Non-Metallic Materials

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Module - 02

Defects, and reaction kinetics of non - metallic materials, carbonaceous materials

Lecture - 09

Laws of thermodynamics, reaction kinetics (Part - 2)

Welcome to my course Non-Metallic Materials and this particular lecture, I will be talking part of module 2, which is defects and reaction kinetics of non metallic materials as well as Carbonaceous materials, where the Thermodynamics Laws and Reaction Kinetics will be described.

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Concept covered

- Enthalpy, entropy, and free energy are defined and explained
- Condition of equilibrium and mass action expressions
- Chemical stability of binary compounds
- Charged interfaces and Debye lengths
- Kinetic considerations
- Gibbs – Duhem relationship for binary oxides: an illustration

In the last lecture as a part 1 of lecture 8, I already discussed about enthalpy, entropy and free energies followed by the condition of equilibrium and mass action expressions. And in this lecture, mainly I will take four topics; the first one is the chemical stability of the binary compounds, then I will introduce the charge interface and the concept of Debye lengths. Then kinetic consideration of particularly the oxide systems that will be described and finally, the application of Gibbs Duhem relationship will be illustrated.

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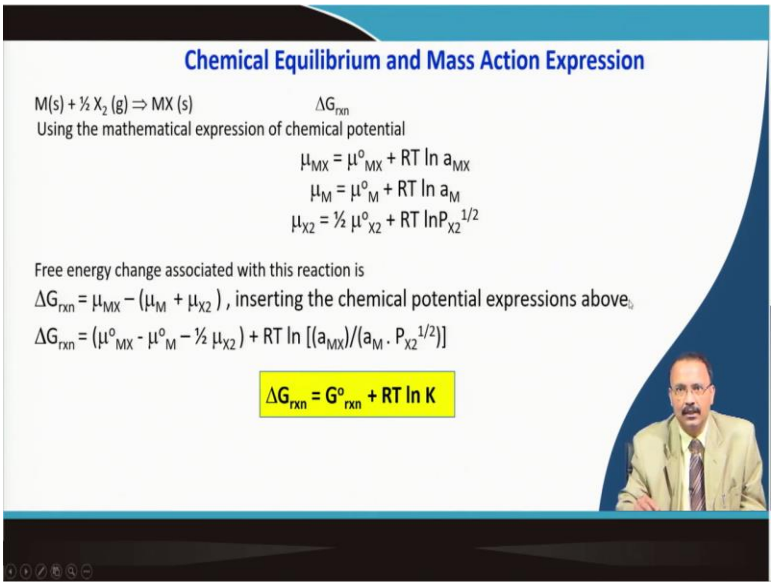

Chemical Equilibrium and Mass Action Expression

$M(s) + \frac{1}{2} X_2 (g) \Rightarrow MX (s)$ ΔG_{rxn}

Using the mathematical expression of chemical potential

$$\mu_{MX} = \mu^o_{MX} + RT \ln a_{MX}$$
$$\mu_M = \mu^o_M + RT \ln a_M$$
$$\mu_{X2} = \frac{1}{2} \mu^o_{X2} + RT \ln P_{X2}^{1/2}$$

Free energy change associated with this reaction is

$\Delta G_{rxn} = \mu_{MX} - (\mu_M + \mu_{X2})$, inserting the chemical potential expressions above

$\Delta G_{rxn} = (\mu^o_{MX} - \mu^o_M - \frac{1}{2} \mu_{X2}) + RT \ln [(a_{MX})/(a_M . P_{X2}^{1/2})]$

$$\boxed{\Delta G_{rxn} = G^o_{rxn} + RT \ln K}$$

So, in earlier part of my lecture, sometimes I go little bit fast, because of the time constraint. So, if you find particularly any topic difficult; then in a live session, I will clarify your doubts. And I will try to go a bit slow, so that these concepts are well illustrated.

Because for you it is important to understand the basic concepts whatever I am teaching in these module courses. So, I will start with the old expression, where a solid is reacting with a gaseous component to form a ionic solid and denoted by MX, and the free energy change for this reaction that is define as del G rxn.

Now, I have already defined what is chemical potential; so for each individual component, if you write the chemical potential equation, so that will take the form something like this. So, mu of MX this compound, this will be mu for it is standard state plus gas constant into respective temperature and log of its activity.

Similarly, you can write the expression for the pure metal and you can also write the expression for the gaseous component. And in case of gaseous component, the activity that is replaced by the partial pressure of this gas; this already I have described in the part 1 lecture. Now, if you want to estimate the free energy change associated with this particular reaction, so that is just the difference of the chemical potentials.

So, the chemical potential of the reactant minus chemical potential of the constituent solid and the gaseous phase; so, you do that and then put the relevant equations of mu MX and other component. And then you will find that this free energy change for this reaction, this is this will form this particular expression.

And the first term under this parenthesis, you can termed it as the free energy under standard condition that is G 0 rxn and RT will remain as it is an ln of this one is the equilibrium constant. So, that is denoted by K. I thought that I should explain the genesis of this reaction; because in the last lecture I have used this particular relation.

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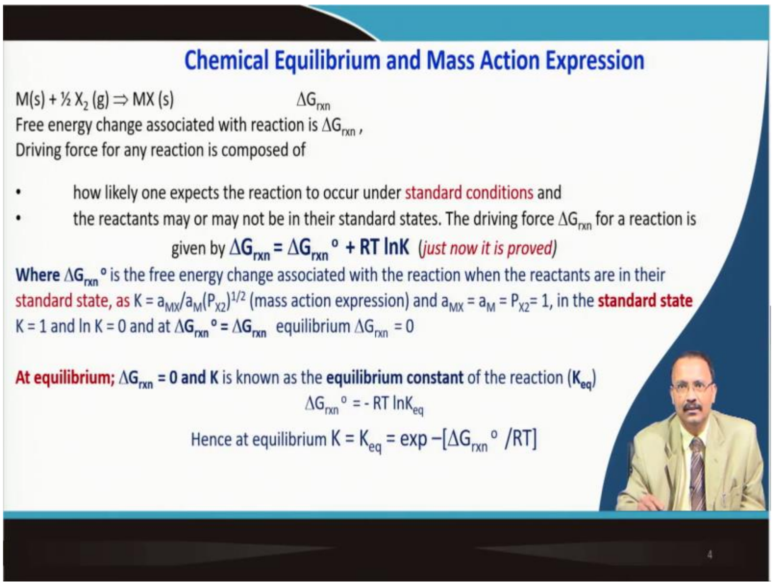

Chemical Equilibrium and Mass Action Expression

$M(s) + ½ X_2 (g) \Rightarrow MX (s)$ ΔG_{rxn}

Free energy change associated with reaction is ΔG_{rxn} ,

Driving force for any reaction is composed of

- how likely one expects the reaction to occur under standard conditions and
- the reactants may or may not be in their standard states. The driving force ΔG_{rxn} for a reaction is given by $\Delta G_{rxn} = \Delta G_{rxn}{}^{o} + RT \ln K$ *(just now it is proved)*

Where $\Delta G_{rxn}{}^{o}$ is the free energy change associated with the reaction when the reactants are in their standard state, as $K = a_{MX}/a_M(P_{X2})^{1/2}$ (mass action expression) and $a_{MX} = a_M = P_{X2} = 1$, in the **standard state** $K = 1$ and $\ln K = 0$ and at $\Delta G_{rxn}{}^{o} = \Delta G_{rxn}$ equilibrium $\Delta G_{rxn} = 0$

At equilibrium; $\Delta G_{rxn} = 0$ **and K** is known as the **equilibrium constant** of the reaction (K_{eq})

$$\Delta G_{rxn}{}^{o} = - RT \ln K_{eq}$$

$$\text{Hence at equilibrium } K = K_{eq} = \exp -[\Delta G_{rxn}{}^{o} /RT]$$

Now, we will continue with this and again write the same old equation solid plus gas and it is forming this compound. And again the free energy change associated with this reaction is del G rxn. Now, if you consider the driving force for this reaction; the first one is; how really one expect the reaction to occur in standard condition.

So, when the condition is standard; that means the activity of MX and activity of metal as well as partial pressure of the gas is 1. So, partial pressure is 1 atmospheric. And second one the reactants, it is possible that may or may not be in their standard state; so, the driving force for this reaction as I have just now proved. So, this is followed by this particular relation.

So, in the earlier explanation, I can find out that del is missing; but del G will be there. So, del G rxn will be there. So, this is the free energy change associated with the reaction when the reactants are in their standard state, right. So, the equilibrium constant is given by this activity of MX divided by activity of metal and gaseous constituent and as standard state as I told that this activity is 1.

So, eventually your K will be 1 and ln K will be 0. So, whatever you are getting that is nothing, but the standard state free energy.

So, at equilibrium, your del G rxn is 0. So, when this del G rxn is 0; then the equilibrium constant is known as, this K constant is known as equilibrium constant and it is denoted by K equilibrium so I can write the relation. So, then your standard state reaction free energy will be minus RT ln K equivalent. So, if you just want to evaluate this term K equivalent; that is exponential of minus del G rxn 0 divided by R T.

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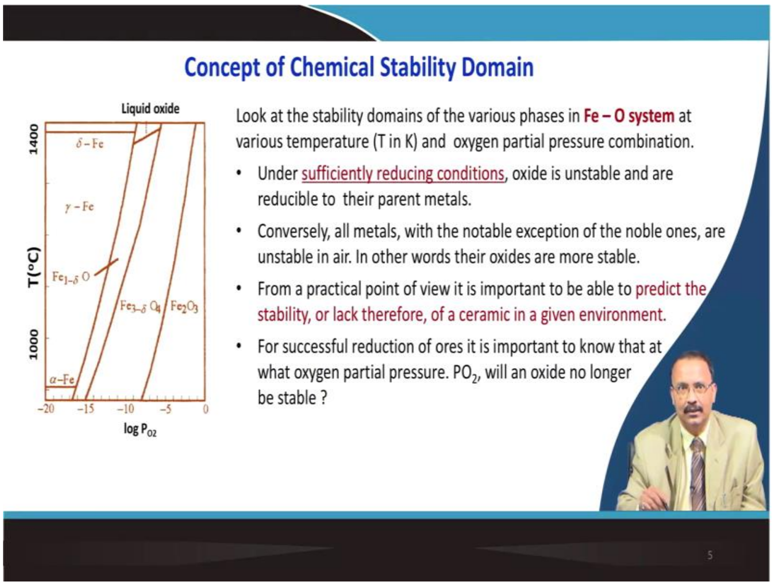

Concept of Chemical Stability Domain

Look at the stability domains of the various phases in **Fe – O system** at various temperature (T in K) and oxygen partial pressure combination.

- Under sufficiently reducing conditions, oxide is unstable and are reducible to their parent metals.
- Conversely, all metals, with the notable exception of the noble ones, are unstable in air. In other words their oxides are more stable.
- From a practical point of view it is important to be able to predict the stability, or lack therefore, of a ceramic in a given environment.
- For successful reduction of ores it is important to know that at what oxygen partial pressure. PO_2, will an oxide no longer be stable ?

Now, this concept now we will be using to understand the chemical stability domain, which is so important for the oxide material. You know that the oxide material to know the chemical stability is very important. You would like to know whether the material will get oxidized or you would also like to know whether a ore, which is a basically oxide that you can reduce down to the constituent metals so for that it is important.

So, this is a typical diagram of temperature versus partial pressure of oxygen for an iron oxygen system. So, at various temperatures, you can see the phase phases, the single component phases that you can see; at lower temperature as well as lower pressure, you see this iron is stable.

So, oxide is unstable, so iron is stable. And as you increase the oxygen partial pressure progressively, it is oxidized to a Fe-O; some non-isometric will also be there. And followed by ferrosoferric oxide and finally, it will form $Fe_2 O_3$ so the these three oxides will form.

So, one notable exception is for the noble metal which does not get oxidized; but most of the metal gets oxidized, particularly at higher oxygen partial pressure. So, we need to determine the stability of this oxide, based on the thermodynamic concept. So, as I said for the successful reduction of the ore, it is important to know at what oxygen partial pressure this oxide will no longer be stable. So, then it will form the metallic part.

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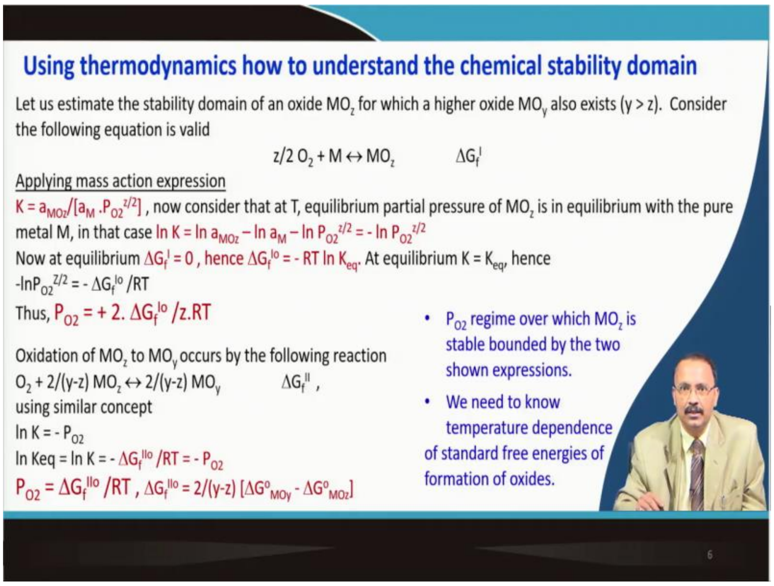

Using thermodynamics how to understand the chemical stability domain

Let us estimate the stability domain of an oxide MO_z for which a higher oxide MO_y also exists ($y > z$). Consider the following equation is valid

$$z/2\ O_2 + M \leftrightarrow MO_z \qquad \Delta G_f^{I}$$

Applying mass action expression

$K = a_{MOz}/[a_M . P_{O2}^{z/2}]$, now consider that at T, equilibrium partial pressure of MO_z is in equilibrium with the pure metal M, in that case $\ln K = \ln a_{MOz} - \ln a_M - \ln P_{O2}^{z/2} = - \ln P_{O2}^{z/2}$

Now at equilibrium $\Delta G_f^{I} = 0$, hence $\Delta G_f^{Io} = - RT \ln K_{eq}$. At equilibrium $K = K_{eq}$, hence

$-\ln P_{O2}^{Z/2} = - \Delta G_f^{Io} /RT$

Thus, $P_{O2} = + 2. \Delta G_f^{Io} /z.RT$

Oxidation of MO_z to MO_y occurs by the following reaction

$O_2 + 2/(y-z)\ MO_z \leftrightarrow 2/(y-z)\ MO_y \qquad \Delta G_f^{II}$,

using similar concept

$\ln K = - P_{O2}$

$\ln Keq = \ln K = - \Delta G_f^{IIo} /RT = - P_{O2}$

$P_{O2} = \Delta G_f^{IIo} /RT$, $\Delta G_f^{IIo} = 2/(y-z)\ [\Delta G^o_{MOy} - \Delta G^o_{MOz}]$

- P_{O2} regime over which MO_z is stable bounded by the two shown expressions.
- We need to know temperature dependence of standard free energies of formation of oxides.

So, we will use the thermodynamical concept to understand the chemical stability. And here as I said that, one oxide is there which is MO_z and a higher oxide of its also possible. So, we started with Fe O; then we thought that Fe_2O_3 or $Fe_3\ O_4$ that is also possible.

So, some kind of relationship exists. So, I will write an equation, oxygen is reacting with the metal to form the MO_z and then I will apply the mass action expression. So, I will write the constant K that is related with the activities of the constituents, reactant as well as the initial constituent. And remember this is at a particular temperature T. And as you know that this metal and metal oxygen, metal oxides, they are in equilibrium.

So, the activity of these two that can be taken as one; so, I have just written as equation of ln k and eventually that is related with a partial pressure of oxygen. At equilibrium again as I showed that, for this particular reaction; reaction number 1, this del G f is 0. So, your standard free energy change is nothing, but RT ln of K equivalent.

So, as we told that at equilibrium K is equal to K equivalent; hence you can get the partial pressure of oxygen to the power z by 2 is the expression which is taking this standard free energy change 0 divided by RT. So, you can get a partial pressure of oxygen expression.

Similarly, this particular oxide, this is again oxidize to MO y. So, I have written a balanced equation here and again I put in the similar concept, I have evaluated the value of K, which is now a partial pressure of oxygen the log of K. I have written the equilibrium K equilibrium expression and found this expression. And this oxygen partial pressure for this higher oxide is given by this relation.

And this change of the free energy in standard condition or equilibrium condition; so this is given by this relation. So, here basically I got two partial pressure of oxygen regime, where these respective oxides are still. So, now, I can apply it to a practical system, the system that already I have shown; but in order to get the value of the partial pressure of oxygen where these oxides are stable, I need to know the temperature dependence of the standard free energies.

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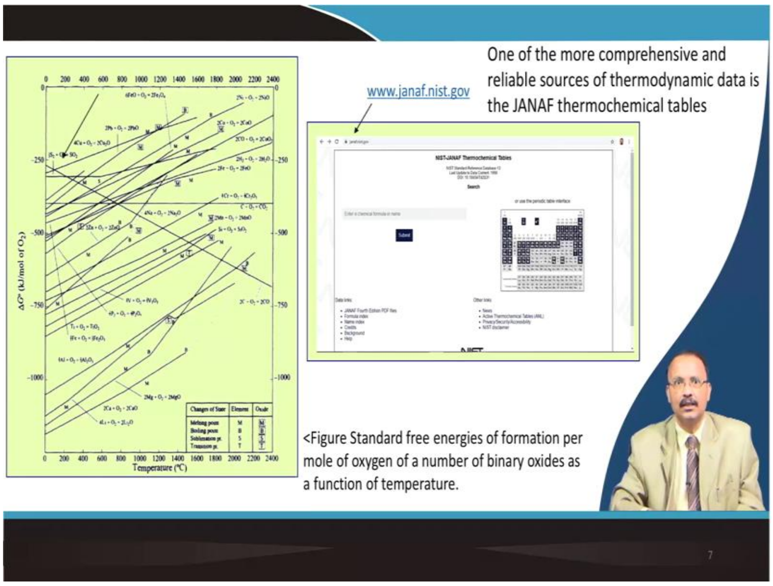

One of the more comprehensive and reliable sources of thermodynamic data is the JANAF thermochemical tables

www.janaf.nist.gov

<Figure Standard free energies of formation per mole of oxygen of a number of binary oxides as a function of temperature.

So, usually that is given, the del G 0 as a function of temperature. So, as you can see that a complicated curve is there; but NIST in US they have developed this JANAF thermochemical tables and where you can just put the constituent elements and you get all possible values related to this type of calculations. So, that is a one thing which is important.

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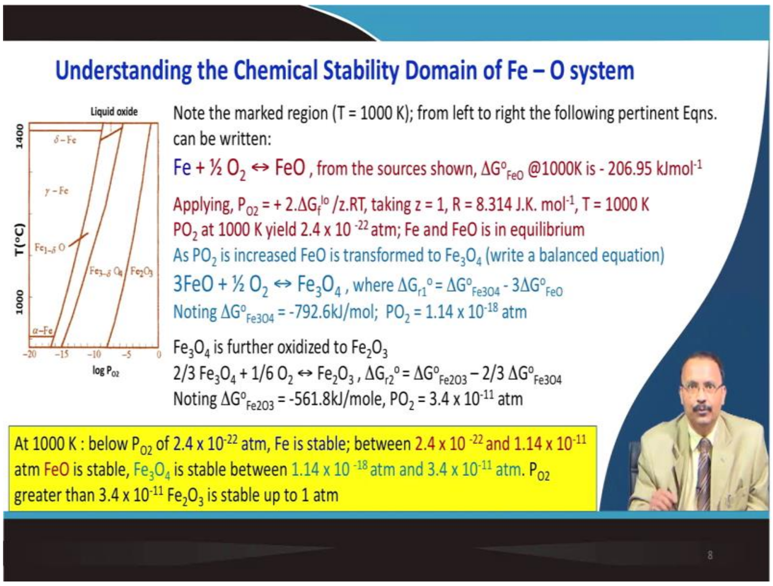

Understanding the Chemical Stability Domain of Fe – O system

Note the marked region (T = 1000 K); from left to right the following pertinent Eqns. can be written:

$Fe + ½ O_2 \leftrightarrow FeO$, from the sources shown, ΔG^o_{FeO} @1000K is - 206.95 kJmol^{-1}

Applying, $P_{O2} = + 2.\Delta G_f^{lo} /z.RT$, taking z = 1, R = 8.314 J.K. mol^{-1}, T = 1000 K

PO_2 at 1000 K yield 2.4 x 10 $^{-22}$ atm; Fe and FeO is in equilibrium

As PO_2 is increased FeO is transformed to Fe_3O_4 (write a balanced equation)

$3FeO + ½ O_2 \leftrightarrow Fe_3O_4$, where $\Delta G_{r1}^o = \Delta G^o_{Fe3O4} - 3\Delta G^o_{FeO}$

Noting ΔG^o_{Fe3O4} = -792.6kJ/mol; PO_2 = 1.14 x 10^{-18} atm

Fe_3O_4 is further oxidized to Fe_2O_3

$2/3\ Fe_3O_4 + 1/6\ O_2 \leftrightarrow Fe_2O_3$, $\Delta G_{r2}^o = \Delta G^o_{Fe2O3} - 2/3\ \Delta G^o_{Fe3O4}$

Noting ΔG^o_{Fe2O3} = -561.8kJ/mole, PO_2 = 3.4 x 10^{-11} atm

At 1000 K : below P_{O2} of 2.4 x 10^{-22} atm, Fe is stable; between 2.4 x 10 $^{-22}$ and 1.14 x 10^{-11} atm FeO is stable, Fe_3O_4 is stable between 1.14 x 10 $^{-18}$ atm and 3.4 x 10^{-11} atm. P_{O2} greater than 3.4 x 10^{-11} Fe_2O_3 is stable up to 1 atm

So, this is the relation, I mean this is the expression figure for iron oxide oxygen system. And now we want to know the stability of the phases at low temperatures, say temperature is 1000 Kelvin. And again I have written this relation, first iron will get oxidized. And then using the earlier concept, I have estimated what will be the partial pressure value. Then again partial pressure is increased.

So ferrosoferric oxide is formed here as you can see. So, again I have written a balanced equation and calculate the partial pressure of oxygen. Then again the ferrosoferric oxide will oxidize to iron oxide $Fe_2 O_3$. Then again I have written this relation estimated the partial pressure of oxygen. And finally, now I can say that at 1000 K, below the partial pressure of oxygen which is 2.4 10 raise to minus 22 atom. Iron metallic form is stable, which is quite understandable at very low oxygen partial pressure.

Then you change the respective pressure and you see whether this phase is stable Fe O stable or $Fe_2 O_3$ is $Fe_3 O_4$ is stable or finally, $Fe_2 O_3$ is stable. So, this kind of calculation it will give you a vivid idea about the kind of stability that you are getting in the oxide system.

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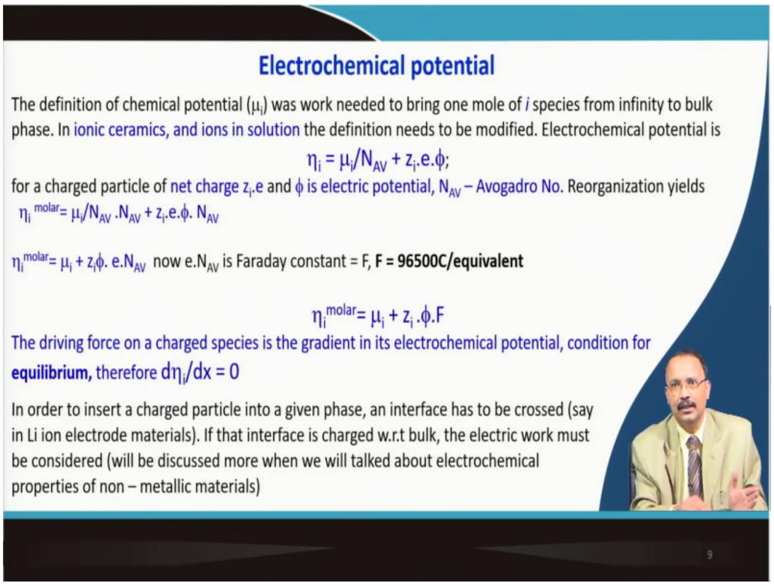

Electrochemical potential

The definition of chemical potential (μ_i) was work needed to bring one mole of *i* species from infinity to bulk phase. In ionic ceramics, and ions in solution the definition needs to be modified. Electrochemical potential is

$$\eta_i = \mu_i/N_{AV} + z_i.e.\phi;$$

for a charged particle of net charge $z_i.e$ and ϕ is electric potential, N_{AV} – Avogadro No. Reorganization yields

$$\eta_i^{molar} = \mu_i/N_{AV} .N_{AV} + z_i.e.\phi. N_{AV}$$

$\eta_i^{molar} = \mu_i + z_i\phi. e.N_{AV}$ now $e.N_{AV}$ is Faraday constant = F, **F = 96500C/equivalent**

$$\eta_i^{molar} = \mu_i + z_i .\phi.F$$

The driving force on a charged species is the gradient in its electrochemical potential, condition for **equilibrium,** therefore $d\eta_i/dx = 0$

In order to insert a charged particle into a given phase, an interface has to be crossed (say in Li ion electrode materials). If that interface is charged w.r.t bulk, the electric work must be considered (will be discussed more when we will talked about electrochemical properties of non – metallic materials)

Now, in ceramic, the chemical potential is slightly different what exactly we are interested in. So, we are interested in a electro chemical potential, not only the chemical potential; because in deriving the chemical potential term, we told that a species, when you are bringing from infinite to a bulk which is in uncharged condition and that is its chemical potential.

But actually the ceramic system many of them, they are ironically conducting service. So, it is a charge system, so we are bringing something from outside. So, you will have to consider this electric potential term to get what we call electro chemical potential; it is a summation of a molar quantity of chemical potential and this electro chemical potential.

So, I have done some kind of jugglery here by multiplying it to the Avogadro number to get a molar electrochemical potential. And finally, this Avogadro number and this charge e is nothing, but Faraday constant. So, this molar electrochemical constant gets the form something like this. And remember the driving force for these charge species, the gradient of its electrochemical potential is important.

And at equilibrium, the differentiation of this electrochemical potential with distance is 0. So, in order to insert a charged particle in a given phase, an interface has to be crossed, right. It is important for the battery, where lithium ion is coming and going inside the electrode phase.

So, if the interface is charged with respect to bulk, the electric work must to be considered. So, we will discuss more this when I will be talking about the electrochemical properties of the material; but this concept is important.

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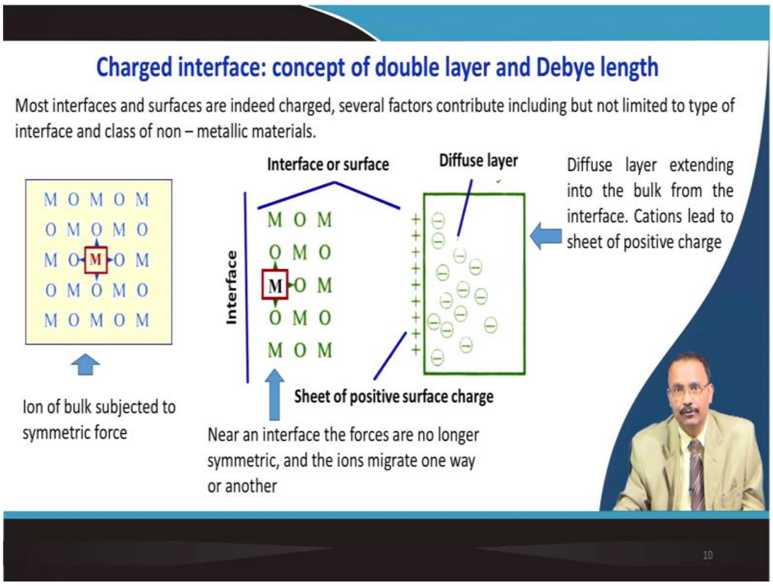

Charged interface: concept of double layer and Debye length

Most interfaces and surfaces are indeed charged, several factors contribute including but not limited to type of interface and class of non – metallic materials.

Interface or surface

Diffuse layer

Diffuse layer extending into the bulk from the interface. Cations lead to sheet of positive charge

Ion of bulk subjected to symmetric force

Sheet of positive surface charge

Near an interface the forces are no longer symmetric, and the ions migrate one way or another

Now, once I talked about the charged interface; then you can see the charged interface all these, these metal bonds are properly satisfied. But when you are creating an interface, you are breaking this metal from here; then these dangling bonds are there. So, these dangling bonds are unsatisfied.

So, if I consider it is a positive middle cation; so the surface will be positively charged. So, something in the bulk of the material must be negative in order to maintain the electric charge neutrality. So, usually when a metal you are considering, say metal interfacial or a metal interfacial let us consider this.

So, there must be some kind of metallic vacancy and I have already described the metallic vacancy is negative. So, it will form some kind of diffused double layer. So, when this interface is there, I mean where this interface is there; then this negative charge will be more and towards a bulk, if you move out, then you will get this is a diffuse condition and a double layer will be formed.

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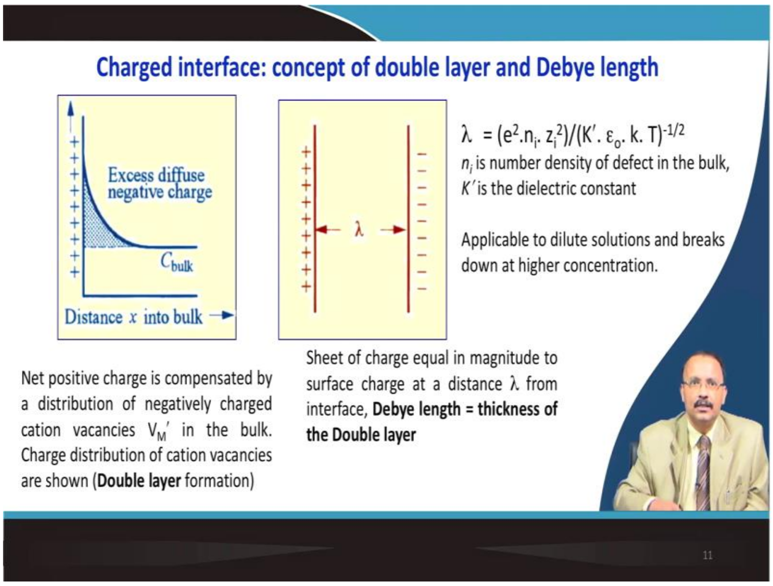

Charged interface: concept of double layer and Debye length

$\lambda = (e^2.n_i.\ z_i^2)/(K'.\ \varepsilon_o.\ k.\ T)^{-1/2}$

n_i is number density of defect in the bulk, K' is the dielectric constant

Applicable to dilute solutions and breaks down at higher concentration.

Net positive charge is compensated by a distribution of negatively charged cation vacancies V_M' in the bulk. Charge distribution of cation vacancies are shown (**Double layer** formation)

Sheet of charge equal in magnitude to surface charge at a distance λ from interface, **Debye length = thickness of the Double layer**

Now, this double layer is something like this. So, you have negative charge here and this is your positive charge. So, where it is exactly gets neutralized in the bulk, this distance we call it is a Debye length and one can estimate the Debye length by this expression, which takes the number density of defects in the bulk.

Then (Refer Time: 18:01) is basically its balancing, dielectric constant is involved; epsilon 0 is the free space dielectric permittivity, Boltzmann constant and the respective temperature. So, this Debye length is important and this Debye length is nothing, but the thickness of the double layer that actually is being formed.

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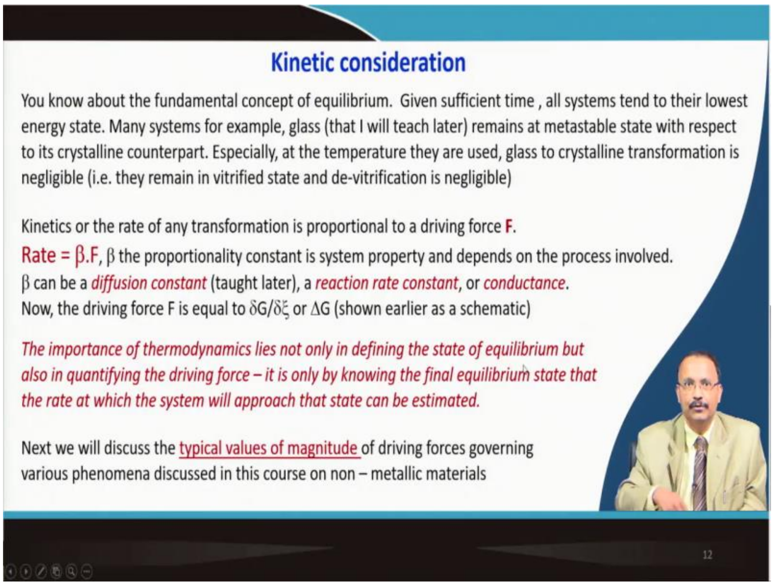

Kinetic consideration

You know about the fundamental concept of equilibrium. Given sufficient time , all systems tend to their lowest energy state. Many systems for example, glass (that I will teach later) remains at metastable state with respect to its crystalline counterpart. Especially, at the temperature they are used, glass to crystalline transformation is negligible (i.e. they remain in vitrified state and de-vitrification is negligible)

Kinetics or the rate of any transformation is proportional to a driving force **F**.

Rate = $\beta.F$, β the proportionality constant is system property and depends on the process involved.

β can be a *diffusion constant* (taught later), a *reaction rate constant*, or *conductance*.

Now, the driving force F is equal to $\delta G/\delta\xi$ or ΔG (shown earlier as a schematic)

The importance of thermodynamics lies not only in defining the state of equilibrium but also in quantifying the driving force – it is only by knowing the final equilibrium state that the rate at which the system will approach that state can be estimated.

Next we will discuss the typical values of magnitude of driving forces governing various phenomena discussed in this course on non – metallic materials

So, having known this, let us now consider the kinetic consideration; you must know the fundamental concept of the equilibrium that you already know. So, if sufficient time is given, then all system they try to go to their minimum energy state; but many of the system they do not go, like for example, glass.

So, glass is a metastable system; if allowed for a prolonged time, then glass will devitrified, it will form crystal in mass. So, we need to know the kinetic consideration; so, time dependence. So, it is very simple way the rate can be defined is a linear equation. So, beta is a proportionality constant which is a system property and this depends on the process that is involved.

It could be diffusion coefficient, it could be a reaction rate constant, it could be conductance and the driving force as I have shown that, this is nothing but change in this free energy with some kind of reaction coordinate. So, the importance of the thermodynamics that lies not only in defining the state of the equilibrium, but also quantify the driving force.

It is only by knowing that the final equilibrium state that, the rate at which the system will approach that the state can be estimated. So, if you now see the typical values of the magnitude of this kind of driving force; then this will be a bit clearer for you. So, I go back to the slide, sorry I am sorry.

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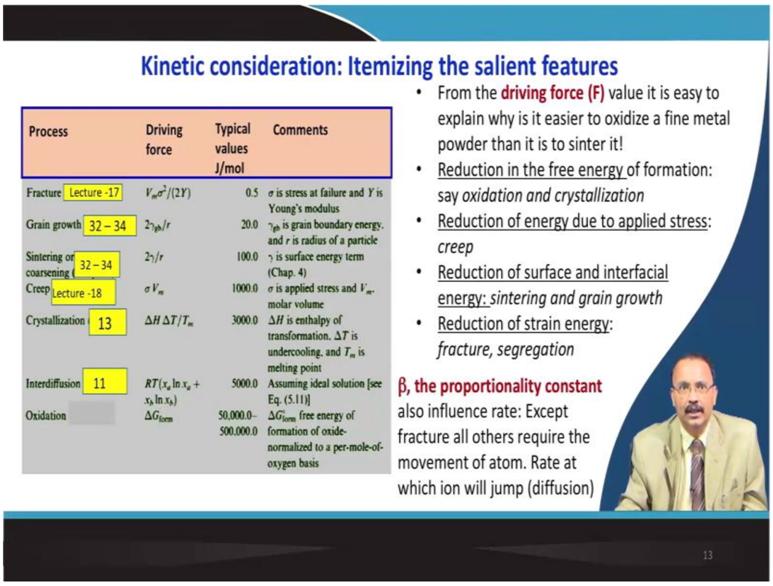

Kinetic consideration: Itemizing the salient features

Process	Driving force	Typical values J/mol	Comments
Fracture Lecture -17	$V_m\sigma^2/(2Y)$	0.5	σ is stress at failure and Y is Young's modulus
Grain growth 32 – 34	$2\gamma_{gb}/r$	20.0	γ_{gb} is grain boundary energy, and r is radius of a particle
Sintering or coarsening 32 – 34	$2\gamma/r$	100.0	γ is surface energy term (Chap. 4)
Creep Lecture -18	σV_m	1000.0	σ is applied stress and V_m, molar volume
Crystallization 13	$\Delta H \Delta T/T_m$	3000.0	ΔH is enthalpy of transformation, ΔT is undercooling, and T_m is melting point
Interdiffusion 11	$RT(x_a \ln x_a + x_b \ln x_b)$	5000.0	Assuming ideal solution [see Eq. (5.11)]
Oxidation	ΔG_{form}	50,000.0–500,000.0	ΔG°_{form} free energy of formation of oxide-normalized to a per-mole-of-oxygen basis

- From the **driving force (F)** value it is easy to explain why is it easier to oxidize a fine metal powder than it is to sinter it!
- Reduction in the free energy of formation: say *oxidation and crystallization*
- Reduction of energy due to applied stress: *creep*
- Reduction of surface and interfacial energy: *sintering and grain growth*
- Reduction of strain energy: *fracture, segregation*

β, the proportionality constant also influence rate: Except fracture all others require the movement of atom. Rate at which ion will jump (diffusion)

So, if you see that driving force for all different types of process which I will be describing in this course for example, fracture, brain growth, sintering, creep mechanism, crystallization, inter diffusion; then the respective driving force, as you can see they have different driving force, but see the typical values here. So, the for example, fracture, it is a very small values as compared to the oxidation, right.

So, the driving force it is very easy to explain that, why it is easier for a fine metal to get oxidized, but to sinter it; because you see the sintering is having relatively typical large values. So, reduction of free energy formation, it is important for oxidation and crystallization; reduction of free energy you apply stress, it is relevant for creep; reduction of surface and interfacial energy, sintering and grain growth it is important.

Reduction of strain energy, that is important in fracture and segregation of dopamine. So, this is this all things I will try to correlate in my forth coming lecture, where you can see the connection of this thermo dynamical concept and the actual process that is relevant in oxide systems.

Apart from this driving force, that proportionality constant beta is also important. So, it influence the rate, as you can see the rate is beta into the driving force. So, except fracture, all others require the movement of atom, right; so, rate at which the atom will jump; so this is nothing but diffusion, which I will be taking in my next class.

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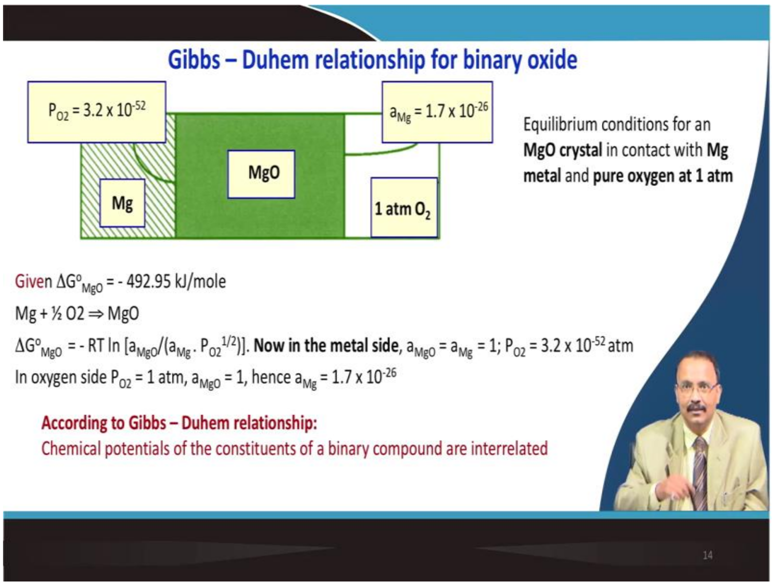

Gibbs – Duhem relationship for binary oxide

Equilibrium conditions for an **MgO crystal** in contact with **Mg metal** and **pure oxygen at 1 atm**

Given $\Delta G^o_{MgO} = -492.95$ kJ/mole

$Mg + ½ O2 \Rightarrow MgO$

$\Delta G^o_{MgO} = - RT \ln [a_{MgO}/(a_{Mg} . P_{O2}^{1/2})]$. **Now in the metal side,** $a_{MgO} = a_{Mg} = 1$; $P_{O2} = 3.2 \times 10^{-52}$ atm

In oxygen side $P_{O2} = 1$ atm, $a_{MgO} = 1$, hence $a_{Mg} = 1.7 \times 10^{-26}$

According to Gibbs – Duhem relationship:

Chemical potentials of the constituents of a binary compound are interrelated

Finally, let us talk about the so called Gibbs Duhem relationship for chemical thermodynamics and let us see how we can apply it here. So, here is a simple system magnesium and it is getting oxidized. So, magnesium oxide is here and then at other end, you have oxygen in typical one atmospheric pressure. So, equilibrium condition for magnesium oxide crystal, that is in touch with magnesium metal and pure oxygen which is 1 atmosphere.

So, we know that this del G 0 from this table, the NIST table we can take this value; we will write this relation, magnesium is getting oxidized. We will write the expression for the free energy at standard state which is given by this. Now, as you can see in the metal side, these two are in equilibrium. So, magnesium activity and magnesium oxide activity is 1 and partial pressure you can always calculate from the relation, the way I have showed you earlier.

So, that is coming about 3.2 into 10 to the power minus 52 atmospheric, just work it out and see whether it is correct. So, I have written it here; in oxygen side, then partial pressure as I have already told it is 1 atmosphere, but activity on magnesium oxide changes, sorry magnesium oxide is also 1 here, this activity will remain same, but activity of magnesium you can calculate.

So, we can estimate this as 1.7 into 10 to the power minus 26. So, the activity of these constituents you are estimating based on our earlier knowledge. Now, Gibbs Duhem relationship it says that, the chemical potential of the constituent of a binary compounds are interrelated.

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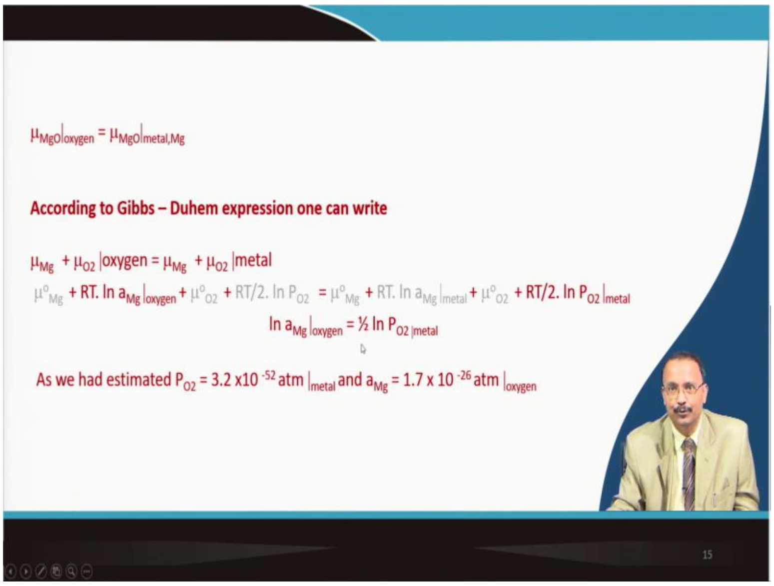

$\mu_{MgO}|_{oxygen} = \mu_{MgO}|_{metal,Mg}$

According to Gibbs – Duhem expression one can write

$\mu_{Mg} + \mu_{O2}\,|oxygen = \mu_{Mg} + \mu_{O2}\,|metal$

$\mu^{o}_{Mg} + RT.\ \ln a_{Mg}|_{oxygen} + \mu^{o}_{O2} + RT/2.\ \ln P_{O2} = \mu^{o}_{Mg} + RT.\ \ln a_{Mg}|_{metal} + \mu^{o}_{O2} + RT/2.\ \ln P_{O2}|_{metal}$

$\ln a_{Mg}|_{oxygen} = ½ \ln P_{O2\,|metal}$

As we had estimated $P_{O2} = 3.2 \times 10^{-52}$ atm $|_{metal}$ and $a_{Mg} = 1.7 \times 10^{-26}$ atm $|_{oxygen}$

Now, let us see how it works. So, here the chemical potential of magnesium oxide in oxygen environment; so that is the right part and chemical potential of magnesium oxide in metal, so that is the left part; here I will apply the Gibbs Duhem relationship. So, I will just divide the constituents.

So, chemical potential of magnesium and chemical potential of oxygen in the oxygen side, and similarly magnesium potential and oxygen potential in the metal side these two are equal. So, if these two are equal, I will write the corresponding expression. And here as you can see that, all these faded things, they all cancel out; this part and this part it will cancel out this and this also will be cancelled out.

So, we are leaving with RT ln activity of magnesium in oxygen equal to half log partial pressure of oxygen in metal. So, this relation you are getting. Earlier you see we have already measured the partial pressure of oxygen which is 3.2 10 to the minus 52 atmosphere.

And activity of metal is this much; so it I just leave it on you, just to see whether in this kind of reaction your Gibbs Duhem expression that is valid; because you will get exactly the same value if you put in this particular relation.

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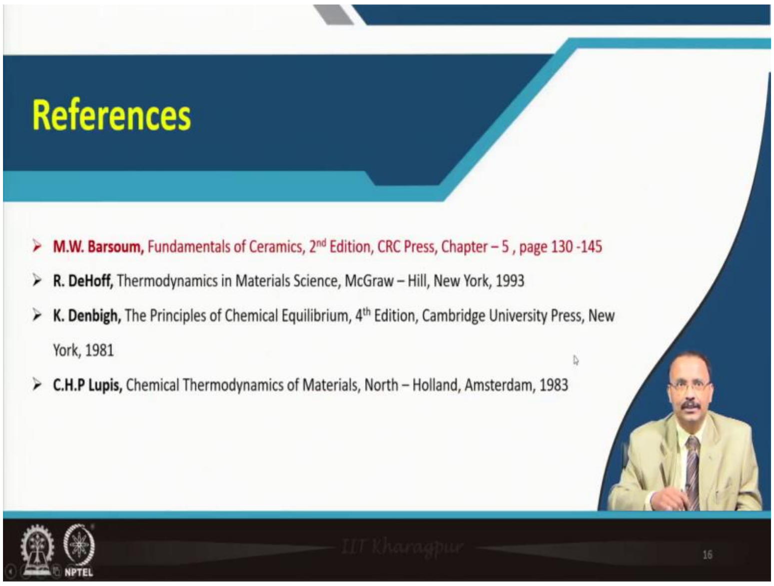

References

- **M.W. Barsoum,** Fundamentals of Ceramics, 2nd Edition, CRC Press, Chapter – 5 , page 130 -145
- **R. DeHoff,** Thermodynamics in Materials Science, McGraw – Hill, New York, 1993
- **K. Denbigh,** The Principles of Chemical Equilibrium, 4th Edition, Cambridge University Press, New York, 1981
- **C.H.P Lupis,** Chemical Thermodynamics of Materials, North – Holland, Amsterdam, 1983

So, here it tells about the thermodynamic concepts I have covered in this particular course. So, this is your study material mostly Barsoum and chapter 5 and these many pages are there to clarify the idea. And apart from that also, you can go through this references, which I think will be very relevant to strengthen the concept that you have developed.

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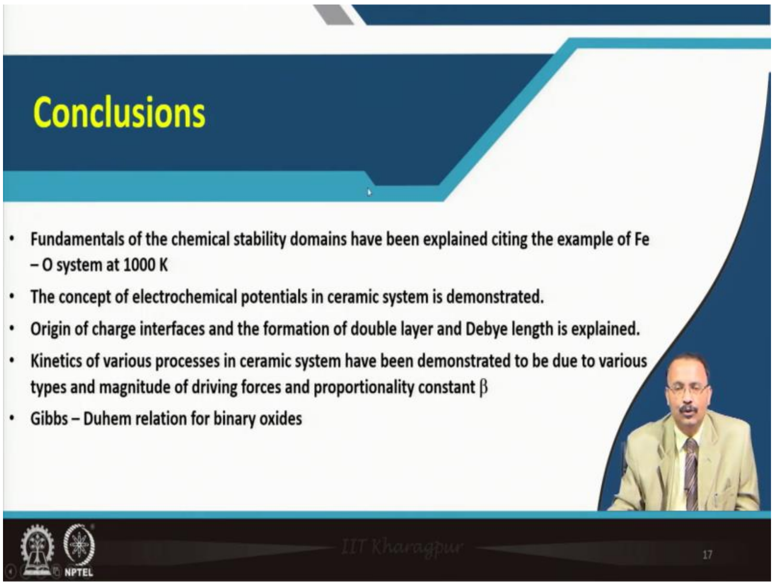

Conclusions

- Fundamentals of the chemical stability domains have been explained citing the example of Fe – O system at 1000 K
- The concept of electrochemical potentials in ceramic system is demonstrated.
- Origin of charge interfaces and the formation of double layer and Debye length is explained.
- Kinetics of various processes in ceramic system have been demonstrated to be due to various types and magnitude of driving forces and proportionality constant β
- Gibbs – Duhem relation for binary oxides

So, we started with the fundamentals of chemical stability domains and that has been explained by citing the example of iron oxygen system which is measured at 1000 Kelvin. And this is just an example; you can apply the same principle in many of the simple oxide system.

So, I just leave it on you to do these calculations and you will have to get the value of the free energy change in the standard condition as a function of temperature and that NIST table may be useful for you. And then you can depending on the transformation, this that is by the way is the transformation from metal to oxygen and maybe in certain cases higher oxides are also there.

For example, in iron I have told you that, iron first oxidized to iron oxide and then eventually to ferrosoferric oxide and then eventually to $Fe_2 O_3$. So, this kind of relation if it is there, it is important for you to know the phase stability that, at what partial pressure which phase is forming and this is also temperature dependent.

So, at a particular temperature, you need to know the value of the free energy change and like way the stability of the oxide system you can very well estimate. So, this part is just one example I have showed. And how to calculate the partial pressures from the relevant data like del G rxn 0 is one of them apart from that the gas constant and the temperature dependence.

So, T will also be there, so you will have to calculate this partial pressure. So, that thing is important. The second concept for electrochemical potential is particularly important in oxide system, oxide ceramic system. So, it is not only this is the consideration for a uncharged surface; but a charged surface you will have to calculate the electric potential involved.

And as I said that when I will be talking about electro chemical system, which is relevant for this non-metallic materials; particularly when I will be talking about the batteries, then the usefulness of the this relation, this chemical potential its variation with chemical potential and electric potential, this will be important, I mean this will be useful for you to understand. So, that is also developed.

And origin of the charge interface and the formation of the double layer, particularly the Debye length; this is explained in terms of a material, where I considered that the interstitial cation that is moving towards the surface. And it is forming some kind of charge interface. And as I told that eventually the system will have to be completely electrically neutral.

So the vacancy of metal vacancy, cation vacancy which is negatively charged, so that will act as a counter ion; and for the solid system, I tried to show you that how exactly it works; but it is implication is far-fetched, I mean many other system it is quite important for you to understand the effect of this double layer.

So, in ceramic processing for example, this is very important. In case of ceramic processing, we usually form during slip casting; for example, you will have to make a ceramic powder which is suspended in a liquid. And this liquid suspension will have to be stable, it should not get precipitated. So, and partial precipitation is also not allowed. So, when it is eventually dispersed inside the system, we call this is as a charged system which is completely de flocculated. So, it is a stable system.

And this stable system is used for slip casting. So, you use this slip in a plaster mold, you just pour it and get the article out of it. So, that is one idea of using it. Apart from that, you can do electrophoretic deposition. So, it is a stable suspension. So, you apply electric field. So, charged particle will go and it will start to deposit on a conducting substrate. So, many types of applications are there.

But for this particular lecture, I concentrated myself that, within the material itself what kind of your defect is moving, pausing a charge interface and how the counter defects they are maintaining the charge balance and how the double layer is forming and how to estimate the thickness of the double layer. But I did not talk about ceramic in a suspension, where your counter ion is coming from a fluid which is there in the suspension.

So, that thing is the origin of the charge interface, that of course is not very simple to just tell that this is what is exactly the origin; there are as we progress I will talk more about it; and the kinetics of various process that you have seen that has been demonstrated due to mainly two factors and one is the driving force f and for various process, the driving force of course is different and also a proportionality constant, which is defined as beta.

And progressively I will tell you that how exactly it works; how this concept we can translate for our other lectures, how we can correlate it that is part of my job. And finally, Gibbs Duhem relation for the binary oxide that is defined and based on the thermodynamical calculations I have shown that, indeed the partial pressure calculation is in line to the so called Gibbs Duhem relationship.

Thank you for your attention [FL].