Thermodynamics: Classical to Statistical

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Lecture - 11

Phase Diagram of one component systems

Today, we will discuss phase rule and phase diagram of one component system. What is phase rule? **Phase rule** is a relation between the number of components (and we denote component by C), the number of phases (we represent phase by P) and the variable parameters (we call degrees of freedom and we define degrees of freedom by F) of a heterogeneous system in equilibrium. The phase rule was first introduced by Gibbs in the year of 1876 and the phase rule it is expressed as, $F = C – P + 2$. So it deals with the effects which changes in pressure, temperature and concentrations will have on the equilibria of heterogeneous systems. Now what is phase? In order to understand phase rule we need to understand component, we need to understand phase. So first we will start with what is **phase**? A phase is defined as a physically distinct but homogeneous part of a system separated from other parts by boundary surface. So how do you define phase? Phase is defined as a physically distinct but homogeneous part of a system separated from other parts by boundary surface. For example, simplest example is liquid water is in equilibrium with water vapor (Figure 1).

Figure 1

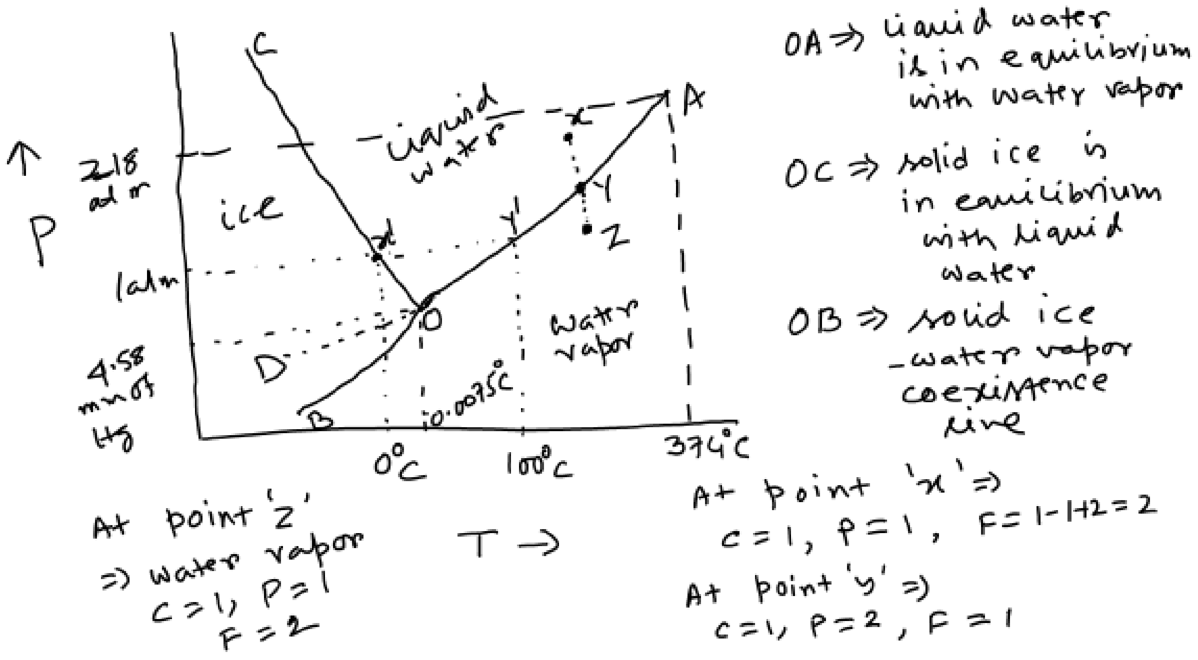
So the liquid region is homogeneous, vapor region is homogeneous and they are separated by a surface or interface. Thus, we can write, a heterogeneous system is composed of two or more phases. So homogeneous phase is only one phase, heterogeneous system means two or more number of phases. So we can write the gas mixer is homogeneous. Similarly, homogeneous solution is also homogeneous. Whatever the number of components in the solution are.

On the other hand, if you consider the decomposition of solid calcium carbonate into CaO and CO_2.

$$CaCO3\ (s)\ \text{------------->}\ CaO\ (s) + CO_2\ (g)\ \text{-------}(1)$$

Here, we have how many phases? We have three phases one for calcium carbonate solid, another is calcium oxide, another is carbon dioxide gas. So each solid surface or each and every solute constitutes a separate phase. So it says each solid solute or each solids constitutes a phase. So this is a three phase system. So CaCo3 is in equilibrium with CaO and CO2 is a three phase system so we have defined phases. Now, what is **component**? Component, we can define like, the minimum number of independent chemical constituents by which the composition of phase of the system can be expressed, determines the number of components. One thing you should remember is, the components of a system are not synonymous with the constituents of the system. We should remember that, we will discuss this one with one example. Now, let us see how we can determine components, we will consider several examples. For example, water (liquid) is in equilibrium with water (vapor) (Figure 1). Here number of components is 1. Now, for the case of CaCO3 (equation 1), we just discussed. CaCO3 solid is in equilibrium with CaO solid + CO_2 gas. So in this case or in this equilibrium we have three chemical constituents, but total number of components is not three here. So here we have three chemical constituents. But C is not three here, because there is one restriction here because of the restriction, what is the restriction? The restriction here is the amount of CaO and CO_2 must be equivalent. So, we can write number of components C is number of constituents C prime minus number of restriction. Similarly, we can consider aqueous solution of NaCl (aqueous sodium chloride solution), another case we are considering. For this case how many constituents are there? Three, H_2O, Na^+ and Cl^-, but restriction is what? Restriction is number of sodium ion is equal to number of chloride ion. So it depicts that C or number of component is 2 here.

Next, we consider a phase diagram of water. We will consider first one component system. One component systems are comprised of pure substances only. For example water. The simplest and a typical example will be that of a system containing water. So today we will discuss phase diagram of water. Under ordinary conditions there are three possible phases of water. What are those three phases? Ice and then we have liquid water and then we have water vapor. These are the three phases one can have at ordinary conditions. Now, if we draw pressure temperature diagram for water, we are plotting here pressure versus temperature (Figure 2).



OA ⇒ liquid water is in equilibrium with water vapor

OC ⇒ solid ice is in equilibrium with liquid water

OB ⇒ solid ice – water vapor coexistence line

At point 'z' ⇒ water vapor $c = 1$, $P = 1$, $F = 2$

At point 'x' ⇒ $c = 1$, $P = 1$, $F = 1 - 1 + 2 = 2$

At point 'y' ⇒ $c = 1$, $P = 2$, $F = 1$

Figure 2

We get like this. This is suppose 1 atm and this is 0° C. Now, if we level them this is suppose point O, this is A, this is B, and this is C and at point O the pressure is 4.58 millimeter of mercury and then a temperature at point O is 0.0075° Celsius. So here we have liquid water in this region we get ice in this region, and in this region we get water vapor. Now, OA, every points on OA gives liquid water is in equilibrium with water vapor. So along line OA, along the curve OA liquid water is in equilibrium with water vapor. Similarly, along line OC, solid ice is in equilibrium with liquid water or OC represents solid liquid coexistence line. Similarly OA represents liquid vapor coexistence line, similarly we can write for OB this is nothing but solid ice water vapor coexistence line, so along this line solid ice and water vapour are in equilibrium with each other. Now, suppose we start with a point from here x, x is falls in liquid water, at point x, number of component is always one, we are considering one component system (pure water). We have only liquid water at point x, so number of phase is 1, so what is F?

$$F = 1 - 1 + 2 = 2$$

So this region is bivariance means you can change both pressure and temperature without disturbing the system. Suppose you can take point x somewhere here, here or here or here or here. So you can do that without disturbing the system. Now suppose, we keep the temperature fixed and if we start from point x and if we decrease the pressure to point Y like this. At point Y, what do we get? At Point Y, again C is 1, how many phases are there as we mentioned along line OA, we have 2 phases so number of phase is 2, means there we have liquid water as well as water vapor.

$$\text{So, } F = 1 - 2 + 2 = 1$$

So it gives F is 1, degrees of freedom is 1 at Point Y, means we can change either pressure or temperature not both simultaneously. Now, if we decrease the pressure further keeping the temperature constant, what we get? We arrive at a point Z. So at point Z we have only water vapor number of component is 1, phase is again 1,

$$\text{So, } F = 1 - 1 + 2 = 2$$

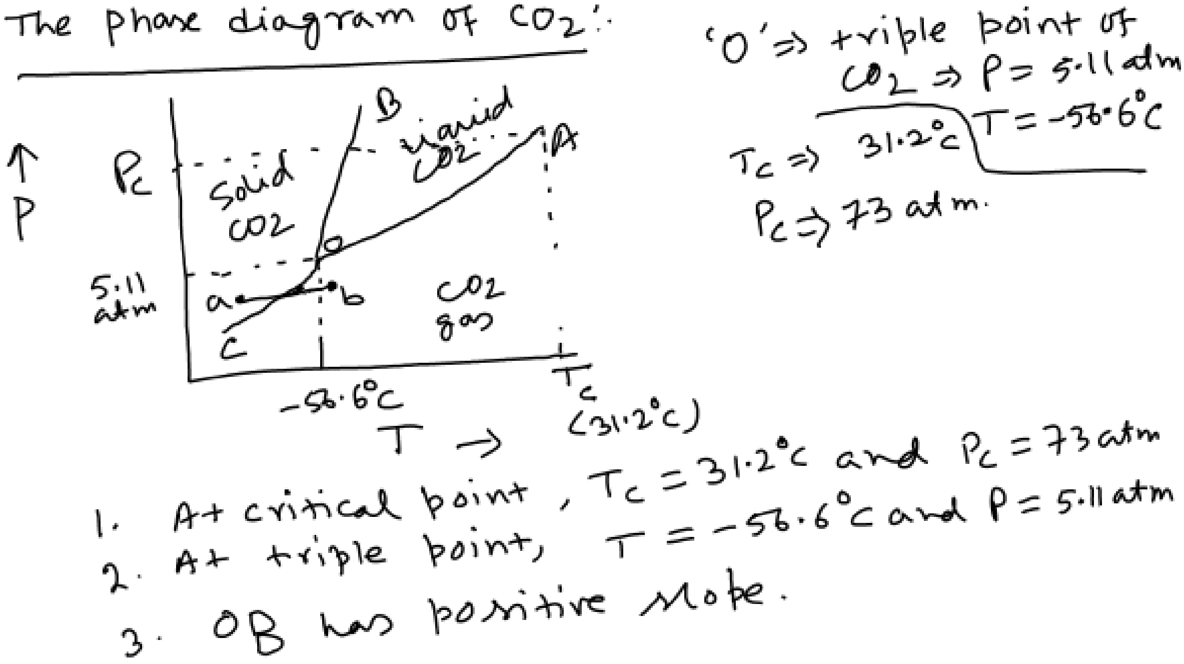
F is 2, so here also like point x we can change both pressure and temperature. Now, what is at point O? At point O all three phases of water coexist. You get all the three phases and at point O,

$$\text{So, } F = 1 - 3 + 2 = 0$$

F is 0. So degrees the number of degrees of freedom at point O is 0. So you cannot change anything there, it is fixed. The next thing is at one atmospheric pressure, here the point on OC line, suppose this is we say this is x`, so x` solid ice and liquid water coexist and the temperature of point x` is 0° Celsius. So x` represents the freezing point of water. Similarly, the point Y`, Y` again falls on OA line and at Y` the temperature is 100° Celsius, so it represents the boiling point of water. What is point A here? You cannot extend point A, at Point A temperature is 374°

Celsius and the pressure at point A is 218 atmosphere. So point ‘A’ is known as critical point. At critical point you cannot distinguish the liquid phase from the vapor phase. So this temperature, the 374° Celsius, known as critical temperature or T_C and 218 atmospheric pressure, it is known as critical pressure or P_C. Next, we can make a note here, it is possible to cool water below its freezing point without solidification. The liquid below its freezing point is said to remain in super cooled state. So this state is not quite stable but it is possible to cool water below its freezing point without solidification. If we extend this line or this OA to here OD, we can get liquid water without getting ice, without solidification. So that is we discussed, so far we discussed the phase diagram of water.

We will discuss now the phase diagram of carbon dioxide (Figure 3).



The phase diagram of CO_2:

‘O’ ⇒ triple point of CO_2 ⇒ P = 5.11 atm, T = −56.6°C

T_c ⇒ 31.2°c

P_c ⇒ 73 atm.

1. At critical point, $T_c = 31.2°c$ and $P_c = 73$ atm
2. At triple point, $T = -56.6°c$ and $P = 5.11$ atm
3. OB has positive slope.

Figure 3

It is very similar to that of water except one thing. We will see that. This is the phase diagram of carbon dioxide. Again O is triple point of CO_2, where pressure is 5.11 atmosphere and temperature is minus 56.6° Celsius. What is the difference there between the phase diagram of water and CO_2? Here the solid liquid coexistence curve for CO_2, the slope of this curve OB is positive here, and for water the slope of the solid liquid coexistence curve is negative, that is the difference here. Now what we can infer from this phase diagram. Let us see his is T_C, critical temperature of CO_2 and this is 31.2° Celsius and this is P_C, P_C is critical pressure is 73 atmospheric pressure. So what we can infer here?

i) At critical point T_C is 31.2° Celsius and P_C is 73 atm.

ii) At triple point temperature is minus 56.6° Celsius and pressure is 5.11 atm.

iii) OB has positive slope unlike that of water or phase diagram of water.

iv) This point is very important, liquid CO_2 cannot exist below 5.11 atm whatever the value of temperature is. If you look at the phase diagram of CO_2 what you find? Below 5.11 atmospheric pressure, suppose at this point here, you cannot get liquid CO_2, even if you increase the temperature, if you increase the temperature you get CO_2 gas, if you decrease the temperature you get solid CO_2. So you cannot get liquid CO_2 below 5.11 atmospheric pressure whatever the temperature is, remember that.

v) At normal pressure means P is 1 atmospheric pressure if we move from point ‘a’ to point ‘b’ what we get? Sublimation occurs, means we get CO_2 gas from solid CO_2, we obtain sublimation.

vi) Since the triple point pressure is higher than the external pressure (suppose external pressure is 1 atmospheric pressure) solid CO_2 reaches to the CO_2 gas without melting. So basically, point v and vi are very similar. So why we get a sublimation if we go from point ‘a’ to point ‘b’? Because the triple point of CO_2 is higher than one atmospheric pressure. So that is why we get sublimation at normal pressure that is all about the phase diagram of CO_2.