Corrosion - Part II
Prof. Kallol Mondal
Department of Materials Science and Engineering
Indian Institute of Technology - Kanpur

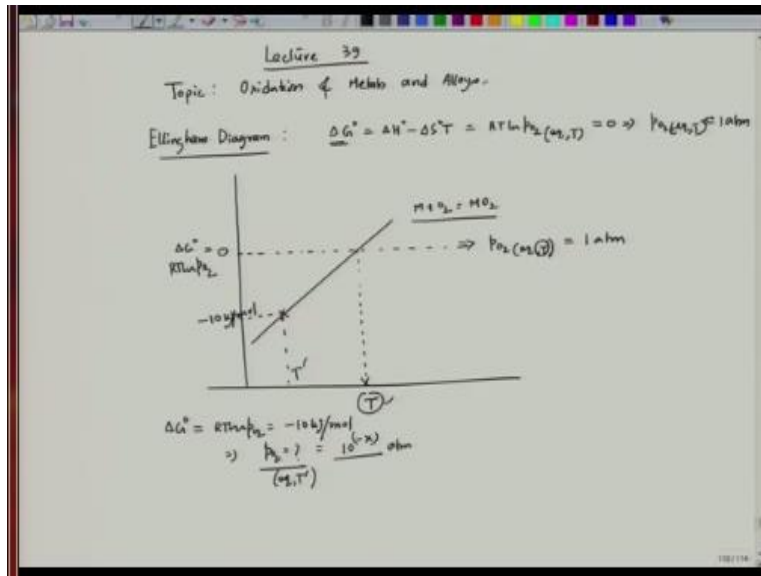**Lecture - 39**
Construction of Ellingham Diagram (II)

Hello everyone, today we have lecture 39 and our discussion point our topic is oxidation of metals and alloys and we will continue our discussion on Ellingham diagram. Last class we have seen how to plot Ellingham diagram which is nothing but the plot between RT ln pO2. Considering 1 mole of oxygen is consumed for metal oxidation forming metal oxide and the assumptions are metal is pure, metal oxide is stoichiometric and the system is closed system and the system is trying to reach equilibrium.

Because the temperature of the system is kept fixed and we are plotting RT ln pO2 with temperature and we could see that within a certain temperature regime that the variation of del G0 or the RT ln pO2 is almost is linear to temperature where del H0 is basically the enthalpy change which is constant for an oxidation process and del S0 is the slope of that particular plot between RT ln pO2 and temperature and this has a positive slope.

Because the entropy change for the oxidation process we have also noticed that it is almost equal to minus of individual entropy of oxygen gas in standard state and that is what an entropy of a particular component or gas is always positive. Since there is a negative sign, so that is what the slope becomes positive, so now today also we started mentioning that at every point in that particular plot indicates a particular partial pressure of oxygen which is an equilibrium in that particular system.

Now what we can do we can take values corresponding to each temperature on that line and from that we can get pO2. But there is one interesting way to find out pO2 from graph without doing any much of calculation, so we will explain that part today and then we will get to kinetics of oxidation.

(Refer Slide Time: 03:19)

So today's lecture is lecture 39 and topic oxidation of metals and alloys and we started talking about Ellingham diagram and it is a plot between delta G0. So this is we can write it to RT ln pO2 which is equilibrium temperature and we have also noticed in case of Ag2O ok how this pO2 is varying and this pO2 reaches 1 atmosphere when these value goes to 0. So that corresponds to pO2 equilibrium T = 1 atmosphere.

Now the plot between RT ln pO2 and T is this and let's say I am considering only one case

$$M + O_2 = MO_2$$
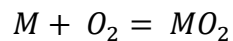
And let's say this is the 0 value and which is equal to delta G0. So it corresponds to pO2 equilibrium temperature = 1 atmosphere and that equilibrium temperature when pO2 is 1 atmosphere is this one this is the T we are talking about this T and this T both are same. Now in order to find that different location, for example let's say I want to find out pO2 in equilibrium with this oxidation reaction.

So I just corresponding value let's say this value is - 10 kilo joule per mole, so I will just equate it equal

$$\Delta G_T^o = RT \ln \ln p_{O_2} = -10 \ kilo \ joule \ per \ mole.$$

So it will give me some pO2 value, if you do calculation you will get some pO2 value which will be definitely 10^{-x} quantity and this is atmosphere. So this will be definitely less than 1 atmosphere pressure. Now in order to find out this p equilibrium this is temperature let say T prime.

So this is equilibrium T prime you have to do lot of calculations though it is a simple calculation but still you have to do the calculations. But there is a way out and from the graph you can find out what is this value.

(Refer Slide Time: 06:57)
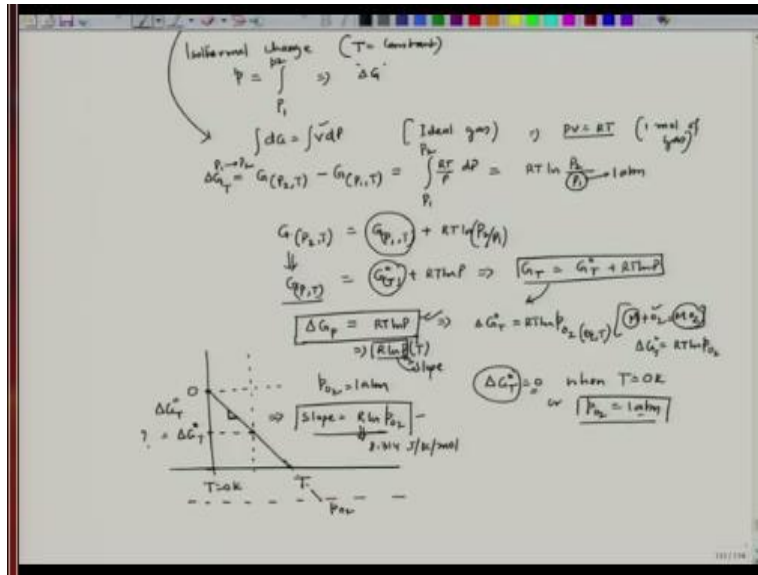
In order to do that let me go back to one interesting equation which is

$$\Delta G = VdP - SdT$$

So these equation is a kind of one of those Maxwell's equations. Now here I can do this particular and this is valid for even if we are considering fixed composition and constant temperature and closed system and this indicate equilibrium condition. So now if I consider isothermal change that means temperature is constant.

So that case I can find out if pressure P is change from P1 to P2, I can find out what is going to be change in free energy. So in order to do that I will simply take this since the temperature is constant, so this part goes to 0, so del G = Vdp if I integrate, so G I can say P2 temperature - G P1 temperature equal to this for ideal system ideal gas. For ideal gas I can take it as RT P dp P1 P2, now since the equation of state for ideal gases

$$PV = RT$$

for 1 mole of substance 1 mole of gas.

So this will become

$$\Delta G_T^{P_1 \rightarrow P_2} = RT \ln \frac{P_2}{P_1}$$

Now so that means we need to know both the pressures and find out this difference which is nothing but delta G P1 to P2 at a constant temperature. Now if we take P1 to be 1 atmosphere then I could see that RT ln P1 becomes 0. So then I can say that G P2 temperature = G P1 temperature + RT ln (P2/P1). Now since P1 is taken 1 atmosphere, so corresponding value this value would become G0 or node which is the standard condition at that temperature + RT ln P.

So now that time this becomes G P temperature, so at a constant temperature if we change the pressure, so then free energy change. So this becomes this would be equal to RT, I can say P, I can say that this is my equation or I can say this is my equation I can write this equation to be

$$G_{(P,T)} = G_{(T)}^o + RT \ln P$$

and there from I can get this. Now interestingly if I notice that this value is also equivalent to I can write it equivalent to

$$G_{(P)}^o = RT \ln P$$

Now if there are number of gases that case in if I try to understand with respect to oxygen only, since in this particular oxidation process

$$M + O_2 = MO_2$$
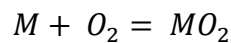
So this is the only gaseous phase the other phase of course while derivation we take vapor phase but that derivation is bit complicated we have not considered in our discussion. But now if I say that final equilibrium condition is given as RT ln pO2 which is the partial pressure of oxygen.

So this can also be written as pO2 partial pressure of oxygen, this is equilibrium at that temperature of consideration. So now you could see that if I try to plot T versus delta G0 and let's say I take T = 0K and then this value is the value corresponding to O2 = 1 atmosphere, so this point becomes 0. So delta 0 T can be 0 when T = 0K or = 1 atmosphere, so we are taking this condition at the same.

So this condition if we take, so these point correspond to G0 this value this particular point. So the difference becomes 0 means we are taking this difference corresponding to 1 with 1 atmosphere pressure. Now at any temperature let's say I take this temperature and at this point I want to measure the partial pressure of oxygen in if so what I have to do I just have to draw a line like this which is a connecting the 0 point.

So that means slope if I try to see this is delta G0 T equal to some value, so now if I, so if I try to take the slope of this particular straight line connecting the 0 point at 0K this slope becomes this becomes my slope because this is 0 and this is del G 0 T, so this is the point. So this slope becomes from this equation if I see this equation if I write it like this, so this becomes my slope, so this particular slope is nothing but R ln pO2.

Now I can take R if I take SI unit then 8.314 joule per Kelvin per mole, now if I take this particular temperature axis let's say this is 0 this is some value. So now I take an arbitrary scale, so I take a line like this which will be connecting this straight line.

(Refer Slide Time: 16:12)
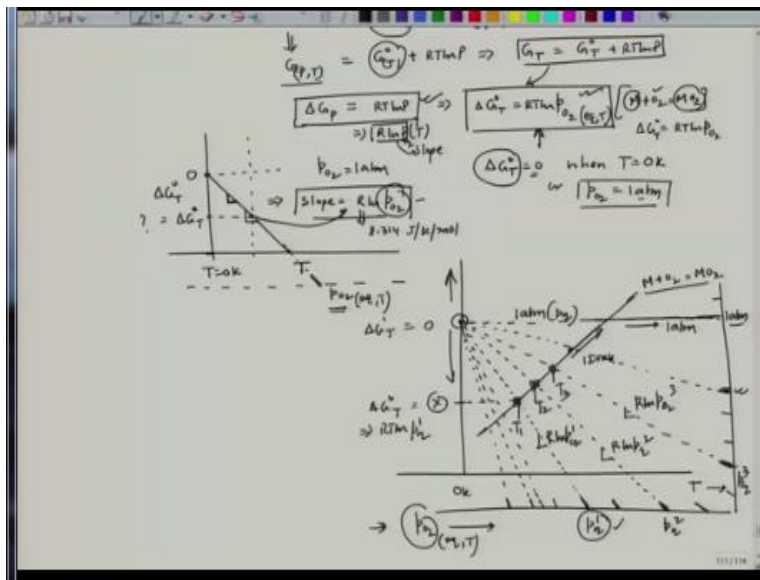
And here if I put pO2 equilibrium T, so this particular slant line connecting to the 0 point at 0K is indicating of pO2 at that particular temperature. Because at that temperature the slope is nothing but this and where just adjustment of R can give you the partial pressure of oxygen at that point.

So the same principle is applied here, now if I take if I draw our diagram again with reference to this is 0K this is temperature.

Now let's say I take metal + O2 this metal oxide reaction this is the 0 point equal to delta G0 node, now if I try to find out the at this point what is the equilibrium partial pressure of oxygen. So I just draw this straight line connecting this with a 0 point which is indicative of 1 atmosphere pressure of pO2. So now these point and then there is a pO2 line which is like this, now let's say if I have to draw you have a find out what is the equilibrium partial pressure of oxygen.

I just draw this straight line connecting this 0 point and this temperature what we are considering then if I see that this will be the pO2 at this temperature. Similarly, if I try to find out at this temperature then this will be the point this is the line which will direct towards this 0 point at 0 Kelvin. So now you will see in a Ellingham diagram that in the pO2 part there are some lines which are indicating half there are some line which are having kind of appearance like this.

And if we draw this extend every time they are going and connecting the 0 point, so this axis is nothing but pO2 in equilibrium for a temperature. So at this temperature what will be the pO2 this will be the pO2 1, this is at this case this will be the pO2 2, at this case this is where pO2 3. So like that way without doing any calculation I have to just look at the Ellingham diagram see those points in the pO2 scale this is a pO2 scale and this slash lines which are actually meeting to the 0 point on del G axis.

So those line indicates the equilibrium pO2 at that temperature where this line cuts the oxidation Ellingham line, okay. So these are the pO2 scale, so at this point if I see this point is indicating a 1 atmosphere, fine. So that way the scale has been generated without doing calculation another way to find out this equilibrium pO2 at this point instead of looking at this you can take the value X equal to

$$\Delta G_T^o = RT \; lnP_{O_2}^1$$

So then we can find out pO2 but without doing this calculation one can find out this and the slope of this line is nothing but RT R ln pO2 1. And in this case the slope is R ln pO2 2, in this case the

slope is R ln pO2 3, so these 1, 2, 3 are the 3 different temperatures, so these are the 3 different temperatures this is T 1 this is T 2 this is T 3. So like that way you can read partial pressure of oxygen at any temperature on this particular line.

By looking at what you have to do for exam unknown temperature let's say this is the unknown temperature you want to find out or let's say this is the let's say 200 Kelvin temperature. I want to find out what is the partial pressure of oxygen for that oxidation process in this case it is metal + oxygen = MO2 you what you have to do you have to just connect this and extend it and see where this line is meeting on this pO2 scale.

So that point is nothing but the partial pressure of oxygen why it is so because we could see that this particular equation is valid here also and these particular equation is coming because of the vary assumption that the 1 partial 1 pressure is considered to be 1 atmosphere and here 1 pressure is considered is here this particular line is nothing but 1 atmosphere pressure. So that is what whatever point you consider on this particular line they will be nothing but delta G0 T0 right, fine.

So this is one information you can get out of Ellingham diagram where you do not have to do a detail calculation without doing calculation by looking at the scale of pO2 you can find out what is the partial pressure of oxygen at any temperature on that oxidation line by just connecting the 0 point at 0K on the RT ln pO2 axis and stretching it to the partial oxygen scale and see where it connects.

So that point it gets the pO2 because that comes from the slope of this particular equation. This particular equation that slope tells me what is that pO2 and since R is a constant that is what we could construct that scale. So this scale was determined done by Richardson ok, so that paper if we see that paper this is of seminal paper on that FD Richardson and J. Getis the thermodynamic of substances of interest in iron and steel making from 0 Kelvin 0 degree Celsius to 2400 degree Celsius.

And this was published in Journal of iron and steel institute 1948 and this was a seminal paper by them and where the scale was drawn. See there are other scale in the Ellingham diagram also you

will find CO CO2 scale H2 H2O scale. But since our consideration is only oxidation in presence of only oxygen that is what we are only indicating pO2. So now what is the benefit of this oxide scale, this oxygen partial pressure of oxygen scale, now let's understand that benefit.
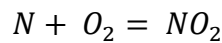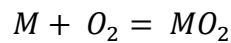
(Refer Slide Time: 24:18)
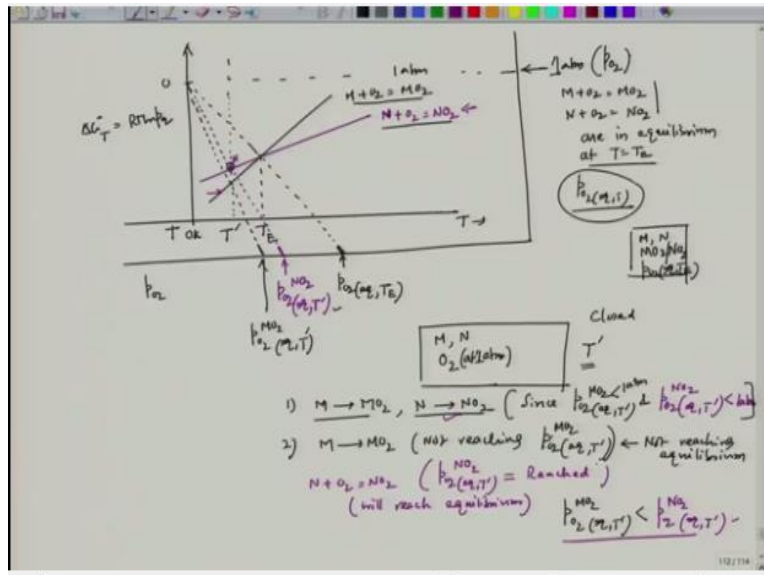
So let's say I have this particular

$$\Delta G_T^o = RT \, lnP_{O_2}$$

This is 0 point 1 atmosphere. Now let's say that 2 oxidation process in this case this is N.
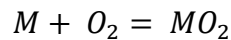
$$N + O_2 = NO_2$$

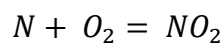Another case it is

$$M + O_2 = MO_2$$

Now oxide scale is this one, this is pO2 scale, now at this point if I connect and extend I will see that this is touching this particular point and this indicates pO2 let's say and this equilibrium T E.

So let's say this is temperature axis, fine, so now at this point both the reactions

$$M + O_2 = MO_2$$

as well as

$$N + O_2 = NO_2$$

are in equilibrium at T equal to T E, fine. And we could see that, so since they have same for both the reactions that is what if this partial pressure is maintained in a close system. Let's say in this

closed system I have M, N, MO2 as well as NO2 and partial pressure of oxygen equilibrium T E this is maintained I would see that oxidation this process both the oxidation reactions will reach equilibrium.

But now let's say I take some temperature which is below T E, let's say this is T prime, now at this temperature I could find out what is the equilibrium partial pressure for N + O2. So I can draw I can connect this point, I can extend and see where it is meeting, so this is pO2 equilibrium T prime for NO2. I am just writing NO2 this oxidation process. Now for this I can also find what is the equilibrium partial pressure, I have to just connect this point extend it and see that here it is cutting.

So this is pO2 MO2 equilibrium T prime, now if I have a system where I have M, N and O2 at 1 atmosphere pressure this is kept at T prime. So then of course I could see that both M the first event what will be observed M will go to MO2 as well as N will go to NO2 since this partial pressure and the 1 atmosphere partial pressure is here as per the scale this is the 1 atmosphere pO2, ok.

So now we could see that partial pressure of pO2 for MO2 or the formation of MO2 at T prime is less than what atmosphere or partial oxygen and even pO2 for N oxidation or NO2 formation at T prime this is also less. So both these oxidations will start, now because this system would try to reach equilibrium, so once it reaches to this point it will be satisfying the equilibrium condition for oxidation reaction N + O2 = NO2.

But this particular reaction has got much lower since second event M MO2 not reaching pO2 MO2 and here since, fine and so oxidation both the oxidation will take place. But this will and one since this is closed system, where we are not allowing any oxygen to come in from outside or oxygen to come out from inside. So the oxygen partial pressure would start decreasing from 1 atmosphere and first it will try to reach pO2, this will be reaching. This will reach.

So, N + O2 NO2 will reach equilibrium and this will not be reaching equilibrium why because, fine, because of this phenomena because of this situation. Because since this partial pressure for

MO2 formation is less than this which are in equilibrium at T prime that is what this particular reaction will reach equilibrium. Because the oxygen partial pressure is gradually decreasing and finally it will reach here and it will reach equilibrium. But since with this particular reaction needs further oxidation and needs further reduction in oxygen partial pressure, so that is what this will go on.

(Refer Slide Time: 32:41)
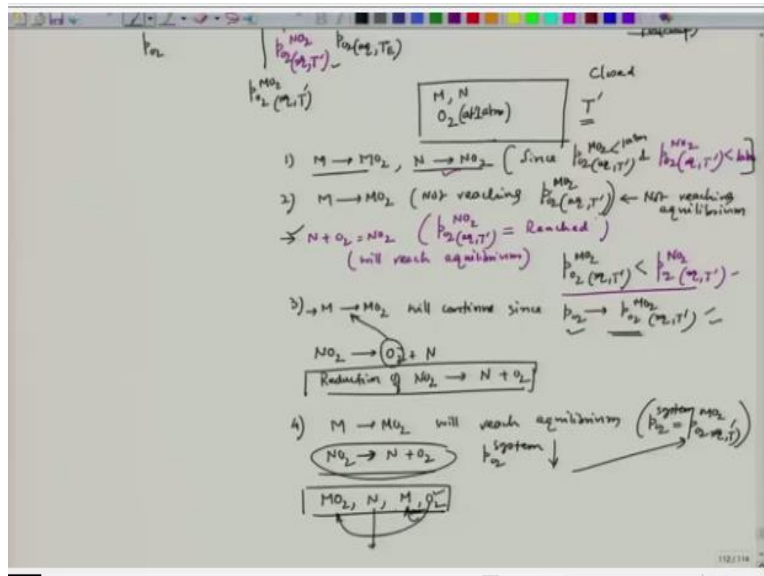
And the third event is MO2 will continue till since pO2 tries to reach T prime, so oxidation of M to MO2 will take the oxygen content further down. Now once it goes below this, fine, so then it has to take more oxygen that metal needs to have more oxygen to reach to this. But once it crosses this particular point around this region oxygen is depleting but metal M needs more oxygen for oxidation.

So this excess oxygen it has to get where from it has to get that excess oxygen to reach this equilibrium condition because already this has reached equilibrium once it has reached to this particular point. So that is what NO2 will try to move to O2 + N and this oxygen will be supplied to this in order to have more oxidation and that is what it is possible then only it will be possible to reach this partial pressure of oxygen in the system to tends to be pO2 of MO2 at that temperature, fine.

So that means we could see once this particular partial pressure is achieved this reaction reaches equilibrium then in order to reach this reaction to reach equilibrium that means the partial pressure attainment of this partial pressure. We need more oxygen and that more oxygen will be provided by the reduction of NO_2 to N and O_2. So these process will start happening, so finally it will reach here it will reach in this particular location.

So and there will be the fourth stage then M this reaction will reach equilibrium equal to pO_2 MO_2 equilibrium temperature prime and NO_2 will keep getting reduced to $N + O_2$. So and if this happens then we could see that my partial pressure of oxygen of the system will decrease and it will try to reach this. So the final system will contain MO_2, N and M this will be the final of course I will have oxygen also.

And this oxygen will be in equilibrium with these two and N will be the product in that particular simple system provided we have sufficient M ok. So which will allow the oxidation and N will be the final product, so N will not oxidize, M will oxidize. So this is the condition which can be set this is the temperature I can set when I would like to prevent oxidation of N metal and how can I do that.

I have to have another strong oxide forming element which will have a much lower partial pressure of oxygen in equilibrium at that temperature, where both M and N are there in that system. So this is one way to decide ok which metal in at a particular temperature which metal will oxidize and which metal oxide will reduce. So this a very good information we can get out of this particular Ellingham diagram, similarly if I try to see a temperature.

(Refer Slide Time: 37:39)
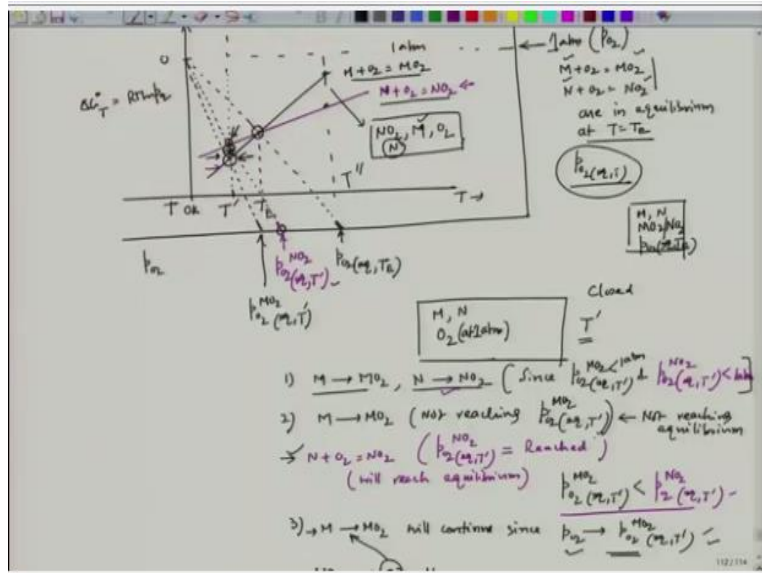
Let's say here T double prime what will be the product you just do that similar process you will see the final product would be NO2, M and O2 and of course N and I must have sufficient N. So that metal oxidation for the metal M is prevented and you have to do the similar operation and but at this temperature I would have all those phases M, N, MO2, NO2 as well as oxygen provided we have sufficient amount of M and N ok.

So this is about Ellingham diagram and one important information what we are getting that to understand whether a metal will oxidize or not we have to see that whether this particular we have to see the partial pressure of oxygen in equilibrium with that metal in that system. If it is more than the partial pressure of oxygen in equilibrium, then oxidation will take place if it is less than the partial pressure of oxygen in equilibrium then the oxidation will not take place rather reduction of that oxide will take place.

And also it tells us if we have 2 oxides depending on the situation that means depending on the temperature I could get 1 metal oxide is getting reduced another would keep on oxidizing or the reverse can happen if we choose a different temperature depending on where these 2 oxide lines are cutting, okay. So this is about Ellingham diagram we will stop here, we will continue our discussion in our next lecture. We will talk about kinetics of oxidation, thank you.