Diffusion in Multicomponent Solids
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Lecture 04
Equilibrium, stability & Phase Diagrams in Single Component Systems

In the last class we saw how the entropy changes are calculated during an irreversible process and most importantly we saw that interdiffusion is an irreversible process. It basically drives the system from non-equilibrium state to an equilibrium state. So how do we define an equilibrium state?

We have seen before that we can define the equilibrium state in terms of entropy and internal energy. At constant internal energy and volume, the equilibrium state corresponds to the maximum entropy or at constant entropy and volume, the equilibrium state corresponds to minimum internal energy.

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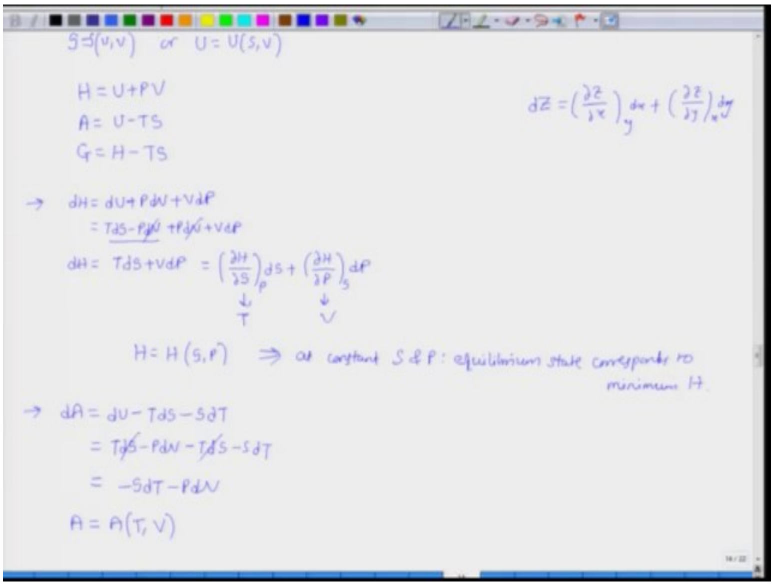

$S=S(U,V)$ or $U=U(S,V)$

$H=U+PV$

$A=U-TS$

$G=H-TS$

$dZ=\left(\frac{\partial Z}{\partial x}\right)_y dx+\left(\frac{\partial Z}{\partial y}\right)_x dy$

→ $dH=dU+PdV+VdP$

$=\underline{TdS-P\cancel{dV}}+P\cancel{dV}+VdP$

$dH=TdS+VdP=\underset{\overset{\downarrow}{T}}{\left(\frac{\partial H}{\partial S}\right)_P}dS+\underset{\overset{\downarrow}{V}}{\left(\frac{\partial H}{\partial P}\right)_S}dP$

$H=H(S,P)$ ⇒ at constant S & P: equilibrium state corresponds to minimum H.

→ $dA=dU-TdS-SdT$

$=T\cancel{dS}-PdV-T\cancel{dS}-SdT$

$=-SdT-PdV$

$A=A(T,V)$

That means to define equilibrium state in terms of S or V, we need to select the appropriate independent variable. In terms of S, we need to select U and V as independent variable or in terms of U we need to select S and V as independent variables. These pair of variables are not really convenient to handle. Imagine you are carrying out certain process in which you want to keep volume constant and vary internal energy systematically or you want to keep volume constant and vary internal entropy systematically or you want to control the entropy which looks really difficult.

So, these are not really convenient variables to handle and so you define the criteria of equilibrium, in terms of variables, which are easily manageable and easily controllable by us. Which are those variables? - temperature, pressure and volume, more specifically temperature and pressure. So we need to define other state functions which can define the criteria of equilibrium in terms of these variables.

And that is how the next state functions are defined. There are 3 more state functions - enthalpy which we define as $U+PV$, Helmholtz free energy which we define as $U-TS$, and Gibbs free energy, which we define as $H-TS$. Let us analyze them one by one. Let us try to see which independent variables we can use in order to be able to use these new state functions for criteria of equilibrium.

If Z is a function of X and Y:

$$dZ=\left(\frac{\partial Z}{\partial X}\right)_Y dX+\left(\frac{\partial Z}{\partial Y}\right)_X dY$$

X and Y are here independent variables. If we take the differential of enthalpy,

$$dH=dU+PdV+VdP$$

and by combination of first law and second law we have:

$$dU=TdS-PdV$$

Using the above equation:

$$dH=TdS+VdP$$

which we can write in the form:

$$dH=\left(\frac{\partial H}{\partial S}\right)_P dS+\left(\frac{\partial H}{\partial P}\right)_S dP$$

By definition, the partial of H with respect to entropy becomes T or partial of H with respect to pressure becomes volume V. So now, we know H can be expressed as a function of S and P and we can show that at constant S and P, equilibrium state corresponds to minimum enthalpy. Hence, we got a criteria of equilibrium in terms of H, but again this is not very convenient. Let us try to figure out what happens with A, the Helmholtz free energy.

If you take the differential of A:

$$dA = dU - T\,dS - SdT$$

substitute for dU as given above, we have:

$dA = -SdT - PdV$

So we know that A can be expressed as a function of T and V and with this we can express the criteria of equilibrium. At constant temperature and volume, equilibrium state corresponds to minimum in Helmholtz free energy.

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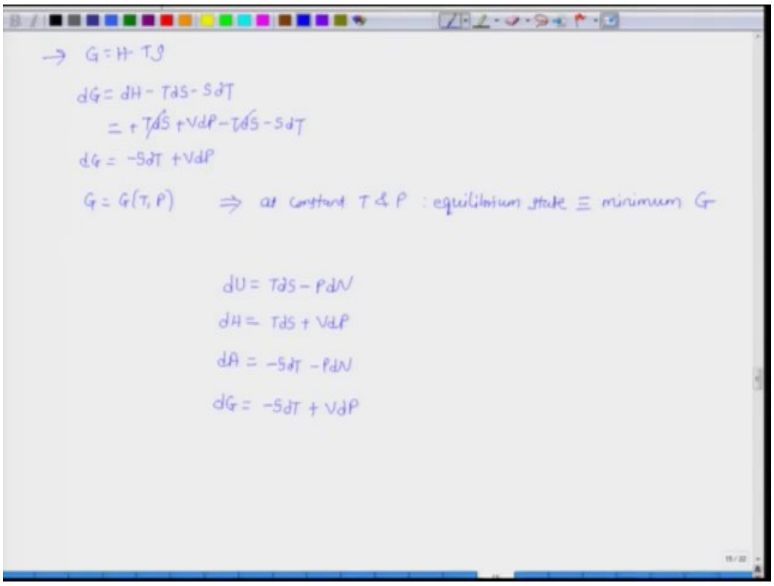

$\rightarrow G = H - TS$

$dG = dH - TdS - SdT$

$= +\cancel{TdS} + VdP - \cancel{TdS} - SdT$

$dG = -SdT + VdP$

$G = G(T, P) \Rightarrow$ at constant T & P : equilibrium state $\equiv$ minimum G

$dU = TdS - PdV$

$dH = TdS + VdP$

$dA = -SdT - PdV$

$dG = -SdT + VdP$

Now, let us try to apply it to G also. Since,

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

And dH we know is:

$$dH = TdS + VdP$$

Therefore,

$$dG = -SdT + VdP$$

Now, we have a state function, which can be expressed as a function of T and P and the criteria of equilibrium becomes - At constant T and P, equilibrium state corresponds to minimum in G. G is the Gibbs free energy. Now this is convenient.

We have Helmholtz free energy if we want to use temperature and volume as the independent variables. We can use Gibbs free energy to define criteria of equilibrium if we want to use temperature and pressure as independent variables. Both are important through the experimentalist’s perspective. As an experimentalist, we usually handle temperature and pressure as independent variables. For example, we carry out isothermal diffusion experiments or annealing at constant temperature.

Let us say we define the annealing temperature to be 800 $℃$and most of the time, we assume the pressure is at one atmosphere. That means we are using temperature and pressure as independent variables. So, we need to use Gibbs free energy as our criteria for equilibrium. For experimentalists, Gibbs free energy is a very important state function. But through the theoretician’s perspective, they would like to use Helmholtz free energy, because they would like to keep volume constant. And the reason is by keeping volume constant, the energy levels are fixed. So, the theoreticians will use Helmholtz free energy – A for the criteria of equilibrium. For this class, we will most of the time use temperature and pressure as independent variables.

We will now focus on the Gibbs free energy. In terms of all these variables, now we have developed what we call as equations of state. In terms of internal energy or entropy, we define:

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP.$$

So far, we have assumed constant composition throughout our analysis as we did not let the composition of the system change. But, what if the composition changes? We know that all this state functions U, S, H, A, G they are all extensive properties, which means they depend upon the size of the system. So when we allow the change in composition, then we need to also take into account, number of moles of each of the species.

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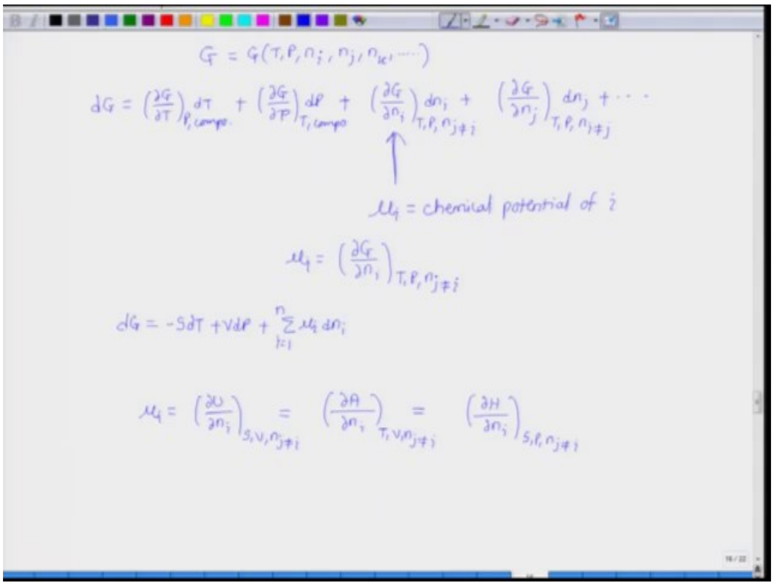

$$G = G(T, P, n_i, n_j, n_k, \ldots)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,\,compo.} dT + \left(\frac{\partial G}{\partial P}\right)_{T,\,compo} dP + \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} dn_i + \left(\frac{\partial G}{\partial n_j}\right)_{T,P,n_{i\neq j}} dn_j + \cdots$$

$$\uparrow$$

μ_i = chemical potential of i

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

$$dG = -SdT + VdP + \sum_{i=1}^{n} \mu_i dn_i$$

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j\neq i}}$$

For example, instead of expressing G as a just a function of T and P, we need to write G is a function of T, P and number of moles of all the components. Then the differential of G is expressed as:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,Comp} dT + \left(\frac{\partial G}{\partial P}\right)_{T,Comp} dP + \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} d n_i + \left(\frac{\partial G}{\partial n_j}\right)_{T,P,n_{i\neq j}} d n_j + \ldots$$

Now, this partial is an important quantity. What is this partial basically? It expresses the change in Gibbs free energy because of addition of one mole of i at constant temperature, pressure and constant number of moles of other species and this is called as chemical potential. the chemical potential of i is defined as:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

Remember that chemical potential is also a function of composition. When you make this addition of one mole of i, the composition of the material should not change. When we define this chemical potential, the addition of one mole of i is done to a large bulk of the material such that addition of one mole of i does not change the composition significantly. You can express this either in terms of per mole or per atom. If n_i is number of moles, this is joules per mole. If you express in terms of atom, how much Gibbs free energy changes by addition of one atom of i at constant temperature, pressure and constant number of atoms of all other elements, that is then it will be joule per atom.

And this is an important quantity in our class on interdiffusion. As I mentioned in the last class, the fundamental driving force for diffusion is the gradient in chemical potential. So you need to understand this. Now with this, we can modify our equations of state to take into account the changes in composition as well:

$$dG = -SdT + VdP + \sum_{i=1}^{n} \mu_i \, dn_i ,$$

The summation goes over all the components i equal to 1 to n.

This chemical potential can also be defined in terms of Helmholtz free energy or enthalpy or even internal energy. In terms of internal energy, you can define as change in internal energy due to addition of one mole of i at constant entropy, volume and n_j not equal to i (as we know U is a function of S and V):

$$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_{j \neq i}}$$

Or it can also be equally defined using Helmholtz free energy – A as:

$$\mu_i = \left(\frac{\partial A}{\partial n_i} \right)_{T,V,n_{j \neq i}}$$

Or change in enthalpy H which is a function of S and P:

$$\mu_i = \left(\frac{\partial H}{\partial n_i} \right)_{S,P,n_{j \neq i}}$$

Now, we know how to define the equation of state even when there is a change in composition. This change in composition may be because of two things. The first way the change in composition is brought about is you allow the system to be open system. The mass can be exchanged and obviously, the composition will change.

But even within a closed system, during a particular reaction or during a particular transformation, the composition of different phases can change. All that will be taken into account if we apply this new equation of state which considers the chemical potentials. So now with that, we also know the criteria for equilibrium in terms of Gibbs free energy.

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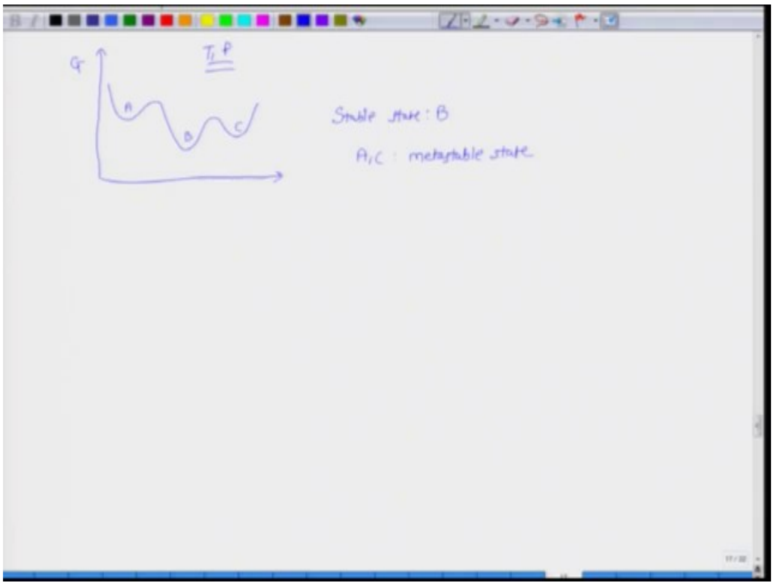

Stable state : B

A, C : metastable state

We will now next move to the stability because that is our main interest to define the stability of different phases. For example, if I consider a process at constant T and P, I need to use Gibbs free energy as a criteria for equilibrium and I track Gibbs free energy as a function of some arbitrary unit for example, atomic arrangement. If I continuously change atomic arrangements at constant T and $P$and see how the Gibbs free energy changes I may get some variations, schematically like this. I need to define now which is the stable state. So how many equilibrium states are here? We know for equilibrium the Gibbs free energy has to be minimum. Locally we see there are three minima. Let us denote them by A, B and C. There are three equilibrium states A, B and C. How many stable states are there?

Student: Only one stable state.

Professor: There is only one stable state which corresponds to the global minimum in the Gibbs free energy and that is B. The stable state here is B. A and C are equilibrium states but they are not stable state. The criteria for stability is the Gibbs free energy has to reach the global minimum and global minimum here is B. A and C are referred to as metastable state. They are called metastable because during a particular process or during a particular transformation, since the Gibbs free energy there is minimum those states can be realized temporarily. Now, that temporarily timeframe will depend upon the kinetics. What is the example that you know of a metastable state? Diamond is metastable phase or in steels we have martensite. Typically iron at room temperature will exist as BCC or in mild steel the low temperature stable phase is BCC or alpha. But if you quench it fast, austenite instead of transforming to alpha will transform to martensite and that martensite is a metastable phase. It means that over certain amount of time, it will eventually transform to BCC but since the kinetics are very slow, so it takes a very long time. So you feel as if the martensite is a stable phase that is why it is called a metastable phase. But ultimately it will transform to the final equilibrium state. So that is the difference between stability and equilibrium. Equilibrium, we just say that Gibbs free energy is minimum at constant T and P. For stability the Gibbs free energy has to reach global minimum. The phase which has the least Gibbs free energy among all possible phases will be the stable phase.

Now, there may be more than one phases, which have the same Gibbs free energy and which happens to be the global minimum in the Gibbs free energy. In that case, both the phases are stable. Then we say that the two phases coexist in equilibrium.

Now let us see what drives the transformations. And for that, we need to analyze the Gibbs free energy as a function of temperature and pressure. So first, let us try to look at how the Gibbs free energy varies first, with temperature at constant pressure, then with pressure at constant temperature, and then we will see if we vary both, how the Gibbs free energy changes.

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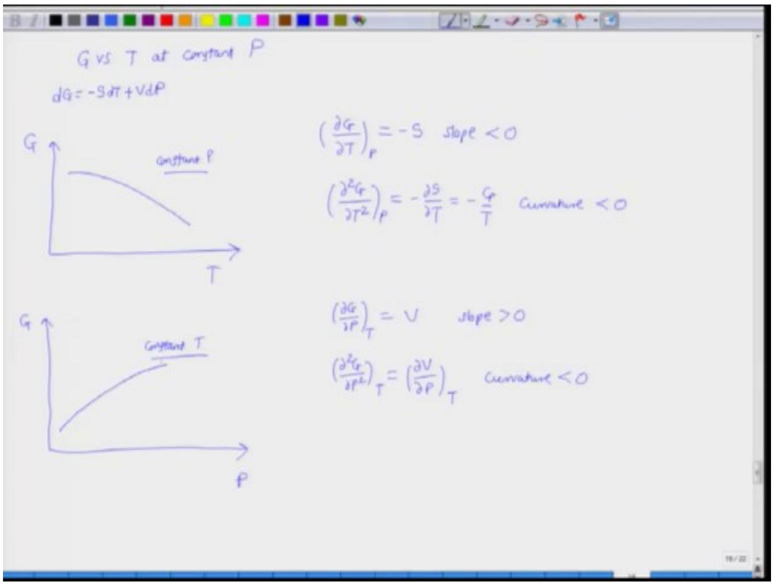

G vs T at constant P

$dG = -SdT + VdP$

$\left(\frac{\partial G}{\partial T}\right)_P = -S$ slope < 0

$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\frac{\partial S}{\partial T} = -\frac{G}{T}$ Curvature < 0

$\left(\frac{\partial G}{\partial P}\right)_T = V$ slope > 0

$\left(\frac{\partial^2 G}{\partial P^2}\right)_T = \left(\frac{\partial V}{\partial P}\right)_T$ Curvature < 0

Let us first try to look at how the Gibbs free energy changes with temperature at constant pressure. We know that:

$$dG = -SdT + VdP$$

And to start with we are analyzing single component systems, which means the composition is constant. Single component system means the system contains only one component. That component may be a pure element or it may be a chemical species or a molecule which does not dissociate over the range of temperature and pressures that we are studying. For example, if you want to analyze the phase transformations in water, how it transforms from ice to water, water to vapor and there is no reaction occurring or no decomposition of water occurring then we use water as a single component system. Since the composition is constant, we do not need to include μ_i terms and we want to analyze how the Gibbs free energy varies with temperature at constant pressure. What will be the slope of the plot?

Slope means variation of G with respect to temperature at constant pressure. From the above equation, this slope should be equal to $-S$ and entropy is always positive. the slope of G versus T curve has to be negative. What will be the curvature? Curvature is the second derivative that is basically:

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = \frac{-\partial S}{\partial T} = \frac{-C_P}{T}$$

Again C_P is positive, T is always positive as we are considering the temperature in Kelvin, which is the thermodynamic temperature scale and so the curvature should be negative.

As the temperature increases, Gibbs free energy decreases, Gibbs free energy of a phase or of a system decreases with temperature. What about variation of G with P at constant temperature? Again if we try to see the slope from the equation of state:

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

It is volume and volume is always positive. So the slope should be greater than 0 and the curvature, which is the second derivative at constant temperature should be:

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_T = \left(\frac{\partial V}{\partial P}\right)_T$$

If you increase the pressure, the volume will decrease. $\left(\frac{\partial V}{\partial P}\right)$ is negative and the curvature is less than 0. If you try to plot G versus P at constant T, schematically it will have a shape something like this.

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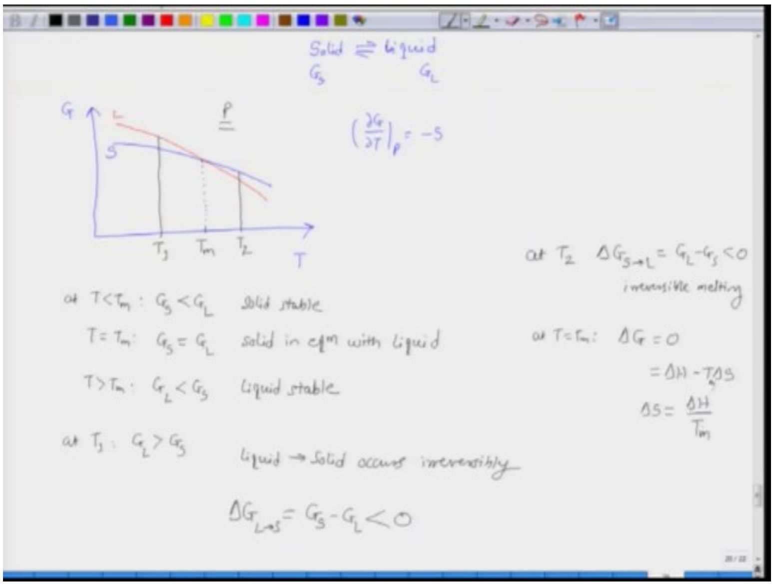

Solid $\rightleftharpoons$ liquid

G_S G_L

$\left(\frac{\partial G}{\partial T}\right)_P = -S$

at T_2 $\Delta G_{S\to L} = G_L - G_S < 0$

irreversible melting

at $T<T_m$: $G_S<G_L$ Solid stable

$T=T_m$: $G_S=G_L$ solid in eq^m with liquid

$T>T_m$: $G_L<G_S$ Liquid stable

at $T=T_m$: $\Delta G = 0$

$= \Delta H - T\Delta S$

$\Delta S = \frac{\Delta H}{T_m}$

at T_1: $G_L > G_S$

liquid → Solid occurs irreversibly

$\Delta G_{L\to S} = G_S - G_L < 0$

Now, let us try to analyze the phase changes in the context of Gibbs free energy change. Let us consider transformation of solid to liquid. The Gibbs free energy of solid is denoted as G_S and Gibbs free energy of a liquid as G_L. If you plot Gvs T at constant pressure to see how the Gibbs free energy of solid and liquid changes, obviously I know the kind of shape of the 2 curves. So I draw one curve for solid and one curve for liquid. The one that I drew first is solid and the second one is Liquid why? How do you know?

Student: Gibbs free energy at low temperature

Professor: From the slopes. Because we know the slope of Gvs T is $-S$ and entropy is a measure of disorder and we know the solid is more ordered than liquid. the entropy of solid is lesser than liquid. the slope of G versus T curve is more negative for liquid than for solid. So they will intersect at some point and this is the equilibrium melting point T_m. At any temperature below T_m, we know the Gibbs free energy of solid is less than that of liquid and so solid is stable.

Student: Is there any difference between equilibrium melting point and melting point?

Professor: Equilibrium means both solid and liquid are in equilibrium at that time. See at T equal to T_m we have the Gibbs free energy of solid equal to Gibbs free energy of liquid. Both are stable phases. That is why we say that solid is in equilibrium with liquid and this is denoted as equilibrium melting point. AtT greater that T_m, G_L is less than G_S and liquid is stable.

Suppose, we could cool the water below T equal to T_m let us say at T_1. We know at T_1, G_L is greater than G_S. Liquid is an unstable phase, so it has to transform to a stable phase which is solid. Liquid to solid transformation will occur irreversibly. There is an irreversible freezing of the liquid because it is associated with decrease in Gibbs free energy. If you calculate ΔG for this change of liquid to solid , it will be final state minus initial state:

$$\Delta G_{L\rightarrow S}=G_S-G_L<0$$

The change decrease in Gibbs free energy is a driving force for this freezing here.

Similarly, if we could heat this solid to a temperature greater than T_m, we know that the solid has a higher Gibbs free energy and it has to transform to liquid. There will be an irreversible melting.

$$\Delta G_{S\rightarrow L}=G_L-G_S<0$$

So at T_2 there will be an irreversible melting. But at exactly T equal to T_m both Gibbs free energies are same, so there is no driving force. Both phases are stable.

By any chance if you start with completely solid phase and if you heat it to T equal to T_m and stop there what should happen? Exactly at T equal to T_m the solid will remain as solid because there is no driving force. Only when you try to increase the temperature, some solid will transform to liquid. Similarly, if you cool the liquid from T_2, slowly to temperature T_m and stop there, what will happen? The liquid will not immediately transform to solid. If you stop, then the liquid will remain as liquid at T_m because liquid is also stable at T_m. Only when you try to cool further then the liquid will transform to solid. Exactly at T equal to T_m, ΔG is equal to 0 and at constant T and P, we can write:

$$\Delta G=\Delta H-T\Delta S=0$$

And so:

$$\Delta S=\frac{\Delta H}{T_m}$$

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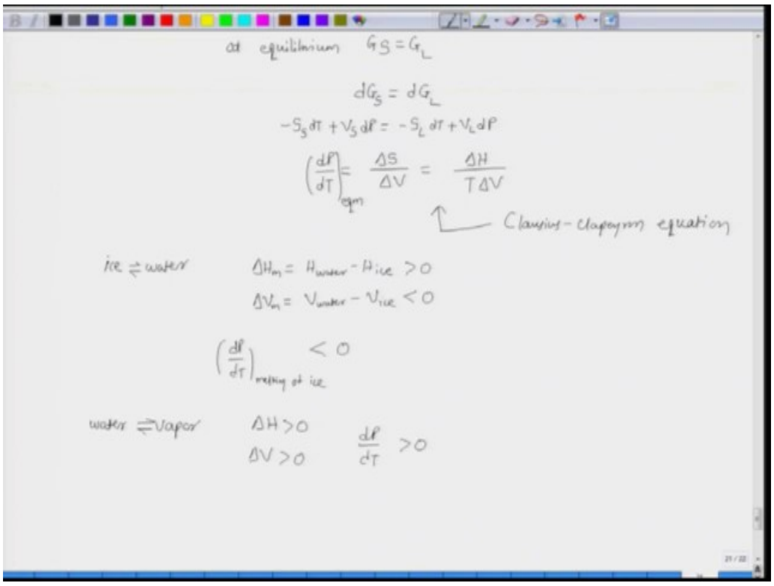

at equilibrium $G_S = G_L$

$$dG_S = dG_L$$

$$-S_S dT + V_S dP = -S_L dT + V_L dP$$

$$\left(\frac{dP}{dT}\right)_{eqm} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V}$$

↑ Clausius-clapeyron equation

ice $\rightleftharpoons$ water $\Delta H_m = H_{water} - H_{ice} > 0$

$\Delta V_m = V_{water} - V_{ice} < 0$

$$\left(\frac{dP}{dT}\right)_{\text{melting of ice}} < 0$$

water $\rightleftharpoons$ vapor $\Delta H > 0$

$\Delta V > 0$ $\frac{dP}{dT} > 0$

There is an equilibrium melting point or equilibrium melting temperature at a given pressure. If I change the pressure, how the equilibrium will shift? In other words, if I change the pressure and if I still want to maintain the equilibrium between solid and liquid which way the temperature should change. Let us try to analyze that. At equilibrium we know that:

$$G_S = G_L$$

Now, we are changing the state, but we are still maintaining the equilibrium between solid and liquid. So, whatever change in Gibbs free energy of solid, the same change in Gibbs energy of liquid should accompany. We can write:

$$d\,G_S = d\,G_L$$

and if you substitute for dG:

$$dG = -SdT + VdP$$

We obtain:

$$-S_S d\,T + V_S dP = -S_L dT + V_L dP$$

And if we rearrange to write

$$\left(\frac{dP}{dT}\right)_{eq.} = \frac{\Delta S}{\Delta V}$$

We know:

$$\Delta S = \frac{\Delta H}{T}$$

So,

$$\left(\frac{dP}{dT}\right)_{eq.} = \frac{\Delta H}{T \Delta V}$$

This is the Clausius-Clapeyron equation. More specifically we denote this as $\frac{dP}{dT}$ at equilibrium. Why? Because, we are observing if I change the temperature a little bit and still maintain the equilibrium between the two phases, how much change in pressure has to be carried out or if I change the pressure a little bit and still want to maintain the equilibrium between the two phases, which way the temperature should change.

Now, this we analyze for solid to liquid or liquid to solid, but this is equally applicable for any transformation. If we know ΔH and ΔV, we should be able to know which way the temperature should be shifted. For example, let us try to analyze the melting of ice. For melting of ice, we know ice to water transformation, what should be ΔH?

$$\Delta H_m = H_{water} - H_{ice}$$

Should it be positive or negative?

Student: Positive.

Professor: Positive because higher temperature phase will have higher enthalpy that appears in the latent heat of fusion. Heat is absorbed because water has higher enthalpy. What about ΔV? Molar volume of water minus molar volume of ice, it should be negative or positive?

$$\Delta V_m = V_{water} - V_{ice}$$

Normally for melting, the volume will increase because liquid phase will have higher volume than solid phase. But for water, it is reverse because ice has lower density than water around near to 0 ℃. Because of that, melting will be associated with reduction in volume, water will have lower volume than ice. And so:

$$\Delta V_m < 0$$

So basically for melting of ice:

$$\frac{dP}{dT} < 0$$

which means if I increase the pressure, the equilibrium melting point should be reduced. This is the reason why ice skating becomes possible. When the skater is skating, there is certain pressure applied on the ice. And because of that pressure, the melting point of ice which is in contact with the skate comes down. And so the ice melts and there is a thin layer of water that forms between the ice and the skate and it helps in skating as it acts as a lubrication. What is another example? You can also consider the water to vapor transformation or boiling of water. Now here, what will be ΔH? Obviously positive because water is converting to vapor, and vapor has higher enthalpy. What about ΔV ? It should also be positive as obviously the vapor has higher molar volume than water. And so:

$$\frac{dP}{dT} > 0$$

If we decrease the pressure, the equilibrium boiling point should decrease. And that is the reason at higher altitude the boiling point of water comes down. if we try to cook rice at higher altitude, it is difficult. At higher altitude the atmospheric pressure is lower. And so the equilibrium boiling point of water reduces. If you try to cook rice in open pot, the water will start boiling before the rice is cooked and that is why you have to use pressure cooker. In pressure cooker you can maintain the pressure near to one atmosphere, then it is easy to cook rice.

Clausius-Clapeyron equation is a very useful equation, because we can use this to develop phase diagrams. What we are doing here basically is tracking how the equilibrium shifts if I make some changes in temperature or pressure. If you plot the locus of pressure and temperature at which the equilibrium exists, you are basically plotting the boundary between the two phases. And that is what you need in the phase diagram.

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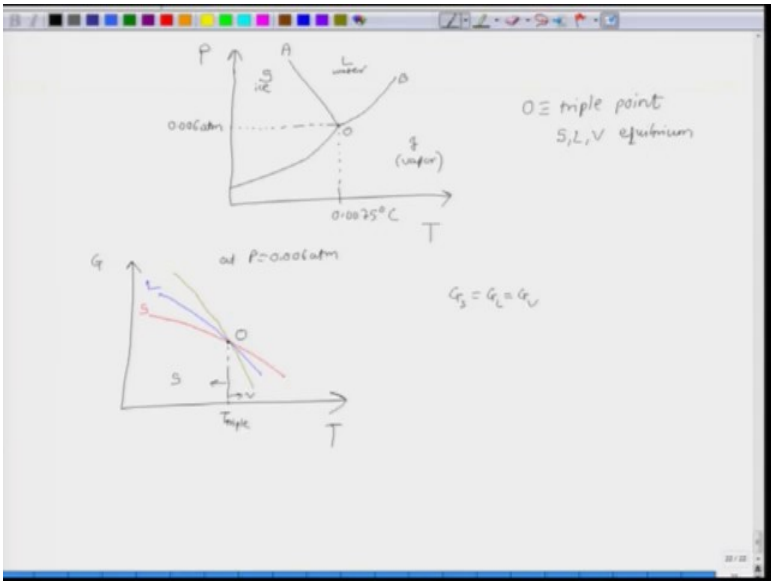

For example, you can consider the phase diagram of water. For single component system we draw the phase diagram as pressure versus temperature. This is how the phase diagram for water looks like, so there are regions of solid ice, liquid or water and gaseous region or vapor. Now, if you look at this curve, let us call this OA it is the boundary between solid region and liquid region and exactly along AO, the solid and liquid two phases exist in equilibrium. This is basically the equilibrium melting.

Now, you can see from the Clausius-Clapeyron equation as we have seen earlier that:

$$\frac{dP}{dT} < 0$$

for solid to liquid transformation in water. And this line has a negative slope. But liquid to vapor or boiling, which is the line OB has a positive slope. Similarly solid to vapor has a positive slope. Now, you can see these three curves intersect at one point O, that means at this point all 3 phases coexist in equilibrium. This is the triple point. So at triple point solid, liquid and vapor all three phases coexist in equilibrium.

This is at around 0.0075 $℃$and 0.006 atmosphere. If we try to plot, let us say $G vs\ T$ for water at constant pressure of 0.006 atmosphere, how would it be? Now we have 3 possible phases, so we need three curves. If we see at 0.006 atmosphere, as we increase the temperature, what happens? First the solid is stable at low temperature and as we keep heating at 0.0075 $℃$, we reach the point O which is the triple point. all 3 phases are in equilibrium and then we enter the vapor region. Basically at point O, the Gibbs free energy of solid is equal to Gibbs free energy of liquid is equal to Gibbs energy of vapor. When I say

Gibbs free energy, these are basically the molar Gibbs free energies as Gibbs free energy is an extensive quantity. The molar Gibbs free energies of solid, liquid and vapor are equal at point 0.006 atmosphere and 0.0075 ℃.

I will have three curves which intersect at one point. If I draw these three curves, let us say one for solid, one for liquid and then one for vapor, all the three curves should pass through one point or intersect at one point O. And this is the triple point. So at temperature below this solid is stable, at temperature about this vapor is stable and exactly at the temperature equal to triple point temperature, all the three Gibbs free energies are equal. So this is how we can develop the single component phase diagram based upon the Gibbs free energy changes. All right, any question? we will stop here for today.

Keywords:

Criteria for equilibrium, Helmholtz free energy, Gibbs free energy, Extensive and intensive properties, Partial quantities, Chemical potential, Stable state, Metastable state, Clausius-Clapeyron equation, Phase diagram of H2O, Triple point