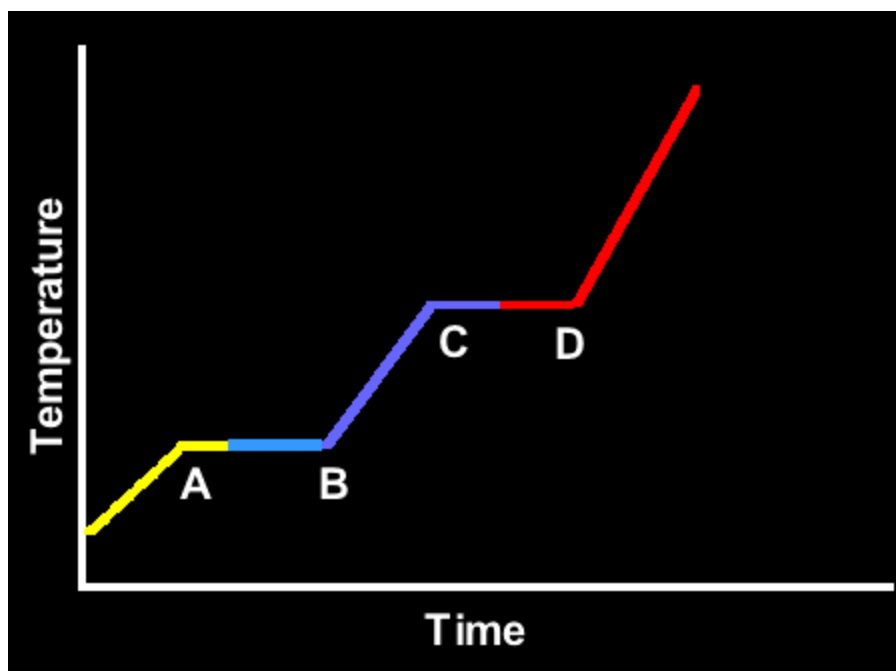
Critical pressure and critical temperature define the **critical point** of a substance.

## Section 10.12: Liquid – Solid Equilibrium

Cooling a liquid transforms it into a solid. This process is called **freezing** or **crystallization**. Conversely, heating a solid transforms it into a liquid. This process is called **melting** or **fusion**.

The melting point of a solid or the freezing point of a liquid is defined as the temperature at which the solid and liquid phases coexist in equilibrium. The normal melting point or the normal freezing point is defined as the temperature at which the substance melts or freezes at a pressure of 1 atm.

Consider the heating curve of a substance. The heating curve is a plot of temperature vs. time.



When a solid is heated, its temperature increases gradually up to point A. At point A, the solid begins to melt. This is defined as the melting point of a solid.

As the substance is further heated from A to B, heat is being absorbed but the temperature remains constant. Under these conditions, the solid and liquid are in equilibrium. The molecules in the solid overcome the attractive forces by absorbing heat.

As the liquid absorbs more heat, the kinetic energy of the liquid molecules increases resulting in an increase in temperature and the curve goes from B to C.

At point C, the liquid begins to convert to vapor. This is defined as the boiling point of the liquid. While the liquid to vapor transformation takes place, the temperature remains constant. Under these conditions, the liquid and vapor are in equilibrium.

All the liquid is converted to vapor at point D. After point D, the absorption of heat simply increases the temperature of the vapor.

$\Delta H_{\text{fus}}$  is defined as the **molar heat or enthalpy of fusion**. The molar heat of the fusion is the amount of heat required to melt one mole of a solid.  $\Delta H_{\text{vap}}$  is defined as the **molar heat or enthalpy of vaporization**. The molar heat of vaporization is the amount of heat required to vaporize one mole of a liquid. The magnitude of  $\Delta H_{\text{fus}}$  is small

compared to  $\Delta H_{\text{vap}}$  because more intermolecular interactions are lost during vaporization than during melting.

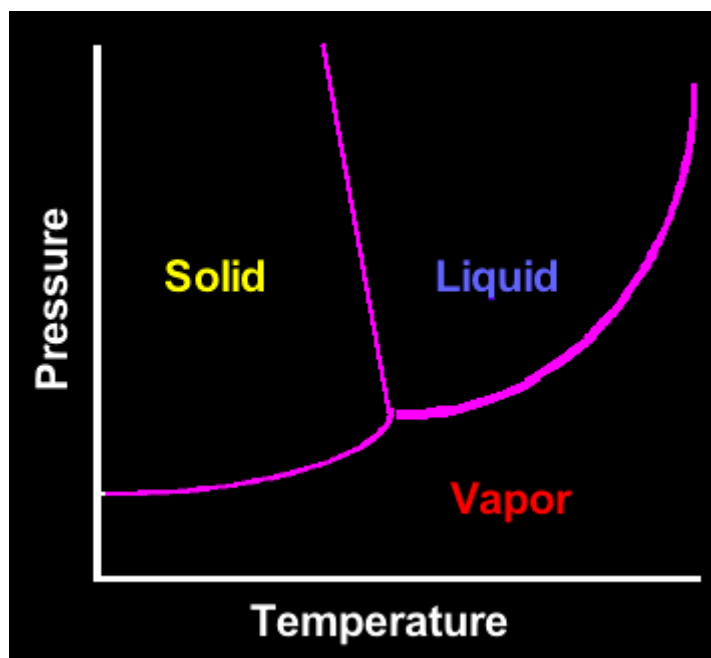
### Section 10.13: Solid – Vapor Equilibrium

Certain solids evaporate and therefore have a vapor pressure. A process in which the solid goes directly into the vapor phase is called “**sublimation**”. A process in which the vapor goes directly into the solid phase is called “**vapor deposition**”. At a certain temperature and pressure the solid and vapor are in equilibrium.

This is expressed as:  $\text{Solid} \rightleftharpoons \text{Vapor}$ .

### Section 10.14: Phase Diagram of H<sub>2</sub>O

A graph depicting the conditions of pressure and temperature where the solid, liquid and vapor phases exist or coexist is called the **phase diagram**. A phase diagram is shown below in the case of H<sub>2</sub>O:



The phase diagram is a plot of pressure vs. temperature which is divided into three regions: **solid**, **liquid** and **vapor**. Each region represents a **pure phase**.

The line separating any two phases indicates conditions in which these two phases **coexist** in equilibrium. Hence, these lines or curves are called **coexistence curves**.

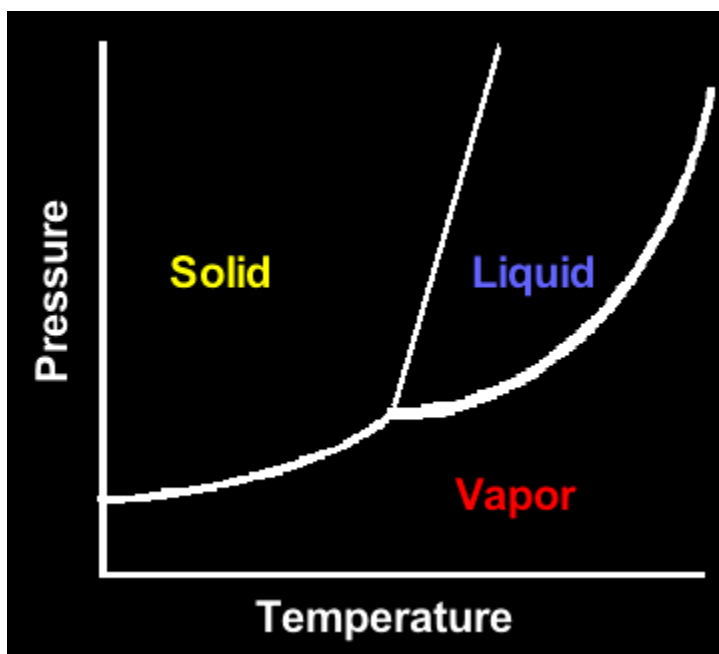
The point at which all three curves meet is called the **triple point**. The triple point is defined as the point at which all three phases can coexist in equilibrium with one another. For H<sub>2</sub>O, the triple point temperature is 0.01 deg.C. and pressure is 0.006 atm.

Phase diagrams predict the changes in the melting and the boiling points as a result of changes in pressure.

- The normal melting point of H<sub>2</sub>O is 0 deg.C. at 1 atm and the normal boiling point of H<sub>2</sub>O is 100 deg.C. at 1 atm.
- An increase in the pressure leads to a decrease in the melting point and an increase in the boiling point for H<sub>2</sub>O.
- Conversely, a decrease in pressure will lower the boiling point and increase the melting point for H<sub>2</sub>O.

### Section 10.15: Phase Diagram of CO<sub>2</sub>

A phase diagram is now shown for CO<sub>2</sub>:



Again, the phase diagram is divided into three regions: solid, liquid and vapor. The triple point of CO<sub>2</sub> occurs at 5.2 atm and - 57 deg.C.

The phase diagram of CO<sub>2</sub> is in many ways similar to that of H<sub>2</sub>O, except that the melting point of CO<sub>2</sub>, like the melting point of most substances, increases with increasing pressure.

Note: The entire liquid phase of CO<sub>2</sub> is well above the atmospheric pressure (1 atm). This is the reason why solid CO<sub>2</sub> sublimates at 1 atm. In fact, solid CO<sub>2</sub> is called “**dry ice**”. It is called dry ice because it looks like ice, but it does not melt.

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