Lecture 5

Learning Objectives:

- Phase behaviour of pure substances.
- Learn what is a phase diagram.
- Become familiar with pure substance phase diagrams

4.4 Phase Behaviour of Single Component Systems

Single component means a pure substance. Application of phase rule relates the degrees of freedom to number of phases present.

$F = C + 2 - P$; $C = 1$, therefore $F = 3 - P$

Since the degrees of freedom cannot be negative, we can have at most three phases. We must also have at least one phase; the pure substance has to exist in some form. Therefore, we have three possibilities in terms of the number of phases; single-phase systems, 2-phase systems and three-phase systems. Let us examine these in some detail.

4.4.1 Single Phase Systems

In the phase rule, we now have $C = 1$ and $P = 1$. Therefore the degrees of freedom are

$F = C + 2 - P = 1 + 2 - 1 = 2$.

It means we have to specify two intensive variables to completely fix the state of the system. These two variables often are the temperature and pressure. Once you have fixed the temperature and pressure, all other intensive properties are fixed, since there are no degrees of freedom left. Of course, you could have selected other intensive variables in place of the temperature and pressure such as density and the refractive index. In that case also, fixing the two intensive variables fixes the values of all other intensive variables. However, it is often most convenient to specify the temperature and pressure, since these variables are easiest to relate to or visualize. Then the values of all other variables become functions of the temperature and pressure.

For example, if T & P are used as independent variables then
Density, $\rho = f(P,T)$ and
Specific volume $V = V(P,T) = 1/\rho$.

The single phase that the substance exists as can be a solid, liquid or gas. Which phase it would be at the given temperature and pressure depends on the substance involved. <u>The phase rule does not tell you anything about the nature of the phase.</u>

The relationship between the density (or specific volume) and the temperature and pressure is called equation of state. We will study equations of state in the next two chapters.

Two-Phase Systems:

By two-phase systems, we mean two phases existing at equilibrium. These could be

- Vapour - liquid
- Vapour - solid
- Liquid - solid
- Solid - Solid

Now we have P = 2, in the phase rule. This gives

F = C + 2 - P = 1 + 2 - 2 = 1.

It means we have only one degree of freedom. Fixing one intensive variable will fix the values of all other intensive variables.

<u>Liquid -Vapour Systems</u>
Let us consider a liquid vapour system first. If the pressure is fixed, the liquid and vapour can coexist only at one fixed temperature. This temperature is the boiling point of the liquid. When the pressure is one atmosphere (101.325 kPa), then the temperature is called normal boiling point.

If you fix the temperature first, the system can have coexisting liquid and vapour only at a particular pressure. This pressure is called the bubble point pressure if the phase change is from liquid to vapour and the dew point pressure if the vapour is condensing to form a liquid.

<u>Solid-Liquid Systems:</u>
A pure substance can have coexisting solid and liquid phases only under some conditions. If the pressure is fixed, the temperature at which solid and liquid coexist is called the freezing point of the liquid or the melting point of the solid.

<u>Solid-Vapour Systems</u>
At relatively low pressures, it is possible for a pure solid to coexist with a vapour phase, without any liquid in the system. The process of transformation of a solid to vapour

without going through a liquid phase is called sublimation - the reverse is called de-sublimation. At fixed pressure, this occurs at a particular temperature, called sublimation temperature.

Table 4-4 presents some data for water. At low pressures and temperatures (first three rows), we have ice and vapour present, but no liquid. The last five rows have liquid and vapour present, but no solid.

The fourth row shows all three phases present. It corresponds to the so-called triple point.

4.4.3 Three-phase Systems:

Now P = 3, C = 1, therefore F = C + 2 - 3 = 0.

There are no degrees of freedom. A pure substance can form three coexisting phases only at very special conditions, called triple point.

These are characteristic of the pure substance. The temperature and pressure at which three phases coexist is fixed. For water, at 0.01°C, and 0.6113 kPa, ice, liquid water and water vapour can coexist.

Note that a pure substance that forms more than one solid phase can have more than one triple point. When we examine the phase behaviour of water in detail, we will see that there are other triple points for water involving different forms of ice.

More than Three Phases:

According to the phase rule, the degrees of freedom would be negative if more than three phases of a pure substance were coexisting. This can be taken as being impossible.

We have seen that a pure substance exists in different phases depending on the conditions of temperature and pressure. If you know the temperature and pressure of a pure substance, you can determine what phase (or phases) it will exist as in two ways: (1) by experimentation and (2) by looking up the information in a handbook that is based on experimentation by others.

It is useful to present this information in a compact way – in diagrams. Such diagrams are called "phase diagrams." Phase diagrams are basically maps that divide the two-dimensional space defined by two intensive variables into territories occupied by different phases. Any two intensive variables can be used, but we will consider only two pairs: (1) Pressure & Temperature and (2) Pressure and Specific Volume.

4.4.5 The P-T diagram of a pure substance

It describes the phase behaviour in the two-dimensional space defined by pressure and temperature.
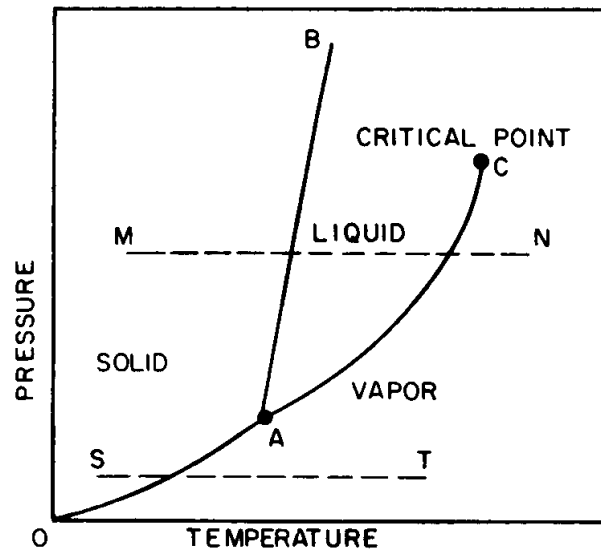

Figure 4-1 is such a diagram. Let us see what it represents.

What does a point Represent on this map?

— Each point on the diagram represents a unique combination of pressure and temperature.
— If you want to look up the information for specified pressure and temperature, you start by locating the point that represents that combination.
— Once you have located the point, you can see which region it falls in and decide what phase the material will exist as.
— These regions in this diagram are labelled solid, liquid and vapour.
— Note that both pressure and temperature can vary considerably without one crossing over to a region of a different phase. Therefore you have two degrees of freedom in these regions.

What does a line joining two points represent on this diagram?
— A line on an ordinary map (say map of Alberta) represents a path, say a trail or road or the path that a river follows.
— A line on this diagram also represents a path. It describes one specific way of going from one point to another.
— The line also represents a relationship between temperature and pressure. If you want to move on the line, pressure and temperature are no longer independent.

What if the point falls on the boundary between two phases?
— When the point is on the boundary between two phases, the substance has one foot in

each phase.
- It is the condition at which two phases can coexist.
- These boundaries are fixed lines on the map; if you specify either temperature or pressure; the point can be located on the line.
- Hence you have only one degree of freedom.

What about point A where three regions meet?
- It represents the condition at which three phases can coexist.
- Because it is a fixed point, you have no degrees of freedom.

Let us now examine the lines that form phase boundaries.
- If you move along these lines you will continue to have two coexisting phases.
- Thus they represent the two-phase locus.
- There are also special names attached to these boundary lines.

    OA -- Sublimation line
    AC -- Boiling point curve
    AB -- Freezing point curve or melting point curve

Curve O-A-C is the vapour pressure curve. At pressures below this curve, only vapour can exist; above it the material condenses to liquid or solid depending on the temperature.

There are also two special points on diagram.
A -- Triple Point, representing temperature and pressure at which three-phases coexist
C -- Critical Point, it represents the condition at which the liquid and vapour properties become indistinguishable. If the temperature and pressure are higher than the critical point values, the substance is called a super-critical fluid. We will examine the critical point more closely later in this course.

Now let us see what this diagram tells about changes in the phase of the substance by heating.

- Let us assume that you start at point M and increase the temperature at constant pressure.
- You will move along the line M-N by increasing temperature at constant pressure. The point, at which the line MN crosses the line AB, represents the melting point of the substance. The solid will start melting into the liquid phase at that point.
- Further increase in temperature will move you to the right and you will eventually hit the AC line.
- The point where you cross the AC line is the boiling point of the liquid. It will start boiling into a vapour phase at that point.
- So you go from solid to liquid to vapour by heating and the phase diagram tells you the

temperatures at which the phase change will occur.

If we had started at point S, the constant pressure heating will be along the line S-T. Now you will cross the sublimation line and the solid will change to a vapour phase without going to liquid first.

Let us look at pressure increase at constant temperature.

Let us say we start at point x, which is below the triple point temperature and increase the pressure along the line x-z. The point x is clearly in the vapour region. We will cross the sublimation line at point y. At that point there is a phase change, and since we have vapour below the sublimation line and solid above it, we know the change will be from vapour to solid. Further increase in pressure to point z will only increase the stress in the solid but no phase change will take place.

Now let us see what happens when you start at point Q, which is above the triple point temperature. You first cross the liquid-vapour line, AC at point R, which implies that the vapour will condense into a liquid phase. Further increase in pressure will take us to point S where the solid-liquid line is crossed. Now the increase in pressure will cause the liquid to solidify at point S. Beyond that you are only compressing the solid.

*So far we have only looked at a generic phase diagram, without identifying the pure substance involved. This was meant to give you the general idea of what phase diagrams are all about. Now you should be ready to look at some real substances. We will examine a substance of great interest to all engineers, namely **water.***
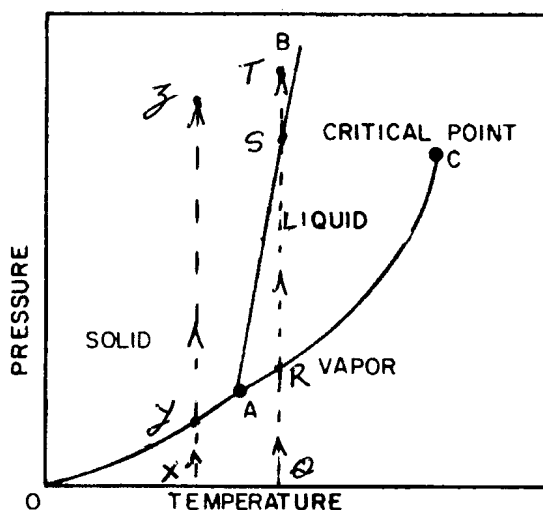
We all know that water can exist as steam in vapour phase, ice in the solid phase. You are now going to learn that ice comes in different varieties, which are actually distinct crystalline phases of water.

Let us first look at the big picture. Note the pressure scale, it is in **Giga-Pascals. One gigapascal is about 10,000 atm.** So we are talking about very high pressures. Note that there are several points where three different phase regions meet. These are all triple points.

Because of the scale used you cannot see the vapour region; it is so small on this map that it disappears into the x-axis line. It takes an expanded scale diagram to see what is going on at lower pressures. This is shown in Fig 4-2b.
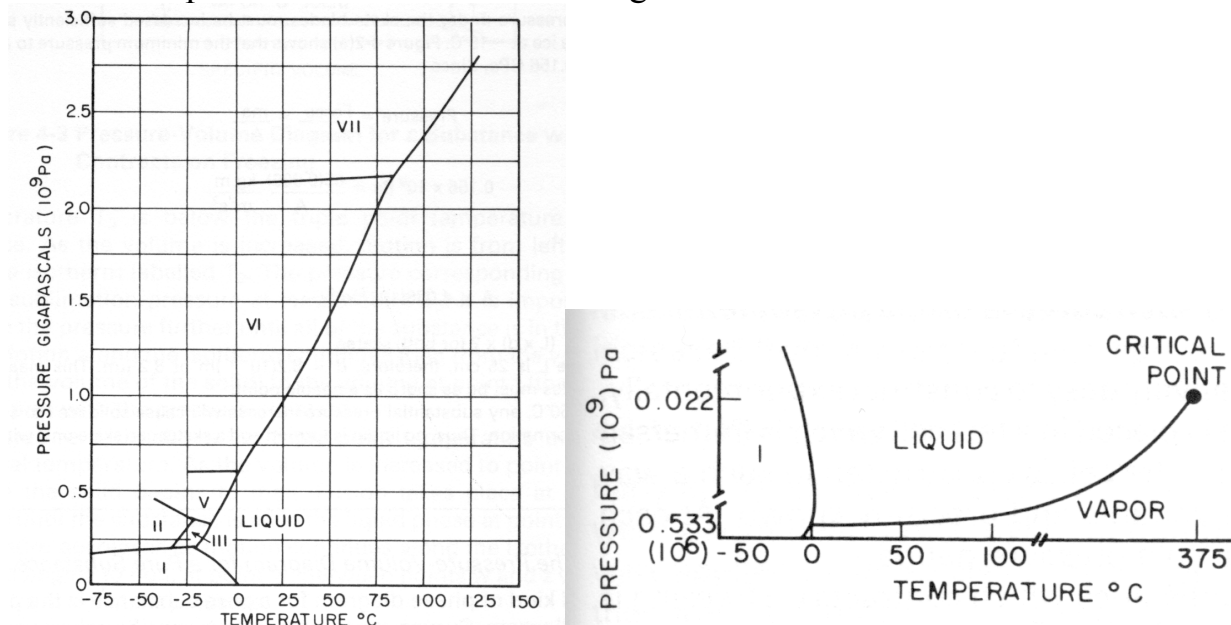
At low pressure we have vapour, liquid and ice-I as the three phases. These are the phases you see in everyday life. The triple point is between Ice-I, liquid and vapour. It occurs at 0.01°C and 0.6113 kPa. The critical point of water is at 375°C and 22 MPa pressure.

P-v Diagrams
So far we have seen only one type of pure substance phase diagram using pressure and temperature as the intensive variables. However, as we saw earlier the state of the system can be described using any intensive variables. Phase diagrams can also be made with other intensive variables.

Another useful combination for pure substances is pressure and specific volume.

<u>Specific Volume</u>, v = volume per unit mass = 1/density in units of m^3/kg.

It is also possible to use volume/kmol, i.e. m^3/kmol. **<u>Pay attention to the scale used in calculations.</u>**

A P-v phase diagram uses v in place of T. Let us examine a typical P-v diagram for a pure

substance. For example, that shown in **Figure 4-3** in the textbook is for a substance that contracts on freezing.
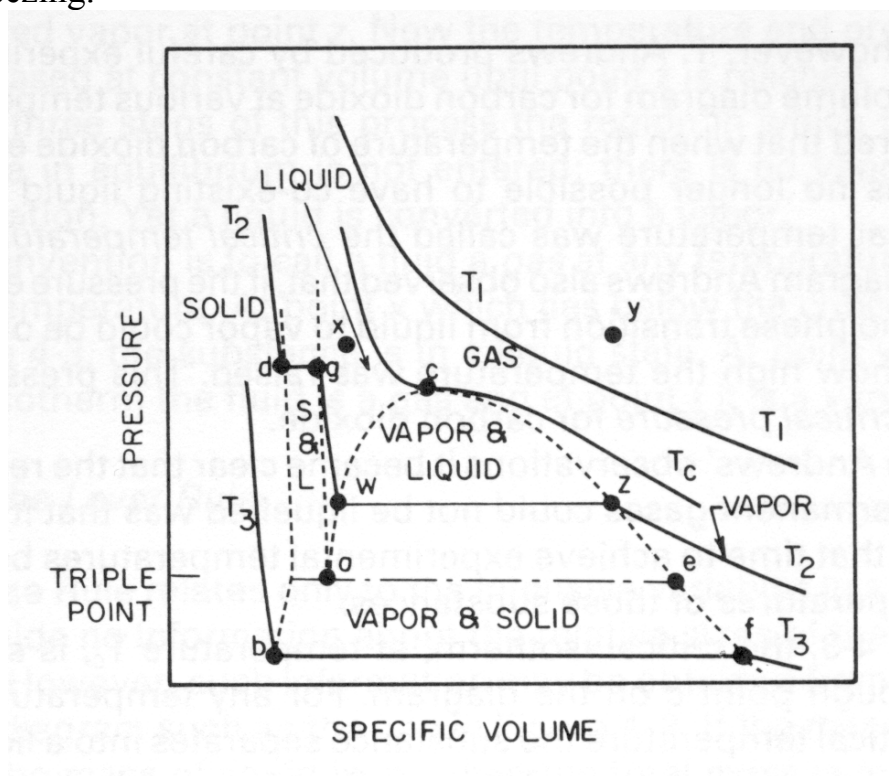
This diagram looks a lot more complicated than the P-T diagram. The reason is that it is trying to show information on what happens when pressure changes at constant temperature by plotting paths of constant temperature. These lines are called isotherms, which literally means constant temperature.

Let us ignore the solid lines labelled T_1, T_2 & T_3 and focus on the dashed lines only. Now this diagram also represents different regions divided by boundaries. **However, there is one big difference. All regions here do not represent single-phase situations. There are regions labelled V+L, V+S and S+L.** These are two-phase regions. In the area labelled V+L, vapour and liquid coexist. Similarly in the area S+L, solid and liquid coexist. Line o-e represents the triple point, where solid, liquid and vapour coexist. Note that the triple point is now represented by a line, along which the volume can change, but pressure and temperature remain constant.

- If you were given a pressure and specific volume value, you can determine from this diagram what kind of phases the substance would exist as.
- If the point falls in vapour-liquid region, the substance will be in the form of coexisting liquid and vapour.
- We will learn later how to determine what fraction will be liquid and what fraction will be solid.
- This information can also be inferred from the phase diagram.

There are three isotherms plotted on the diagram.

T_3 < triple point temperature; Increase in volume at constant temperature takes the system from all solid to all vapour through the solid-vapour region. The phase change for a pure substance at a specified temperature occurs at constant pressure. The reason is that the two-phase system can have only one degree of freedom. If the temperature is fixed, the two-phase pressure is automatically fixed.

Triple point < T_2 < Critical pt. Temp. There are two phase changes involved along this isotherm. The first represents melting of solid at constant pressure and the second is boiling of the liquid, again at constant pressure.

The isotherm T1 is at a temperature above the critical temperature; it involves no phase change.

4.4.7 The Critical Point

At critical point the coexisting liquid and vapour phases have identical properties, i.e.

$$\rho_l = \rho_v$$

This requirement uses one degree of freedom in the two-phase system. Since the two-phase system has only one degree of freedom to start with, and this gets used up by the requirement of equal density, there is no degree of freedom left. **The critical point is a fixed point for all pure substances. T_c, P_c and all other intensive properties have unique values at the critical point.**

The critical isotherm passes through the critical point and just touches the two-phase envelope. It is the borderline isotherm, if the temperature is above the critical point; there will be no phase change, if it is below the critical point, there will be phase change by expansion. At the critical point, there is a phase change, but since the properties of the two phases do not differ, you will not see it happen experimentally.

A fluid above its critical point temperature is called gas. Below T_c it is called vapour or liquid depending on the specific volume.