Concepts of Chemistry for Engineering
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Lecture – 59
Ellingham Diagram

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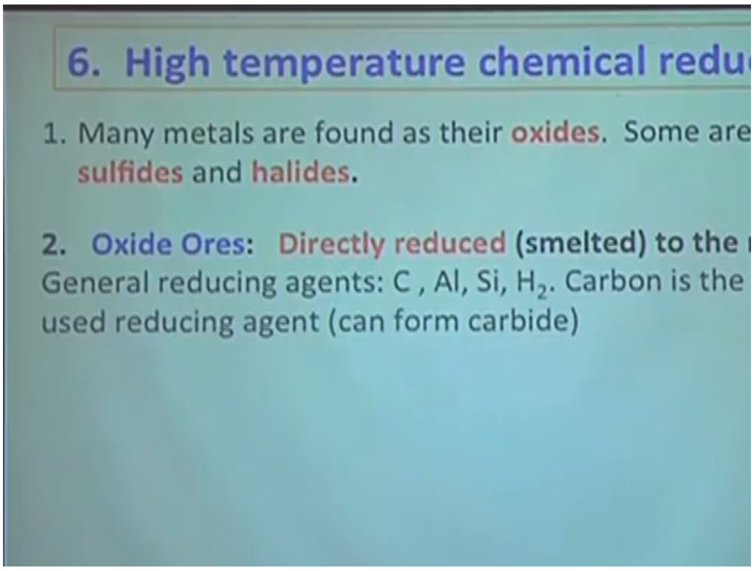

6. High temperature chemical redu

1. Many metals are found as their oxides. Some are sulfides and halides.
2. Oxide Ores: Directly reduced (smelted) to the General reducing agents: C , Al, Si, H_2. Carbon is the used reducing agent (can form carbide)

We are going to get into something high temperature chemical reduction; this is where Ellingham diagram is coming in. Now, of course every metal oxide and every metal sulfide can be heated to some really high temperature; extremely high temperature. And you can break it down to its corresponding metal and oxygen; 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 have to have that facility in a industrial scale; it is going to a cost a lot.

At the end you may get 1 rupees of metal and you ended up spending let say thousand 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 net result you are going to get exactly the same metal in reduced form; but without heating at it to a high temperature. You want to heat it at a moderate temperature instead of 3000 degree centigrade; let 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. Some of them are present in metal sulfide or metal halide form. Usually what happens is we try to convert metal suphides 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 convert into 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. So, that is why we will just mainly try to focus on metal oxides; all the details are given you can read it.

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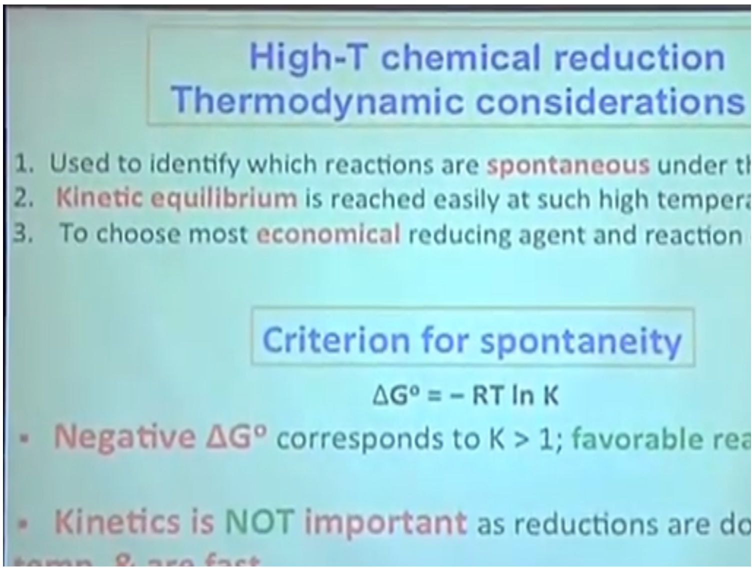

High-T chemical reduction
Thermodynamic considerations

1. Used to identify which reactions are spontaneous under t
2. Kinetic equilibrium is reached easily at such high temper
3. To choose most economical reducing agent and reaction

Criterion for spontaneity

$\Delta G^{o} = - RT \ln K$

- Negative ΔG^{o} corresponds to K > 1; favorable rea
- Kinetics is NOT important as reductions are do
temp. & are fast

Now, since we are talking that we need to heat it at a very high temperature 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 very fast reaction. Since we are talking about really very high temperature, that reactions are going to be; and we are 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; it will be converted very fast.

Only thing we really need to worry about is the thermodynamics; whether it is a favorable reaction or not. What is a favorable reaction? 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? Let say this reaction carbon plus oxygen giving you carbon monoxide. Now, this is a solid, 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. In fact, one equivalent of gas is giving you two equivalent of gas, so entropy is increasing; that means more degrees of freedom you are having. So, delta S is going to be positive for this reaction; of course, you most of you know 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 for this reaction is going to be positive; combined it is going to be negative, for a spontaneous reaction will look for negative delta G. 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 trouble 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 lot less of a problem anyway. So, criteria's 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 these cases; kinetics is not important as reductions are done at high temperature, and these reactions are very fast.

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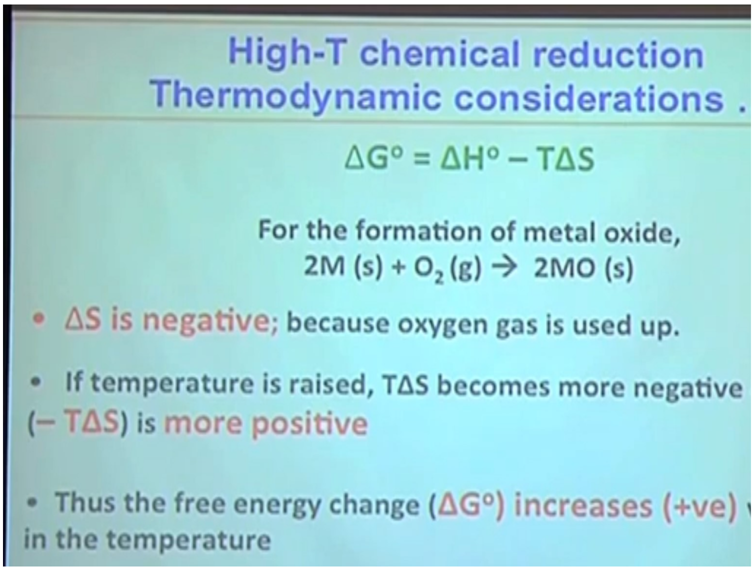

High-T chemical reduction
Thermodynamic considerations .

$\Delta G^\circ = \Delta H^\circ - T\Delta S$

For the formation of metal oxide,
$2M\ (s) + O_2\ (g) \rightarrow 2MO\ (s)$

- ΔS is negative; because oxygen gas is used up.
- If temperature is raised, $T\Delta S$ becomes more negative ($-T\Delta S$) is more positive
- Thus the free energy change (ΔG°) increases (+ve) in the temperature

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 oxide solid.

Now, for this 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 negative. So it is not a spontaneous reaction that we are going to get. So, for these cases, if temperature if you are increasing, let say you are hitting from 100 degree centigrade to 500 degree centigrade; your delta G is becoming more and more positive.

See, delta G maybe you are starting from negative something; negative, let say 500. But, as you are increasing temperature, delta G is becoming more more and more positive. If the absolute value still could be negative, but it is becoming more positive; minus 500 to minus 400 minus 300 minus 200 as you are going to increase the temperature. Thus, the free energy change that is delta G increases with increase in the temperature.

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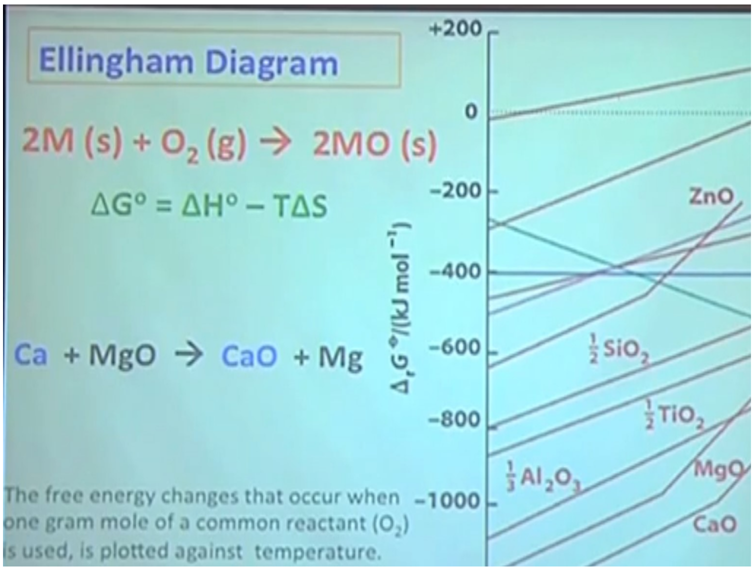

Ellingham Diagram

$2M(s) + O_2(g) \rightarrow 2MO(s)$

$\Delta G^\circ = \Delta H^\circ - T\Delta S$

$Ca + MgO \rightarrow CaO + Mg$

The free energy changes that occur when one gram mole of a common reactant (O_2) is used, is plotted against temperature.

Let me show you the show you the curve for one case. So, let say this is the calcium oxide curve. Now delta G for calcium oxide formation was at 500 degrees C; this is something like minus 1200, or so kilojoules per mole delta G. As you are increasing temperature 500 to 2500, you can see that the delta G is increasing. Of course, you started with negative value that is why it is staying 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 over here at 2500 degrees 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.

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 any thing feasible, whether it can happen or not; you should have delta G negative. Anything below 0 you can have these metal oxide formation.

For example, silver oxide, we were saying that silver oxide can be heated to get or to give you silver plus oxygen. So, that means at this temperature where delta G is becoming positive; so, it is a little negative right over here. If you heat it 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 at 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. So, this is the temperature you are looking for.

But as you see for most of the metal that temperature, let say a copper oxide; yes, it is something 2000 degrees C; but that temperature is very high. For most of the metal oxide, it is not crossing this delta G is 0 at a reasonable temperature. So, they will stay even if you keep on heating your own 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. For only if it is possible for sodium iodized azide, sodium azide iodized is explosive. But silver oxide, you have to be careful with sodium azide; but silver oxide, you can just heat off a little bit, and you can get pure silver.

But as you see, almost nothing else is crossing up to 2500 degrees 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 read? What can you use to reduce? Well, the problem here is all these metal oxide curves. Of course, technically speaking, you can take one from the top.

For example, technically speaking, you can take calcium, and you can hit 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; are you going to sacrifice calcium to get magnesium? No, it is not possible. Although thermodynamically 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; you can argue that anything else you can take. Bu technically speaking, even if there is some price difference, if you are getting 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 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 equivalent of oxygen is giving you one equivalent of carbon monoxide; so, which is gas. So, this is a favorable very very delta; delta S is going to be positive for these reactions. 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. So, technically speaking that is what the advantage of charcoal. Carbon monoxide or CO is gas; but metal oxide any form M2O 3, MO2 or whatever it is; 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 having, this is having a downward slope; means that reaction is going to help almost the mankind to give the pure metal at a very cheap rate; 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. So, what we are trying to say; one more time I think a few of you are having queries.

How delta G is going to be positive more positive with respect to temperature more, more and more positive. So, some reaction if you are looking at this reaction, metal solid is; and reacting with gas to give you metal oxide. This is the reaction where you were 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, if the delta G is becoming more and more positive, if you are increasing the temperature; delta is negative here negative, negative. So, as you increase the temperature from 25 to 100 to 300; you are going to have more and more delta G positive.

So, if you are starting from 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 800 or 600 and so on. It is becoming more positive; does not necessarily mean that value 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 G0, which is kind of 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.

Carbon monoxide gas form half 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 almost all the metal oxide curve that you see in here.

Technically speaking, wherever this curve this green curve is crossing the red curve; 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 over here or here are more favorable.

So, if this is the 1000 degrees centigrade where the green curve is crossing the red curve, at that point right after that point you can react metal oxide. 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, this is crossing 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; so, that that is the crucial temperature we are going to look at. So, carbon plus, let us 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 change of state definitely; so metal this was solid, metal itself was solid, oxygen was gas. Now, if up to for example, calcium oxide, calcium metal was in the solid form up to 1500 degree centigrade. After 1500 degrees centigrade, what happened that calcium is becoming calcium liquid, solid to calcium liquid.

So, you are initially you are having metal solid plus oxygen gas giving you metal oxide solid; delta S for this reaction was negative. Now, metal equals your calcium up to 1500 degrees centigrade that is what is happening. Above 1500 degrees centigrade you have metal liquid, plus oxygen gas giving you metal oxide solid; that solid remains at solid.

Now, what is happening here? It is a solid plus gas was giving you solid. Now it is a liquid, which is having more of an entropy more free material, liquid solid to liquid; so, liquid plus gas is giving you solid. So, delta S is going to be, so delta S is going to be more negative just double negative.

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 of free flow material is going into the solid material; delta S becoming negative. So, you just relate to delta G equals delta H 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 more. And thereby you are going to get more unfavorable or more unfavorable delta G. Same is true if if it is becoming gas; instead of liquid, metal is metal; instead of metal being liquid, if metal is becoming gas. At such certain temperature you will get further increment in the slope.

So, now other things to look at from the periodic, from that Ellingham diagram is very simply. These are the metals which are electropositive metal; if you are looking at that electrochemical series, these are the ones which are going to be in the on the top. That means they tend to stay in metal oxidized form. So, that you have seen that 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. It is there is of course some clear correlation with those electrochemical series; and that of the Ellingham diagram. The more positive material which tends to stay in positive state; electropositive material is at the bottom, those which are less electropositive they are on the top.

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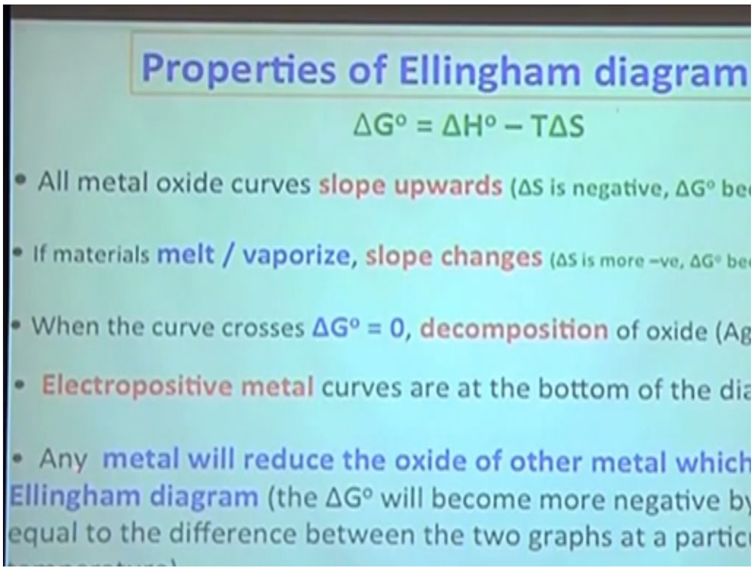

Properties of Ellingham diagram

$\Delta G^o = \Delta H^o - T\Delta S$

- All metal oxide curves slope upwards (ΔS is negative, ΔG^o be
- If materials melt / vaporize, slope changes (ΔS is more –ve, ΔG^o be
- When the curve crosses $\Delta G^o = 0$, decomposition of oxide (Ag
- Electropositive metal curves are at the bottom of the di
- Any metal will reduce the oxide of other metal which Ellingham diagram (the ΔG^o will become more negative b equal to the difference between the two graphs at a partic

As I said previously any metal will reduce the oxide of other metal which is above in that Ellingham diagram.

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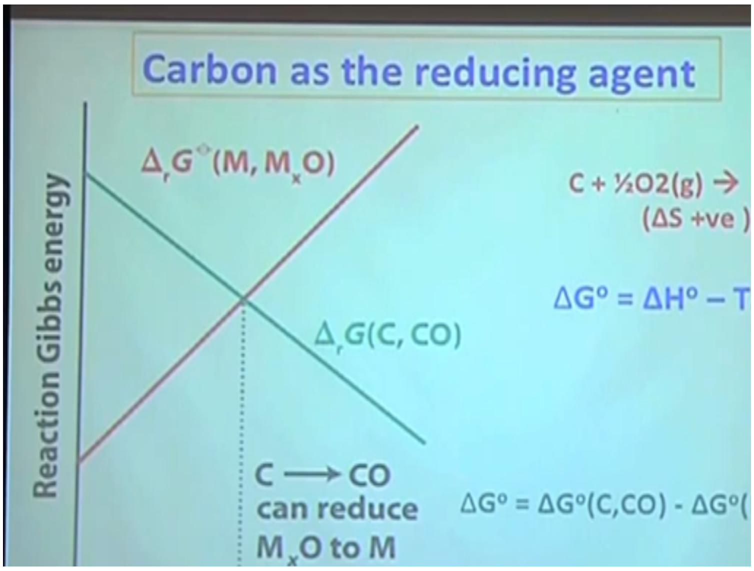
Carbon as the reducing agent

$C + ½O2(g) \rightarrow$

(ΔS +ve)

$\Delta G° = \Delta H° – T$

C ⟶ CO can reduce M_xO to M

$\Delta G° = \Delta G°(C,CO) - \Delta G°($

Now, of course, we need to also understand how carbon can be oxidized to carbon monoxide or carbon dioxide; and how how their plots are relating to each other. Now, this is usually as we are discussing usually this is the metal oxide for plot; metal going to metal oxide and this is the usually carbon going to carbon monoxide plot. So, at any temperature above this crossing point above this point, you will be having carbon monoxide formation. At this temperature you will have carbon monoxide formation and metal oxide will be converted to corresponding metal.

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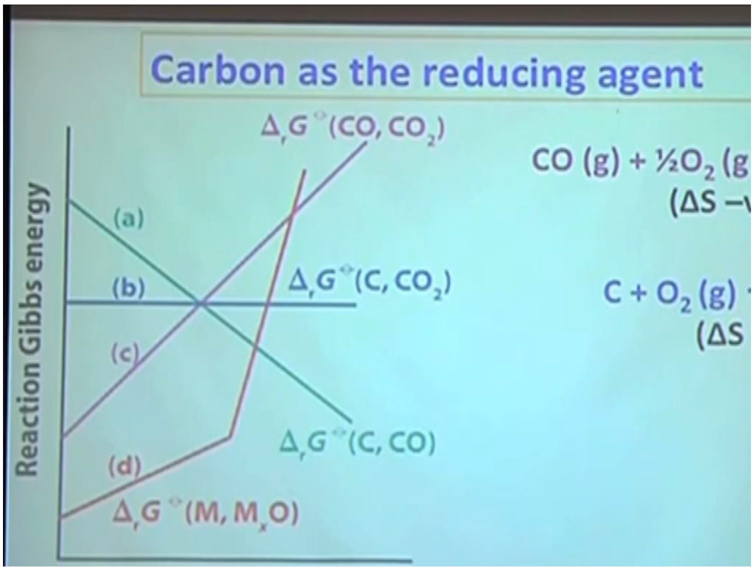
Carbon as the reducing agent

$CO\ (g) + ½O_2\ (g$

(ΔS –

$C + O_2\ (g)$

(ΔS

Now, if you were 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. So, for carbon monoxide case, it is a gas plus gas giving you a gas; but it is a one and a half equivalent of gas is giving you 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. Thereby the plot you see over here this purple color one over here.

So, with respect to temperature as you are increasing temperature, it is becoming more and more unfavorable. It is just all depends on delta S, whether delta S negative or delta S is positive; in this case one and a half equivalent of gas giving you one equivalent of gas. So, this is the purple line over here for carbon monoxide going to carbon dioxide. Now, the warning 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; 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 we it is delta of delta S. So, usually you can say it is zero; but it is better to put constant, it is it is not changing. It is a change that we are looking for. With respect to temperature, I think it is better to say zero maybe with; so, only delta H will matter. 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. Let me see you in over here.

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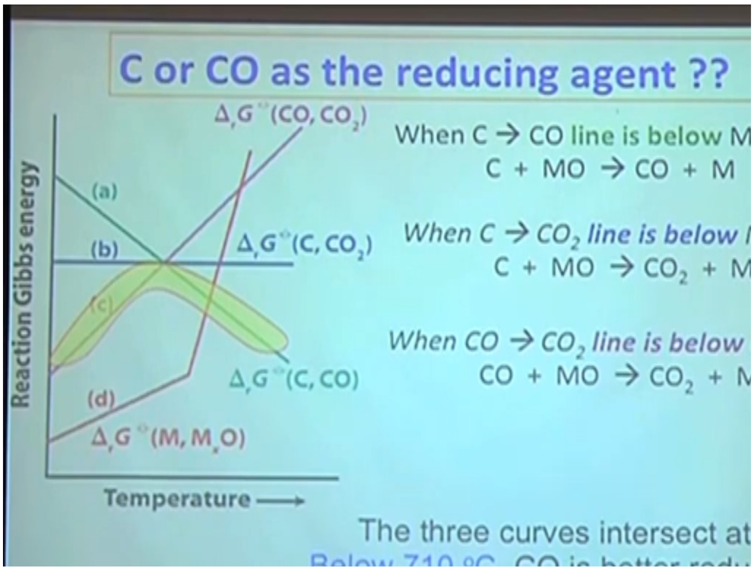

C or CO as the reducing agent ??

When C → CO line is below M
$C + MO \rightarrow CO + M$

When C → CO_2 line is below
$C + MO \rightarrow CO_2 + M$

When CO → CO_2 line is below
$CO + MO \rightarrow CO_2 +$

The three curves intersect at

During this period, up to the 710 degrees C or so, carbon monoxide to carbon dioxide formation is more favorable. Because co2-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. 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 degrees C anything you do it is going to be carbon to carbon monoxide formation; so, of course you have the option to choose. But practically speaking usually we are heating the ore at a rely on, 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. Anyway, now I think the same thing we have discussed already.