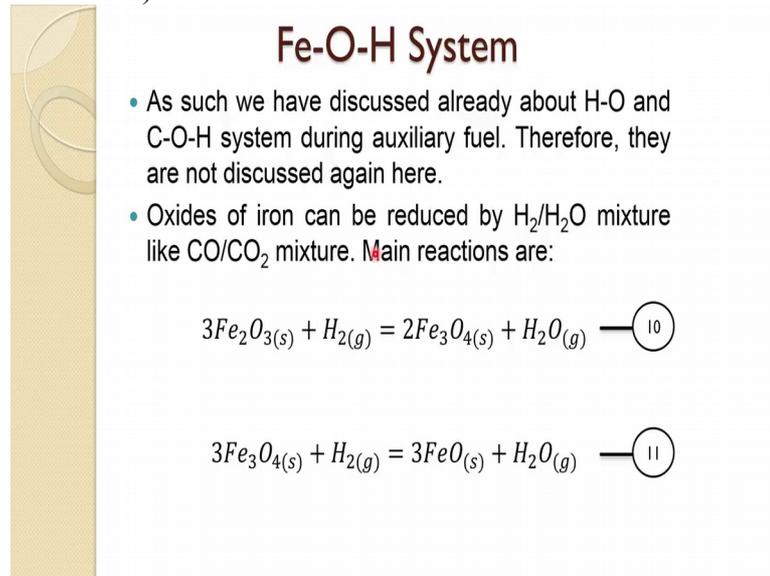


**Iron Making**  
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**Lecture - 11**  
**Iron Making**

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**Fe-O-H System**

- As such we have discussed already about H-O and C-O-H system during auxiliary fuel. Therefore, they are not discussed again here.
- Oxides of iron can be reduced by H<sub>2</sub>/H<sub>2</sub>O mixture like CO/CO<sub>2</sub> mixture. Main reactions are:

$$3Fe_2O_{3(s)} + H_{2(g)} = 2Fe_3O_{4(s)} + H_2O_{(g)} \quad \text{--- (10)}$$
$$3Fe_3O_{4(s)} + H_{2(g)} = 3FeO_{(s)} + H_2O_{(g)} \quad \text{--- (11)}$$

Now, we come next to the Iron Oxygen Hydrogen System. As you know in there were blast air, sometimes you put the moisture and you would be aware that hydrogen is a more, had more reducing power than carbon. And, so many times to increase the reducing power of the gas, as you use hydrogen. So, either through oil or sometime putting some moisture or water, as we have already discuss about it in the previous lectures. So iron oxygen hydrogen is also an important system, and how the hydrogen reduce these oxides; we will discuss in this.

So s, as so hydrogen oxygen we had discussed before during the fuel injection lecture, and under auxiliary fuel, so we are not discussing this here. So, oxides of iron can be reduced by hydrogen and water mixture; like CO CO 2 mixture in the same way. So, main reaction are magneti hematite getting reduced to magnetite, and magnetite is getting reduced to boostite, and then finally boostite is getting reduced to iron.

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$$\text{FeO}_{(s)} + \text{H}_{2(g)} = \text{Fe}_{(s)} + \text{H}_2\text{O}_{(g)}$$

$$\Delta G_{12}^{\circ} = 7800 - 4.22T \text{ J} \cdot \text{mol}^{-1}$$

$$\text{Fe}_3\text{O}_{4(s)} + 4\text{H}_{2(g)} = 3\text{Fe}_{(s)} + 4\text{H}_2\text{O}_{(g)}$$

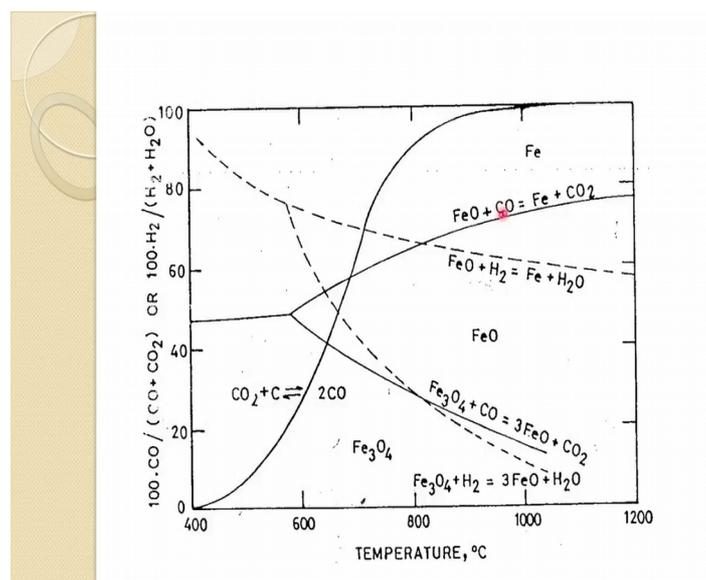
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- The different phases of iron oxides in equilibrium with H<sub>2</sub>/H<sub>2</sub>O mixture are shown in figure. Reduction of FeO with H<sub>2</sub> is endothermic. So, the curves in the figure inclines downwards with increasing temperature. This figure also shows the Fe-O-C system for comparison. The two curves of FeO reduction with CO and H<sub>2</sub> intersect at 1094 K (821°C) where both the gasses have some reducing power over CO at this temperature.

And this is like endothermic reaction in the overall reaction is given by this equation.

So, the different phases of iron oxide in equilibrium with hydrogen and water mixtures is given in the next figure. So, reduction of FeO hydrogen is endothermic, because this reaction are mostly endothermic. So, the as you know the slope of the curves and the figure would be downward. So, the curve incline toward the downward with increasing temperature.

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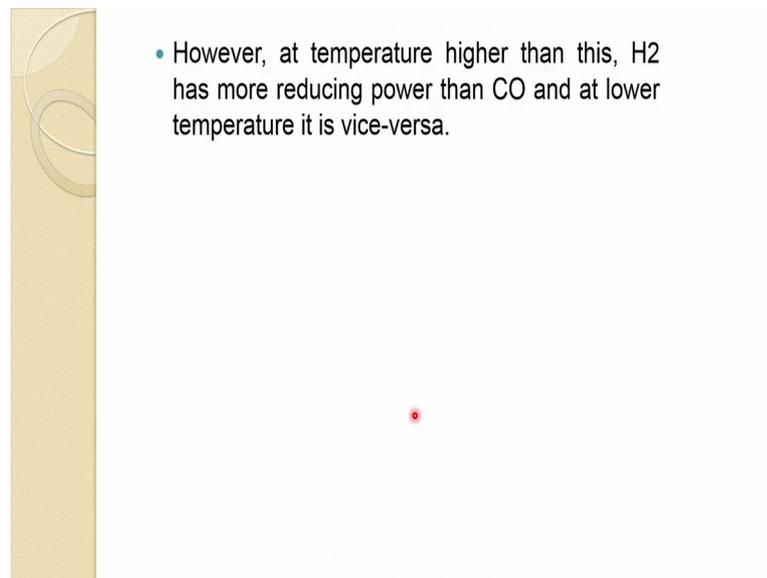


And that is as we said even for when we were discussing with carbon, that slope of this this is exothermic. So, it is upward, but for this was endothermic so it downward. And in the system of iron oxygen hydrogen, these reactions are mostly endothermic. So, these are more in the downward direction. So, you can see at 800 degree Celsius also, there is a intersect hydrogen and carbon bond line which is getting intersects.

And what is it mean? Which you need a less probably CO below this temperature to reduce the magnetite, but you may need a higher hydrogen potential to reduce the magnetite below that temperature. So, that one can clearly see however, it is higher the temperature, then you need a less hydrogen power than the CO 2 to reduce the magnetite; so as the temperature increases, reducing power of hydrogen increases; then the CO.

So, here as two curves of FeO reduction with CO and hydrogen intersect at 821 degree, where both the gasses have same reducing power over CO at this temperature. As we discuss here this is about 821 degree Celsius.

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• However, at temperature higher than this, H<sub>2</sub> has more reducing power than CO and at lower temperature it is vice-versa.

However, at temperature higher than this, hydrogen has more reducing power than CO, and at lower temperature it is vice versa. That point again we discussed over here. So, that is. So, the importance of both hydrogen and CO system and how it could be useful; so at high temperature it is much better that, and lower temperature CO is having a more reducing power than the hydrogen.

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## Rist Diagrams

- These are the graphical representation of heat and mass balances in BF, considering BF reactions. There are many such diagrams. One example is given below, based on simple mass balance of oxygen and carbon, ignoring reduction by hydrogen, dissolution of C in hot metal and reduction of other minor oxides except  $\text{Fe}_2\text{O}_3$ .
- Therefore,  
$$\text{O}_2 \text{ input (from air blast + iron oxide)} = \text{O}_2 \text{ output (as CO and CO}_2 \text{ in top gas)}$$

Now, we come to one, another topic is about the rist diagram, and these are the graphical representation of heat and mass balances in blast furnace. You know in chemical engineering, do have many of these graphical representation of many processes even for like Reynold's number, friction factor, and like that. So, empirically as you can get the values from those graph it is similarly in this, same thing is happen in heat and mass balance in chemical engineering. And the same sort of principle has been applied here, to for this one. So, it is like a graphic representation of heat and mass balances in the blast furnace, considering large furnace B F reaction. And there are many such diagrams,. So, one simple example is given below, which is based on the mass balance of oxygen and carbon, ignoring reduction by hydrogen, dissolution of carbon in hot metals and reduction of other minor oxide, except the hematite.

So, you can include these one, you can make it more complex, as you can include other reaction, similarly heat balance and you can then make the diagram more complex and more realistic. But how does it work? That one which is showing it here in a simple way. So, therefore, oxygen input mostly from the air blast which is coming and from the iron oxide, whatever you are feeding in. And output is mostly in CO and CO<sub>2</sub> in top gas, which is going out.

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- In terms of Fe

$$nO^B + \left(\frac{O}{Fe}\right)^X = nC^A \times \left(\frac{O}{C}\right)^g$$

Where,

$\left(\frac{O}{Fe}\right)^X$  and  $\left(\frac{O}{C}\right)^g$  are the composition of incoming iron oxide and outgoing gases. X is mole ratio and for hematite it is 1.5.

$nC^A$  is moles of carbon input through coke per mole of Fe and  $nO^B$  is moles of oxygen in blast air per mole of Fe.

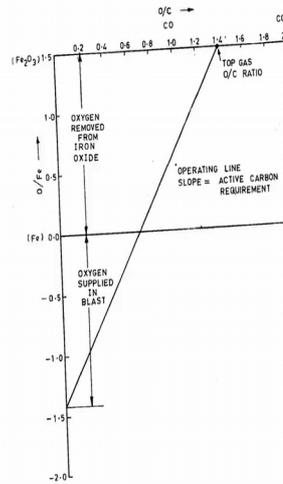
So, if we do this in terms of iron. So, oxygen associated with the oxide, and oxygen in the blast air, and the oxygen which is going out in the form of C associated with the CO<sub>2</sub> and CO, and this is the number of moles of carbon which are being input.

So, this. So, these are the composition of incoming iron oxide and outgoing gases. X is a mole ratio for hematite if it is, or to an Fe<sub>2</sub>O<sub>3</sub>. So, gives 1.5, for in case of hematite. And this is the mole of carbon input through coke per mole of iron, which is needed. And is the mole of oxygen in the blast air per mole of iron. So, all the calculations are based on the per mole of iron.

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The above equation is presented in graphical form in figure in which the slope of the line is  $nC^A$  i.e carbon required to produce 1 mole of Fe which is a coke rate of B.F under simplified conditions. Similarly, more complex Rist diagrams can be constructed considering heat and mass balance and adding more reactions etc.



And so, the above equation it is a represented in a graphical form for oxygen iron ratio oxygen carbon ratio. So, the upper zone, oxygen is removed from the iron oxides. So, this. So, the graphical representation and the slope of this line is nothing.

It is a this. So, this is essentially, this is the line which you are doing this, for says this; and intercept also you will get it. So, the slope of this line is the number of carbon required to produce 1 mole of iron, which is a coke rate of blast furnace under simplified condition. So, by a making it more and more complex, as you can they know how much coke is required under that condition, what should be your CO C O 2 ratio, and other thing and more rist, rist diagram can be made on, based on mass balance and even the heat balance you can include.

So, the over time it just to be, even now also at many places they use it. But with the advent of more modelling tool and others, though they are much more reliable and important, people are going or going away from these now.

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Example 1:  
A gas mixture of 20% CO, 20% CO<sub>2</sub>, 10% H<sub>2</sub> and 50% N<sub>2</sub>(by volume) is fed into the furnace at 900 °C. Find the equilibrium composition of the gas inside the furnace.

Given:

$$C(s) + \frac{1}{2}O_2(g) = CO(g); \quad \Delta G^0_1 = -111.71 - 0.0877T \text{ KJ/mole}$$
$$C(s) + O_2(g) = CO_2(g); \quad \Delta G^0_2 = -394.17 - 0.00088T \text{ KJ/mole}$$
$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(g); \quad \Delta G^0_3 = -246.44 - 0.0548T \text{ KJ/mole}$$

Consider one mole of gas mixture at room temperature as the basis of calculation. The number of chemical species are 5 (CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>). Number of elements are 4 (C, O, H, N). Therefore the number of equilibria is (5-4) i.e. 1.

Considering following equilibrium :

$$CO(g) + H_2O(g) = CO_2(g) + H_2(g) \quad \Delta G^0$$

(1)

$$\Delta G^0 = \Delta G^0_3 - \Delta G^0_1 - \Delta G^0_2 = 1.579 \text{ KJ/mole at } 900 \text{ }^\circ\text{C}$$

There is one example for this. So, a gas mixtures of 20 percent C O, 20 percent CO 2, 10 percent hydrogen, 50 percent nitrogen by volume is fed into the furnace at 900 degree Celsius. Find the equilibrium composition of the gas inside the furnace. So, under these are the data given. So, carbon plus oxygen, free energy how of CO formation, then CO 2 formation the free energy of that in; remember it is given in kilo joule per mole. Ok. And then the water formation, this is also including for mole. So, based on that, we have to find the equilibrium composition of the gas inside the furnace.

Now, because there are about 5 chemical species and 4 elements, so we should have a number of equilibria 1. So, we consider the equilibrium this one between these 5 species. So, CO plus waters, CO 2 plus hydrogen. This is the one nitrogen anyway is not going to change. So, this would be the equilibrium reaction, and that we have to find a equilibrium composition. So, a composition of these, and free energy because data are given. So, free energy can be found for this reaction, which comes around 1.6 kilojoule per mole at 900 degree Celsius, because this is all given at 900 degree; and we have to find the equilibrium composition at 900.

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$$1.579 \times 10^3 = -RT \ln \left( \frac{p_{CO_2} \times p_{H_2}}{p_{CO} \times p_{H_2O}} \right)_e \quad (2)$$

According to Dalton's law:  $p_i = \frac{n_i}{n_T} \cdot PT$

So, at 900 °C,

$$\frac{n_{CO_2} \times n_{H_2}}{n_{CO} \times n_{H_2O}} = 0.85 \quad (3)$$

$$\text{Also, } n_T = n_{CO} + n_{CO_2} + n_{H_2} + n_{H_2O} + n_{N_2}$$

Where,  $n_T$  is total number of moles.

According to the stoichiometric restriction, we have,

$$\text{Carbon Balance : } n_C = n_{CO} + n_{CO_2} = 0.4$$

$$\text{Oxygen Balance : } n_O = n_{CO} + 2n_{CO_2} + n_{H_2O} = 0.6$$

$$\text{Hydrogen Balance : } n_H = 2n_{H_2} + 2n_{H_2O} = 0.2$$

$$\text{Nitrogen Balance : } n_{N_2} = 0.5$$

So, this is the free energy for this reaction, And if you put it this one, this is in kilo joule which is gives you about 10 to the power into 10 to the power 3. So, essentially it is not 1002 3 to 10 to the power 3, and equilibrium constant for this reaction;  $p_{CO} \times p_{H_2}$  5 all in cases phase, divided by  $p_{CO}$  and  $p_{H_2}$  by as we discussed before in equilibrium; and this can be converted in terms of number of moles.

So, that gives you the value when you bring this down. So, substitute universal gas constant and temperature, it will be gives you the 0.85. And also, we know the total number of moles, and the mixture are these. And then doing a simple circulatory analysis for these element for carbon balance, oxygen balance, hydrogen balance, and nitrogen balance this with the nitrogen that you can arrive with these number, because the percentage and other thing is given. So, you can do the balance of all of these. So, it gives you carbon 1.4, oxygen 0.6, hydrogen 0.2, nitrogen 0.5. So, with the help of this for now, equation you can easily calculate in terms of CO to carbon. So, from these you can get the CO in terms of CO 2 and you substitute.

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Carbon balance equation yields,  $n_{CO} = 0.4 - n_{CO_2}$

Substituting above equation in oxygen balance equation, we get,  
 $n_{H_2O} = 0.2 - n_{CO_2}$

Combining all the above equations with equation (3), we get,

$$\frac{n_{CO_2} \times (n_{CO_2} - 1)}{(0.4 - n_{CO_2}) \times (0.2 - n_{CO_2})} = 0.85$$
$$n_{CO_2} = 0.157$$

Substituting  $n_{CO_2}$  in all the equations yields,  $n_{CO} = 0.243$ ,  
 $n_{H_2O} = 0.043$ ,  $n_{H_2} = 0.057$ ,  $n_{N_2} = 0.5$  and  $n_T = 1.0$

Hence the gas at equilibrium at 900 °C have following composition,

CO = 24.3%, CO<sub>2</sub>=15.7%, H<sub>2</sub>O = 4.3%, H<sub>2</sub>=5.7% and N<sub>2</sub> = 50%.

In the other equation; so finally, you get it your CO<sub>2</sub> value is 0.15, because this you substitute back her in this which is equal to 0.85. So, from that you can get the number of moles of CO<sub>2</sub> 0.157.

Once you get this value you have to be as substitute now into these equations, and here you can get and number of moles for CO from here, then from other equation, number of moles for waters, hydrogen, nitrogen and the total anyway be led up to 1, so total number of moles 1. So, once you know the number of moles, you can convert it into the percentage of the gasses. So, CO 24.3, CO<sub>2</sub> 15.7, water is 4.3, and hydrogen is 5.7, and nitrogen it does not react. So, it would be the same as 50 percent. So, that would be the composition of the gasses at equilibrium.