

# *Liquids and Solids*

## **Phase Transitions**

All elements and compounds undergo some sort of phase transition as their temperature is increase from 0 K. The points at which these phase transitions occur depend on the substance being examined. There are three types of phase transition. Two that should be familiar are melting and boiling. The third is called sublimation and is a transition from the solid phase directly into the gas phase. Each type of phase transition has associated with it an enthalpy ( $\Delta H$ ).

Melting (Freezing)	$\Delta H_{\text{fus}}$ (Heat of fusion)
Boiling (Condensation)	$\Delta H_{\text{vap}}$ (Heat of vaporization)
Sublimation (Deposition)	$\Delta H_{\text{sub}}$ (Heat of sublimation)

The heat of fusion is numerically the same as the heat of freezing, only the sign is different.

When a phase transition occurs the temperature does not change. This is because the heat being added to or removed from the system is involved in changing the state of the substance, not in changing the temperature. As a result, the equation used for calculating the amount of heat transferred that we used earlier cannot be used for phase transitions. The heat transferred in a phase transition is equal to the number of moles of the substance times the heat of phase change.

$$q = \pm n\Delta H_{\text{fus,vap,sub}}$$

If we were to plot the temperature of a substance versus the heat added to the substance we would not get a constantly increasing line. There would be plateaus in the line where the phase changes.

When the temperature changes, the heat transferred can be calculated with

$$q = ms\Delta T = C\Delta T$$

When the phase changes we use

$$q = \pm n\Delta H_{\text{fus,vap,sub}}$$

We can get the total heat transferred for the entire heating process by adding the heats from the individual processes (temperature changes and phase changes).

## **Boiling and Vapor Pressure**

We may recall from earlier that the vapor pressure is the partial pressure of a liquid in a closed system at equilibrium. The vapor pressure increases with the temperature. Earlier when we used linear interpolation we assumed that the vapor pressure increased linearly with temperature. In reality it's more complicated. It can be shown that the relationship between vapor pressure,  $p$ , and temperature,  $T$ , is

$$\ln p = -\frac{A}{T} + B$$

In this equation  $A$  and  $B$  are constants that are substance dependent.  $A$  can be shown to be

$$A = \frac{\Delta H_{vap}}{R}$$

where  $R$  is the ideal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ). Often we are concerned with what the vapor pressure is at a particular temperature. If we already know the vapor pressure at one temperature, we can calculate what it should be at the other temperature if we know the enthalpy of vaporization. We can find this relationship by subtracting the above equation from itself at the two different points. We then have:

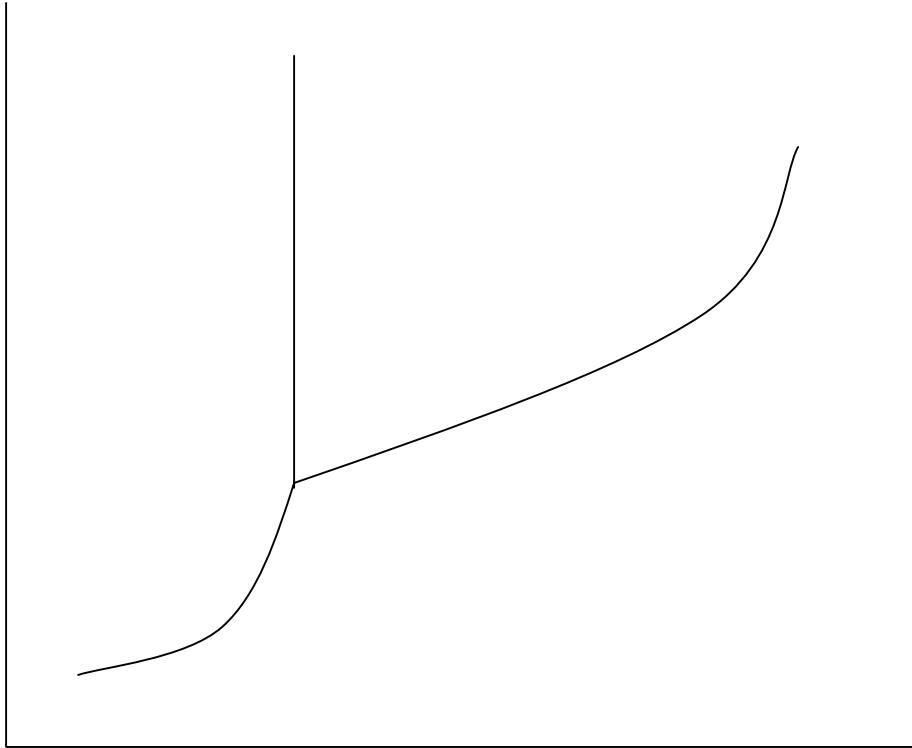
$$\ln \frac{p_1}{p_2} = \frac{\Delta H_{vap}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

When using this equation we need to remember to keep everything straight. If we have  $p_1$  on the top of the left hand side, then we must have  $T_1$  as the last term on the right hand side.

What exactly is boiling? It is the phenomenon where, when a liquid is heated, the vapor pressure increases to be equal to the external atmospheric pressure. The definition of boiling is exactly that. When the vapor pressure of a liquid increases to be equal to the external pressure, the water can start forming bubbles in the bulk of the liquid. This is what we see when a liquid boils. What we mean when we say that the boiling point of water is  $100.0^\circ\text{C}$  is that the **normal boiling point** is  $100.0^\circ\text{C}$ . The **normal boiling point** is the temperature at which the vapor pressure is equal to 1 atm. The boiling point is for any pressure; the normal boiling point is specifically at 1 atm.

### ***Phase diagrams***

We can collect the data about the phase of a particular substance at various temperatures and pressures into a graphical format. This graph is called a **phase diagram**. The phase diagram will tell us what phase something is in if we know the temperature and the pressure. It will also tell us the melting point, sublimation point or boiling point of a substance if we know the pressure. This data can be useful. A phase diagram has the following general form.



The almost vertical line in the phase diagram is the melting point curve. In most substances it leans very slightly to the right. In water it leans very slightly to the left. This is why the solid form of water (ice) is less dense than the liquid form of water. If we apply pressure to ice (compressing it) it converts to the liquid form.

The lower curved line is the sublimation point curve. It is the collection of pressures and temperatures where the solid converts directly into the vapor.

The upper curved line is the boiling point curve. It will give us the boiling point of a substance at any given pressure.

The three lines meet at a given temperature and pressure. The point where they meet is called the **triple point**. The triple point is the temperature and pressure where three phases are in equilibrium with each other. The triple point in the above phase diagram has the solid, liquid and gas phases in equilibrium. There may be more than one triple point in a phase diagram, because there may be more than one solid (or liquid) phase.

The boiling point curve ends abruptly at the upper point. This is different from the melting point curve, which extends indefinitely. We can explain this behavior by imagining we have a liquid in a sealed container that is infinitely strong. As we heat the liquid in the container, the vapor pressure of the liquid increases. However as the vapor pressure increases so does the pressure above the liquid because the vapor cannot escape.

This results in the liquid never boiling. The vapor in the container becomes denser as the vapor pressure increases. Eventually, the vapor and the liquid have the same density. This occurs at the **critical temperature** (the end of the boiling point curve). Above this temperature the liquid phase no longer exists. The **critical pressure** is the pressure at the critical temperature.

### *Intermolecular forces*

All substances can be liquefied or even solidified if the temperature is lowered enough. This is an indication that there are some attractive forces between all molecules and atoms. Some molecules have stronger forces between them than others. Water, for instance, has very strong forces between the molecules. Evidence for this is the fact that water has a very high boiling point for a molecule of its molar mass. All other molecules with a similar molar mass are gases at room temperature and pressure. Only water is a liquid.

What are the forces that hold molecules to each other? What determines what will have a higher or lower boiling point?

The weakest of the intermolecular forces are the **London forces**. All molecules possess London forces. This force arises when two molecules get close to each other. The nuclei on one molecule will start to attract the electrons on the other molecule. This sets up an induced dipole in the molecules. The induced dipole is very temporary; it lasts for only a very small fraction of a second. This is the reason this force is so weak. A molecule that possesses only London forces must get its kinetic energy low enough (a low temperature) to allow the potential energy of the London force to keep it in contact with other molecules (convert to the liquid state). The London force increases with molar mass and molecular volume. A more spread out molecule is more easily polarized than a compact one.

The intermolecular force that comes in the middle is the **dipole-dipole interaction**. This interaction exists only between polar molecules. The positive end of one molecule will attract, through electrostatic interactions, the negative end of another molecule. If the temperature is low enough, this will serve to hold the molecules together in the liquid phase.

**Hydrogen bonding** is the strongest of the intermolecular forces. This force requires a molecule to possess a hydrogen atom attached to a very electronegative atom (such as oxygen, nitrogen or fluorine). The electronegative atom will tend to pull electrons away from the less electronegative hydrogen atom. This leaves the nucleus partially exposed. The hydrogen atom will then try to attract any electrons that come by. Usually, these electrons are the lone pair electrons on the oxygen, nitrogen or fluorine from another molecule. The attraction is actually a weak coordinate covalent bond between the hydrogen on one molecule and the corresponding electronegative element on another molecule.

A molecule that possesses more of these forces will have a higher boiling point than one that does not. This explains why water, which has all three forces, has a higher boiling point than methane, which has a similar molar mass but has only London forces.

## ***Solids***

There are two distinctly different kinds of solids. The first is the amorphous kind of solid, which is represented by plastics and glass. The second is the crystalline solid, which is represented by ionic solids. We will concentrate here on the crystalline solids.

### **Types of crystalline solids**

There are four types of crystalline solids: ionic, molecular, metallic, and covalent network. Each of these types has different physical properties.

#### **Ionic solids**

This type of solid is held together by the attraction of positive and negative ions. As a result, ionic solids tend to be very brittle. They will shatter very easily. Although they are comprised of positive and negative ions, they will not conduct electricity, unless they are melted or dissolved in water. The melting points of ionic solids range from a few hundred to a couple of thousand Kelvin.

#### **Molecular solids**

The intermolecular forces described above hold molecular solids together. They also tend to be very brittle. Because of the weaker interactions between particles the melting points of molecular solids range from a few Kelvin to a couple of hundred Kelvin. These solids do not conduct electricity under any conditions.

#### **Metallic solids**

**Non-directional bonding** holds metallic solids together. Non-directional bonding results from the loosely held valence electrons of metals. Each metal atom in the solid shares its valence electrons with every other atom in the solid. This is also the reason that metallic solids are excellent electrical conductors. Metals are not brittle. They are ductile (can be drawn into wires) and malleable (they can be pounded into sheets). These properties are also explained by the non-directional bonding in metals. Metals have melting points from a couple of hundred Kelvin (Mercury and Cesium) to several thousand Kelvin (Tungsten).

#### **Covalent Network solids**

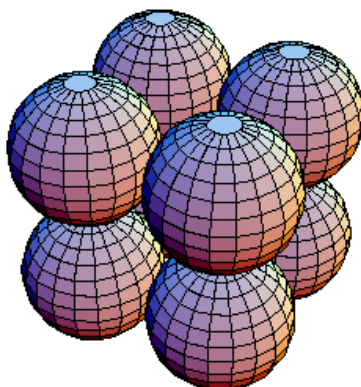
Covalent network solids are essentially giant covalent molecules. Each atom in this type of solid is covalently bonded to at least two other atoms. Covalent network solids tend to be very hard but also brittle. Diamond is an example of this kind of solid. It is the

hardest natural substance known but will shatter if struck with a hammer. Some examples of this type of solid are electrical conductors, like graphite. Most do not conduct electricity. The melting points of covalent network solids are very high, several thousand Kelvin. This is because covalent bonds must be broken to turn it into a liquid.

All crystalline solids have a repeating structure on an atomic level. Usually the geometry of this structure is shown in the shape of crystal on a macroscopic level. The smallest unit of the structure that can be used to reproduce the whole crystal is called the **unit cell**. There are several types of unit cells. We will look at only four of them and only three of them in detail.

### Simple Cubic

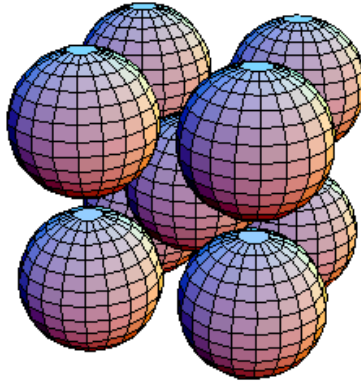
As the name implies this is the simplest of the cubic structures. There is an atom centered at each vertex of a cube and each atom touches the atoms closest to it along the edges of the cube. Because there is one atom at each vertex and eight other cells share it, there is one-eighth of an atom in the unit cell at each vertex. This makes a total of 1 atom in the simple cubic unit cell. Each atom in the structure touches six other atoms. This is called the **coordination number**.



We can find a relationship between the edge length of the unit cell and the atomic radius. Looking at the diagram above we see that the edge length is twice the atomic radius. Edge lengths and atomic radii are often given in units of pm ( $1 \text{ pm} = 10^{-12} \text{ m}$ ).

### Body Centered Cubic (bcc)

The body centered cubic unit cell, often abbreviated bcc, has an atom centered at each of the vertices of the cell and 1 atom at the center of the cell. Using the same logic as for the simple cubic cell, we find that there are two atoms per unit cell. The atoms touch each other along the diagonal of the unit cell. The coordination number in the bcc is 8.



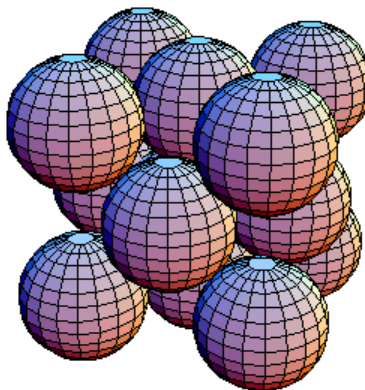
The relationship here is a little more difficult to determine. We need to use the Pythagorean theorem in three dimensions to determine this. The diagonal of the cell is 4 atomic radii long. The relationship can then be derived as:

$$(4r)^2 = e^2 + e^2 + e^2 = 3e^2$$

$$e^2 = \frac{(4r)^2}{3} : e = \frac{4r}{\sqrt{3}}$$

### Face Centered Cubic (fcc)

The face centered cubic unit cell, abbreviated fcc, has an atom centered at each corner and on each face. There is  $\frac{1}{2}$  of an atom at each face and  $\frac{1}{8}$  of an atom at each corner. There are 6 faces and 8 corners on a cube so there are 4 atoms per unit cell. The atoms touch each other along the diagonal of the face of the cell. The coordination number in the fcc is 12.



The diagonal of the face of the cell is equal to 4 atomic radii. The relationship between edge length and the atomic radius is then:

$$(4r)^2 = e^2 + e^2 = 2e^2$$

$$e^2 = \frac{(4r)^2}{2} : e = \frac{4r}{\sqrt{2}}$$

With any unit cell we can calculate the **packing fraction**, or the fraction of the space in the cell that is occupied by atoms. This can be calculated as:

$$\frac{V_{atoms}}{V_{cell}}$$

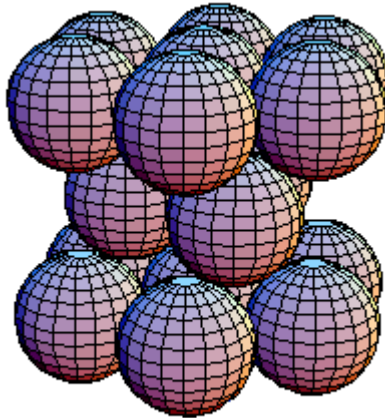
The volume of the atoms is assumed to be the same as the volume of a sphere with the same radius. The volume of the cell is equal to the edge length cubed. For a simple cubic unit cell with 1 atom per cell we have:

$$\frac{V_{atoms}}{V_{cell}} = \frac{\frac{4}{3}\pi r^3}{e^3} = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\frac{4}{3}\pi}{8} = \frac{\pi}{6} = 0.5234$$

or about 52% of the space in the unit cell is occupied by atoms.

### Hexagonal close packed (hcp) and cubic close packed (ccp)

There are two types of close packed structures. A close packed structure has as many atoms packed into the unit cell as is possible. One of these close packed structures is called **cubic close packed** and is identical to the face centered cubic unit cell. The other is called **hexagonal close packed**. This is not equivalent to any cubic structure.



The hexagonal close packed structure and the cubic close packed structure have the same coordination number and the same packing fraction.