Advanced Metallurgical Thermodynamic
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Module #01
Lecture #30
Thermodynamics of heterogeneous system

So far, we have been talking about systems which are liquid and solid systems mostly. So, solidification is something which you have talked about to solid to liquid transmissions, we also talked about solid to solid transformations, variety of solid to solid transformations. Let us start looking at a liquid gas and solid gas interactions. These are what we call them as heterogeneous systems, where the moment gas comes, pressure comes into picture.

So far, we did not actually bother much about the pressure excepting in one case, we talked about Clausius-Clapeyron equation and how the melting point can change as a function of pressure. We have talked about it if you remember.

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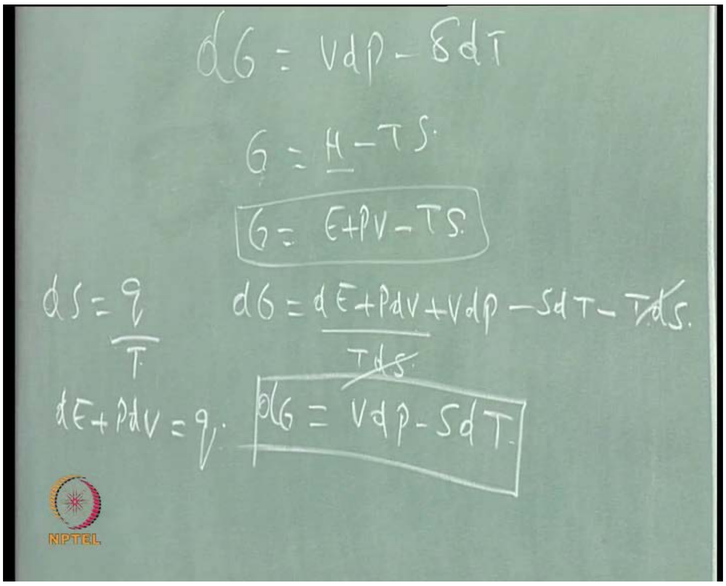

$$dG = Vdp - SdT$$

$$G = \underline{H} - TS$$

$$\boxed{G = E + PV - TS}$$

$$dS = \frac{q}{T} \qquad dG = \underbrace{dE + PdV}_{\cancel{TdS}} + Vdp - SdT - \cancel{TdS}$$

$$dE + PdV = q \qquad \boxed{dG = Vdp - SdT}$$

Basically, we can write dou G as Vdp minus sdT. This is one of the Maxwell equations, the most popular Maxwell’s equation. Do you know how does this come? You know how this can be derived? If you simply know the dG is if you can write G as H minus T S. For example, if you write it G has H minus TS and basically do partial differentiation.

So, you can write it as dH equal to basically dG equal to dH. You can even possibly write it as basically, H is E plus PV minus TS. If you write H is E plus pv, so you can write dG is dE plus PdV plus Vdp minus SdT minus Tds. This is how we can expand the whole thing.

So, once you have this expression, we basically take the differential of it and once you do that, we know the d E plus pdV is Tds. That is the basic definition of the second law of the thermodynamics because you know the ds is equal to Q by T and d E plus p d V is equal to Q. Am I right? That is a heat continent. So, if that is the case, I can write this as Tds. Tds is Q and if write it as Tds, this goes off. So, what is left out is dG is Vdp minus sdT, a very very profound thing and we can express every phase with this expression.

So, basically, it connects the free energy with the state variables, volume, pressure, temperature and entropy. Out of them, some are extrinsic, some are intrinsic. You people know what are the extrinsic variables and intrinsic. Out of this, which are the extrinsic and which are the intrinsic entropy, which have state variables entropy and yes pressure and temperature of the state variables, volume and entropy are not. So, we can do that. So, any way, once we can derive this today, let us look at and we use this expression basically looking at for example, we can write this expression for every phase transmission. We have done this thing earlier for liquid to solid.

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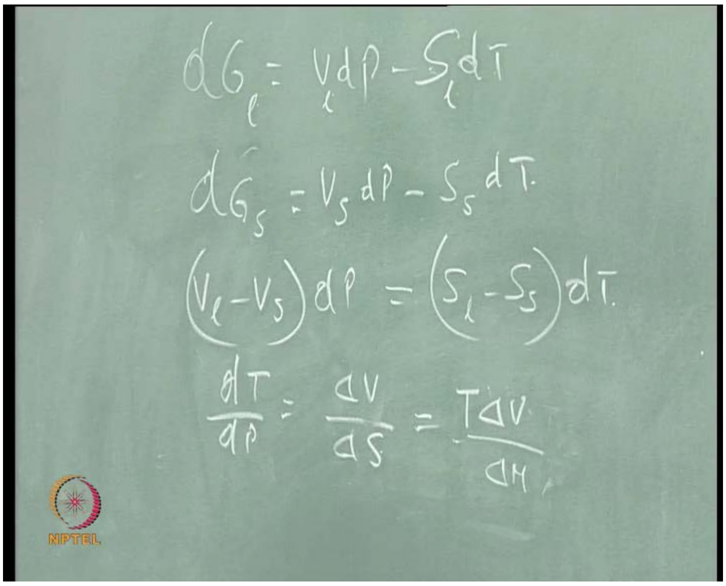

$$dG_l = V_l dP - S_l dT$$

$$dG_s = V_s dP - S_s dT$$

$$(V_l - V_s) dP = (S_l - S_s) dT$$

$$\frac{dT}{dP} = \frac{\Delta V}{\Delta S} = \frac{T\Delta V}{\Delta H}$$

For example, we can write dG of liquid is V of liquid into dP minus S of liquid into dT and we have also written that dG of solid is V of solid into dP minus S of solid into dT and we know that at equilibrium, the both free energies are equal. So, when we equated these 2, we got expression where basically, Vl minus VS into dP should be equal to Sl minus S, S into dT and that is where we got an expression called dT by dP is Sl or we call it as delta S by delta V or we can also write it as delta H minus T into delta V because delta V by delta S. Am I right? You are right. This is delta V by delta S. So, obviously, this will become delta V by delta H into T. It comes up. Am I right? So, this is and if you want to avoid confusion, we can put the T in front. Otherwise, this is delta V t.

So, it is basically, this gives us an idea where delta H is the heat of transformation, delta V is volume change during transformation. So, the change in the transformation temperature, any transformation temperature for that matter is related to the pressure by this expression. This is what we have talked about in Clausius-Clapeyron. Today, let us look at sublimation because when we want to talk about heterogeneous reaction gases, things have to be involved. So, let us start with sublimation. As a reaction, where there is a gas that is involved before we actually start dealing with, solid gas reactions are liquid gas reaction.

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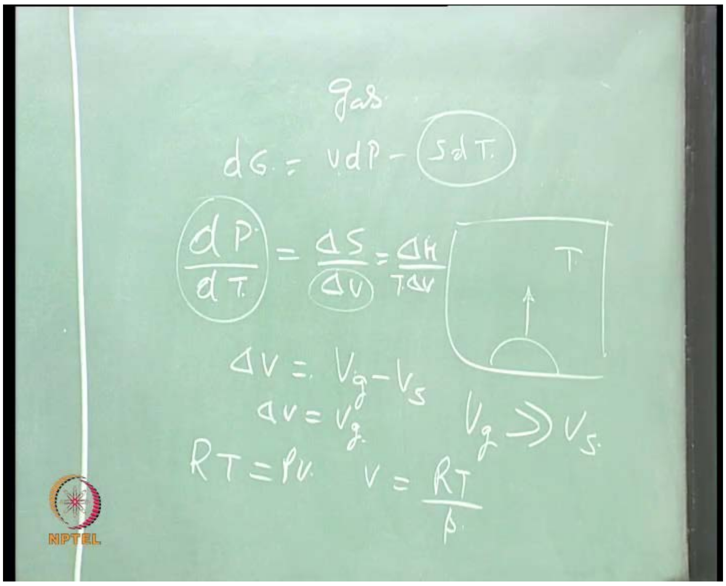

So, let us look at a system where a solid is sublimating into gas. If that is the case, then we can actually start writing the expressions for that in terms of the gas or for the solid.

Again, you can use this kind of an expression and from that, we can bring out a few things. For example, if you want to look at let me just see. So, basically if you want to look at this expression, if you take the gaseous part of it, if you can write this expression for the gas d G is V d p minus s d T and if you imagine that there is a chamber where there is a solid which is sublimating at a constant temperature, if you assume that the temperature is constant, then in principle, then this term actually vanishes. Isn’t it? So, if that term vanishes, then we can talk this as nothing, but V d p.

So, if you want to consider this expression in detail. Yes. So, we can basically write this expression as d p by d T as equivalent to delta s by delta V, which also can be written as delta H by delta V into T, where this expression when we talk about this in terms of delta V here, delta V is basically nothing, but V of the gas minus V of the solid. Am I right? Usually, V of the gas is much larger than the V of the solid. Am I right? It depends on which direction you want to look at it. You can look at that way or this way. Then, both of them became negative, both of them will get cancelled.

So, when we assume that this is much larger than this, we can write delta V can be actually taken as almost this and when there is a gas, we can always use the ideal gas equation where we can write R T equal to p v. So, we can write that V is actually R T by p. Am I right? So, in principle where you have this expression delta V, delta V can be written as V of the gas and the V of the gas can be written as R T by p of the gas.

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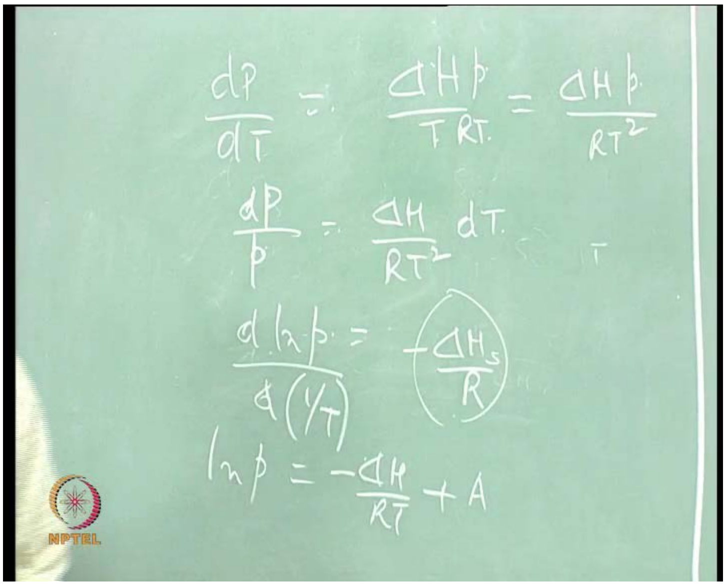

$$\frac{dp}{dT} = \frac{\Delta H p}{T RT} = \frac{\Delta H p}{RT^2}$$

$$\frac{dp}{p} = \frac{\Delta H}{RT^2} dT$$

$$\frac{d \ln p}{d(1/T)} = \boxed{-\frac{\Delta H_s}{R}}$$

$$\ln p = -\frac{\Delta H}{RT} + A$$

So, if you do that, then we can write it as d p by d T as equal into delta H by T delta H by T. This remains same in place of delta V. We are writing it as V because delta V is approximating it to V of the gas because V of the solid is much smaller than V of the gas. Then, this place of V of the gas we can write in terms of R T by p. So, basically, this becomes R T p goes here. So, this basically means delta H into p divided by R T square. Am I right?

So, in principle, then we can write that d p by p is delta H by R T square into d T. Fine? So, this can be basically taken it as d l n p as you can see. If you can further d l n p by d of 1 by T can be taken as minus delta H by R, where you can see that this d T can be brought this side in terms of 1 by T and if that is the case, then we can basically say that if you see how the vapor pressure changes with temperature. It is actually always related to the delta H of sublimation divide by this. So, in principle, we can say now if you try to integrate this, you can always write that l n p is equal to minus delta H by R T plus some constant. You call can call it as A.

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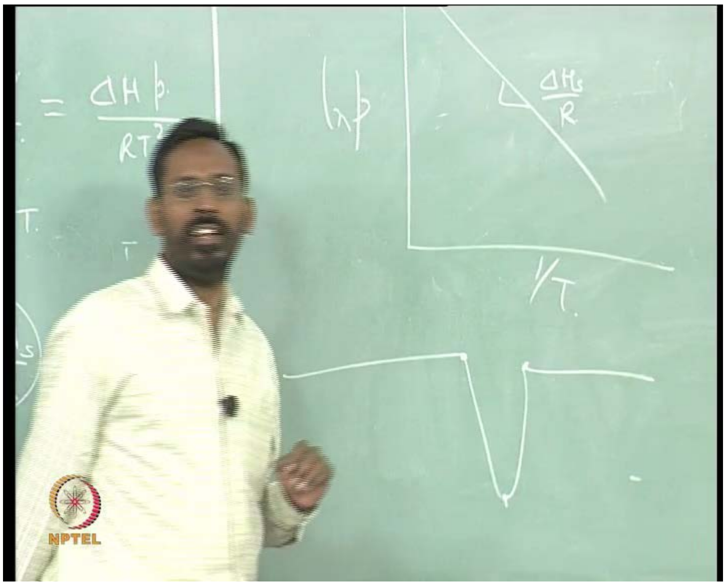

So, in principle, that means if we always plot l n p verses 1 by T, if you plot l n p verses 1 by T, you will always see an expression something of this sort where the slope of this turns out to be delta H by R. So, this is how if one can measure the partial pressure of any gas, where a solid is sublimating and there is a gas inside the chamber and as you change the temperature, how this partial pressure of the gases is changing. If you try to measure that partial pressure of gas as a function of the temperature, you would see these two are related to this and the higher the sublimation delta H, the higher this value, smaller will be the partial pressure. This is expected because if the sublimation enthalpy, the delta H associated with sublimation is very large, then at any given temperature because you need more energy for the sublimation.

So, the amount of gas molecules generated from a solid are always going to be lower if the delta H. So, that means, particularly when we are looking at metals with a higher boiling point, a metal with a higher boiling point basically means, its delta H sublimation is a very large. That is when actually you will have a boiling point being very high. So, whenever the sublimation delta H is very very large, you would say that this material is more difficult to sublimate. So, you need to provide more energy for the sublimation to take place for any solid molecule to be converted into a gaseous molecule. So, if that is a case, the partial pressure of that gas that is generated at any given temperature is going to be proportional to that inversely proportional in principle.

So, as a result, we can say that whenever the sublimation enthalpy is higher is also similar to saying that whenever the melting point, I mean whereas, the heat of fusion is very large. We can say the metal to melt is more difficult. Isn’t it? As simple as you need to because heat of fusion basically is something to be added if be provided to the solid, so that a solid gets converted into a liquid. So, the larger this value, the more difficult is for the solid to melt. Similarly, the larger the heat of sublimation is, the more difficult for a solid to sublimate. So, the partial pressure of the gas that you generate because of the sublimation of a solid is always inversely proportional to these and the larger this value, the smaller will be the partial pressure.

So, by measuring the partial pressure as a function of temperature, even if you do not know this one would be able to get at 4 or 5 different temperatures. You measure the partial pressure of a particular metal vapour in a chamber by certain. There are so many methods of the chromatography methods are available, spectroscopic methods are available to measure the partial pressure of the gases and if you can do those things, then at various temperatures plot, it get a lee square fit for that and from that, you will be able to measure this sublimation temperature.

What is the other method? Does anybody know? If I want to know what the enthalpy of sublimation is, what is the direct DSC is a direct method? So, take a sample in a DSC, provided DSC can go to the temperature, where your sample sublimates. Unfortunately, most of the DSC's go up to, let us say 1500 degrees or so. The one of that we have in our lab goes to 1500 degrees. So, if the sublimation temperature of the material is below 1500 in principle, you would see a strong peak associated with the sublimation. Of course, whether it is this side or that side depends on what is the polarity that we are talking about, but basically sublimation being an endothermic reaction, you get an endothermic peak at the sublimation temperature and this basically represents the onset of the sublimation. What does this represent? Anybody knows in any DSC what does the peak indicate Alisha?

What does the peak indicate in a DSC? You always know that there is a temperature difference between this and this. They are not the same. So, there are 2 temperatures here associated. Within principle, there are 3 temperatures associated with any phase transformation or any reaction in a DSC. What are these 3 temperatures? What is a physical meaning of these 3 temperatures? I take anything. Let us say a melting, a metal solid I get peak again similar and there will be 3 temperatures. There onsets represents being of the melting, then maximum. Then, onset is also a melting point where it completes that is a peak.

What is third one? So, obviously, the first and third are more easy to answer the onset and the completion maximum rate. The peak represents always the temperature, where the rate of transmission is the highest. So, one can, but the thing is in principle, whenever you want to do what is called reaction rates, for example, any transformation rate of transformation if you are interested and what is called kinetics of the transformation. In fact, if you have any phase transmission taking place, let us say I take a metallic glass. I am crystallizing a glass. The moment I am crystallizing a glass, I get a peak. I have to mention to you as possibly numbers of the times.

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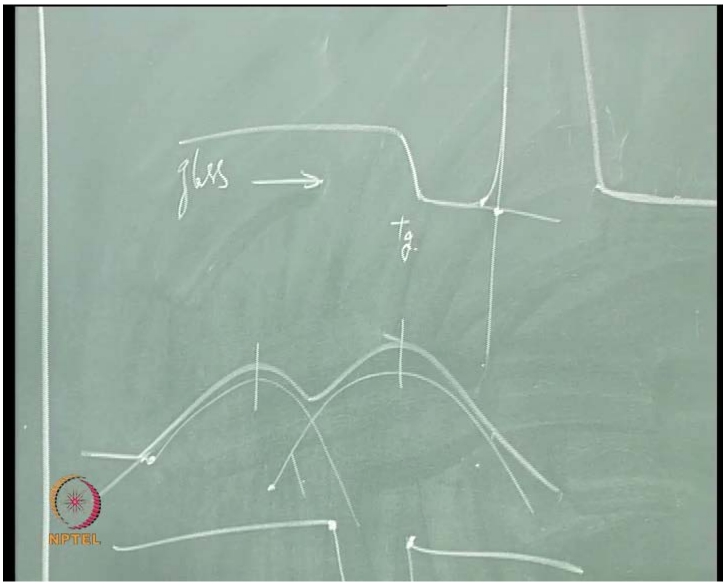

We get a peak like this. Am I right? A glass when you start with and then, you are heating it, you get something like this. What do we call this? What is that T glass transition temperature? So, why this glass transition temperature is like this? Why it is a second order transition? So, glass transition is second order transition and what is the characteristic of the second order transition? Second derivative discontinues. What about the first derivative? They are continued. What does that means in terms of thermodynamic parameters enthalpy? There is no enthalpy involved. There is no enthalpy change involved. Please be careful. So, the delta H for the transmission is 0 and the delta s for the transmission is 0 and the delta V for the transmission is 0.

So, that is a second order transition. A second order transition will be that where the delta V is 0. There is no change in the volume during the transition; there is no change in the enthalpy during the transition, whereas in the first order transition, all these three are discontinued. So, there is a change in enthalpy and that is what we call it as heat of fusion. There is a change in the entropy and that is what we call it as entropy of fusion and there is a change in volume, which is what we call it as volume expansion or volume change during melting or solidification. So, whereas, here now and then, this is what we call it as crystallization and if any time you do a DSC many of times, if the delta H involved in the reaction, if it is a very large, what kind of transformation are those where delta H is involved is a very large? Tell me? When will be the delta H involved in any particular change is going to be large explosive reaction. That is a reaction. Let us not talk about reactions here. We are talking of phase changes, change in the state.

Whenever there is change in a state of the matter, then the delta H is large solid to liquid, solid to gas, liquid to gas. When within a particular state if there is a transmission taking place, solid to solid let us a precipitation, a martensitic transformation, it could be order disorder transition. So, all these things usually excepting order disorder because in order disorder, there is large delta H is negative that is involved between order state and disorder state. As a result, many of at times the order and disorder transitions delta H is very large. So, the peak is going very large, a big peak whereas, all of there.

For example, if I am taking an iron, pure iron and transforming a B c c iron to f c c iron, the delta H is very small and when the delta H is very small, many times this peak is going to be very broad. Particularly, if you are talking about a cold worked material, some of you if you have ever done re-crystallization of a cold worked material and do it by DSC let us say, you get usually a very broad peak because it happens usually. The recovery and re-crystallization tend to overlap and you see a broad peak rather than a very sharp peak and when you get broad peaks, then you identify the onset become very difficult. The way we identify an onset in any peak is you extrapolate this and you extrapolate this. Wherever these two intersect is what we take it as the onset of transformation.

So, whenever the peaks are very broad, if you get broad peak like this, it becomes very difficult for you to identify. You may still say that I will do this and then, find it out some phases. It is more difficult to see and particularly in some places where you have two peaks overlapping. Let us say, so you will see a situation where something like this. In such a case, what is the onset of this? It is very difficult to find out. Then, what I should do? In principally, I should do deconvolution and then, make it as two peaks and then, find out the onset for this and find out the onset for this.

So, under such conditions, people usually consider the peak temperature representing the transformation. Though we know peak temperature is not a temperature where the transformation actually started, we definitely know the peak is not a temperature where the transformation has started, but in case where it is more difficult to find out what is onset, we should do this. Otherwise, for all, I mean theoretical purposes onset should be actually taken as the transformation temperature onset temperature is and in case of melting kind of things, the onset and offset what is called offset. The second one is going to be very close unless you really do very fast heating.

When you do fast heating, then the onset to offset there will be differences. Otherwise, usually they are very close to those, to each other and using this information in principle, one can get lot of kinetic information. For example, doing this if you do this at different heating rates, what will you observe? Let us I have a glass. I take the glass, put it into DSC and heat it at particular rate and take another piece of the same glass and heat it at different rate. Do I get the same pattern? If I do not get the same pattern, what will be the difference in the DSC traces that I get at two different rates?

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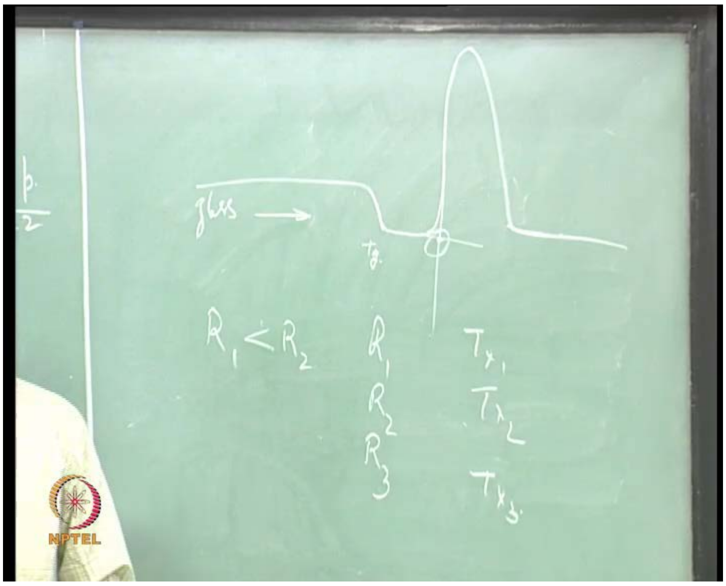

Let us see, one is let us say R 1, another is R 2 where R 2 is greater than R 1. Now, tell me what will be the difference that will you get peak will broaden anything? More peak will be shifting towards what? In which case the peak will be of at a higher temperature? R 2. What is the logic? Basically, it is yeah. Anymore arguments? Anyone else yeah? You are saying something Alisha. It is basically the inertia of the system. Whenever you heat a sample at a higher rate, the sample does not transform at its equilibrium transformation temperature and it transforms at a temperature higher than its equilibrium transformation. This is similar to taking a liquid and under cooling it is very fast. It does not start melting solidifying at the normal regular equilibrium transformation temperature. Instead, it under cools to a lower temperature and the transformation starts at a lower temperature.

Exactly similarly, whenever I am heating the liquid, I mean solid, in principle melting point also shifts. The only difference is the shift in the melting point with a heating rate is not as much as the shift in the freezing point with a cooling rate. The reason is also very obvious that in case of freezing, a new surface has to be created. So, there is a activation barrier and because of the activation barrier, the system when it is being cooled very fast, you are not providing sufficient time for this nucleus to be created. As a result, it under cools where as you heating it a solid into liquid. Then, you see that because there is already surface available, you would see that it does not need that much of an activation as u need it in case of a freezing.

So, as a result, the shift is not as much as possible, but here it is again a solid to solid transformation. A glass crystallizing is not exactly like a liquid I know being freezing. So, as a result, you would see there is significant shift to higher temperature if the heating rate is higher. So, by basically heating it at different rates, 4 or 5 different rates what you get is different temperature, starting temperature for different heating rates R 2, R 3 and so on. You will get what is called TX 1, TX 2, TX 3 and so on. So, identify for each heating rate, what is transmission temperature. If the transmission temperature is sharpness identify, what is the onset. Otherwise, consider the peak temperature and once you have that, you can in principle plot what is called a Kissinger plot which is nothing, but l n beta by TX square versus 1 by T, where beta is the heating rate and TX is the crystallization temperature or each of the heating rates versus 1 by TX.

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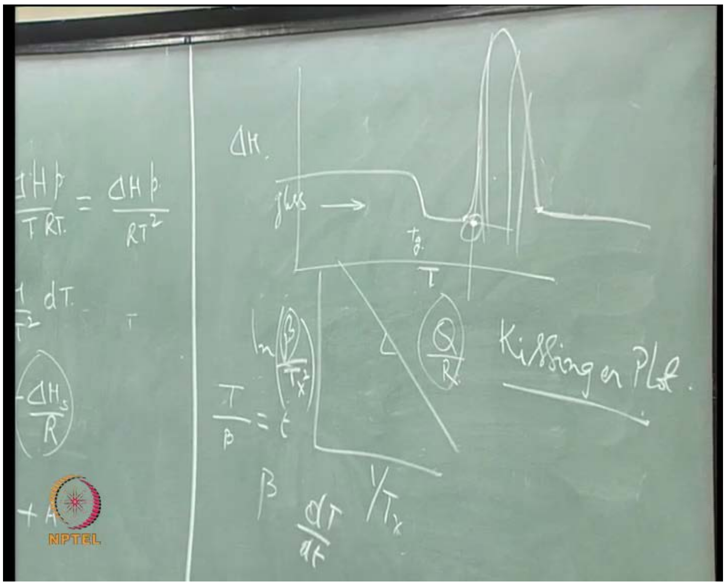

If you do, you will exactly get this and where the slope of it can be taken as Q by R, where Q is the activation barrier exactly similar to what we have done few minutes back for vaporization, where we have taken l n p by 1 by T and plotted it. So, similarly, here you simply take the beta and TX, tabulate the things at least four or five different temperatures. If you do because basically to be able to get consistent plot dually square fitting and this is how for any such reaction, whether it is a polymorphous transformation or an allotropic transition or a crystallization of a glass or any other precipitation, all of them you can use this is so-called Kissinger plot. Of course, by the name of the person who has talked about it which is very famous.

So, all phase transformations, kinetics are done with this and this is all what is called thermal kinetics. What do we mean by thermal kinetics? It means, as the functions of heating at different rates you are doing it, you can also have what is called isothermal kinetics. That means, at a given temperature, you try to have the transformation taking place in principle. If the same transformation I do it in a dac, what we plot is delta H versus temperature. The heat evolved versus the temperature is what we are plotting. You can also plot the heat evolved versus time, basically temperature once I know the heating rating beta. What is beta? It is d T by d T. Am I right?

So, if I take the temperature divided with beta, it should become actually time for me. Somewhere, it should be related to time. Isn't it? So, in principle heating rate if I know and if I know the temperature axis, the temperature axis can be converted into time axis. Hold it at a given temperature and as a function of time, you see how the phase is involved and in this process, you can talk about how much percentage of transformation has taken place. So, here it is onset, here it is complete and at any given time here, you can talk about percentage transformation. It is similar to our T diagram.

At a given temperature, you are talking of onset. I mean start of perlite formation, end of perlite formation. Exactly similar you can do a DSC which is called isothermal DSC, and find out how is the fraction transform and that fraction transform can be correlated to activation energy. We will not talk about it at the moment because this is more too much of kinetics, but some time, if we are interested will talk about it.

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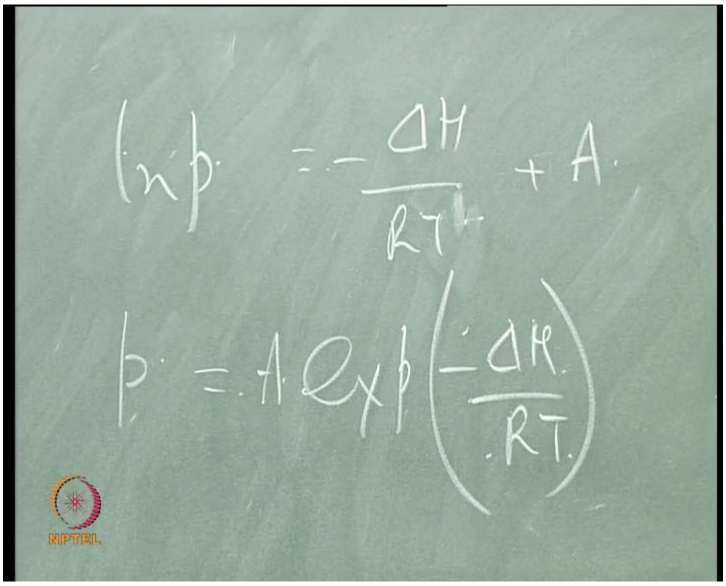

$$\ln p = -\frac{\Delta H}{RT^2} + A$$

$$p = A \exp\left(\frac{-\Delta H}{RT}\right)$$

So, this is all about how we can see that partial pressure l n p of it is related to. We have seen that l n p is minus delta H by R T square, R T. RT naught R T square plus A. Am I right? In principle, if that is the case, one can also write if we can write it in the exponential form. You can write p is exponential; some constant will be there, minus delta H by R T. Am I right? Once you have in the l n version, we can also write this. That means, partial pressure is exponentially related to the temperature, partial pressure of any gas. That is the reason why the temperature is very important in terms of this. We can also see whether how the external pressure influences the partial pressure.

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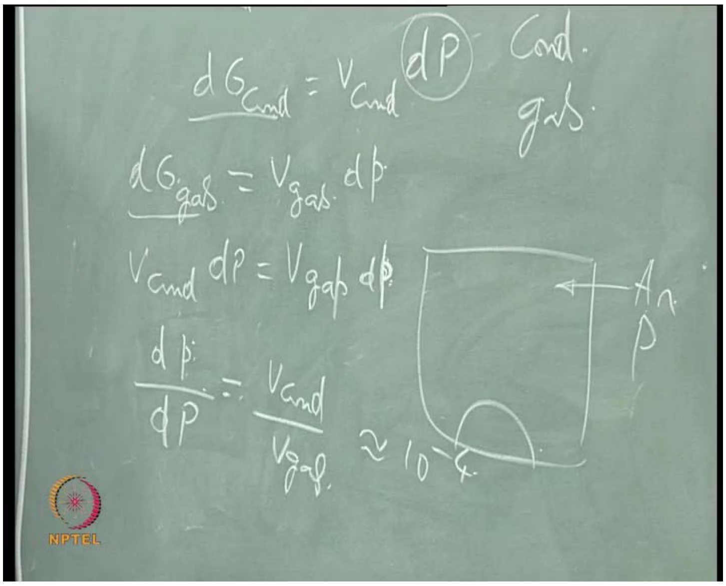

Let us say, I have a solid which is sublimating and I put some pressure, the chamber where I have the solid with is sublimating. I introduce some gas, let us say an argon gas at a certain pressure p and I want to see how this influences it. If you want to see that, then what we can do is let us try to do. Let us write the expression here. In this case, we have a condensed phase. We have a gas phase for both of them. If we write d G expression, d G of the condensed phase can be written as V of the condensed phase into d p minus s d T and because we are again calling it as temperature is constant, in principle we can ignore this. Am I right?

So, in such a case we can write this is the d p. So, we can write the d G of the condensed is equal to V of the condensed. So, if there is any external pressure with change of pressure, the d changes with this. Now, if we do the same thing with a gaseous thing, V of the gas multiplied by d p. Am I right? In principle, we can write this expression that way and in such a case, we can equate both of them. If we equate both of them because at a given transformation temperature, both of them should be equal the free energy of the gaseous phase and the free energy of condensed phase should be same. So, we can equate and say V of the condensed into d p should be equal to the V of the gas into d p.

So, if that is the case, d p minus d of the partial pressure here. In this case, we are using a small p because we are talking of the gas, partial pressure of the gas and there we are talking of the pressure. So, we can even do it the reverse way, d small p, the rate of change of the partial pressure of the gas with the external pressure that we are putting is related to the V condensed by V gas.

Now, if you look at this, this, this, V volume of the condensed phase and volume of the gaseous phase if you compare, the volume of the gaseous phase is much larger than the volume of the condensed phase. Usually, the ratio of it is of the order of around 10 to the power minus 4 at any given temperature usually. So, if that is the case, then you can show that the partial pressure of the gas that we have the sublimated gas that is forming, the change of it with the external pressure that we are introducing is actually very small. So, the external pressure.

Why this becomes important is whenever you are trying to sublimate something, this becomes very important. Particularly for those people who want to make nano materials by gas condensation techniques. Let us say, you take a metal. You want to evaporate and form gas and then, condense it and get nano particles and you want to do it at various pressures. You want to know how this sublimates because the rate of formation of nano crystals is related to the rate of sublimation and rate of sublimation is related to this. So, if I have certain gas inside the chamber, when the gas pressure inside the chamber, how does it affect partial pressure of the gas that is generated because of sublimation.

You can see that the partial pressure of the sublimated gas does not get changed by the external pressure to a large extent, unless this pressure is very large. So, if I take this as one atmospheric pressure, at one atmospheric pressure this p changes only by 10 to the power minus 4, not much. So, this is something which you have to see, whereas if you look at previous thing, the partial pressures changes with temperature is very very significant. You can see here.

P changes we have also written down earlier. It is exponentially related to temperature while the partial pressure is exponentially related to temperature. The partial pressure is not related significantly with the pressure that is a, so these are the two aspects. One has to remember whenever we are talking of gases coming out of the solids and how the temperature and pressure which are two important state variables, how do influence the formation of gases from a solid.

So, this is the first concept that we need to understand when we are talking of heterogeneous reactions involving gases. How pressure and temperature influence? The sublimation influences the partial pressures. Now, also we understand this. Let us go ahead with reactions and start talking about how the reaction rates and the thermodynamics of the reactions depend on pressures, temperatures and things like that for that plotter.

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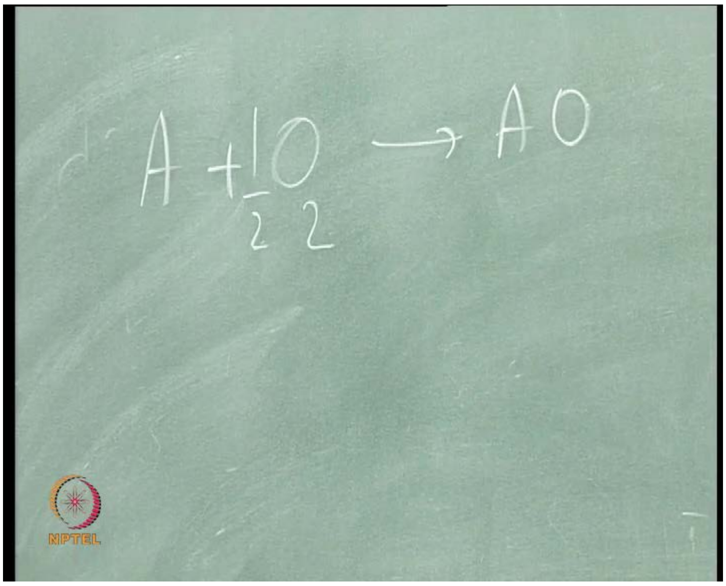

Let us simply take up simple case, where A reacts with O and gives you AO and you can also call it as O2. Then, may be takes it as half of it if you want and then, say that A gives you AO with 1 whole 1 half of the mole of oxygen. If you are taking such a reaction, how do we understand thermodynamics of this kind of reactions? To understand thermodynamics of that kind of reactions, one or two concepts which we should already know which we have possibly done it earlier is one that.. We already know that chemical. If I want to write G free energy of anything, we have written it in different ways.

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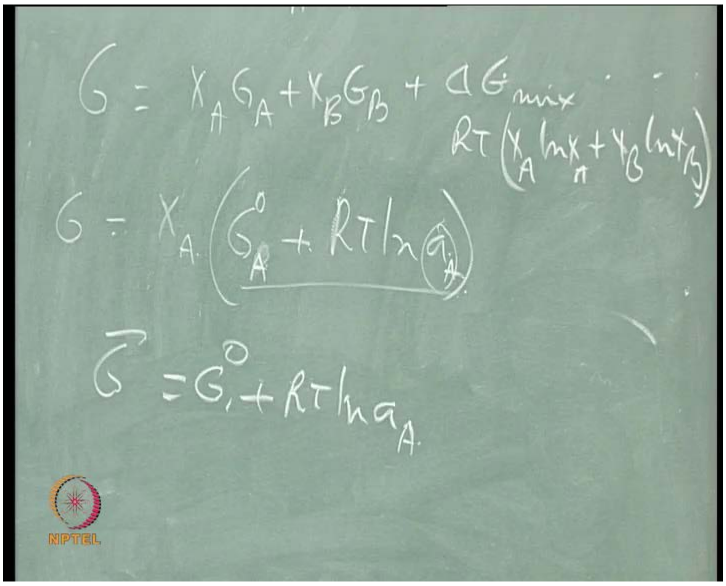

$$G = X_A G_A + X_B G_B + \Delta G_{mix}$$

$$RT\left(X_A \ln X_A + X_B \ln X_B\right)$$

$$G = X_A\left(\underline{G^0_A + RT \ln \boxed{a_A}}\right)$$

$$\bar{G} = G^0_{,} + RT \ln a_A$$

One we have written is what is called X A G bar A plus X B G bar B. You remember this we have written and we can also write. We have also written G as function of the complete plus delta G mixing, of course whatever it is. Am I right? In principle, we can also write this G as X A into G bar A G bar a can be written as G naught plus R T l n a of A. Any chemical potential G naught is the standard state. You can call it usually G naught, put it A G naught of A. So, the chemical potential can be always expressed as this and in fact, from here, you can get the whole expression of this when you talk of a. It is an ideal solution. A is equal to X. Am I right?

If that is a case, then you see here in the case of delta G mixing. You will see this turns out to be R T X A ln X A plus X B ln X B, where delta H mixing goes to 0. So, basically if you put here A in terms of X a, so this equation becomes actually equivalent to this equation accepting that this is X A G A. So, this will become X A R T ln X A and then, you put another expression for the X B, X B into G naught B plus R T ln X B. If you put it, so this whole thing is actually this for the ideal solution.

The moment I say it is not an ideal solution, then I can write A as equal to gamma into X A, where you talk of an activity coefficient and then, talk about this. Then, this gamma actually brings out the delta H mixing. I can put here in place of activity ln a. I can put it as ln gamma X A and that can be split into two parts. One as ln gamma part, another is called ln X A part. The ln gamma part is what is related to the delta H. So, the delta H mixing is always related to the activity coefficient gamma.

So, depending on how you express this equation, whether it is ideal solution or a non-ideal solution, you can express the whole thing in terms of that. What is more important is you can take that this G bar is G naught plus R T 1n a. If you remember this, we can do a lot of things. You hold on there and we will come back to that. Along if you take this expression which where one solid is reacting with another solid and giving you reacting with a gas give you an oxide, both assume that both of them are solids and this is a gaseous phase in such a case.

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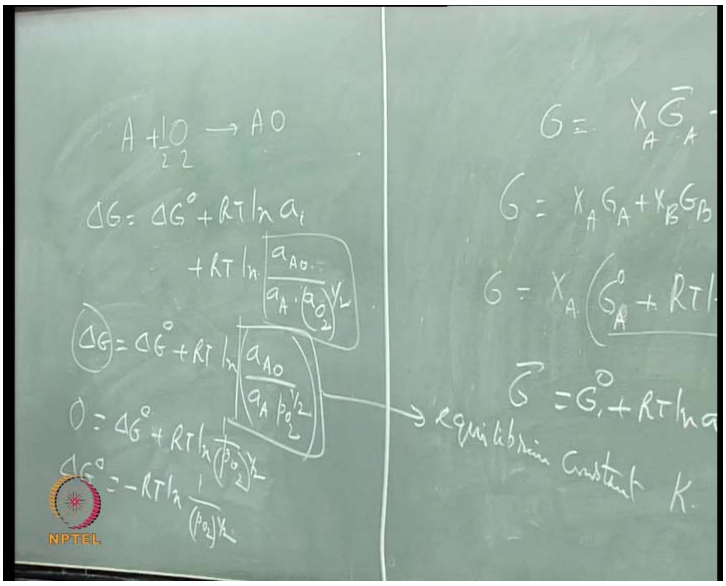

We can write what is called the delta H delta G of this reaction and the delta G of the reaction can be taken as delta G naught plus R T ln a of the reaction when we say the A of the reaction. So, here you have to take it as individual activities of each of them. So, activity of the product which is nothing, but AO divided by activity of the reactants, where you have activity of A into activity of O 2 and then, to the power half because it is half is coming and this activity O 2 we can represent activity in case of gases as partial pressure. So, this becomes pO 2.

So, you can write this whole expression, delta G is equal to delta G naught plus R T ln a of A O into a of a into pO 2 to the power half and in this case, we always know that the activity of solids in their standard states is equal to 1 if they are pure, as long as they are pure. So, if this reaction, if a pure A reacts with oxygen and gives you pure oxide without any impurities there, then this becomes 1 and this becomes 1 and this whole thing we can write it as and for any such a reaction at the equilibrium transformation temperature, delta G is 0.

So, you can write this as 0 is delta G naught plus R T ln pO 2, 1 by pO 2 to the power half. Am I right? This is where we say the delta G naught is equal to minus R T ln 1 by p O 2 to the power half. So, this is how, so if I know what is the partial pressure of oxygen during the reaction, I can actually find out what is the delta G of the reaction without knowing or if I know the delta G of the reaction by some means, if I can find out the delta G of the reaction by, let us say doing a DSC.

If I do DSC, what do I get from the DSC? Delta H of the reaction I will get. If I know the temperature of the reaction and if I know the entropy of the reaction from the delta H basically, in principle I will be able to get the delta G. So, either measure the delta G or measure the pO 2 and you can see both of them are related to each other. This whole reaction kinetics, I mean thermodynamics are all related. How to relate the free energy with this and this whole stuff is what we call it as the equilibrium constant or the reaction constant k, where it is an activity of the products divided by the activity of the reactions.

So, this part is what we call it as equilibrium constant k and people represent this in terms of the constant. It will take few more constants in the next class where we have not simply one gas. There can be a number of gases involved and most of our actual reactions. In metallurgy, we deal with a number of gases that are involved and try to see how these reactions change as function of the free energy and as the function of temperature and also see as a function of pressure how things change with that. We will stop now.