Iron Making
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Lecture - 10
Iron Making

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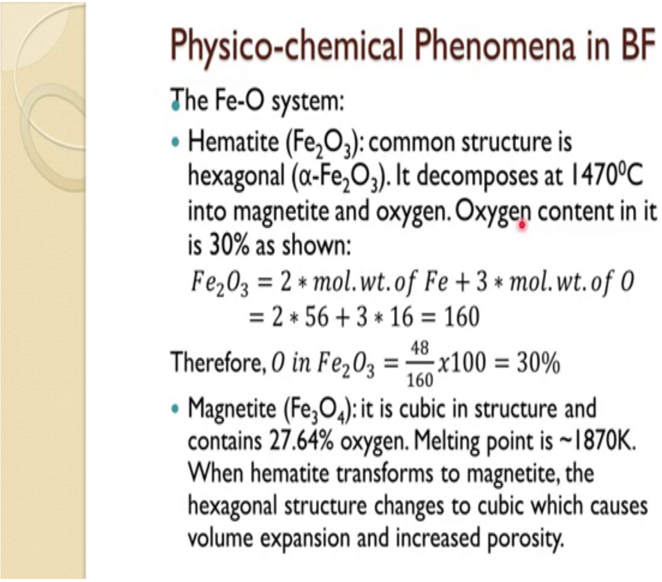

Physico-chemical Phenomena in BF

The Fe-O system:

- Hematite (Fe_2O_3): common structure is hexagonal (α-Fe_2O_3). It decomposes at 1470^{0}C into magnetite and oxygen. Oxygen content in it is 30% as shown:

$$Fe_2O_3 = 2 * mol.wt.of\ Fe + 3 * mol.wt.of\ O$$
$$= 2 * 56 + 3 * 16 = 160$$

Therefore, $O\ in\ Fe_2O_3 = \frac{48}{160} x100 = 30\%$

- Magnetite (Fe_3O_4): it is cubic in structure and contains 27.64% oxygen. Melting point is ~1870K. When hematite transforms to magnetite, the hexagonal structure changes to cubic which causes volume expansion and increased porosity.

Come to another topic in the blast furnace and that is Physico-chemical phenomena in blast furnace. And this is sort of a heart of the blast furnace in one way be we would say because all the chemical reaction which is hankering the thermodynamics behind it, how it can be improved what are the limitation of it this actually we would be discussing in this topic.

So, from thermodynamic, reaction kinetics and in fact, knowing the limitation of the furnace from these few point this topic is very important. So, we will go to various systems in the blast furnace which are of important to us the first one is the iron and oxygen system.

So, iron and oxygen system when we talk about it first one comes to in our mind is about the iron ore which is hematite and which is nothing like Fe 2 O 3. So, the common structure of this is hexagonal in nature which mostly for alpha Fe 2 O 3 and it de decomposes at 1470 degree Celsius into magnetite and the oxygen and oxygen contained in this is about thirty percent Hepson one calculation how do you determine this oxygen content.

So 2 mol of iron 3 mol of oxygen so, that keeps you the molecular bit of Fe 2 O 3 160 and the there for oxygen would be total we have 48 divided by 160 and in the percentage term multiply by 100 that gives you the 30 percent oxygen in hematite.

Similarly we can calculate for other oxides. So, we will not so this calculation we will just refer the percentage, but one can do it. So, magnetite it is cubic in structure and contains about 27.64 percent oxygen it melts about at in 170 degree Kelvin.

When hematite transform to magnetite the hexagonal structure changes to cubic structure and which causes boiling expansion and increase the porosity this is the thing which lead to a little bit expansion of the or in the blast furnace I think in the first few lectures we talked about swelling and other thing and this causes one of the that one is not so this is one region.

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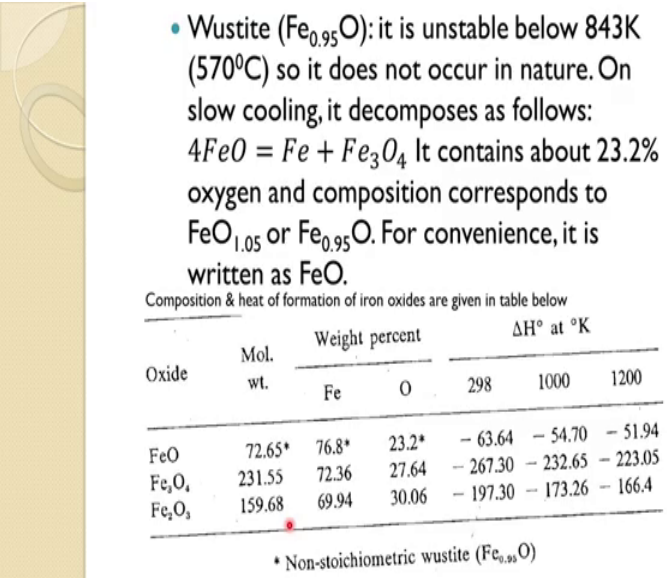

- Wustite ($Fe_{0.95}O$): it is unstable below 843K (570⁰C) so it does not occur in nature. On slow cooling, it decomposes as follows: $4FeO = Fe + Fe_3O_4$ It contains about 23.2% oxygen and composition corresponds to $FeO_{1.05}$ or $Fe_{0.95}O$. For convenience, it is written as FeO.

Composition & heat of formation of iron oxides are given in table below

Oxide	Mol. wt.	Weight percent		ΔH° at °K		
		Fe	O	298	1000	1200
FeO	72.65*	76.8*	23.2*	− 63.64	− 54.70	− 51.94
Fe_3O_4	231.55	72.36	27.64	− 267.30	− 232.65	− 223.05
Fe_2O_3	159.68	69.94	30.06	− 197.30	− 173.26	− 166.4

* Non-stoichiometric wustite ($Fe_{0.95}O$)

Now we have Wustite Fe O it is unstable below 843 3 p degree Kelvin that is 573 degree Celsius so it does not occur in the nature. So, once you know Fe O is not in naturally occurring compound because it is unstable. On slow cooling it decomposes as follows. So, it keeps actually magnetite and iron.

So, it contains about 23.2 percent oxygen and composition corresponding to this ratio. So, this is stoichiometry not right in the form of Fe O because oxygen ion content deform , but in terms of convenience way which has drawn it Fe O and that tells you the heat of formation and composition of all these 3 important oxide which part of the blast furnace. So, molecular weight and the iron content in it and the oxygen content and heat of formation at various temperature.

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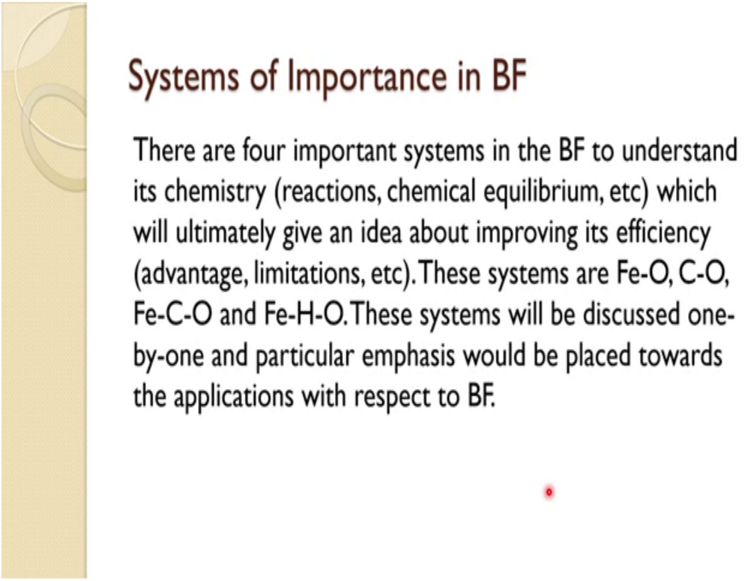

Systems of Importance in BF

There are four important systems in the BF to understand its chemistry (reactions, chemical equilibrium, etc) which will ultimately give an idea about improving its efficiency (advantage, limitations, etc). These systems are Fe-O, C-O, Fe-C-O and Fe-H-O. These systems will be discussed one-by-one and particular emphasis would be placed towards the applications with respect to BF.

So, there are 4 important systems in the blast furnace to understand its chemistry reaction chemical equilibrium etcetera which will ultimately give an idea about improving its efficiency advantage limitation etcetera. So, these systems are iron oxide system which has so that carbon oxygen and carbon oxygen and iron hydrogen oxygen these system will be discussed. Now one by one in the coming slides and application of these system towards the blast furnace applications would be discussed.

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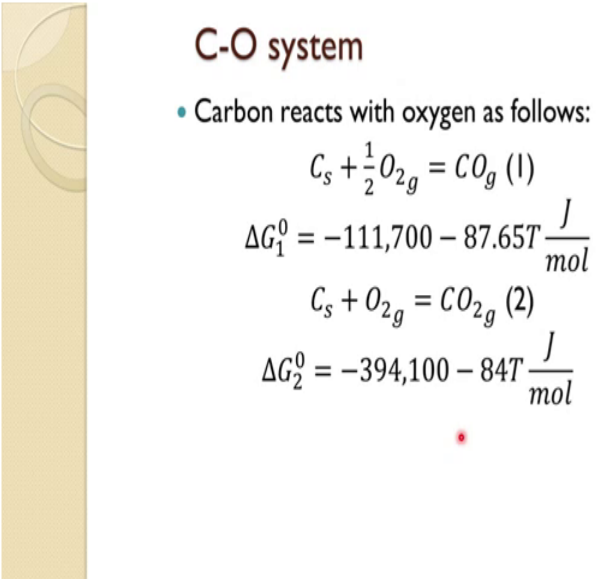

C-O system

- Carbon reacts with oxygen as follows:

$$C_s + \frac{1}{2}O_{2_g} = CO_g \text{ (1)}$$

$$\Delta G_1^0 = -111{,}700 - 87.65T\frac{J}{mol}$$

$$C_s + O_{2_g} = CO_{2_g} \text{ (2)}$$

$$\Delta G_2^0 = -394{,}100 - 84T\frac{J}{mol}$$

So, C-O system carbon react with oxygen as follows. So, 1 mol of oxygen combined with the carbon, 1 mol carbon gives you the one mol of C O and the change in free energy is given from this expression the standard 1 T is the temperature in degree Kelvin joule per mol and the another reaction which forms C O 2 when oxygen compound with carbon it is given oh represent by a reaction number 2 and the free energy expression is given by this again T is in degree Kelvin joule per mol.

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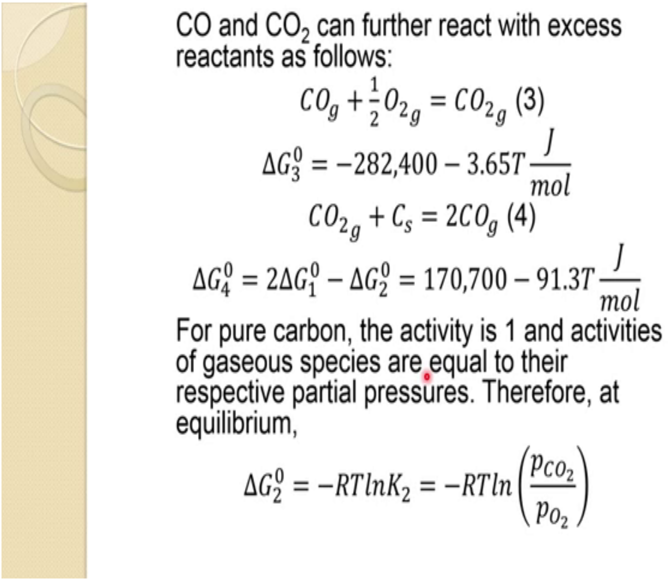

CO and CO_2 can further react with excess reactants as follows:

$$CO_g + \frac{1}{2}O_{2_g} = CO_{2_g} \text{ (3)}$$

$$\Delta G_3^0 = -282{,}400 - 3.65T\frac{J}{mol}$$

$$CO_{2_g} + C_s = 2CO_g \text{ (4)}$$

$$\Delta G_4^0 = 2\Delta G_1^0 - \Delta G_2^0 = 170{,}700 - 91.3T\frac{J}{mol}$$

For pure carbon, the activity is 1 and activities of gaseous species are equal to their respective partial pressures. Therefore, at equilibrium,

$$\Delta G_2^0 = -RTlnK_2 = -RTln\left(\frac{p_{CO_2}}{p_{O_2}}\right)$$

So, you can see both are exothermic in nature and this see when C O form in this it can further react with oxygen it form C O 2 and a free energy is given again for this reaction.

Similarly, C O 2 which is forming here can react with carbon can gives you C O 2 C O these 2 reactions or even the this reaction is possible when reactants are more in quantity. So, whatever is formed they again react and because a especially at higher temperature C O is stable.

So, it is again from the C O and when C O 2 is converting reacting with carbon and forming C O that is usually a an endothermic reaction. So, for pure carbon that activity is taken as 1 and activities of gases species are equal to their respective partial pressure which I am sure all of you might be aware of these activities free energy and other thing from your thermodynamic powers or reaction kinetics force.

So, we are not going to tell about these terms and we expect that you would be knowing about it so that is why this can be converted into partial pressure. So, therefore at equilibrium if we look at the this reaction number 2 that we have put their free energy can be written RT log K 2 and this K is nothing its equilibrium constant for the particular reaction. So, we have considering this reaction and you can easily write the equilibrium constant K equal to p C O 2 divided by p O 2 and S C S so that is activity of carbon and activity of carbon is we said we are considering it is a pure carbon it has been assumed 1. So, the equilibrium constant goes down to this expression p C O 2 divided by p O 2 for this reaction.

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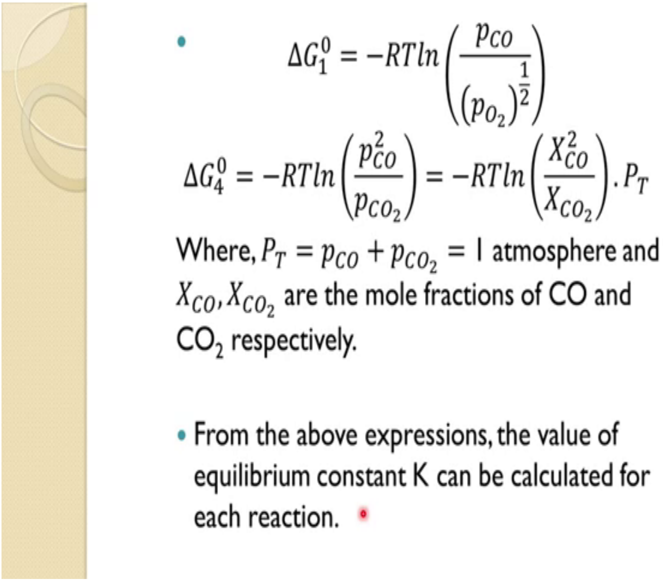

- $$\Delta G_1^0 = -RTln\left(\frac{p_{CO}}{(p_{O_2})^{\frac{1}{2}}}\right)$$

$$\Delta G_4^0 = -RTln\left(\frac{p_{CO}^2}{p_{CO_2}}\right) = -RTln\left(\frac{X_{CO}^2}{X_{CO_2}}\right).P_T$$

Where, $P_T = p_{CO} + p_{CO_2} = 1$ atmosphere and X_{CO}, X_{CO_2} are the mole fractions of CO and CO_2 respectively.

- From the above expressions, the value of equilibrium constant K can be calculated for each reaction.

So, and we substitute that equilibrium constant over here and we know the then the free energy this is for the others reaction that the first one where the half mol is converted into C O so that gives for the free energy expression in terms of partial pressure.

Similarly for other we can put it for the number 4 for this we can write again 2 moles of C O R are forming so the equilibrium constant is this and now this can be written in terms of mol fraction and we are assuming pure system whereas C O and C O 2 only are there. So, total pressure would be one atmosphere.

So, these thing one can interchange can write in mol fraction volume fraction partial pressure and other way and I hope you read those who are taking this course they are familiar with these terms. So, from the above expression the value of equilibrium constant K can be calculated for each reaction.

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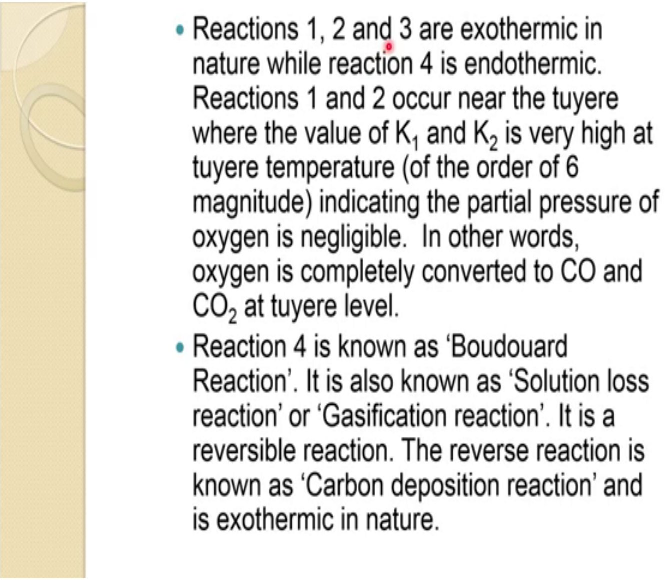

- Reactions 1, 2 and 3 are exothermic in nature while reaction 4 is endothermic. Reactions 1 and 2 occur near the tuyere where the value of K_1 and K_2 is very high at tuyere temperature (of the order of 6 magnitude) indicating the partial pressure of oxygen is negligible. In other words, oxygen is completely converted to CO and CO_2 at tuyere level.
- Reaction 4 is known as 'Boudouard Reaction'. It is also known as 'Solution loss reaction' or 'Gasification reaction'. It is a reversible reaction. The reverse reaction is known as 'Carbon deposition reaction' and is exothermic in nature.

So, reaction 1 2 and 3 are exothermic in nature as we said before because this having a negative for free energy why reaction 4 is endothermic. Reaction 1 and 2 occur near the tuyere where the value of K 1 and K 2 is very high at tuyere temperature of the order of 10 to the power 6. So, this value you can calculate for this 1 at tuyere temperature taking about 1900 2000 degree Celsius and free energy is you already know.

So, log K as you can get it in this you put it log K and delta G expressions you already know for these reaction put it there and you can R it is universal constant gas constant T is the temperatures. So, temperatures suppose it 2000 degree Celsius at tuyere level or nineteen hundred one can calculate the equilibrium constant value. So, equilibrium constant value at that comes very high of the order of 6 and in fact, another one is of the order of 9.

So, indicating that partial pressure of oxygen is negligible. So, naturally the partial pressure of the this if this is of the order of 10 to the power 6, partial pressure of oxygen would be very low and which indicate that all the carbon converted into C O and C O 2 at the tuyere level.

So, reaction four is very important reaction what we call it is a boudauard reaction in metallurgy in iron making and you also call it gasification reaction. Even solution loss reaction they have various way of telling about that reaction number four. So boudauard reaction, solution loss reaction, gasification reaction, whose carbon is losing so if a in the reverse reaction is known as.

So, if it goes in a reverse direction. So, what is happening carbon is coming out from the C O so it is called the carbon deposition reaction and C O 2 is forming and that is when it is going in the reverse direction depending on the temperature in the kinetics of this. So, the reverse direction reaction actually is exothermic in nature those you can see it is an endothermic in nature forward direction, but in reverse direction it is in exothermic in nature this reaction.

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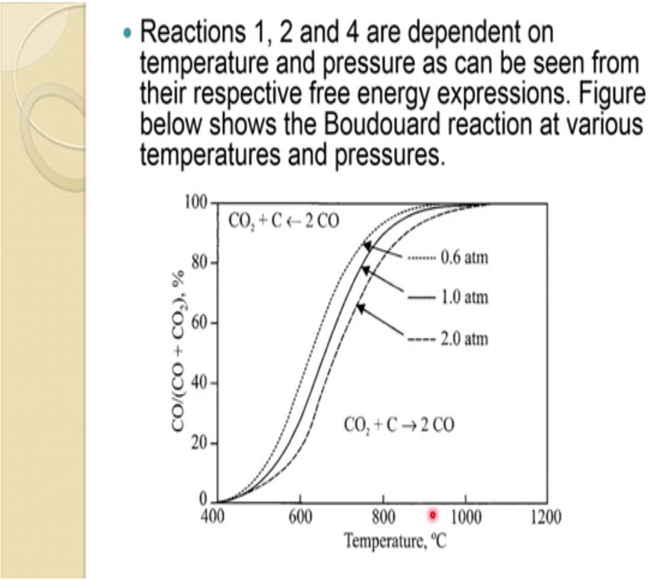

- Reactions 1, 2 and 4 are dependent on temperature and pressure as can be seen from their respective free energy expressions. Figure below shows the Boudouard reaction at various temperatures and pressures.

So, reaction 1 2 and 4 are dependent on temperature and pressure as we have seen with the free energy relation with respect to free energy expression. So, these can be plotted in graphical forms. So, figure below shows the boudouard reaction at various temperature and pressure. So, this is boudouard reaction carbon gasification reaction and one can see plotted temperature versus C O C O plus C O 2 ratio.

So, this actually tells how much C O is being utilized and as you can see below 600 this becomes quite sluggish oh 50 or below 500 400 in fact, this reaction its almost sees as in reverse direction though a 1000 degree Celsius you can see it fully converted into C O and C O 2 is no more there really, but in this one the reverse is occurring, but after this it is almost serious the reaction.

And as the, but the most unstable region actually is this where disturb between I would say 600 to 800 where this is changing rapidly this is the region which is very unstable and you can see with the slope of the curve.

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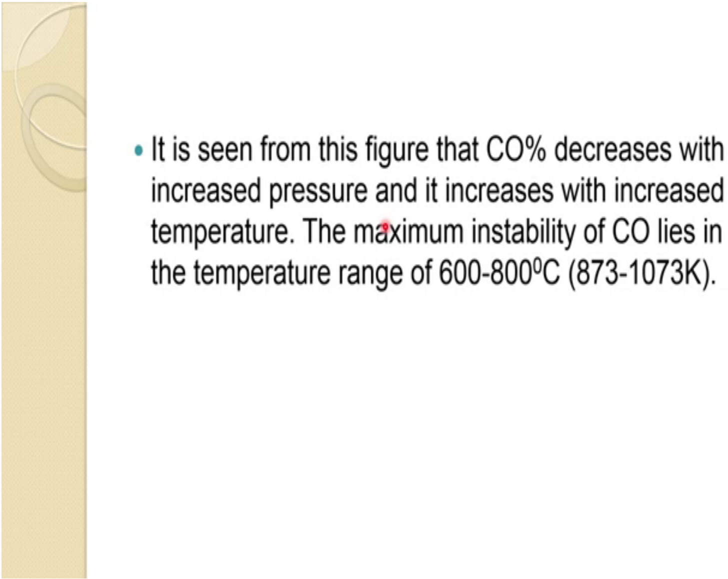

- It is seen from this figure that CO% decreases with increased pressure and it increases with increased temperature. The maximum instability of CO lies in the temperature range of 600-800^{0}C (873-1073K).

So, so, it is seen that C O percentage decreases with increased pressure a so with the increased pressure C O percentage decrease at the same temperature we will take it , but it increases with temperature.

So, with the temperature C O percentage is increasing and the maximum instability of C O lies between the temperature range of 600 to 800 degree Celsius and our in the blast furnace mostly reaction is occurring after 800 to 1000 where we have a chemical or thermal results zone. So, this that is where it is reaction in the blast furnace occurs reduction reaction now the decomposition of C O is a very slow process after 400 degree Celsius as we said is almost see this up to 400 so decomposition is very slow.

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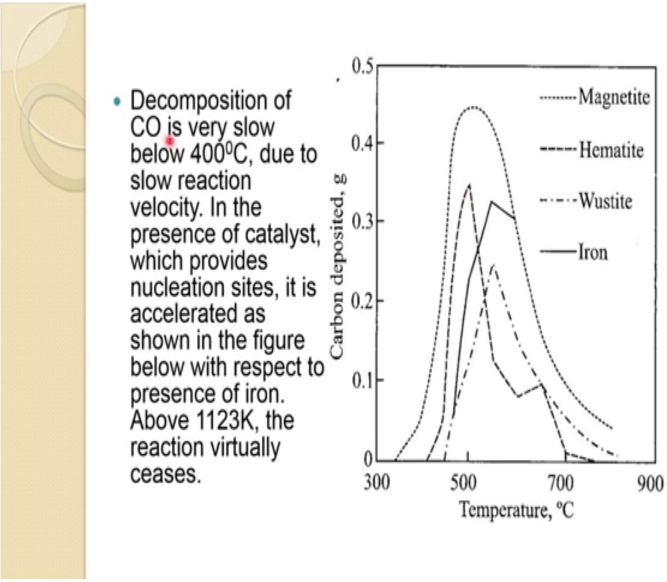

- Decomposition of CO is very slow below 400^{0}C, due to slow reaction velocity. In the presence of catalyst, which provides nucleation sites, it is accelerated as shown in the figure below with respect to presence of iron. Above 1123K, the reaction virtually ceases.

In the presence of catalyst which provides nucleation sites it is accelerated as shown in this figure and this is with respect to presence of iron so iron becomes as a catalyst and so this reaction is accelerated. So, above 1123 Kelvin, 900 degrees see the reaction virtually sees as we mentioned in this one above 9 900 degrees. See this is almost over this reaction does not occur that 1 so you can see the in the presence of magnetite carbon deposits is maximum.

So, when hematite in the stake region at the top is reducing to magnetite that time and that time temperature is also favorable in the stake region carbon deposition occur magnetite actually accelerate that and that is a maximum you are getting it at 5 hundred and hematite of course, as a and Wustite is the lowest one and iron is in the middle.

So, magnetite is the one which will favor or accelerate this reaction and that is in the stake region and at the top where the free heating zone and these thing which we discussed temperature goes from up to 6 700 so that is the reason when this carbon get deposited it has a many disadvantage.

So, beside some advance some advantage and mostly disadvantage. So, deposition of carbon in blast furnace reduces the stack diameter. So, it deposit an so diameter of the stack decrease in the terms of more mass has been added so that causes breakdown of charge material also retards burden descent and finally, leads to the hanging of the furnace.

So, these are the major problem which occur due to the deposition of carbon and one has to be careful and design in the in a way the blast furnace reaction or the temperature zone that it should be minimized one cannot completely get rid of this why should be minimized.

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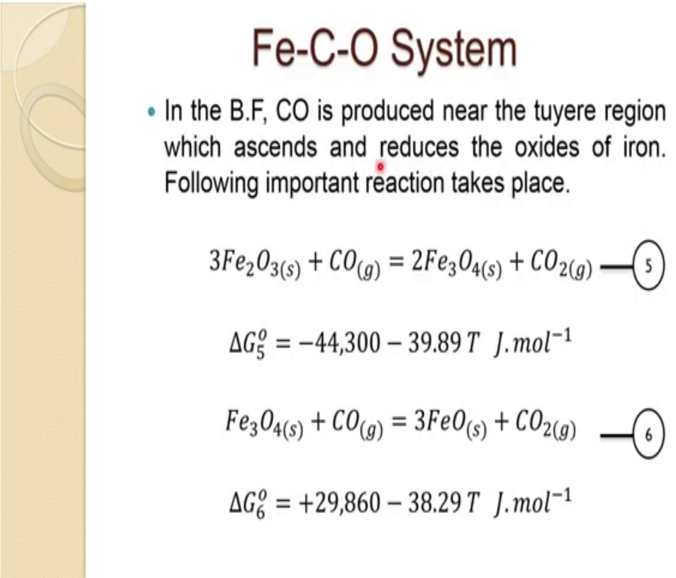

Fe-C-O System

- In the B.F, CO is produced near the tuyere region which ascends and reduces the oxides of iron. Following important reaction takes place.

$$3Fe_2O_{3(s)} + CO_{(g)} = 2Fe_3O_{4(s)} + CO_{2(g)} \text{ —⑤}$$

$$\Delta G_5^o = -44{,}300 - 39.89\,T \quad J.mol^{-1}$$

$$Fe_3O_{4(s)} + CO_{(g)} = 3FeO_{(s)} + CO_{2(g)} \text{ —⑥}$$

$$\Delta G_6^o = +29{,}860 - 38.29\,T \quad J.mol^{-1}$$

Now we come to the third system is iron, carbon, and oxygen system. So, and this is the one which is quite prevalent in the blast furnace so in the blast furnace C O is produced near the tuyere region which ascends and reduces the oxides of iron following important reaction that place.

So; obviously, the first one we are going from the top as soon as you charge the ore which is mostly hematite is reduces its carbon monoxide C O 2 magnetite C O 2 you can see this is a an exothermic reaction then magnetite when we further go down magnetite convert into Wustite and this is an endothermic reaction form the free energy.

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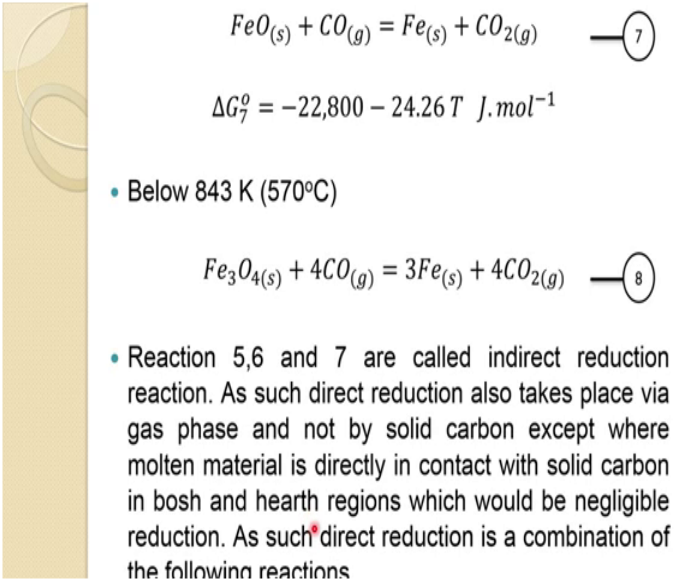

$$FeO_{(s)} + CO_{(g)} = Fe_{(s)} + CO_{2(g)}$$ ⑦

$$\Delta G_7^o = -22{,}800 - 24.26\,T \quad J.mol^{-1}$$

- Below 843 K (570ºC)

$$Fe_3O_{4(s)} + 4CO_{(g)} = 3Fe_{(s)} + 4CO_{2(g)}$$ ⑧

- Reaction 5,6 and 7 are called indirect reduction reaction. As such direct reduction also takes place via gas phase and not by solid carbon except where molten material is directly in contact with solid carbon in bosh and hearth regions which would be negligible reduction. As such direct reduction is a combination of the following reactions

And then this Fe o converts into iron it is slightly exothermic reaction, but , but you know this Fe O which has formed must be more than 570 degree Celsius the temperature otherwise if it is formed below that temperature then it build dissociate as we discussed before because it is not stable and it will form iron and C O 2 in fact, some of the iron fiscal has been found in the upper zone of the blast furnace. So, this also reaction sometime occur below 843 Kelvin. So, reaction 5 6 and 7 are called indirect reduction reaction.

ah So you can see the getting indirectly reduced by C O. So, this 3 reaction are called indirect reduction and you must have heard about the direct reduction , but as such really there is no direct reduction takes place via so direct reduction takes place via gas phase only and not by solid carbon except where molten material is directly in contact with solid carbon which is mostly in the bosh and the hearth region. So, by that time most of the Fe O is already reduced; however, that is why this direct reduction the ways you represent it actually it goes via gaseous phase.

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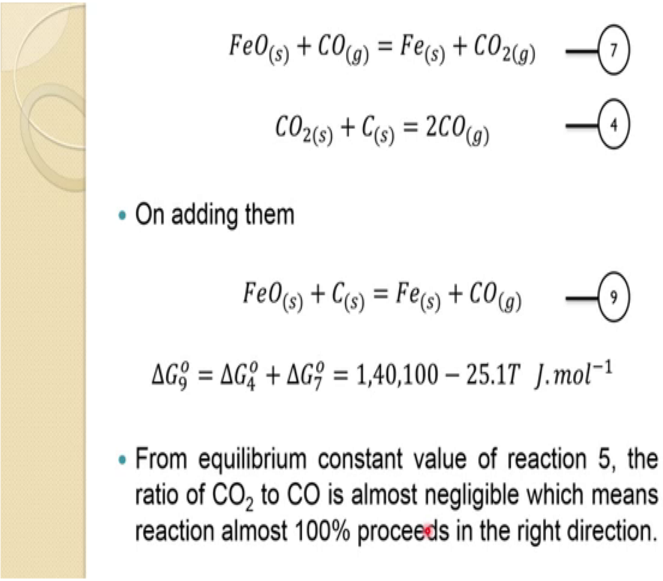

$$FeO_{(s)} + CO_{(g)} = Fe_{(s)} + CO_{2(g)}$$ ⑦

$$CO_{2(s)} + C_{(s)} = 2CO_{(g)}$$ ④

- On adding them

$$FeO_{(s)} + C_{(s)} = Fe_{(s)} + CO_{(g)}$$ ⑨

$$\Delta G_9^o = \Delta G_4^o + \Delta G_7^o = 1{,}40{,}100 - 25.1T \ J.mol^{-1}$$

- From equilibrium constant value of reaction 5, the ratio of CO_2 to CO is almost negligible which means reaction almost 100% proceeds in the right direction.

So, Fe O plus C O iron plus C O 2 C O 2 plus C gives you 2 C O. So, gasification of carbon is occurring and when you add both of them this gives you this reaction which what you called I the direct reduction essentially it is not the carbon directly is reducing it is a via gaseous phase it is getting reduced overall reaction is non this one which you call it a direct reduction.

So, the overall free energy for the this and you can see highly endothermic reaction very high endothermic reaction. So, it needs quite a lot heat to get that. So, from equilibrium constant value of reaction 5 the ratio C O 2 to C O is almost negligible which means the reaction almost goes with hundred percent proceed in the right direction so this is the reaction 5 this magnet hematite.

So, the this reaction is a ratio of C O 2 to C O so, almost 100 percent which means the reaction proceeding in the right direction and almost 100 percent get completed.

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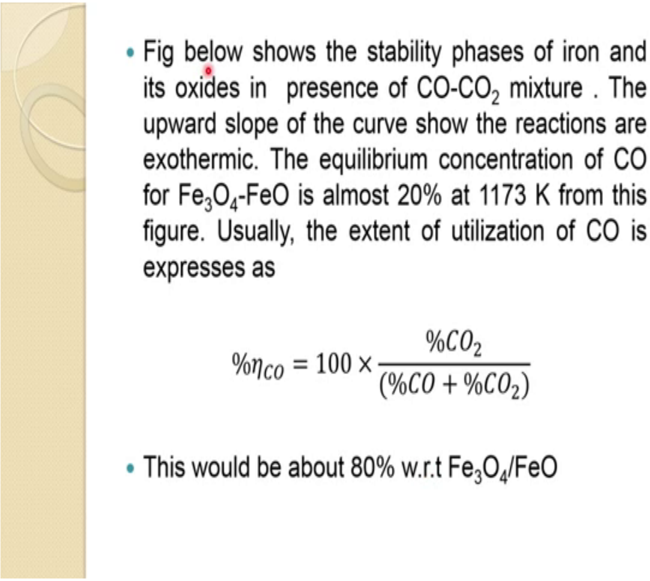

- Fig below shows the stability phases of iron and its oxides in presence of CO-CO_2 mixture . The upward slope of the curve show the reactions are exothermic. The equilibrium concentration of CO for Fe_3O_4-FeO is almost 20% at 1173 K from this figure. Usually, the extent of utilization of CO is expresses as

$$\%\eta_{CO} = 100 \times \frac{\%CO_2}{(\%CO + \%CO_2)}$$

- This would be about 80% w.r.t Fe_3O_4/FeO

Note the other reactions of figure on the next slide you will show the stability phases of iron and its oxide in presence of C O C O 2 mixture. So, the upward so this is the Fe c and O system where you are having so, this is the line which you have seen for the C O system carbon and oxygen.

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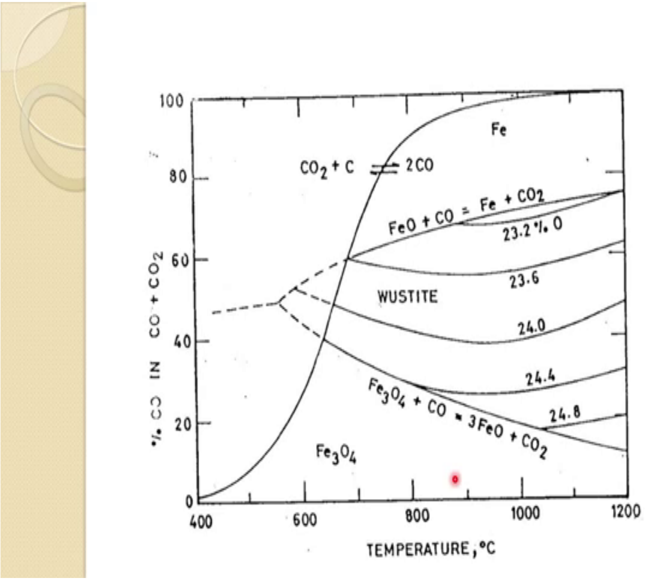

So, it has been superimposed and on the Fe C O system just to say how the deduction will take place. So, essentially Fe C O system is this one with these lines are there so above this line iron this table Wustite is in between and this is your magnetite region and this is what iron.

So, you can see at this point 570 degree Celsius which we talked that is where the Fe O which is here Wustite is no longer exist below that and getting directly at twist magnetite and iron at this. So, this is invariant point of that because oxygen content in Wustite changes because stoichiometry it is not 1 mol of a p and one mol of oxygen which changes that is how this other lines are given here.

Now in the curve so as I the upward slope of the curve shows the reaction are exothermic so you remember the this upward one you know this reaction are with exothermic and we found one is endothermic actually the downward one

So, so, the equilibrium concentration of C O for Fe 3 O 4, Fe O is almost 20 percent at 1173 degree Kelvin and from so this is a Fe 3 O 4 a Fe O contain and usually we talk around 900 degree Celsius are so at that if you see its about 20 percent coming to about 20 percent C O and that is where what equilibrium concentration of C O is about 20 percent.

And usually the extent of utilization of C O is expressed in terms of the efficiency of the carbon which sets that so this is the efficiency of utilization of C O equal to percentage of C O 2 divided by the per total percentage of C O plus C O 2 the ratio of this tells you about the percentage of utilization of C O for the particular reaction.

So, with respect to that what we discussed that now, it would be for magnetite Fe O 20 percentage utilization it would be 80 percent efficiency of C O for this reaction. Similarly for others one can calculate and this is the C O C O carbon gasification line which tells where this reaction will occur and how it is going to reduce or deduce let us say the Fe O what sort of how much C O you need it to reduce at a particular temperature a particular oxide.