Basics in Inorganic Chemistry
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Lecture - 05
Ellingham Diagram

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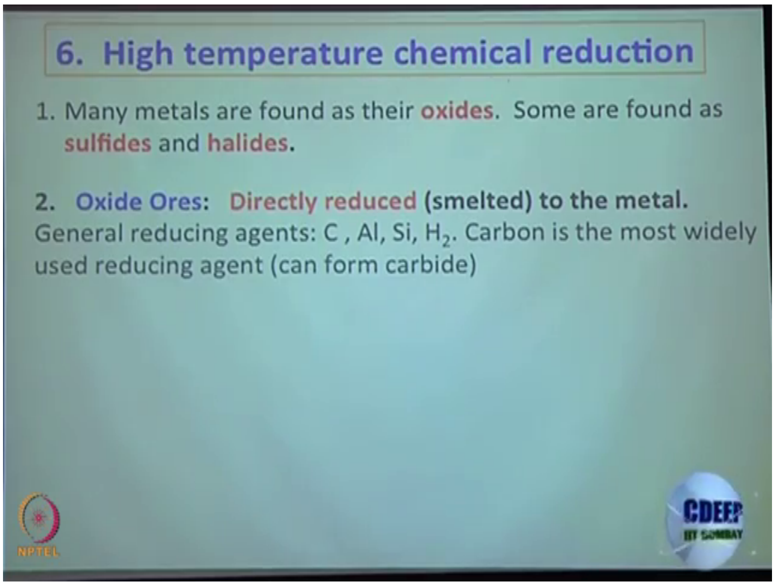

We are going to get into something high temperature chemical reduction ok. This is where Ellingham Diagram is coming. Now of course, every metal oxide and metal sulfide can be heated to some really high temperature extremely high temperature and you can break it down to its corresponding metal and let us say oxygen right, but that is not going to be feasible.

See if you want to heat something at 3000 degree centigrade, the cost for that is going to be a lot. It is not just you know you have to have that facility in a industrial scale, it is going to cost a lot you know at the end you may get 1 rupees of metal and you ended up spending let us say 1000 rupees. So, it is not going to be practically possible to just heat anything any metal compounds at any given temperature although you know that if you can heat it at a suitable temperature, you can break it.

It is possible theoretically, but practically you are never going to do this. So, this is when we need to understand the thermodynamics. What can you do what type of reaction can you do and met result you are going to get exactly the same metal in reduced form, but without heating at a too high temperature. You want to heat it at a moderate temperature instead of 3000 degree centigrade; let us say you want to heat it at 1000 degree centigrade which is much more achievable and you can get exactly same pure metal.

What you need to use some sort of reducing agent when or how you determine that, that is what we are going to discuss. So, most of the metal in ore is present in metal oxide form ok. Some of them are present in metals sulfide or metal halide form. Usually what happens is we try to convert metal sulfides to their corresponding metal oxide because that way thermodynamic parameter works out better.

So, if you understand how metal oxides are converted to their corresponding metal, you will understand how metal sulfides are converted to their corresponding metal because metal sulfides are converted first to metal oxide and then metal oxide is going to converted to corresponding metal it is a two step process for metal sulfide. For metal oxide, it could be one step process; for metal sulfide, it is usually two steps process ok. So, that is why we will just mainly try to focus on metal oxides all the details are given, you can read it ok.

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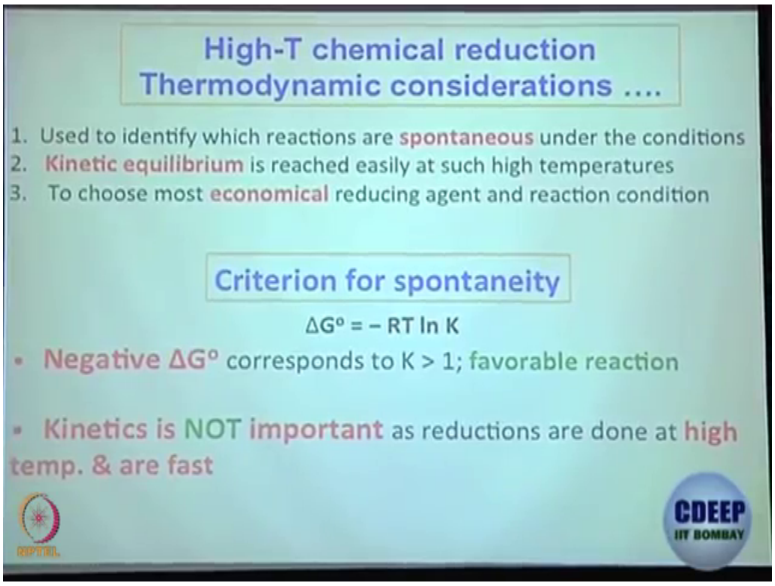

Now, since we are talking that we need to heat it at a very high temperatures something like 1000 degree centigrade at least or 500 to 700 all those temperature. So, these reactions are going to be spontaneous. These are going to be a very fast reaction. Since we are talking about really very high temperature, the reactions are going to be and we have to looking for a spontaneous reaction, reactions are going to be fast.

So, kinetic parameter how fast it is, it is something we do not need to worry because it is going to be very fast, it is not a slow process it is not going to take days ok; it will be converted very fast. Only thing we really need to worry about is the thermodynamics whether it is a favorable reactions or not. What is a favorable reaction?

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So, we have I am sure you have learned before to some extent for any reaction we try to calculate delta G, free energy change and this is equated with delta H fantastic minus T delta S. Now usually this delta H term is a small one, it is not a huge term or the contribution is not that huge compared to T delta S. So, we can kind of neglect this term because it is you know it is kind of negligible contribution.

What all we need to understand or we need to deal with is this T delta S. Since temperature is always a positive quantity like 25 degree centigrade 100 degree centigrade of course, you can you have to convert it to Kelvin and then 500 1000 essentially what it boils down to is you have to look at the delta S. What is delta S? That is the entropy change. How to easily relate the entropy change?

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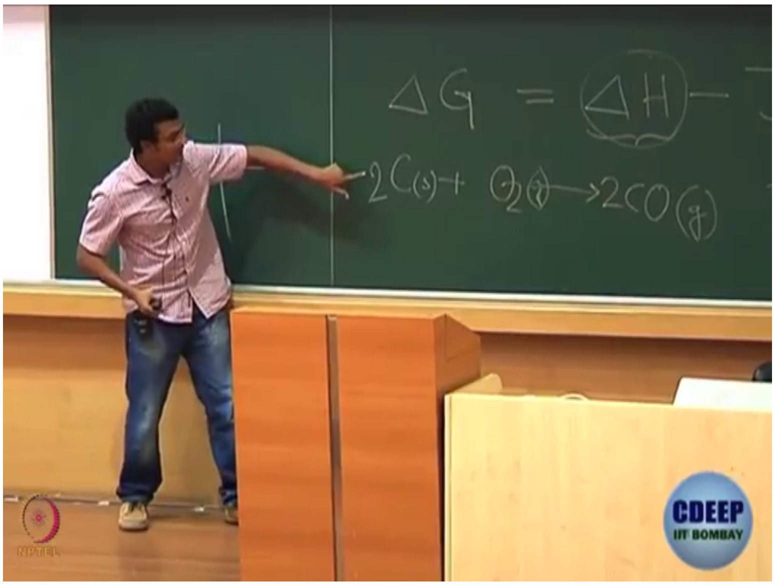

Let us say this reaction carbon plus oxygen giving you let say carbon monoxide ok. Now this is a solid right; this is a solid, this is a gas. You cannot see this is a solid carbon is a solid oxygen is gas. So, solid plus gas is giving you a gas ok. In fact, one equivalent of gas is giving you two equivalent of gas. So, entropy is increasing; that means, you know more degrees of freedom you are having. So, delta S is going to be positive for this reaction of course, you most of you now that.

Now, for such reaction delta S is going to be positive plus and this minus T is always plus T delta S term this term is going to for this reaction is going to be positive combined, it is going to be negative. For a spontaneous reaction, we will look for negative delta G ok.

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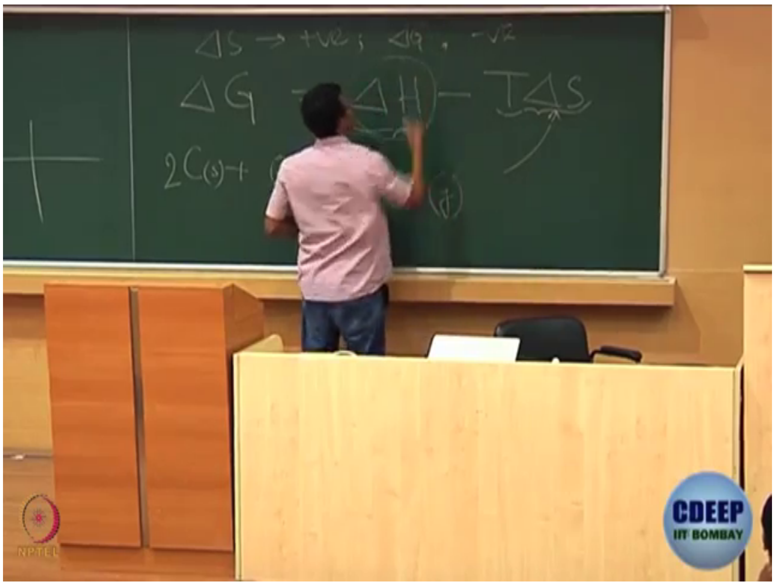

So, for a spontaneous reaction delta S should be positive and delta G should be negative that is what exactly we are looking for. Now, the problem is somewhere else, where is the trouble? Metal oxide that reaction you will find or metal plus oxygen when you are reacting metal with oxygen, it is a gas that is oxygen you are reacting metal oxide most often is a solid.

Metal plus oxygen going to metal oxide, delta S is not going to be positive that is what the problem is otherwise I mean I guess we could have lost lot less of a problem anyway. So, criterion for spontaneity is very simple as we say we need a delta G that is negative for a favorable reaction. So, equilibrium constant has to be greater than 1 for this cases, kinetics is not important as reductions are done at high temperature and this reactions are very fast.

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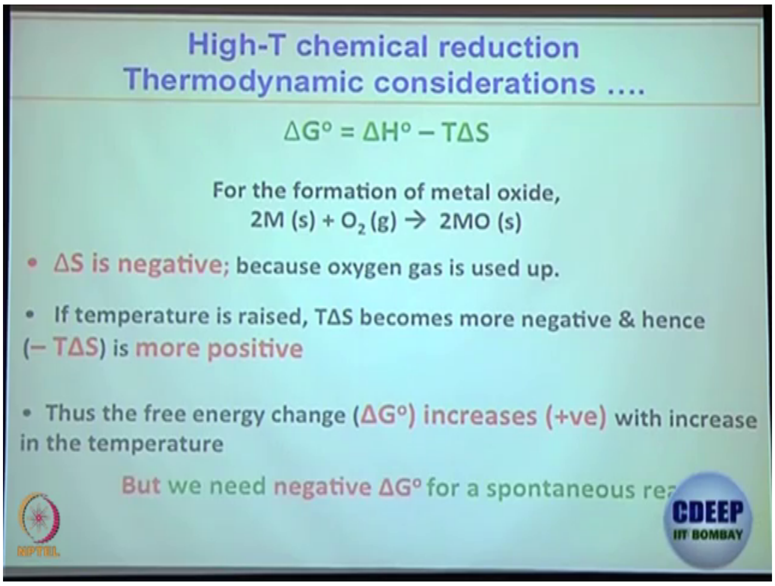

So, delta G as I wrote in here delta G equals delta H minus T delta S for the formation of metal oxide metal is in solid form oxygen is in gaseous form. So, what we get is metal oxides solid. Now for these sort of reaction, we have delta S negative of course, oxygen gas is used up solid plus gas is going to solid. So, entropy change is going to be you know negative. So, it is not a spontaneous reaction that we are going to get right.

So, for these cases if temperature if you are increasing let us say you are heating from 100 degree centigrade to 500 degree centigrade, your delta G is becoming more and more positive. See delta G may be your starting from let us say negative something; negative let us say 500, but as you are increasing temperature delta G is becoming more and more positive. If the absolute values still could be negative, but it is becoming more positive minus 500 to minus 500 minus 300 minus 200 as you are going to increase the temperature ok. First the free energy change that is delta G increases with increase in the temperature.

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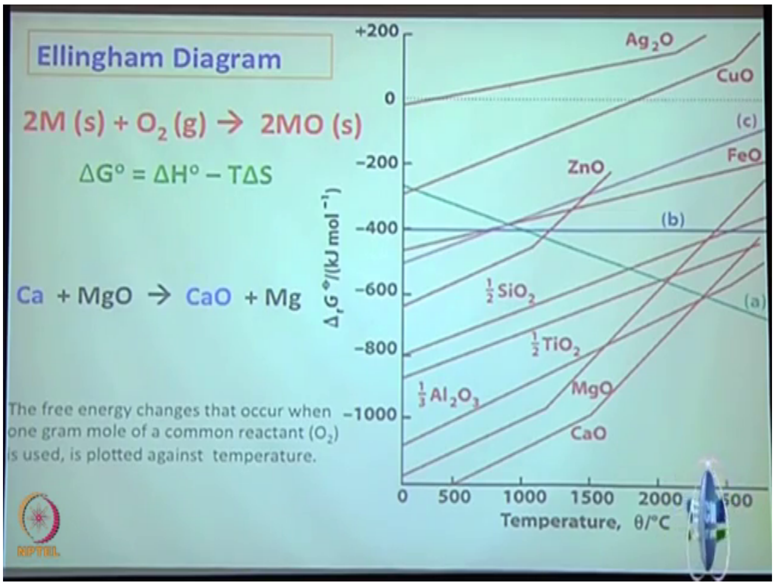

Let me show you the show you the curve for one case. So, let us say this is the calcium oxide curve. Now delta G for calcium oxide formation was at 500 degree C, let say this is something like minus 1200 or so, kilo Joule per mole delta G. As you are increasing temperature 500 to let say 2500, you can see that the delta G is increasing. Of course, you started with negative value that is why it is saying still negative because 0 is here. It is still negative value, but overall delta G is becoming more and more positive.

You started with somewhere minus 1200 or 1300, you are going to get up to let us say over here at 2500 degree C you are going to minus 400. So, delta G is increasing with respect to temperature. If you are heating keep heating the reaction mixture, the reaction is becoming more and more unfavorable right. Now so, delta G is becoming more positive that is understood this is the 0.

This is delta G equals 0 anything below that is thermodynamically feasible means it is a favorable process for any spontaneous reaction for anything feasible whether it can happen or not, you should have delta G negative ok. Anything below 0, you can have these metal oxide formation

Let us say for example, silver oxide; we were saying that silver oxide can be heated to get or to give you silver plus oxygen right so; that means, at this temperature where delta G is becoming positive. So, it is little negative right over here; if you heat it let us say 50 degree centigrade, now this delta G is becoming more than 0 means positive. The moment it is becoming positive, the silver oxide will not exist and silver oxide, it will break down to silver. If delta G is not negative that species is not going to or that oxide is not going to stay over there, it will disintegrate into corresponding metal and oxygen right.

So, this is the temperature you are looking for, but as you see for most of the metal that temperature let say copper oxide; yes, it is something 200 degree C, but that temperature is very high. For most of the metal oxide, it is not crossing this delta G 0 at a reasonable temperature right.

So, they will stay even if you keep on heating your ore, you are not going to get anything out of it. You can melt it, you are having a solid mixture you can melt it, but still you cannot get your pure metal right. For a only it is possible let say for sodium azide as I was saying sodium azide is explosive, but silver you have to be careful with sodium azide, but silver oxide you can just heat off little bit and you can get pure silver, but as you see almost nothing else is crossing up to 2500 degree C except this copper oxide.

So, just simple heating is not going to be enough, you need a reducing equivalent; you need something to reduce. What can you reduce; what can you use to reduce? All the problem here is all this metal oxide curves of course, technically speaking you can take one from the top ok. For example, technically speaking you can take calcium and you can heat calcium with magnesium oxide and calcium oxide will form because calcium oxide formation is more favorable than magnesium oxide.

But in practically speaking, are you going to do that I mean are you going to sacrifice calcium to get magnesium? No, it is not possible. Although thermodynamically it is it should technically work out calcium oxide formation at any point looks like going to be more favorable. So, delta G as long as delta G is more negative for some metal oxide formation. You can kind of trade off, you can just sell one to get another one. You can sell calcium to get magnesium, but it is not a feasible process because it is not going to be economically favorable ok.

You can argue that anything else you can take, but you know technically speaking even if there is some price difference; if you are getting let say 50 rupees worth of metal by using 40 rupees worth of another metal, you are not going to do that you need 50 rupees worth of metal by using 50 paisa of worth of something some reducing agent. What all you need to know is what is a suitable reducing agent.

This is where charcoal carbon all the industry you see all the charcoal; all those you know metallurgical extraction charcoal works out why charcoal works out. Now as I was saying charcoal works out because it is just working opposite way charcoal is solid, oxygen is gas one equivalent of charcoal and half a equivalent of oxygen is giving you one equivalent of carbon monoxide right.

So, which is gas? So, this is a favorable very very delta S is going to be positive for this reaction. Over here what you are saying metal plus oxygen going to metal oxide. This metal oxide is going to be solid, but this carbon monoxide is going to be gas or it is gas right. So, technically speaking that is what the advantage of charcoal carbon monoxide or CO is gas, but metal oxide any form M 2 or 3 M O 2 or whatever it is going to be solid.

So, as you are increasing the temperature, this curve is becoming more and more positive metal oxide curves are becoming more and more positive, but the green one over here which is not written that is for your carbon plus oxygen going to carbon monoxide. This is a having this is having a downward slope means that reaction is going to help almost the man kind to give the pure metal at a very cheap rate right that is what all we are looking for. We need an alternate solution or we need a solution which can work out for most of the metal right.

So, what we are trying to say one more time, I think few of you are having queries how delta G is going to be positive more positive with respect to temperature more and more positive. So, some reaction if you are looking at this reaction, metal solid is going and reacting with gas to give you metal oxide right. This is the reaction where you are going to have delta S negative because gas is consumed and you are forming solid delta S is going to be negative.

Now if delta S is going to be negative, the delta G is becoming more and more positive if you are increasing the temperature delta S is negative here negative. So, as you increase the temperature from let us say 25 to 100 to 300, you are going to have more and more delta G positive. So, if you are starting from let us say over here 1100 or 1200, it is minus 1100 or minus 1200, it is becoming more and more positive. So, minus 1200 you are getting let us say 800 or 600 and so on.

It is becoming more positive does not necessarily mean that value it itself will be becoming absolutely positive from minus 1200, it is going to minus 1000 minus 600 minus 400 and so on. Eventually it can reach to the 0 delta G is 0 which is kind of you know the point where you will be able to break it disintegrated. Now since the other reaction which you are going to look at is the carbon reacting with oxygen that is the charcoal we are talking about.

It is a good reducing agent and that is a good reducing agent basically because this carbon monoxide gas is formed ok. Carbon monoxide gas from half a equivalent of oxygen one equivalent of carbon monoxide is formed. Therefore, delta S is going to be more positive. So, delta S is going to be positive and thereby with respect to if delta S is going to be positive for carbon plus oxygen this carbon monoxide formation. So, delta G is becoming more and more negative as you can see as you are increasing the temperature.

So, you keep on increasing the temperature delta G is becoming more and more negative this is just opposite to all most all the metal oxide curve that you see in here. Technically speaking wherever this curve, this green curve is crossing the red curve. Let us say this is the temperature for zinc oxide, this is the point where carbon monoxide curve carbon going to carbon monoxide curve is crossing. So, right after that temperature right after that cross section, carbon monoxide formation is more favorable.

Delta G for carbon monoxide formation let us say over here or here are more favorable. So, if this is the 1000 degree centigrade where the green curve is crossing the red curve at that point right after that point, you can react metal oxide ok; you can react metal oxide with carbon, you can get carbon monoxide plus corresponding metal that is what all I think Ellingham diagram has to tell you.

At any temperature or the temperature where it is crossing, any temperature above that let us say this is crossing at 1000 degree C 1001 degree centigrade if you are heating carbon monoxide formation is more favorable compared to the metal oxide formation. So, metal oxide will be reducing to corresponding metal carbon will get oxidized to carbon monoxide right ok. So, that is the crucial temperature we are going to look at.

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So, carbon plus let say metal oxide going to carbon monoxide plus metal. Now you see that at some point this curve is breaking or seems like breaking, what is happening there? It is a change of state definitely.

So, metal this was solid metal it iself was solid oxygen was gas. Now if up to let us say for example, calcium oxide calcium metal was in the solid form up to 1500 degree centigrade; after 1500 degree centigrade, what happen that calcium is becoming calcium liquid solid to calcium liquid right.

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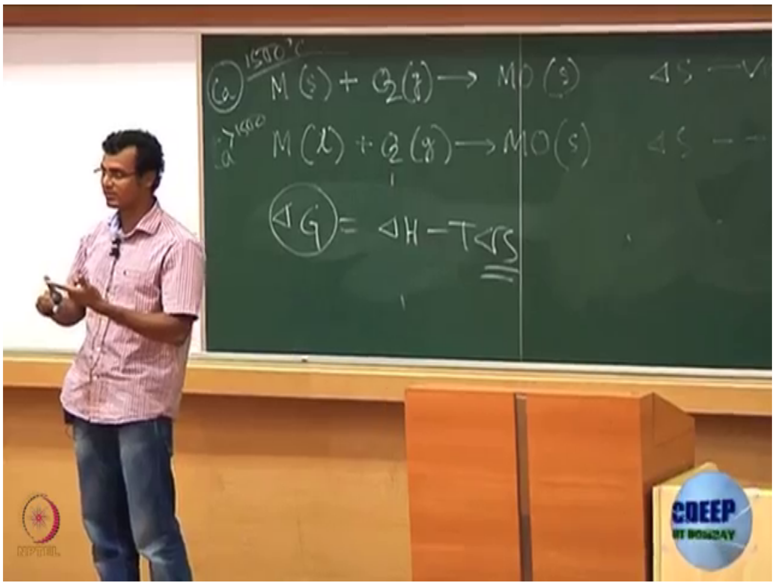

So, you are initially you are having metal solid plus oxygen gas giving you metal oxide solid right. Delta S for this reaction was negative right. Now let us say let say metal equals your calcium up to 1500 degree centigrade that is what is happening, above 1500 degree centigrade, you have metal liquid right plus oxygen gas giving you metal oxide solid that solid remains as solid right.

Now, what is happening here? It is a solid plus gas was giving you solid now it is a liquid which is having more often entropy more free material liquid solid to liquid. So, liquid plus gas is giving you solid.

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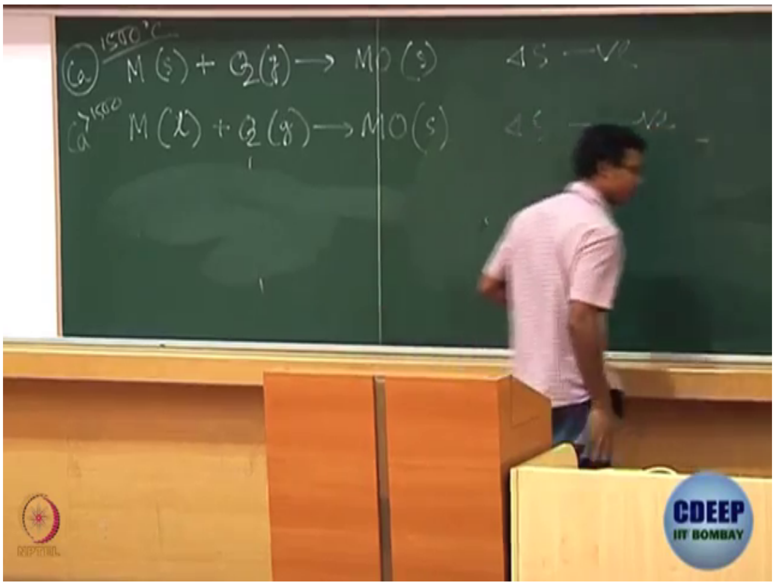

So, delta S is going to be so, delta S is going to be more negative. Let us say juts double negative let us say, what is? So, if delta S is becoming more negative because it is a liquid plus gas is going to solid. Previously solid plus gas was going to solid, now it is a liquid plus gas more freely you know freely free flow material is going into the solid material delta S becoming negative. So, you just relate to delta G equals delta S minus T delta S.

If it is more negative delta G is becoming more and more positive. So, it was going positive, but the slope changes. So, the it was going very slow positive, it was coming with respect to temperature it was going very slow slope was less the point calcium melts the slope increases; that means, it is becoming more and more unfavorable quickly this is happening or I mean this change is better or slope is becoming more and thereby you are going to get more unfavorable or more unfavorable delta G ok.

Same is true if it is becoming gas instead of liquid; if metal is metal instead of metal being liquid if metal is becoming gas at certain temperature, you will get further increment in the slope alright.

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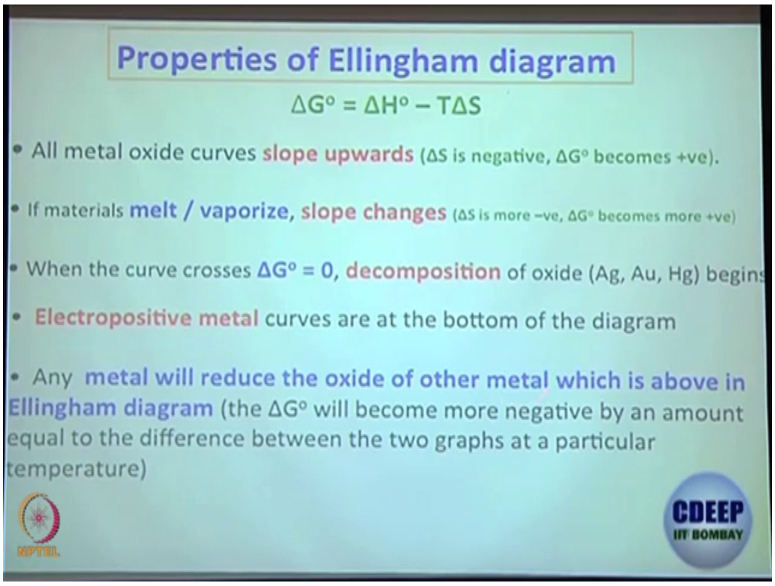

So, now other things to look at from the periodic from that Ellingham diagram is very simply these are the metal which are electro positive metal. If you are looking at that electro chemical series these are the one which are going to be in the on the top; that means, they tend to press stay in metal oxidized form right.

So, the your seen the reduction potential is very less for these cases; that means, they will tend to go to the reduced form; silver oxide will tend to go to silver, but calcium oxide will prefer to stay in calcium 2 plus right. It is there is of course, some I mean clear correlation with those electrochemical series and that of the Ellingham diagram.

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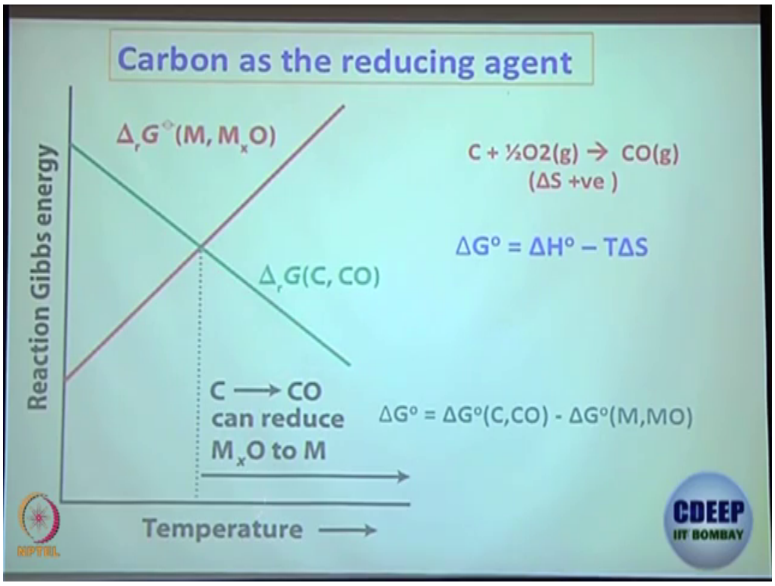

The more positive material which tends to stay in positive state electro positive material is at the bottom those which are less electro positive there on the top ok. As I said previously any metal will reduce the oxide of other metal which is above in the Ellingham diagram ok. Now of course, we need to also understand how carbon can be oxidized to carbon monoxide or carbon dioxide and how they are plots are relating to each other right.

Now, this is usually as you are discussing usually this is the metal oxide fog plot metal going to metal oxide and this is the usually carbon going to carbon monoxide plot. So, at any temperature above these crossing point above this point, you will be having carbon monoxide formation. Let us say at this temperature you will have carbon monoxide formation and metal oxide, you will be converted to corresponding metal right.

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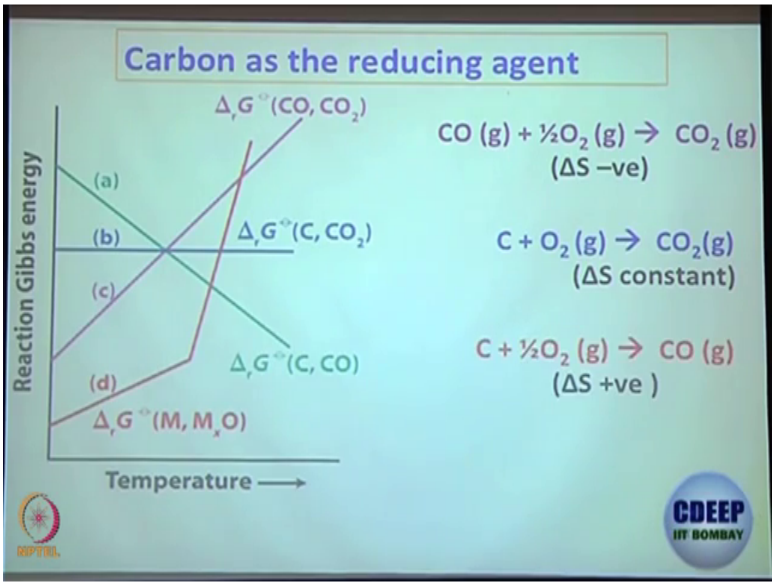

Now, if you are to relate how it is with carbon monoxide plus oxygen reacting with carbon dioxide this is of course, another reaction which is possible in these cases. If you are taking charcoal and reacting with metal oxide, you are going to get usually a mixture of carbon monoxide and carbon dioxide right. So, for carbon monoxide case, it is a gas plus gas giving you a gas, but it is a one and half equivalent of gas is giving you a one equivalent of gas.

So, delta S is going to be negative. Unlike the carbon case carbon solid plus oxygen giving you carbon monoxide here carbon monoxide plus oxygen delta S is going to be negative ok. Thereby the plot you see is over here, this purple color one over here. So, with respect to temperature as you an increasing temperature it is becoming more and more unfavorable ok.

It is just all depends on delta S whether delta S is negative or delta S is positive. In this case one and half equivalent of gas giving you one equivalent of gas right so, this is the purple line over here for carbon monoxide going to carbon dioxide.

Now, the one in green here is the carbon going to carbon monoxide, what is happening for carbon going to directly carbon dioxide. So, carbon is solid oxygen is gas it is going to gas right delta S remain constant; one gas is going to another gas. So, overall, it is going to stay constant. Delta S should be I mean you know, we it is delta of delta S right.

So, usually you can it 0, but it is better to put constant it is not changing it is a change that we are looking for. Now with respect to temperature, I think it is better to say 0 may be with. So, all the delta H will matter ok. So, delta S is not changing anything. Now that is the; that is the curve for carbon going to carbon dioxide, this is carbon monoxide going to carbon dioxide and this is the one going carbon to carbon monoxide. Now, clearly the idea here is very simple which is most negative for all these area when we say you in over here.

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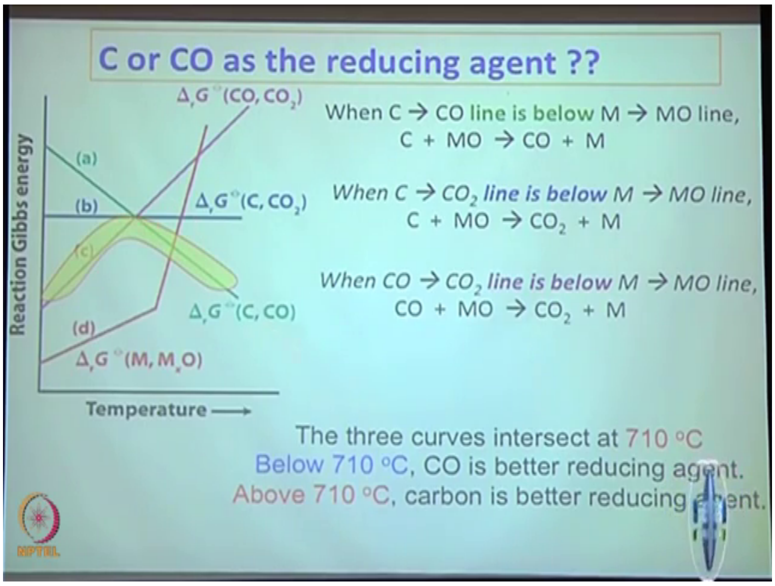

During these period up to the 710 degrees c or so, carbon monoxide to carbon dioxide formation is more favorable because CO 2 CO2 graph carbon monoxide to carbon dioxide graph as you can see, it is in the purple. So, it is more negative. So, all you need to consider is which is more negative which curve is more negative ok. If you are looking for any reaction below 710 degree C, it is better to utilize carbon monoxide to carbon dioxide curve or that is the reaction which is more favorable.

Above 710 degree C anything, you do it is going to be carbon to carbon monoxide formation ok. So, of course, you have the option to choose, but practically speaking usually we are heating the ore at a you know kind of a high temperature. So, we do not really worry about everything mostly carbon going to carbon monoxide is the one you need to worry about any way. Now I think same thing we have discussed already.