

Advanced Metallurgical Thermodynamics
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Lecture No. # 31
Thermodynamics of heterogeneous system

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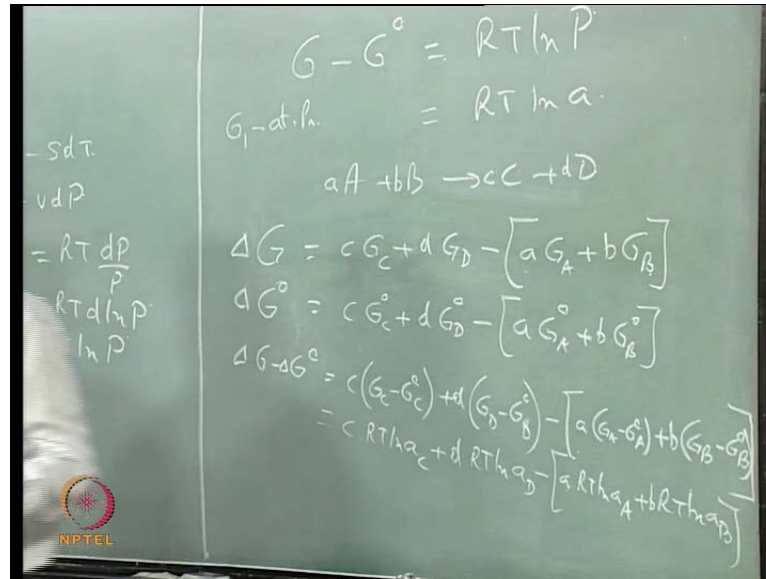
$$\begin{aligned}dG &= v dp - S dT \\ \text{at const temp: } dG &= v dp \\ RT &= PV \quad dG = RT \frac{dp}{P} \\ V &= \frac{RT}{P} \quad = RT d \ln P \\ G &= RT \ln P \\ G_1 &= RT \ln P_1 \\ G_2 &= RT \ln P_2 \\ G_2 - G_1 &= RT \ln \frac{P_2}{P_1}\end{aligned}$$

Yeah we started talking about reactions. Let us continue and know a few aspects about various reactions. We start with first of all the relation between the G and a. This is well known, but still I thought it is better; we look at it once carefully before we go ahead. If we look at basically the expression dG is V dP minus S dT; this is what we all know, am I right? So, in principle at constant temperature, this turns out to be nothing but V dP. So at constant temperature this dG is V dP, and if we assume that there are gases involved in the reaction, we can use the ideal gas relation and where RT equal to PV. And then, use this V in terms of RT and P, and write V equal to RT by P. Once we write that we can write that dG as RT dP by P. RT dP by P is RT dln P. So, that is how you actually get this expression, and in this now if I simply look at two pressures, let us say.

I can say dG 1 can be written as RT dln P 1. I can write another dG 2 as RT **ln** dln P 2 or if we can write it in terms of G alone, you can simply even not write this; simply write G equal to RT ln P, where d can be removed. So, and once you write it, you can write G 1 equal to RT ln P 1 and G 2 equal to RT ln P 2. So, whenever you want to look at

differences in the free energy at various pressures, you can simply take as G_2 minus G_1 is equal to $RT \ln \frac{P_2}{P_1}$. So, I can simply write G_2 minus G_1 is equal to $RT \ln \frac{P_2}{P_1}$. So, like these we can simply look at how the free energies change as a function of pressures, and if one of them, let us say P_1 is a standard pressure, what is the standard pressure for us? Atmospheric pressure.

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So if I take it as atmospheric pressure, I can write it as G minus G° . I will take G_1 as related to atmospheric pressure can be written as $RT \ln P$. Because if P_1 is equal to 1 if I take P_1 as 1, then P_1 goes off in this equation. So you can write G_2 minus the G_1 , I will call it as standard free energy at atmospheric pressure. So, that I will refer it to as G° ; so we always refer free energy at atmospheric pressure as G° . So I can write G minus G° is equal to $RT \ln P$ and the same thing if you are talking in terms of activities, I can write the same thing as $RT \ln a$. If we are talking of a mixture of it, infact there also if you are talking of a mixture of gases, you can write G_i minus G_i° .

I can be written as $RT \ln P_i$ for a particular gas. If there are mixtures of a number of gases, for a particular gas we can write i th gas; you can always write this expression. So this is how, we can express the free energy changes in terms of activities. And once we know this, we can start looking at various equations; various reactions **that are** that take place and look at, how we can correlate the free energies with the activities. And then,

from that get to know information about whether the reaction will go in the forward direction; whether the reaction will go in the backward direction. All this can be accumulated, once we are aware of it.

So, you can see starting from a simple Maxwell's equation which is $dG = V dP - S dT$ and this I hope all of you know, how we derived it. I will not need to derive it. So, we are simply assuming the temperature to be constant and from there, we have arrived at this; for a given atmospheric pressure, one pressure being a atmospheric pressure. And from there we have come to the activity. Now, let us look at a equation, a reaction where let us say A is reacting with B and giving you C plus D. And here, to make it more specific, we will call it as some a moles of A is reacting with b moles of B to give you c moles of C and d moles of D.

And you can see this kind of reaction variety of reaction, where certain numbers of moles of a particular component are involved in the reactions. For example, if you take Mg simple example, magnesium plus oxygen gives you Mg O. When we say, when you need to balance the equation, you need to see 2 moles of magnesium would give you 2 moles of Mg O with 1 mole of oxygen. So, that these numbers are the numbers that we are talking here. When I say small a b c d, small a b c d referred to those moles and if that is the case, then the free energy change for such a reaction is nothing but the free energy of the products minus the free energy of the reactants **am I right**.

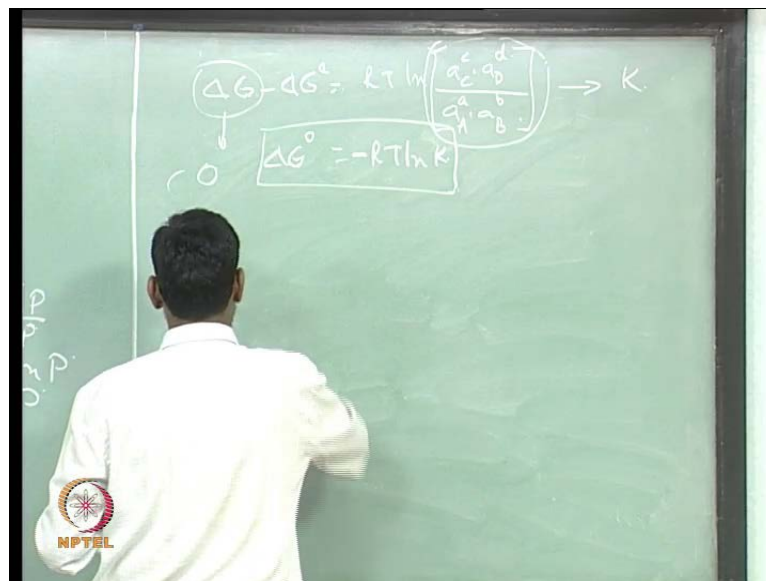
So, I can say the G of the reaction is nothing but I can write it as c into G of C plus d into G of D minus I can write a into G of A plus b into G of B. This is the reactants; this is the products; this is the free energy of c plus the free energy of d minus the free energy of a and I can also write the same thing at a standard state; **sorry** I will put naught on the top that means at atmospheric pressure. If this reaction is happening, then I can write it as c into G C naught plus d into G D naught minus a into G A naught plus b into G B naught. Everything see means the same excepting that, we are talking at the standard state.

So, if that is the case, now I can write $G - G_{naught}$. For example this is **this is** actually ΔG change in the reaction; change in the free energy. I should not put G; I should put ΔG_{naught} . So, ΔG is this; ΔG_{naught} at the change in the free energy for the reaction at the standard state, standard conditions is this. If I take the difference of this two, difference of this two is basically nothing but the difference of this

two. So I can write c into G_C minus $G_{\text{naught } C}$ **am I right** plus d into G_D minus $G_{\text{naught } D}$ minus of whatever it is. If you want more specific, we will write a into G_A minus $G_{\text{naught } A}$ plus b into G_B minus $G_{\text{naught } B}$. Here if you look at this part, this part is nothing but this.

We already know that, G minus G_{naught} is $RT \ln a$. So I can write this as, c into $RT \ln a$ of C at activity of component c and then, plus d into $RT \ln a$ of D minus a into $RT \ln a$ of A plus b into $RT \ln a$ of B . Basically, now we have got the whole free energy change in terms of activities **am I right**. Any confusions? We simply looked at the free energy change of the reaction. We took it as products minus reactants and then, we looked at the same free energy change at the standard state. And the difference between the two brings out that, there is a component, which is a free energy in at any given condition minus the free energy in the standard state and this difference is always $RT \ln a$.

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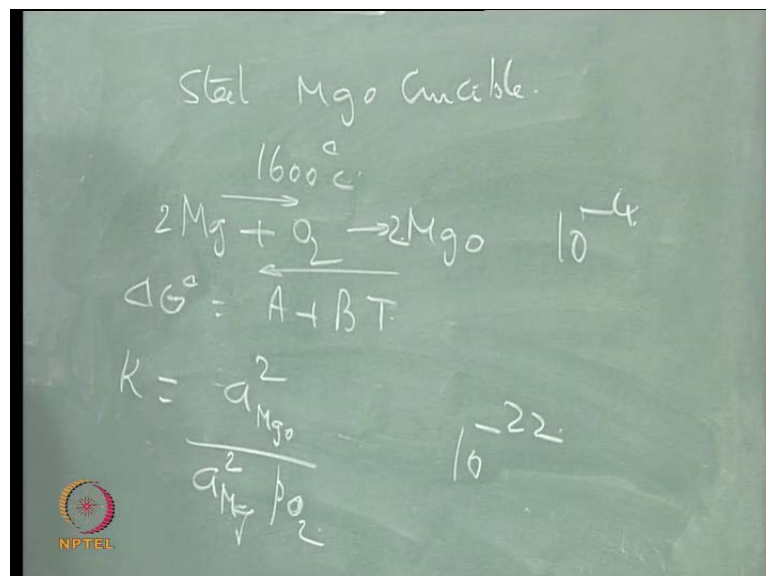
And so from this, I can write that, ΔG minus ΔG_{naught} is $RT \ln$ of C to the power c into a of D to power d divided by a of A to the power a and a of B to the power b . Are we right? Because these are \ln 's, we can take the \ln out and then do multiplications. So here basically, we are simply multiplying and because this is negative it comes to the denominator; positive is in the numerator. So this particular thing is what we call it as this, the bracketed item is what we call it as K , equilibrium constant. And we learnt a lot of things from this as we go along; we will see, how does this influence the

whole reaction and this, the whole reaction, whether it will go in the forward direction or the backward direction always depends on that.

So, I can write this as $R T \ln K$ and ΔG here, if this the reaction is taking place; if under equilibrium conditions; if there is equilibrium that is established between the reactants and the products, then this ΔG is 0. Whenever there is equilibrium between anything, we have seen liquid to solid transformation ΔG is 0. So, the same argument I can hold even for magnesium plus oxygen reacting to give you Mg O. The change in free energy for such a reaction should be 0, if all the 3 components whether it is products and the reactants; if everything is under equilibrium, then the ΔG is 0.

And if that is the case, then you can say ΔG_{naught} is minus of $R T \ln K$; if there is a minus there, that comes here. This is a very crucial equation; which will tell you that, we can correlate change in the free energy of a reaction in a standard state to the equilibrium constant; which is nothing but activities of various components. And this is how, we will be able to see how to understand reactions and maybe, I will just take one or two examples just to give you. Whatever we have done so far, is it clear? So you can see for example, let us take any example. I will take an example.

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Let us say, you are melting steel in a magnesia crucible at some temperature 1600 degree centigrade or so. You want to know, whether this magnesia crucible will be intact at the temperature, or will it dissociate into magnesium plus oxygen. If it dissociates, obviously

you cannot melt the steel at in that crucible; it is no more stable. So, if you want to melt anything in a crucible, that crucible material should be stable at the temperature. So if that is the case, how do I find out that? Simply, what you do is find out what is the reaction that goes on? Mg plus O₂ gives you Mg O. So 2 Mg plus O₂ should give you 2 Mg O.

If this is the case, then find out what is the delta G naught for this reaction? If the delta G naught for the reaction is available, usually delta G naught is given in the form of A plus B T. Whenever you look at various why it is written in the form of A plus B T is basically, because delta G naught is delta H minus T into delta S. So, whether the B is negative or positive, let us not bother about it. So basically, because it is delta H minus T into delta S. So, you would always see the expression for the delta G naught is always given in form of two constants and linear dependents on temperature.

Once you know the A and B terms, for that particular reaction which are available based on basically, people have done such reactions at various temperatures and found out, how the free energy is changing. How do you find out the free energy change for a reaction from c p change anything else? Look at particularly, the thing that is easily measurable for any reaction is the enthalpy change. Because that is something you can measure using a calorimeter. So measure the enthalpy change at various temperatures for a reaction.

And once you measure the enthalpy changes at various temperatures for a reaction, from that you can actually get how the and keep the pressure constant; because we are all talking of delta G naught there. At atmospheric pressure, do this reaction at various temperatures. At various temperatures, measure how the delta G H is changing and from that, you can actually get this. Infact, people have done this and for various reaction and these values are standard values are available. If you go to any standard hand book shop, on thermodynamics, you will see for various reactions.

What is this in terms of temperature is what are they? Particularly, what are the A B values? For various oxidation reactions, various reactions where sulphites form; sulphide form; sulphates form and such reactions they are all tabulated. You go to any thermodynamics hand book, you will see it. For example, the book one of the good one's is what is called kubaschewlki . If you go to this particular book, it is thermo chemistry.

A book on thermo chemistry, which gives you towards the end so many appendices and each appendix, gives about various such reactions, what is the value of A and B.

Once I know this, A itself is a function of temperature you mean? No, A and B are constants and if there are the functions of temperature, then obviously these functions becomes more complicated. So, A and B are usually fixed. Because that is how in principle, if you go a little detail, if you think these two are nothing but $\Delta H - T \Delta S$. These two are also functions of temperatures, in principle yes. But for in such a case, this whole expression becomes a little complicated expression where in each of them, you will get temperature dependence. But to a large extent, people have seen that A and B are constants for most of the reactions.

You simply take A and B as constants and do it and that works out for most of the reactions. Yeah why are you see the question is, if this magnesia crucible at that temperature will it dissociate? That is what, we are interested in. you know At any temperature, whether the reaction will go in this direction or whether the reaction will go in this direction; we do not know. What does it depend on? Whether the reaction will go in this direction or in this direction depends on what is called partial pressure of oxygen. For this reaction, there is a equilibrium partial pressure.

How do I calculate the equilibrium partial pressure? Simply, find out what is the K? So, I know K of this reaction. I can write it as, activity of Mg O square divided by activity of magnesium square into partial pressure of oxygen. In case of gases, we call yeah Mg O giving you Mg plus O₂. We are we are trying to find out, whether that will happen or not? Correct. The point is, at that particular temperature and pressure that we have whether this will happen or not. For example, this melting is taking place e may furnace let us say, where there is certain oxygen partial pressure.

My furnace is under certain oxygen partial pressure. Now, for that oxygen partial pressure, which is available in the furnace whether this reaction will happen or not? Whether the whether the Mg O will dissociate or whether the Mg O is stable? How will I know? If I know what is the partial pressure of equilibrium partial pressure of oxygen for this reaction at that temperature; for example, if I know the ΔG naught as a function of temperature, by putting 1600 degree centigrade in to it. Mind it; you should remember that, whenever we are talking of any thermodynamics, we talk of temperature in Kelvin.

So, come let into Kelvin; put it into this. So, you will know ΔG° and ΔG , we know is nothing but $-\text{RT} \ln K$. So, from once I know ΔG° , I will know K and once I know K , I will know P° ; P° , partial pressure of oxygen, which is the equilibrium partial pressure of oxygen at that temperature, which will keep on changing at different **different** temperatures. So, once I know that and what is the actual pressure inside the furnace if I know, and if the actual pressure of oxygen is higher than the equilibrium partial pressure of oxygen, then what will happen?

Reaction should happen in the forward direction. Whenever oxygen content is more, the Mg should get oxidized. It should go in this direction. If the oxygen content inside the furnace is lower than what is the P_{O_2} of the reaction, then what happens is the system would go in such a way that, oxygen is created in the **in the in the** process. So that, it maintains the oxygen partial pressure inside the furnace equivalent to the equilibrium oxygen **pressure** partial pressure. So, if the actual oxygen partial pressures inside the **...** let us say you are doing this in vacuum. Let us say at 10^{-4} bar.

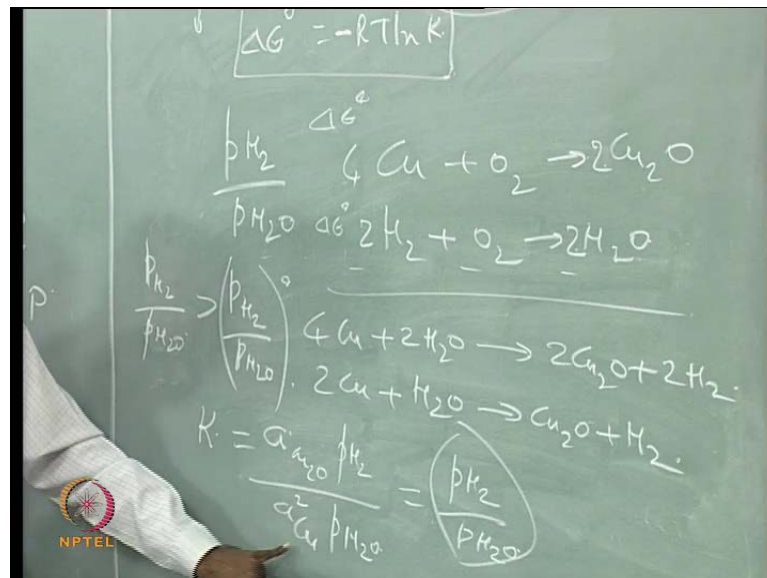
So, if the melting is taking place in vacuum and then you find, what is the P_{O_2} for that reaction at this temperature? Infact, if you do it, what you would get is that partial pressure of oxygen will be actually 10^{-22} . You will get as **as** 10^{-22} **minus 22** or 10^{-23} , it comes out. So, this value is much smaller than this. As a result at this particular vacuum level, at this particular pressure level, because the actual oxygen partial pressure is much larger than the equilibrium partial pressure of oxygen. The reaction would not go in this direction; would go in this direction, because **oxygen** excess oxygen is available than the oxygen partial pressure of the reaction.

If the oxygen that is available is less than the partial pressure of oxygen that is required to maintain the equilibrium, then what happens is MgO will dissociate and will give you oxygen, by the way. So, that this oxygen joins the atmosphere to maintain the equilibrium. So, this is how, I can simply calculate, what is the partial equilibrium partial pressure and find out what is the actual partial pressure inside the thing? And then, find out whether this MgO is stable or not stable? This can be done for any of the things when say all meltings are done in certain crucibles; whether it is alumina crucible or silicon carbide crucible or whatever kind of crucibles, so you need to make sure that, these crucibles are stable.

Particularly, when I am why I have to be bothered is whenever I am doing melting in vacuum; vacuum means lower pressure. Whenever the pressure is low, the volume has to be high. P and V are inversely proportional. As a result, the reaction will go in such a direction, which will increase the volume of the system. So, what can increase the volume of the system, if the oxygen can come out? So, as a result, there is always a tendency. Whenever I am melting a material in vacuum, the oxide which is there in the crucible may dissociate to give you oxygen provided.

That particular pressure in the furnace is smaller than the oxygen partial pressure under equilibrium conditions, only if it is smaller than and if it is larger than, then it will not happen. So, this is one such example, we can think of many **many** such examples. Take say, you are trying to annealing copper in **in a in** a atmosphere, which is containing hydrogen and H₂O. Most of the time annealing is always done in **a in** furnaces, which are actually heated by oiled; various oils. So where, there is always hydrocarbons; these hydro carbons will break and give you some hydrogen and some moisture is also expected in the reaction.

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So, there is what is called partial pressure of P H₂ by P H₂ O. If I know what is the actual P H₂ by P H₂ O; that is being maintained in the furnace. One can do what is called mass spectroscopy and things like that, to measure the actual partial pressures of oxygen; I mean various gases in any furnace atmosphere. And if I can measure and find

out, what is the actual value inside the furnace. Now, **I will** I would like to know whether this copper, which is being annealed in the furnace, is going to get oxidized or not. How do I know that? To know that, first of all look at the copper oxidation reaction. This is Cu_2O .

So, that means basically 4 copper plus 2 oxygen should give you $2\text{Cu}_2\text{O}$ and the other reaction, that is possible is H_2 plus O_2 giving H_2O . Again, you say you do this; now, look at combination of these two reactions. If you subtract these two and you can say that, 4Cu plus $2\text{H}_2\text{O}$ will give you $2\text{Cu}_2\text{O}$ plus 2H_2 **am I right**. Basically, oxygen goes off; this is minus **minus** I am taken it that side; this minus, I have brought it this side, simply. So, that means copper, H_2O can oxidize copper and to give you Cu_2O and H_2 can reduce copper oxide to give you Cu . What does that depend on?

It depends on what is the actual values of Cu , H_2 and partial pressures of H_2 and H_2O . So, if you look at the equilibrium constant for this. For example, if I know the free energy change for this reaction, ΔG_{naught} for this reaction and I also know the ΔG_{naught} for this reaction, let us say; as a function of $A + B/T$ kind of thing. If I know that, by **by** adding those two or subtracting one from the other, I will be able to know that ΔG_{naught} for this reaction. And because you can see, there are 4 moles and 2 moles in both the sides, I can actually make it simplified; 2Cu plus H_2O gives you Cu_2O plus H_2 .

Whenever I am dividing with 2, obviously the ΔG of the reaction also has to be divided with 2; this has to be kept in mind. So, whatever ΔG_{naught} I am getting by, subtracting ΔG_{naught} of this minus ΔG of that has to be divided by 2; So that, you know the free energy change for this particular reaction. And for that reaction, if I now want to write down what is K ? K is nothing but now activity of Cu_2O into partial pressure of hydrogen divided by activity of Cu square and partial pressure of H_2O . And if we assumed that, this reaction is giving you a pure copper oxide and a pure copper is getting oxidized in this particular condition.

There are no impurities in that, then whenever it is pure, the activity is equal to 1. So, there is no second component. **Second** whenever there is second component, then we have to consider what is the activity of it. So, activity basically becomes 1, when it is a pure component. So, if **if** pure copper is getting oxidized and giving you pure Cu_2O ,

then the activities are 1's for these two. Then, I can write K as nothing but P_{H_2} / P_{H_2O} minus $\Delta G^\circ / RT$. So, I can find out if I know the ΔG° of the reaction. What is the equilibrium partial pressure ratio of H_2 to H_2O ? This can be easily found out.

Once I know the ΔG° and simply, I will put this equation and from that, I can find out K and K is nothing but this. So, I will know what is the equilibrium and once I know, what is the actual value of P_{H_2} / P_{H_2O} in the furnace and if that actual value of P_{H_2} / P_{H_2O} is greater than this value, then what does it mean? I have an excess hydrogen in the furnace. When I say the actual P_{H_2} / P_{H_2O} is greater than P_{H_2} / P_{H_2O} , remember always use partial pressure as small p of the standard state. If this is higher than this, then that means you have excess hydrogen inside the furnace.

Then, what is there for the standard reaction? If there is excess hydrogen, then that means what? the reaction will go in this direction. If this value is smaller than this, then the reaction will go in that direction; that means copper will get oxidized. So this is very, very important, whenever you are doing annealing. For example, steel you want to do hot rolling of steel. Before hot rolling of steel, you have to heat the steel at 900 degrees or 1000 degree centigrade to for some time, before you start rolling it. And you do not want this whole steel to get oxidized at that temperature.

So, if that is the case you need to know what is the partial pressure of H_2 by H_2O ; that I should maintain inside the furnace; so that, the steel does not get oxidized. So, you can see that, all these actual practical applications of the thermodynamics come. When you want to use simply hydrogen in annealing of copper or **you know** hot rolling of any of the steels or whatever it is aluminum alloys that you are talking about. So all is related to the presence of this; ofcourse, depending on the actual equation, if I am talking of Fe, then I have to actually see what the type of oxide that is forming is. Is it FeO or is Fe_2O_3 or Fe_3O_4 ?

And accordingly, the actual numbers will change a little bit and then, so here also the values will be slightly different. Otherwise you will see that, but as long as the gas molecules are not changing, then this whole thing will not change. Because we are not bothered about, what is the metal and oxides much because we are assuming that, they are **...** But then, this may not be always true for alloys. For example, if I am looking at

the steel. Steel is not pure iron. So, I need to consider when I say activity of iron, there I need to find out how much of iron is there in the steel?

Ofcourse, luckily for plain carbon steel, **you know** we are talking of mild steel. Let us say, is about 0.2 percent carbon. So it is more or less can be treated as a pure iron. So, activity of iron actually is 0.9998. If you are considering a steel containing 0.2 percent carbon, the activity of carbon is accordingly the value 0.0002 and activity of iron will be 0.9998, if it is a binary alloy. So, if it is a **you know** multi component alloy, if it is a stainless steel that I am talking about then accordingly I have to consider what is the activity of?

So the actual activities that we are talking here, which we are equating it to 1; this would not be true, if I am considering alloys. If I am talking of let us say super alloy, where there are various elements present. And I need to look at, let us say oxidation of each of the alloying element; I need to consider what; for example, in a super alloy again super alloy also I am heat treating at certain temperature to do hot rolling of super alloy. Let us say, I want to find out whether nickel of that super alloy will oxidize; whether aluminum of that super alloy will oxidize or not. If you want to find out, you have to actually find out for each of them equations like this.

And the activities of the oxide and the metal that, you are putting in this equation should be accordingly the compositions of those. Once I know the compositions of it mole fractions of it, activity is equal to... And again, this issue activity equal to mole fraction also **is a** is not so easy. When **when** activity is equal to mole fraction? when it is an ideal solution. If I am assuming it be an ideal solution, an ideal solution works out only when in a very dilute conditions. Whenever is a dilute alloy, then I can think of that; but if I have alloying elements of the order of 20, 30 percent, the ideal solution may not work out.

So, that is where you have to consider, then activity is activity coefficient into the mole fraction. So, all these complications will come into picture, when you are talking about materials, where you do not have pure components. So, as long as pure components are there; **there** these equations turn out to be very easy. So, you can see like this, we can talk about many **many** examples, where this kind of knowledge of active the equilibrium

constant and the knowledge of (No audio from 37:07 to 37:22) our basic equation with which we have started.

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$$dG = VdP - SdT$$

$$d\Delta G^\circ = -\Delta S^\circ dT$$

$$d\Delta G^\circ = -\left(\frac{\Delta H^\circ - \Delta G^\circ}{T}\right) dT \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

$$T \frac{d\Delta G^\circ}{dT} - \Delta G^\circ = -\Delta H^\circ$$

$$\frac{\partial(\Delta G^\circ/T)}{\partial(1/T)} = \Delta H^\circ$$

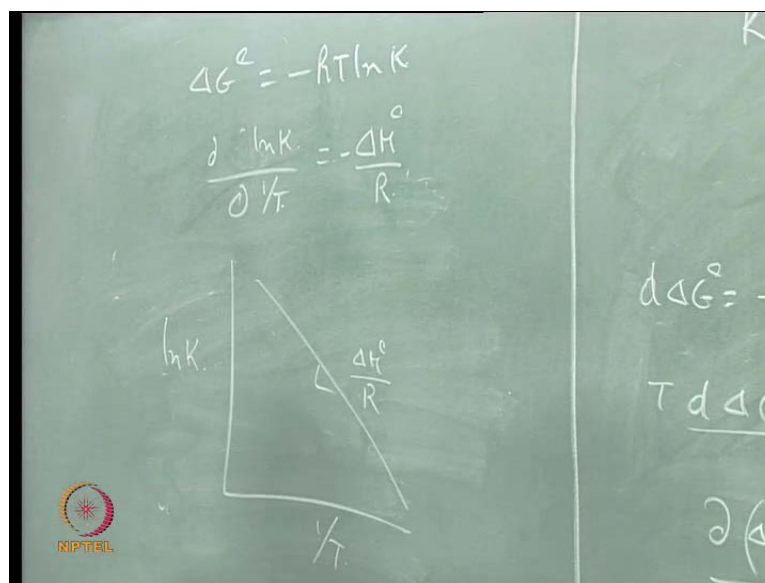
Take dG equal to $V dP$ minus $S dT$ and this time let us assume that, we are doing at atmospheric pressure. The whole reaction is happening at atmospheric pressure. Then, obviously dP becomes 0; pressure is constant. I can write dG is equal to minus $S dT$. And I can write d of ΔG is equal to ΔS into dT and for a standard thing, I can write it as **delta** $d \Delta G$ naught is equal to minus ΔS naught into dT . And we can always write the ΔG naught as ΔH naught minus T into ΔS naught **am I right**. If that is the case, then I can reframe this equation and then say that, ΔS naught is equal to ΔH naught minus ΔG naught divided by T .

Simply, rearranged the things and I put that into that equation and then, I can say that, d of ΔG naught is equal to minus of ΔH naught minus ΔG naught by T into $d T$ **am I right**. Simply in the place of ΔS naught, I am putting this. If I am putting that, then we can write again as (No audio from 39:21 to 39:38). So, you can see that, T if it comes this side, this T into d of ΔG naught minus ΔG naught. We have brought both the ΔG naught in one side. So that, we can actually differentiate them very easily and minus ΔH naught dT if you divide this whole thing by T square...

ΔG naught dT you are right, perfect; dT has to come there. Otherwise, you cannot differentiate; hence, it has to come there. So, if you divide with T square on both the

sides, you will be able to see this whole thing as $\frac{d \ln K}{d(1/T)}$ is equal to actually $\frac{\Delta H^\circ}{R}$. You can actually show that to become actually this. Basically, this becomes $\frac{dG^\circ}{dT}$ and $\frac{dG^\circ}{dT^2}$ and that, if you take it as $\frac{1}{T}$, it turns out to be this. You can do this exercise and what comes out of this is because, we know ΔG° is actually $-RT \ln K$.

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If you put that into that, you will see that $\frac{d \ln K}{d(1/T)}$ is equal to $\frac{\Delta H^\circ}{R}$ and in principle, this R can be brought out and R can come out here. So, you can see that $\frac{d \ln K}{d(1/T)}$; that means, if I have the K values what is called the equilibrium coefficient values as a function of temperature. And if I plot the $\ln K$ if I plot $\ln K$ as a function of $1/T$, I should be able to get a straight line; where the slope is $\frac{\Delta H^\circ}{R}$, where the ΔH° is the heat of the reaction. So, one can find out the heat of the reaction and the K and $1/T$ are related by the heat of the reaction.

This is similar to almost like a link, you know **clinsinger** plot and things like that; that we talked about it in the last class. So, any activation energy more or less, we do the same thing. So, you can see the equilibrium constant is related to the temperature through the ΔH° of the reaction. So, that means in principle, equilibrium constant is not constant. Though we use the word equilibrium constant, so **it is** it is a fixed value for equilibrium

at certain temperature. But as a function of temperature, the same reaction is occurring at different **different** temperatures at the same pressure; pressure being constant.

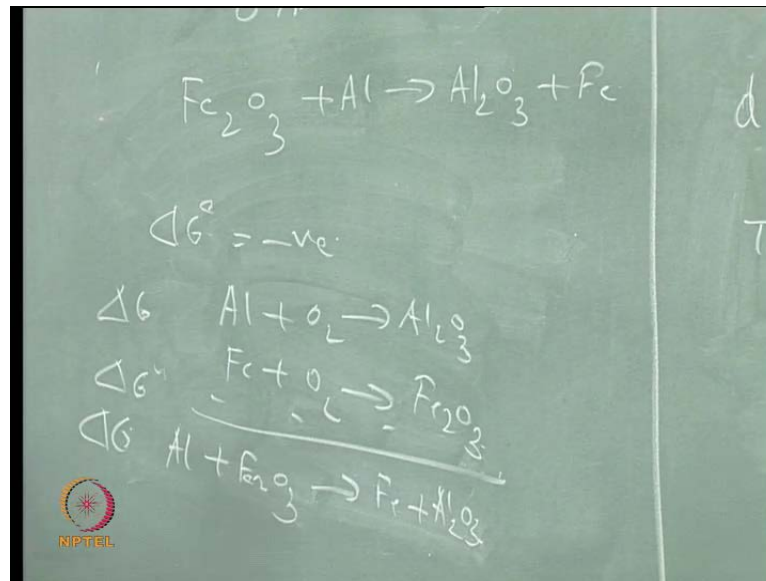
You will be able to see that, this follows such a thing. Ofcourse, it depends on how accurate your measurements are to see, whether this will be a good fit, or not a good fit depends on your actual measurements. And as long as the measurements are right, this gives you a good **(())** do it; let say at 4 different temperatures and find out what is K at all these 4 different temperature. How do I find out what is the K? Basically, I find out delta G naught at various temperatures; at different **different** temperatures, find out the delta G naught and once I know the delta G naught, from that I can find out the K and plot that K with $1/T$.

So, if you have 3 or 4 points in principle, you can plot a straight line and as long as the data is reliable, you will get a good straight line. Because the equation, there is nothing wrong in the equation. If all the points are not falling on the straight line that means, only your delta G naught measurements are wrong. Because if the delta G naught measurements at various temperatures are wrong, then the K that you get out of it will be wrong. If that is wrong, you will not see a good fit. That is why, **that is why** we always whenever you talk of fit like that, in any statistical we talk of what is called confidence level.

So, whether the R square value of the **of the** fit, whenever the R square value of the fit is atleast more than 95 percent, that is when we say the actually the fit is good. So, that again depends on how reliable all these K values. And once you have this, one can find out this K and from that, we will be able to find out at various temperatures, how the reactions take place. So, your point that actually delta H and delta S are related to temperature actually comes here. Because K is related to delta G naught and K itself is a function of temperature; that comes basically, because delta G is a function of temperature.

I think with this, we will stop. If you have any queries, feel free. We will again have one more class, where we will see few more reactions and look at, what is called a **ellingham's** diagrams. Where we are actually going to talk about various stabilities of various oxides, which oxides is more stable than other oxides. And if one oxide is more stable than another oxide in principle, we may be able to reduce one oxide with a metal.

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For example, if you take an example of a very standard example everybody knows. If I take a FeO or Fe₂O₃ plus aluminum, you should be able to get Al₂O₃ plus Fe. Whether this reaction will go in this direction or not depends on whether the ΔG of this reaction is negative or not at a given temperature. At a given temperature, if the ΔG is negative, what is ΔG ? It is the free energy of the products minus the free energy of the reactants. So, if the free energy of the products is smaller than the free energy of the reactants, then only ΔG will be negative and if that means be the case, that means the products have a lower free energy than the reactants, it is like the liquid going to a solid, it happens only when a solid has a lower free energy than the liquid.

So, you can see such reactions happening and for that, what you need to do is basically, find out what is the free energy of aluminum getting oxidized to Al₂O₃? And what is the free energy of iron getting oxidized to Fe₂O₃ and then, find out a combination of these two reactions. By if I do, this negative so I will know aluminum plus Fe₂O₃ will give you Fe plus Al₂O₃. So, I have ΔG of this reaction; I have the ΔG of this reaction.

I will be able to find out the ΔG of this reaction at a particular temperature and at that temperature, if this turns out to be negative, then I can say yes; this reaction would happen. If this turns out to be positive, then actually the reverse will happen. So,

whether these reactions are such reactions are feasible; if that is feasible, then what is called, metalothermic reductions are possible. Even for that matter, if you want in a blast furnace, iron oxide to be reduced by carbon; that reaction of iron oxide plus carbon should give you the iron plus carbon dioxide; that reaction should be negative.

If ΔG is not negative, you will not see that reaction happening. Similarly, if you want iron oxide to be reduced by carbon monoxide to give you carbon dioxide plus iron again; that reaction also should have negative. Again there also, you can simply find out the reaction of iron plus oxygen, carbon plus oxygen reaction; add the two reactions. Then, you will get iron plus carbon monoxide giving you carbon dioxide plus iron; iron oxide plus carbon monoxide giving you carbon dioxide plus iron or iron oxide plus carbon giving you carbon monoxide or carbon dioxide plus iron.

So, you can add such reaction that is one good thing about all these reactions is that, you can simply sum them up, and the free energy is being extrinsic property, you can simply sum them up. So, you can sum them up and get the actual values. And if the actual value becomes negative at a particular pressure and temperature, we are already talking at about a fixed pressure. Because we are talking of ΔG naught and temperature at a given temperature we do this. We will stop here.