Steel Making

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Module No. # 01
Lecture No. # 04
The Science Base of Iron and Steelmaking

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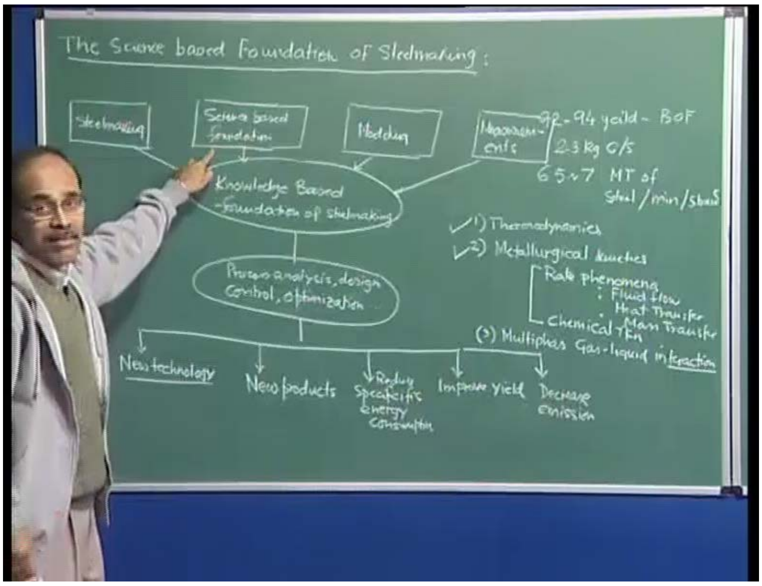

We will now start talking, for the next few lectures, on the science based foundation of steelmaking; because, steelmaking involves a lot of fundamentals and no course in steelmaking, I think, can be appreciated unless the fundamentals are known.

Of course, I am not going to give you a complete coverage of the topics, but it is important for us to revise a few key concepts and show what the fundamental components are, or the science based foundation of steelmaking, which we need to remember all the time as we go and address steelmaking problems - be it process analysis, process design optimization and so on.

Steelmaking is more than 150 years old, when Sir Henry Bessemer first made steel by blowing air into a clay crucible containing molten pig iron. Since the days of Sir Henry Bessemer, the making, treating and shaping of steel has undergone remarkable improvements. Today, if you go to the BOF shop for example, you are talking about 92 to 94 percentage of yield in BOF.

So, that means if you charge 100 kg of iron into BOF you are going to get something like 92 to 94 (( )), extremely efficient process.

In the BOF, the refining inducts yield the converter and combination blown reactors. The refining is so fast, so rapid that you can get something like 2 to 3 kg of carbon per second - that is the rate of carbon removal we are talking about.

If you go and visit the casting bay, for example, in a thin slab casting shop today, you will find that you are talking about 6.5 to about 7 metric tons of steel being produced per minute per strand - so enormously efficient process.

Lot of developments went in the last 150 years and we have been able to reach here - achieve all these marks; because, we have relied, at all stages, heavily on fundamentals. The application of fundamental knowledge is extremely important in steering the technology further because there are going to be many challenges coming up in the future days for steelmaking. For example, stricter environmental regulations and burning of fossil fuels, specific energy consumption, recycling - these are some of the fronts where the steel makers will be more and more concerned to improve, and there we will see that the science based foundation will come to our rescue, and we will have to increasingly apply the fundamental knowledge in order to find the ways out.

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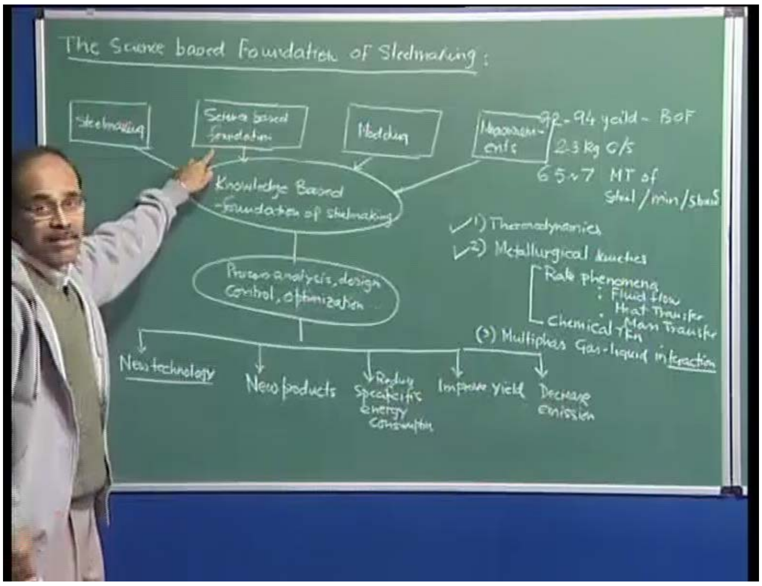

There is a huge knowledge based foundation of steelmaking, this I call as the knowledge based foundation of steelmaking. I will tell you what the components with a top down approach are. If your knowledge based foundation of steelmaking is good what you can do, you can do very well – you can do process analysis, design, control, optimize, and if you can do all these things then what is the net result? The net result is enormous, you can develop new technology; people are looking for direct steelmaking technology, people are looking for technology where they do not have to use coke to produce iron.

You can have new products, every day you see new alloy systems are being developed, new products are being marketed, and what was not possible 20-30 years ago, these are possible today. For example IF grade steel - who heard about IF grade steel 30-40 years ago? Today you can roll sheets, IF grade steels and make thin automobile sheets ready for automobile usage, and these have been the development of sustained application of knowledge.

You can reduce specific energy consumption, you can improve yield, and you can decrease emission and make the process more environmentally friendly.

Today, steel industries are looked down upon in view of the global warming, that we are one of the biggest polluters as far as the greenhouse gases are concerned and we have got to tighten our belt. You will find that in the context of reactor emission, decreasing emission, reducing specific energy consumption, process analysis design will play very big role and this is based on the knowledge based foundation.

What does this knowledge-based foundation comprise of? It has 4 different components, these are very important - steelmaking we say and this is the manufacturing, steelmaking or the alternative that I can put here in the box is the manufacturing, then we have the science based foundation, I have modeling and I have measurements; so manufacturing process, science based foundation, modeling and measurements - they constitute our knowledge based foundation; you cannot omit any of this.

So, you have to know the steelmaking technology, the processes - steelmaking processes - very well, you have to know the science based foundation of steelmaking.

When you talk of the science-based foundation - let us elucidate what it contains. The science based foundation of steelmaking contains, for example, metallurgical thermodynamics, that is why before one student or one takes a steelmaking course, it is so important for him or her to know about metallurgical thermodynamics which is introduced at the second year level or beginning of the third year level in engineering program.

We have to know about metallurgical kinetics and kinetics basically comprises of two components, we will subdivide kinetics into rate phenomena and chemical reaction. Rate phenomena again can be divided into three sections: fluid flow, heat transfer and mass transfer.

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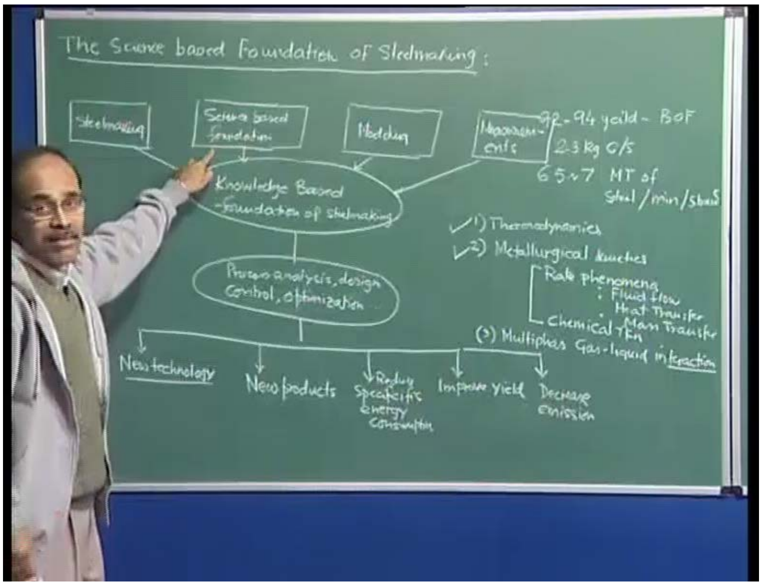

The science-based foundation of steelmaking is extremely vast and on top of that I can say, that multiphase or gas-liquid interaction. Basically, I am talking of gas metal interaction, because these interactions, as in the case of a basic oxygen furnace, these are reacting interaction; on the other hand, in the case of an argon molten steel interaction in a ladle, these are inner interaction - there is no chemical reaction.

So, you have to know thermodynamics well; we have to know metallurgical kinetics well, and there we see that it contains various subjects and each of these can be a topic on their own; in many engineering disciplines like mechanical engineering, chemical engineering, we have full-fledged one semester courses running on this.

You can imagine the breadth of the science and it is here that you get the largest insight; unless your science based foundation is good you will not be able to build models and if you do not built models, you will not be able to make any meaningful interpretation of the measurements that you might intend to carry out.

Therefore, we have to know these subjects well and most of you during your second year stages of metallurgical engineering program have been exposed to thermo-metallurgical thermodynamics, also, a subject titled differently may be transport phenomena or heat transfer. Many of you may not have really done an exhaustive treatment of metallurgical kinetics which comprises of so many things, but in an isolated way you are already exposed to it.

I intend to revise this very briefly, because as I said, they are subjects on their own and when I am delivering few lectures on the topic of steelmaking, perhaps it will be beyond any possibility to address these subjects on their entirety in the context of steelmaking.

Nevertheless, it is important for us to review certain key concepts before we can advance into the discussion of various other topics: basic oxygen steelmaking, ladle metallurgy, continuous casting, etcetera, because there we will see extensive application of the fundamentals. Before we can address all those advanced topics or relevant topics, it is worthwhile for us to briefly examine the key concepts of thermodynamics, metallurgical kinetics, that are relevant to steel making.

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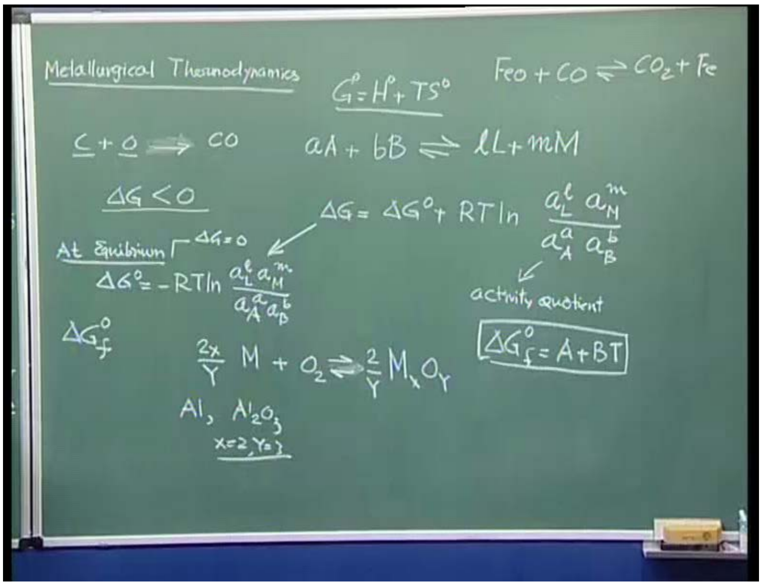

Let us talk very briefly about the key concepts in metallurgical kinetics. First, the metallurgical thermodynamics, this is a vast subject as I have mentioned, but in the context of steelmaking we apply metallurgical thermodynamics, particularly to compute or calculate the state of the equilibrium system.

In many instances we would like to see whether this process reached equilibrium or not, for example, we can say carbon-oxygen reaction is taking place in a basic oxygen steelmaking converter. Is the reaction closer to equilibrium? How far is it from the equilibrium? Is the reaction reaching equilibrium under certain temperature and pressure? What is the composition of the system in terms of its carbon concentration and oxygen concentration?

So, all these equilibrium calculations we wish to calculate, we wish to perform in the context of steelmaking. For example, I have a slag and I want to find out that how much iron oxide will be there in the slag in equilibrium with a certain given concentration of oxygen; so, I will carry out an equilibrium calculation and I am going to find out that what is the level of iron oxide content based on that equilibrium concentration.

It is not necessary that the calculation is going to match the measurements; the calculation is going to match measurements while the process has truly reached the state of equilibrium. Thermodynamics, as you all know it predicts about the feasibility of a process, thermodynamics depends on the initial and the final stages; it does not depend on the path.

To study the feasibility of the process we apply thermodynamic fundamental; so, whether oxygen will react with carbon or not, the feasibility of that process can be examined.

If the process is occurring then it is away from the equilibrium because at equilibrium there is no net rate of the process, it stands still.

So, thermodynamics cannot talk about rate, it can only talk about the feasibility of a process; it can talk about the state of equilibrium of a system.

When the process is occurring spontaneously from left to right, for example, carbon and oxygen reacting to form carbon monoxide, there comes the question of rate - that if it is reacting and the reaction is proceeding in one direction, if it is moving towards the equilibrium but not yet at equilibrium, then the question comes at what rate it is happening.

I have quoted that 2 to 3 kg of carbon per second is the rate of carbon elimination; that means, if you are talking of carbon-oxygen reaction, the reaction obviously is going in the forward direction and certainly it is not close to equilibrium which we represent basically as a reversible sign. When you are talking of 2 to 3 kg of carbon per second of removal, that means, we are talking about the reaction going in the forward direction.

Now, what is the condition for a process to go from the left or a reactant will be converted into a product; or in terms of a system generalized statement we can say that the free energy change is going to be less than 0; for the reaction in that case we can say is going spontaneously from left to right.

So, delta g essentially means that the product has a lesser free energy then the reactant and therefore this is a negative quantity and the free energy becoming negative gives an essential condition for spontaneity of a process.

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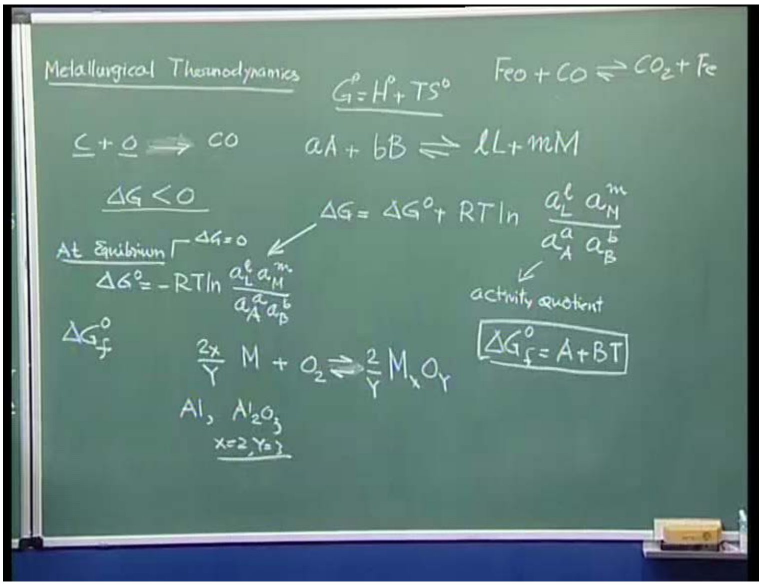

Metallurgical Thermodynamics

$G^o = H^o + TS^o$

$Feo + CO \rightleftharpoons CO_2 + Fe$

$C + O \Longrightarrow CO$

$aA + bB \rightleftharpoons lL + mM$

$\Delta G < 0$

$\Delta G = \Delta G^o + RT \ln \frac{a_L^l \, a_M^m}{a_A^a \, a_B^b}$

activity quotient

At Equilibrium $\Delta G = 0$

$\Delta G^o = -RT \ln \frac{a_L^l \, a_M^m}{a_A^a \, a_B^b}$

ΔG_f^o

$\frac{2x}{Y} M + O_2 \rightleftharpoons \frac{2}{Y} M_x O_Y$

$\boxed{\Delta G_f^o = A + BT}$

Al, Al_2O_3

$x = 2, Y = 3$

This criterion we have applied in many cases, now let us look at when you have a reaction like for example (Refer Slide Time: 16:15 for the example of reaction), and let us say that the reaction is occurring reversibly, that means, it is close operating, close to equilibrium and so this is the chemical reaction that we wish to represent.

So, we have a forward reaction, we have a backward reaction, they are competing with each other and soon the process is going to be under equilibrium condition.

In this particular case the expression that we have seen, we know from our knowledge of thermodynamics is: delta G free energy change for reduction - the standard free energy change, plus the gas constant logarithmic and then we say, it is activity of L raised to the power L activity of M raised to the power m activity of a raised to the power A and activity of B. We know that if the process is occurring close to equilibrium, in that case this, that is the product and reactant will have free energies which will be identical; so, there will be less quantity on the left hand side, will be close to or is equal to 0.

Now, this quantity this is called as we have known mind it I am not trying to introduce all these concepts in great detail because I am expecting that you know the subject, you have been exposed to thermodynamics; we are just revising it very quickly so that we find these concepts to be relevant later and we can remember them often as we advance or move on to different topics in steel making.

So, this is activity quotient and when the process is at equilibrium, the chemical reaction is in equilibrium; I have tried to equate, then we say that delta G naught is equal to this, as shown in the slide (Refer Slide Time: 18: 15). We have applied frequently to solve a variety of problems in thermodynamics particularly for steelmaking systems, for solutions and so on; this term we must denote that this concentration refers to the concentrations at this equilibrium stage. (Refer Slide Time: 18: 45)

So, one should normally represent this with a suffix like a l capital L comma e a small m capital M comma e and so on to indicate specifically that when you write delta G is equal to 0, at equilibrium delta G being equal to 0; so the equation translates to this particular form and this now refers to the equilibrium concentrations and as I have written here, these are essentially activities. (Refer Slide Time: 19:13).

Now, this concept the delta G and delta G naught have been extensively applied and what does the delta G naught essentially implies? It is the standard free energy change. When the elements or the reactants and the products are assumed to be in their standard state, which we say as a one atmosphere pressure, that is the condition at which delta G naught is going to be evaluated in terms of this.

In order to evaluate delta G naught we must understand that we have to have proper activity versus composition relationship, because we will not be able to directly measure activity; activity is a measure of chemical potential in the system. So, we can measure the concentration, based on that we will be able to evaluate these activities. Therefore, there are various models which are available to us which will allow us to convert activity in terms of relevant known parameters.

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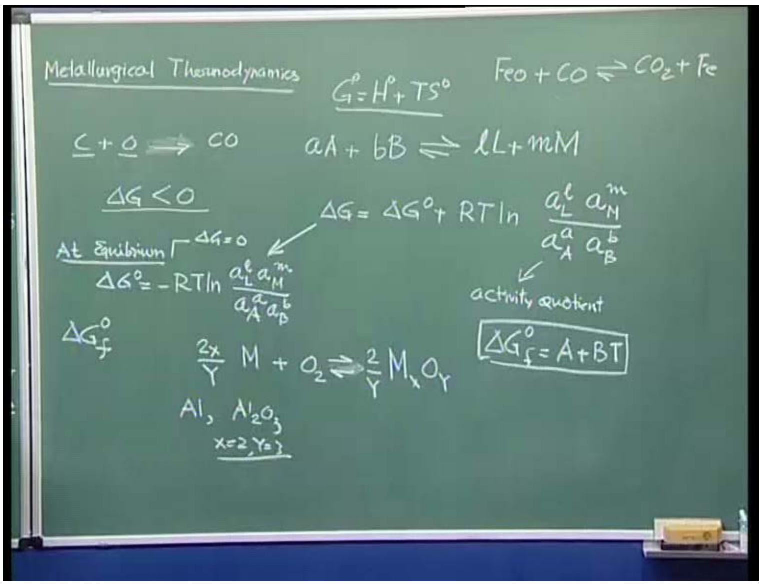

The system that I am talking about, in the context of, particularly solutions because we have talk of steelmaking, molten steel and slag can be visualized as solutions of multi-component system. If I say that activity is roughly equal to mole fraction, in that case, these activities can be converted into corresponding mole fractions and mole fractions can be easily converted into weight fractions, which are measurable quantities through any standard chemical devices. Before I talk about these activity composition relationships, whereby we can convert this equation or expression in a more meaningful form, let us explain the relevance of a parameter called the free energy of formation.

Many a times you will find that, in the later lecture, free energy of formation of compounds is extensively used. For example, if I start with a compound - you will require in order to carry out, what the difference is in the free energies - you will have to know that; the compound that you are taking, what is its free energy of formation.

For example, I can write down, say, a metal plus oxygen and then I say it is M x O y; therefore, it is going to be 2 by Y and this is going to be 2 x by Y, so this is a stoichiometrically balanced equation as you can see here.

This oxide I can use for example; what is the free energy of formation of this particular oxide? What is the relevance of this? Because, I may use this oxide in other calculations also. When I say that I take iron oxide and I want to find out the free energy change for this reaction CO 2 plus Fe, then ratio will come; then, what is the free energy of formation of this compound? Then only I will be able to find out the free energy. So, I will have to find out the free energy of formation of iron oxide, I will have to find out the free energy formation of carbon monoxide; I have to find out - because these are all compounds. Only when I know the free energy of formation of these compounds can I calculate the net free energy change for this particular reaction.

So, we have free energy formation of the sulphides, we have free energy formation of the chlorides, we have free energy formation of oxides, these are the standard information which are needed for carrying out many pyrometallurgical calculations, and I am going to just highlight this free energy formation in the context of oxides which, where it is stimulated, is known as an oxide Ellingham diagram to which all of you been exposed with.

Here, for example, I have written this x and y are the stoichiometric compound, so you can imagine that if I am talking about aluminium then what is a value of x? For aluminium, we know the corresponding oxide is Al 2 O 3, so turns out that x is equal to 2 and y is equal to 3, that is what I am talking about. If it is iron oxide, in that case you can also clearly see what will be the value of x and y; for all other oxides you should be able to visualize.

Now, standard free energy of formation; standard state means that the metal is in the pure state, the oxide is in the pure state. As a function of oxygen partial pressure has been measured by various investigators and for the sake of our convenience, so that we can carry out thermodynamic calculations very easily, these have been tabulated before us. In the Ellingham diagram if one assumes, delta G naught formation can be represented in terms of A and B T.

Now, you can see that this is a Gibbs free energy expression - Gibbs free energy functional is expressed in terms of combined expression of first and second law as enthalpy, temperature and entropy. If you assume that H naught, standard enthalpy and standard entropy of formations are not dependent on temperature, in that case, the free energy of formation of oxide materials can be expressed conveniently in terms of this particular equation. (Refer Slide Time: 24:45)

So, it indicates that the free energy of formation plotted against temperature will yield us a straight line in which A and B are constants, and that is what you actually see when you look at the Ellingham diagram where you have a number of straight lines drawn. I am going to now draw it very briefly and show you what the relative positions of lines in the figure are and what that really indicates.

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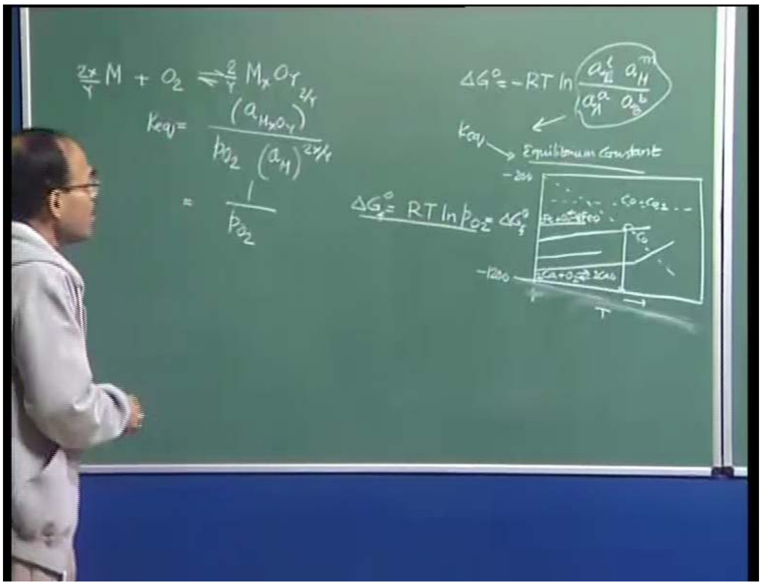

At equilibrium, when delta G is equal to 0, I have shown that delta G naught is equal to this parameter and this, as you all know, is called the equilibrium coefficient or equilibrium constant. If I look at this reaction, operating close to equilibrium, I should also write down the equilibrium coefficient and that is going to be activity of metal oxide raised to the power 2 by y, and then activity of oxygen; if you assume ideal behavior then this is equal to partial pressure of oxygen in the system and then we have activity of metal raised to the power 2 x y.

Since we are talking of standard free energy change, the standard state is pure for metal and metal oxide; therefore, their activity is going to be equal to one; so, this equation is going to come out to be partial pressure of oxygen.

Therefore, now one can measure the partial pressure of oxygen and delta G naught is going to be exactly equal to R T l n p o 2, the negative sign cancels out and that is what it is; therefore, we can now plot. Study the equilibrium of this reaction at 800 degree centigrade, 900 degree centigrade, 1000 degree centigrade, measure the partial pressure of oxygen, along the basis of that we can compute the delta G naught value because R is known, temperature is known, and partial pressure is the equilibrium partial pressure that we have measured through an adequate measuring device.

So, we should, at various temperature be able to plot; so temperature is measured - temperature at which the equilibrium has been obtained, corresponding delta G naught is estimated based on the measured c o 2 value and we should be able to draw.

Now, a straight line between the two, because of the fact that delta h naught f and delta s naught f are largely independent of temperature; if you look at it, in such plots you will find that there are straight lines and only the slope of the straight line changes when there is a phase change.

For example, we may have started with a solid, but then, at some point of time the solid may melt; so, otherwise when the phase is maintained continuously, during - in that case you will see that there is a straight and in this straight line behavior for different metal is different in the system. They need not be parallel as I have tried to indicate, in fact, there is a straight line, there is a line which is horizontal in the Ellingham diagram and there is a line which is actually with a negative slope, these are the two peculiar lines in the oxide Ellingham diagram.

So, this I say as delta standard free energy of formation of oxide, which is actually equal to R T l n p o 2.

So, these are the negative values, for example, this could be something like 1200 kilocalories per mole and this could be about minus 200; so, more negative values standard free energy formation.

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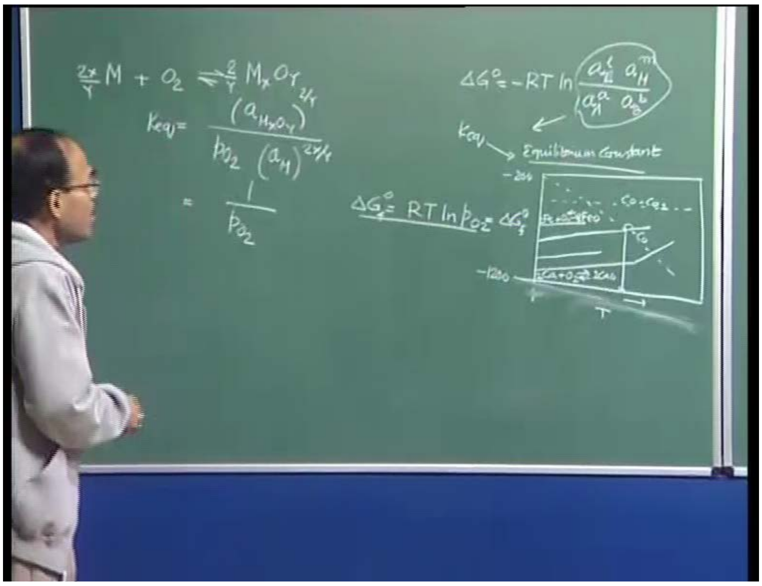

Therefore, this line indicates the values are here; standard free energy change values are far more negative than this value, which essentially indicates that a very little amount of oxygen will be able to oxidize this metal, and then it is possible for this particular metal.

So, very low lines in the figure, for example, will be for 2 calcium plus oxygen and note it so that we can compare the relative affinity of elements or the stability of oxides at a given temperature, all this is done for per mole of oxygen, and this is 2 CaO which essentially indicates that the calcium oxide is a very stable oxide.

On the other hand, if you look at iron oxide for example, 2 Fe plus O 2 it is going to be relatively (Refer Slide Time: 30:02), so this are all at equilibrium therefore I should (( )) maintain, and calcium, then will come magnesium, then will come aluminum, then will come titanium, then will come silicon, and if you go up and then you will see lead oxide, tin oxide, etcetera which are relatively weak oxides.

This line is a C CO line and this is the CO CO 2 line; you must be knowing that why the slope of the lines are different, because of simply the difference in the entropy values for this reaction and with a standard entropy that causes opposite slope for carbon monoxide and carbon dioxide lines, this you must be knowing.

So, we have similar figures which are tabulated and these figures give us important guidelines as far as pyrometallurgical processes are concerned.

For example, at this particular point when carbon-carbon monoxide line intersects this particular line, it tells us that it should be possible to. Below this line, the dotted line carbon-carbon monoxide line hooks by smaller position, lower position.

Therefore, above this temperature carbon monoxide is far more stable than the oxide which is corresponding to this particular line (Refer Slide Time: 31:22); therefore, it indicates that beyond this temperature, carbon monoxide will be able reduce this particular line for the oxide itself.

Now, we see that carbon monoxide line intersects the Fe Fe O line at 800 900 degree centigrade but it intersects the aluminium line for example at more than 2000 degree centigrade; that is why by looking at this diagram we can immediately conclude whether carbothermic reduction of a metal oxide is possible.

Similarly we have sulphide diagrams also, for mole of sulphide we can find out that what is the standard free energy change where you can take a metal, take sulphur gas and then form metal sulphide; exactly the same sort of graph that we can use and which is known as a sulphide Ellingham diagram, which gives us important clue regarding the pyrometallurgical or the sulphide smelting processes.

You see how smartly I have been able to convert, I made one assumption that activity of oxygen is equal to partial pressure of oxygen, an ideal behavior - ideal gas flow has been assumed and thereby I have been able to convert the oxygen activity into partial pressure; so I have assumed an activity composition relationship here.

We have various models particularly for steel melts and slag, one model for particularly solutions. When you are talking of activity, you know we are talking about activity of sulphur in steel melt, so, basically we are talking about activity of (( )) in a solution.

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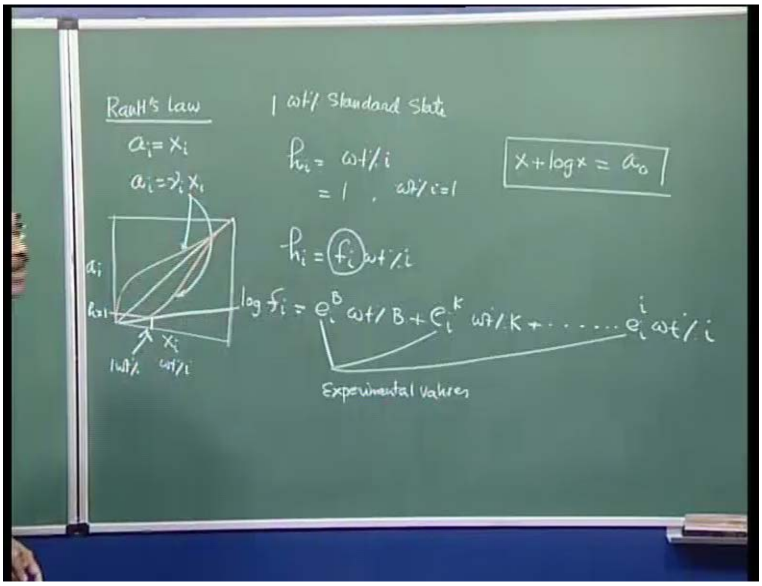

So, for various solutions we have various models available and as you all know Raoult's law is there; so, if you have concentrated solution, in that case you can say, activity is equal to actual activity of i is equal to fraction.

If you have departure from Raoult's law, you introduce what is known as activity of i is equal to, introduce an activity coefficient X i.

For example, iron and manganese, they occupy very close position in the periodic table, the atomic numbers are similar, crystal structures are similar, and so when you mix iron and manganese they form ideal solution. There you can say that if the mole fraction of manganese is 0.5, in that case its activity is also equal to 0.5 because iron and manganese ways.

There are only few solutions, few systems which are truly ideal in nature; most of the systems are non-ideal and departure from Raoult's law is expressed by what is known as the Henry's law where we say that activity is equal to activity coefficient.

This can enhance the activity, can get bigger than the mole fraction or can get smaller than the mole fraction depending on the value of gamma id activity coefficient. If activity coefficient is greater than 1 then we say it is a positive deviation, that means a mole fraction is 5, in that case the activity will feel like it is 0.7 0.8 or something like that because activity coefficient is greater than 1.

So activity coefficient greater than 1 causes positive deviation and activity coefficient less than 1. This is a Raoult's law line, activity is equal to mole fraction with an angle of 45 degree, but what is there - it is activity of i, it is mole fraction, and this is the negative deviation and this is the positive deviation of the Raoult's law; deviation behavior is explained on the basis of this expression (Refer Slide Time: 35:09).

Now, we can have different type of expressions also depending on what we choose as the standard state. In this case, the standard state refers to the pure element but we can also define a standard state, for example we can use Henry's law in the weight percentage standard scale.

So, 1 weight percentage standard scale, this is also a very popular scale and finds extensive application in dilute solutions and there we say that activity of a species i is approximately equal to weight percentage i. Therefore, activity becomes equal to unity when weight percentage i, so, weight percentage i is equal to 1 then the activity is equal to 1.

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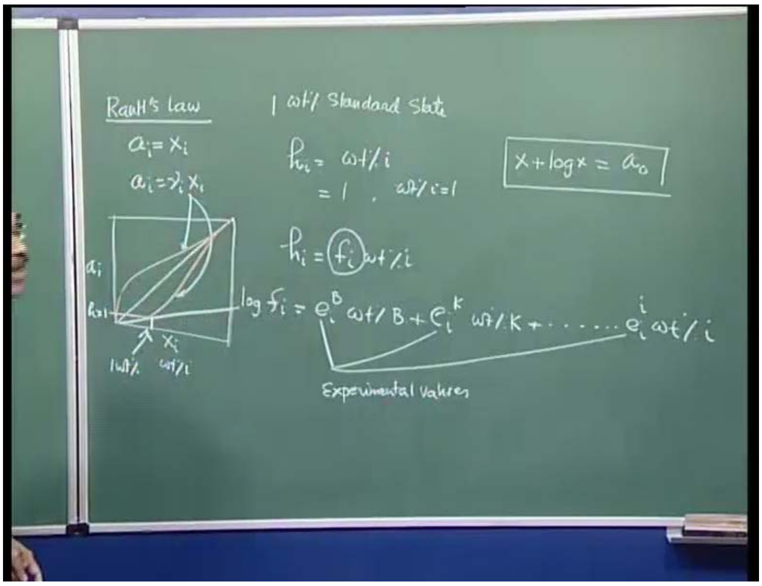

So, this is the henrian activity in 1 weight percentage scale; this is interpreted as the henrian activity in concentration or in the pure state when the elements are in their original solid state or an impure state and this is with reference to 1 weight percentage standard stage.

Standard free energy of formation if you calculate with respect to 1 weight percent standard state or with respect to pure element as the standard state, these values are not going to be related; so, their have to be some difference by some constant amount when the thermodynamic parameters are evaluated with respect to different standard states.

One standard state is like a frame of reference, you can do the coordinate transformation - from one frame of reference you can shift the origin and you can go to another frame of reference, so exactly the same thing is applicable here. It is based only on our convenience that we use sometimes pure elements as the standard state or sometimes pure compound as a standard state or sometimes 1 weight percentage as this one.

So, this will essentially tell that this activity is equal to 1, so this is mole fraction is equal to 1 and this is activity is equal to 1 so this is 1 and this is 1, so mole fraction is equal to, you can say it is not mole fraction but weight percentage; so this point is actually 1 weight percentage and this is actually activity is equal to 1. (Refer Slide Time: 37:15)

So, at the pure state we have reference with the pure elements or pure compounds, we can have one standard state defined and with respect to 1 weight percent standard state we can have again the same kind of an evaluation.

Now, if weight percentage is equal to 2, in that case what happens if Henry's law is obeyed? In that activity does not become equal to 2, it becomes equal to 1 because that is the maximum value of activity, that is actually possible.

Now, this assumes that up to 1 weight percentage Henry's law is obeyed in that 1 percentage standard scale, but if it deviates from that, in that case, we can introduce a parameter which is(( )) weight percentage of i and this f i actually given in terms of the composition of the (( )) and this is multi-component dilute solutions which have lot of impurities and lot of elements present; this sort of analysis is very meaningful in the sense that where we can take into an account the activity of influence of other elements on the activity of the species.

For example, we can say that there is one e i B into weight percentage B plus e i K weight percentage of K, this activity coefficient is given in terms of some e i's which are known as the interaction parameters. Again, these interaction parameters are tabulated in thermodynamic groups, this tells us e i B into weight percentage of B, therefore, it essentially tells us the influence of B on the activity coefficient of i.

Now, you must understand that when I have iron and sulphur for example, I have an activity, I can measure the activity of sulphur.

When you introduce carbon into it, it becomes now three body problem, so there is carbon sulphur interaction, iron sulphur interaction and carbon iron interaction.

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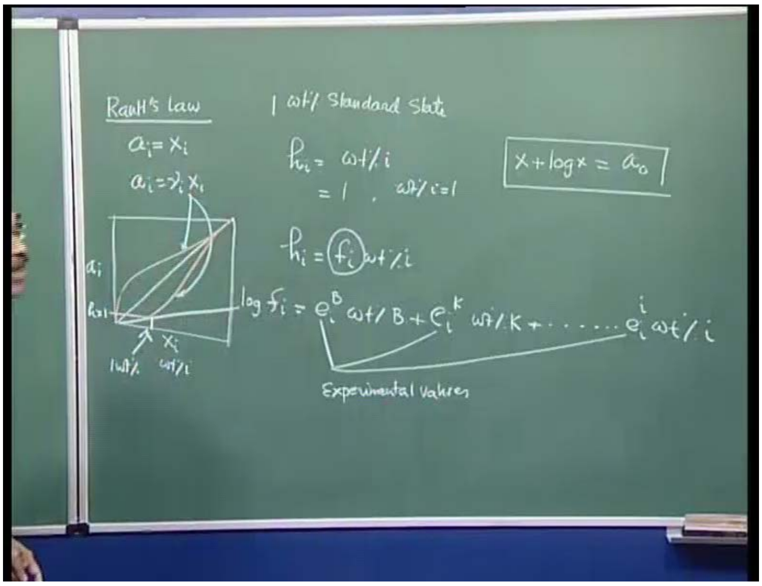

As result of which, in a two component system - iron and sulphur, whatever is the activity that I measure, in the presence of carbon the same activity will not be measured.

Therefore, you understand that the introduction of third element will either increase or decrease the activity of the second element and therefore, all the solutes present in steel melt will have influence on the activity of a given species.

For example, if you take the activity of oxygen, so the activity of oxygen will be dependent on the activity of sulphur, on the activity of phosphorus, how much phosphorus is there? How much silicon is there? How much manganese is there?

So, all these things that is dictated by f i and the dependents of f i in terms of the weight percentage of various species, so you can interpret this to be as oxygen, i is oxygen here and B may be silicon, K may be aluminium; so, we have a multi-faceted influence of all the solute elements over any element and thereby its activity can either increase or decrease.

Now, this essentially tells influence of B on i, we also have parameters called e i i which is called as the self-interaction parameter and the self-interaction parameter sometimes may become 0 and sometimes may not become is equal to 0, but they nevertheless come into the picture when you formulate f i in this particular form.

So, this parameter can be known, but if there are self-interaction parameters then I can know how much percentage of manganese, for example, is there and then I can say that these experimental values are available to us; so, these are known, at this composition B K etcetera can be known.

As you see here that f i itself is a function of w i, therefore, when you solve this kind of an equation we get an equation of this particular form in which a naught is equal to a constant, because the log term is there - log f i; therefore, we can convert the equation in terms of this unknown parameter, so x we can interpret as the weight percentage of i x plus log x i which is known as the transient equation.

You cannot solve this equation analytically so you have to use computational routines and you can imagine that so many such equations are going to be there in multi-component system, one equation will be there for oxygen, another equation will be there for sulphur, another equation will be there for manganese and you know lot of activities you are going to calculate, as a result of which you may carry out many other calculation.

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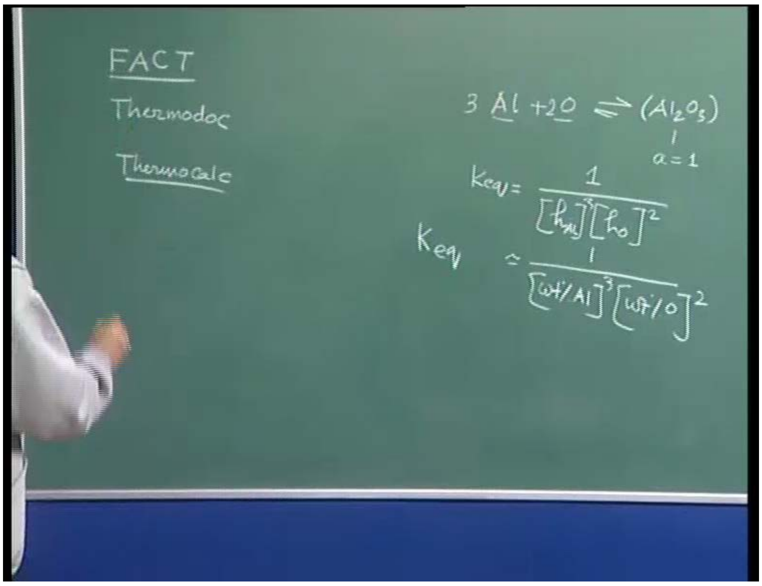

For example, I have aluminum, the deoxidation calculation - aluminium plus oxygen, it giving you Al 2 O 3. If you assume that there is no formation of any slag, just pure aluminum forms, there is no silica, there is no calcium oxide, pure alumina is there, there is no reaction taking place simultaneously. So, aluminum reacts with dissolved oxygen and produces, so we can say 2 times dissolved oxygen and 3 atoms of aluminum producing 1 molecule of Al 2 O 3, and if this is found in the pure phase - there is no formation of any compound, then we can say that is where the activity is equal to Al 2 O 3 is equal to 1.

Then I can write down that the K equilibrium is actually activity, so this is equal to 1 and then I can say this is going to be henrian activity because it is dilute solution, does not obey; so this is h Al and then we have h o and then this is equal to 3 and then this is equal to 2.

If there is an indication that whatever oxygen is there below 1 weight percentage, that you all know as I have indicated it is about the saturation limit, is about 0.20 weight percentage; as an approximation we can say that this is equal to weight percentage aluminum cube and weight percentage oxygen square.

Now, free energy of formation of Al 2 O 3 is available to us. Note that this free energy formation and the free energy of formation in the Ellingham diagram are not going to be identical because here the standard state is different, there the standard state was pure aluminum but here the standard state is 1 weight percentage.

So, the value of free energy of formation for this equation cannot really be directly obtained from the oxide Ellingham diagram, this is a point, because we have changed the standard state.

So, this sign is very important for us, this is an approximate sign, otherwise, if there is a departure you should have introduced the parameter f i into this particular calculation and you should have made the calculation little bit more tedious.

If I substitute in this particular form, in that case, I should be able to use a simple calculator and solve it, but the moment I introduce h i values here, h Al and h o, the calculation becomes complex. We have to take into account manganese concentration, sulphur concentration, silicon concentration and as a result of which we will require computational routines to solve because we generate equations of this particular form which one cannot really solve by analytical means.

Therefore, we have to have today large computational routines in order to calculate the state of the equilibrium; give us the composition, give us the phase concentration, etcetera; many computational packages are available.

So, maybe you have heard about this software which is called the FACT, a Canada based software for thermodynamic calculations, facilities for chemical thermodynamics, calculation of chemical thermodynamics. Then we have thermodoc, this is an enormous software which is available, thermocalc which is another software. There are lots of software platforms, which are now available where we can perform many complex thermodynamic calculations considering multiphases, various types of solutions and innumerable number of possibilities to predict the various states of equilibrium that you may be interested to know.

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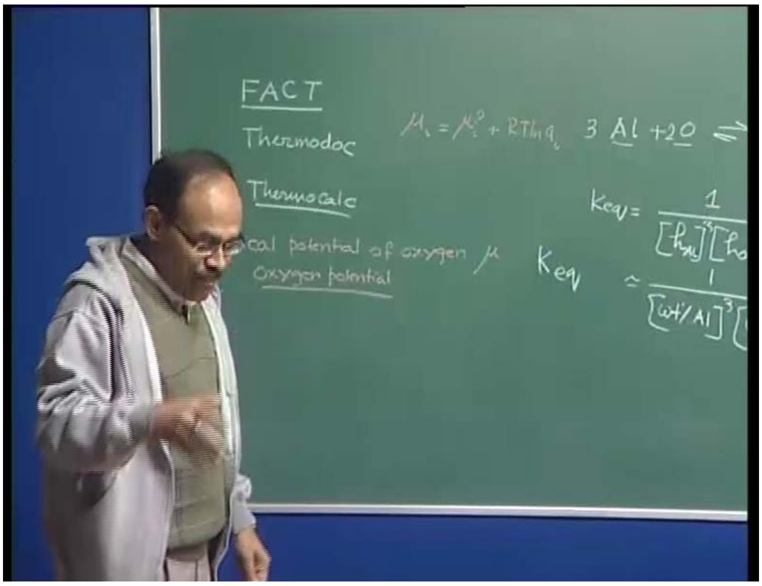

Now, beyond this, one important parameter that we often talk in oxygen steelmaking is a term called oxygen chemical potential or chemical potential of oxygen. This is a very important term which we frequently use and our notation for chemical potential is mu; mu is basically written for a species i is equal to mu i naught plus R T l n a i; that is the chemical potential of - this is the standard formulation accepted, this is the standard chemical potential of the species, this is the activity and this is a chemical potential under consideration at a given condition.

Transport of species from one phase to another phase is driven by chemical potential, so we have thermal potential; thermal potential is created because of a temperature gradient, heat will flow when there is a temperature difference, mechanical potential is going to be created by heat difference or pressure differences; similarly mass transport is going to be created because of gradient in chemical potential which is directly related with activities.

You have studied this famous Darken’s couple; we have seen there that in terms of concentration, it is possible for us to transfer carbon from a region of lower concentration to a region of higher concentration; because, of the simple fact that in the lower concentration region the activity of carbon is much more because of the presence of many other solute elements which have influenced through the activity coefficients and enhanced the activity of carbon.

It is not the absolute value of concentration that dictates the rate of mass transport, rather the possibilities of mass transport or transfer of species from one phase to another phase is going to be dictated by the chemical potential.

Therefore, chemical potential is a very important term in the context of mass transfer studies and also oxygen potential is a very important term, it tells us what the level of oxygen potential in the system is, it tells us the oxidizing power of the system.

For example, oxygen potential in the blast furnace is extremely small - ten raised to the minus 19 atmosphere, this tells us that the environment within the blast furnace is extremely reducing; on the other hand, in oxygen steelmaking converter the oxygen potential because of the presence of the oxygen is tremendously large.

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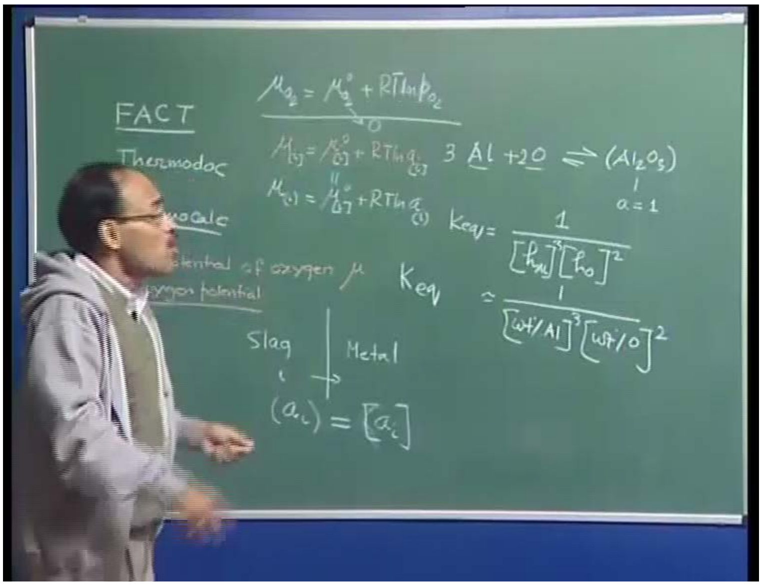

If I have a slag here and if I have metal here and a species i is being transferred from here to here, an equilibrium is going to be achieved, so you visualize it like this - temperature is higher here, temperature is lower here, so heat will flow in this direction and heat flow will come to a standstill when the temperature becomes identical.

If the species i has higher chemical potential in slag, lower chemical potential in slag, the transport is going to take in the direction of slag to metal and a chemical equilibrium, that was the thermal equilibrium when we were talking about temperature; now, a chemical equilibrium is going to be established at the interface, that means, there is going to be no net movement across the interface, provided the activity is identical or chemical potential is identical here.

Therefore, if we assume that the same one is, say, this is metal which I denote as this and this is slag and if I assume that the same standard state condition applies, so I am going to denote by the same bracket although these are first brackets, this is the third bracket; because I am making assumption that the same standard chemical potential holds good or applies to both slag and the metal phase and then we can say that R T l n activity of a i in the slag phase. (Refer Slide Time: 51:11).

Now, since these two quantities have been assumed to be identical, so equality of chemical potential essentially implies that, when there is a chemical equilibrium, activity in the slag phase of i is exactly equal to the activity of i in the metal phase and that is the essential condition of chemical potential.

Now, we can find out chemical potential. Chemical potential of oxygen will be defined as mu o 2 this is equal to mu o 2 0 standard plus R T l n O 2, that is again fundamental definition of chemical potential, and because it is in the pure state, so if we assume that there is only oxygen available then this term is equal to 0; therefore, the chemical potential is going to be directly related with the partial pressure of oxygen.

We can calculate that chemical potential for oxygen potential with respect to this oxygen also and then translate it, convert it to this particular scale because here the standard state and here the standard states are different.

So, this is the fundamental definition of oxygen potential and we can calculate the activity of oxygen and the oxygen potential here and then translate it to this particular format.

So, wherever there is oxygen it is possible for us to calculate the chemical potential of oxygen and thereby tell that what the oxidizing power of the system itself is.