Electroceramics
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Lecture - 7

So, welcome to this new lecture. So, I will just go through the review of last lecture.

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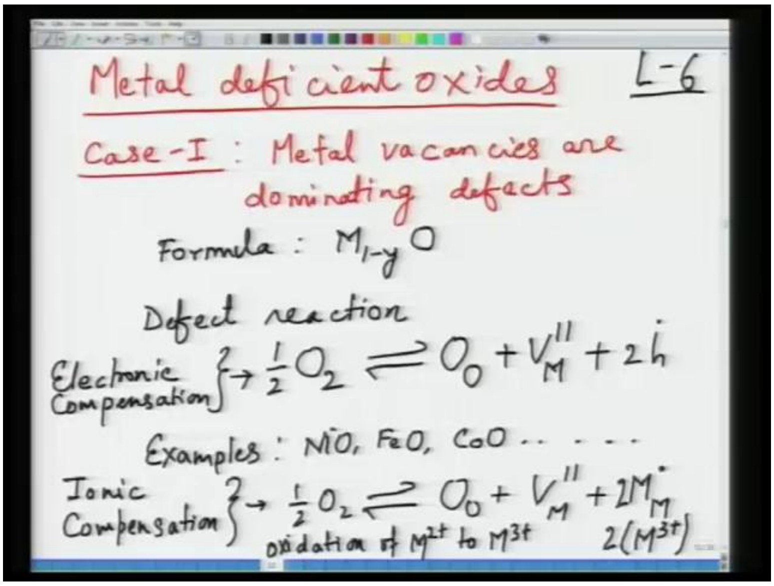

Metal deficient oxides

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Case-I : Metal vacancies are dominating defects

Formula : $M_{1-y}O$

Defect reaction

Electronic Compensation } → $\frac{1}{2}O_2 \rightleftharpoons O_O + V_M'' + 2h^{\bullet}$

Examples : NiO, FeO, CoO .. . . .

Ionic Compensation } → $\frac{1}{2}O_2 \rightleftharpoons O_O + V_M'' + 2M_M^{\bullet}$

oxidation of M^{2+} to M^{3+} $2(M^{3+})$

In the last class, we looked at the defects in non stoichiometric oxides. So, we started talking that the metal deficient oxides and we took two cases. So, the first case in which metal vacancies were dominating defects. So, in this case again, you will have either the metal vacancy formation accompanied by that whole creation or a metal vacancy formation accompanied with oxidation of the metal side.

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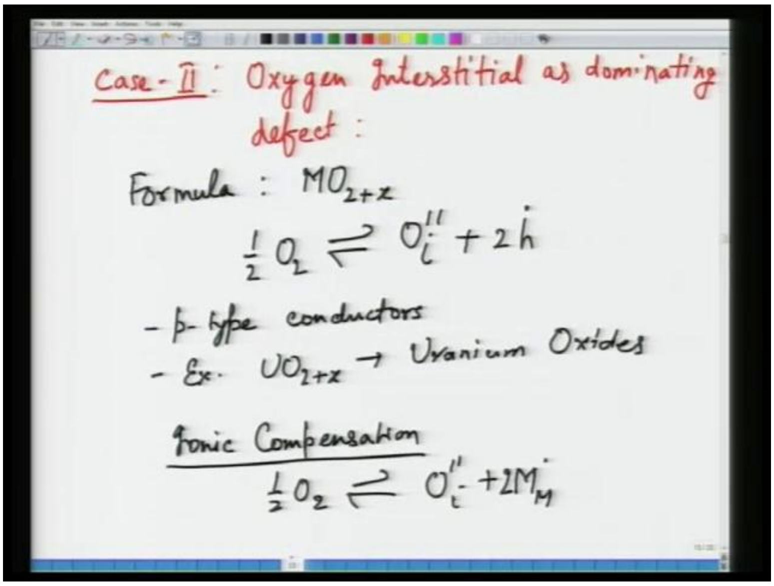

Case - II : Oxygen Interstitial as dominating defect :

Formula : MO_{2+x}

$$\frac{1}{2}O_2 \rightleftharpoons O_i'' + 2\dot{h}$$

- p- type conductors
- Ex. UO_{2+x} → Uranium Oxides

Ionic Compensation

$$\frac{1}{2}O_2 \rightleftharpoons O_i'' + 2M_M^{\cdot}$$

So, second case was oxygen interstitial as dominating defect. In that case again you have compensating effects; defects could be holes or oxidized metal sites. This is a common thing in for example, uranium oxides and which turn out to be p type conductors.

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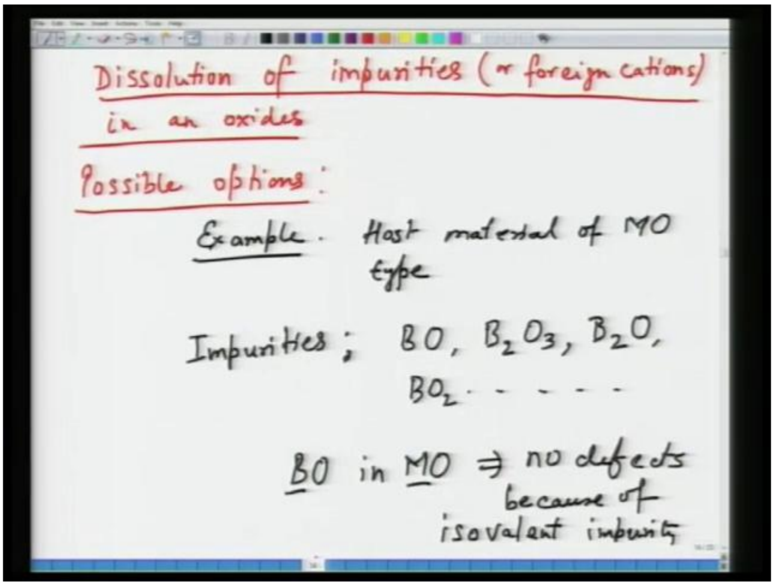

Dissolution of impurities (or foreign cations) in an oxides

Possible options :

Example . Host material of MO type

Impurities ; BO, B_2O_3, B_2O, BO_2 . - - - -

$\underline{B}O$ in $\underline{M}O$ ⇒ no defects because of isovalent impurity

Then we looked at dissolution of foreign atoms or impurities which are intentional or unintentional, whatever the case may be but when you put the impurities, the impurity has its own effect. So, if you have a a impurity of same formula as of or same valence as of parent lattice, in that case you do not have any defect creation. But the moment you have impurity of different valence and different formula you have a defect creation, and these are called as aliovalent impurities.

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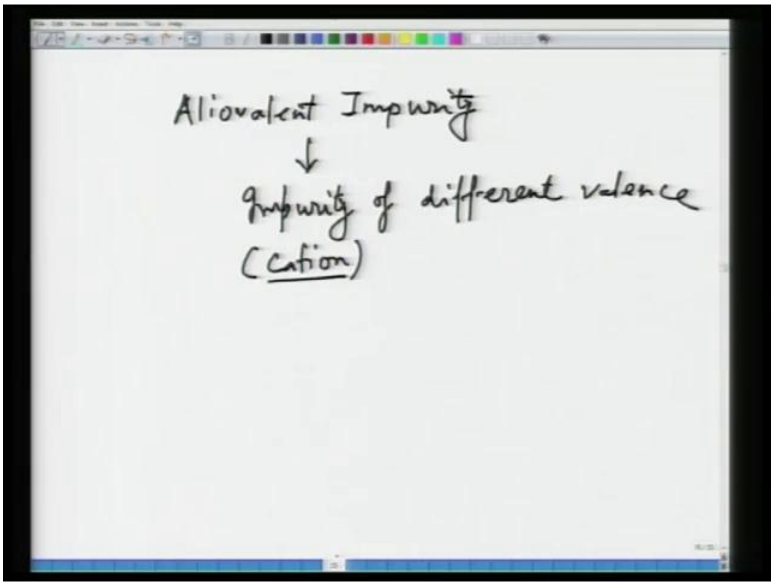

Aliovalent Impurity

↓

Impurity of different valence

(Cation)

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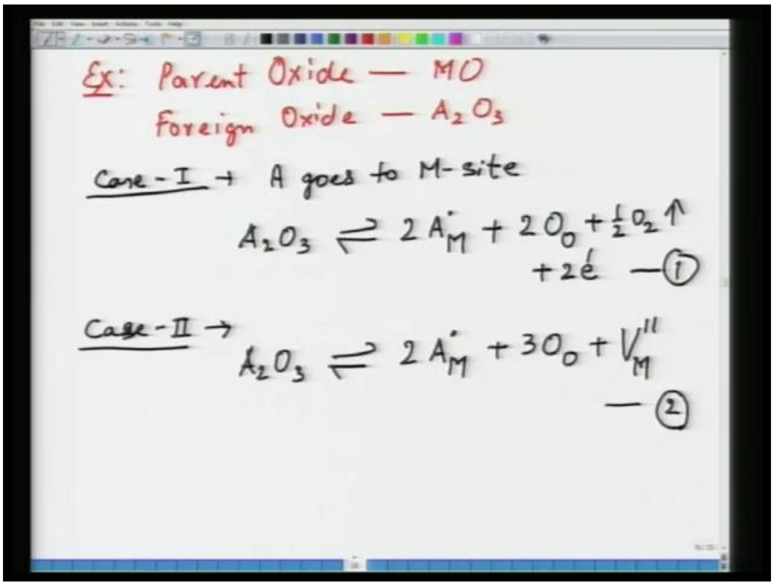

Ex: Parent Oxide — MO

Foreign Oxide — A_2O_3

Case-I → A goes to M-site

$$A_2O_3 \rightleftharpoons 2A_M^{\bullet} + 2O_O + \frac{1}{2}O_2\uparrow + 2e' \quad — ①$$

Case-II →

$$A_2O_3 \rightleftharpoons 2A_M^{\bullet} + 3O_O + V_M'' \quad — ②$$

So, we we looked at the case of dissolution of for instance A 2 O 3 and M O and we looked at what are the possible scenarios, in both the cases we have found that A goes to M side. Now, depending upon the how oxygen distributes itself on the oxygen sides. So, you might have case where only 2 oxygen’s occupy. The oxygen sides maintain the stoichiometry of the crystal and side balance of the crystal, extra oxygen goes out creating one extra, two extra electrons. In the case two, you might have 3 oxygen's going to 3 oxygen sides, which means the disbalances the side balance. So, to maintain the side balance you create another metal side which is empty. So, thereby giving rise to a metal vacancy.

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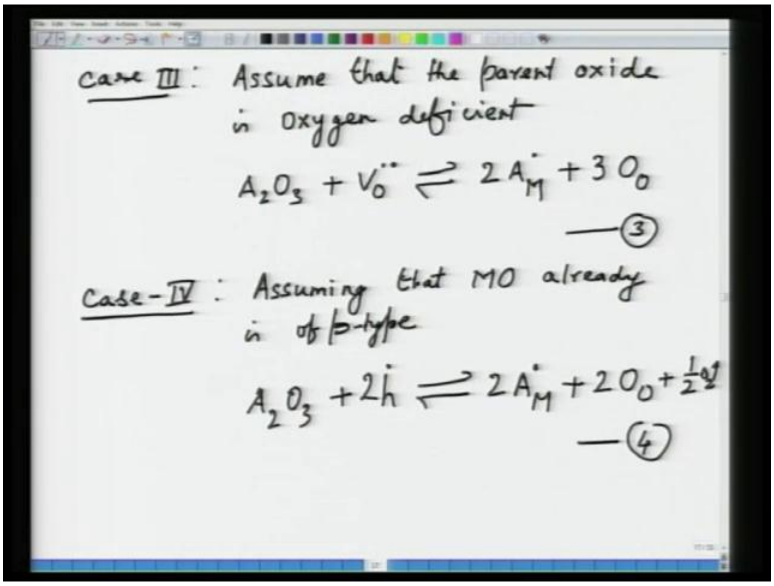

Case III: Assume that the parent oxide in oxygen deficient

$$A_2O_3 + V_O^{\bullet\bullet} \rightleftharpoons 2A_M^{\bullet} + 3O_O \quad — ③$$

Case-IV: Assuming that MO already in of p-type

$$A_2O_3 + 2h^{\bullet} \rightleftharpoons 2A_M^{\bullet} + 2O_O + \frac{1}{2}O_2 \quad — ④$$

Then we looked at the cases in which the oxides, suppose of the of the oxide has reasonable amount of vacancy concentration to begin with or reasonable amount of whole concentration to begin with.

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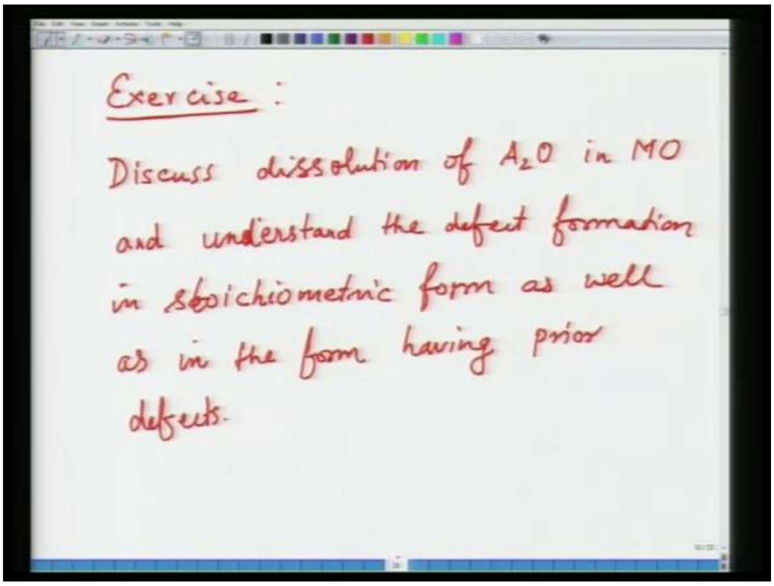

Exercise:

Discuss dissolution of A_2O in MO and understand the defect formation in stoichiometric form as well as in the form having prior defects.

So, as an exercise I asked you guys to to discuss the dissolution of A 2 O in M O, to understand the defect formation in a stoichiometric form as well as in the form having prior defects. So, I will leave this exercise to you.

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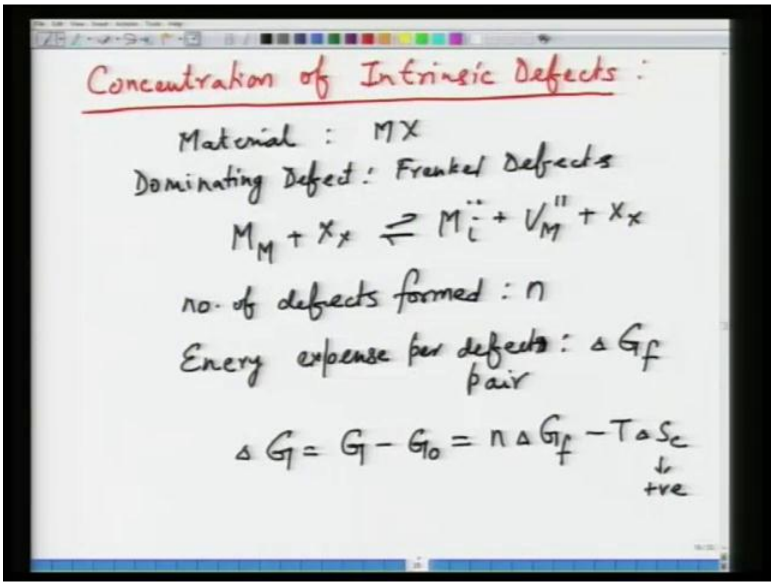

Concentration of Intrinsic Defects :

Material : MX

Dominating Defect : Frenkel Defects

$$M_M + X_X \rightleftharpoons M_i^{\bullet\bullet} + V_M'' + X_X$$

no. of defects formed : n

Enery expense per defects pair : ΔG_f

$$\Delta G = G - G_0 = n\Delta G_f - T\underset{\substack{\downarrow \\ +ve}}{\Delta S_c}$$

Then we worked out what was the concentration of intrinsic defect. This is the thermodynamic basis to calculate the concentration of intrinsic defects. The basis comes from that, if defects are stable that means at certain concentration. The free energy of the crystal will be minimum or the free energy change will be the most negative. So, as a result we worked out the expression for defect concentration, which is nothing but exponential dependence on the free energy expense and temperature. It comes out to be…

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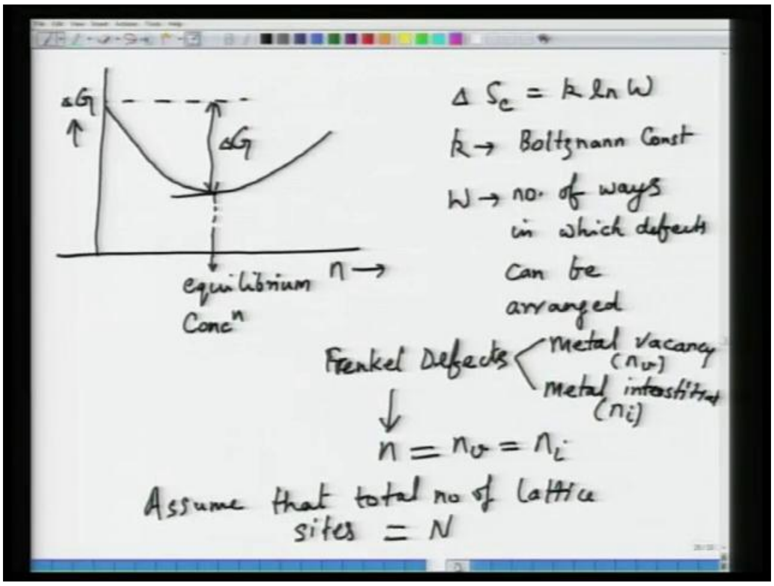

$\Delta S_c = k \ln W$

$k \rightarrow$ Boltznann Const

$W \rightarrow$ no. of ways in which defects can be arranged

Frenkel Defects < metal vacancy (n_v)
metal interstitial (n_i)

$\downarrow$

$n = n_v = n_i$

Assume that total no of lattice sites $= N$

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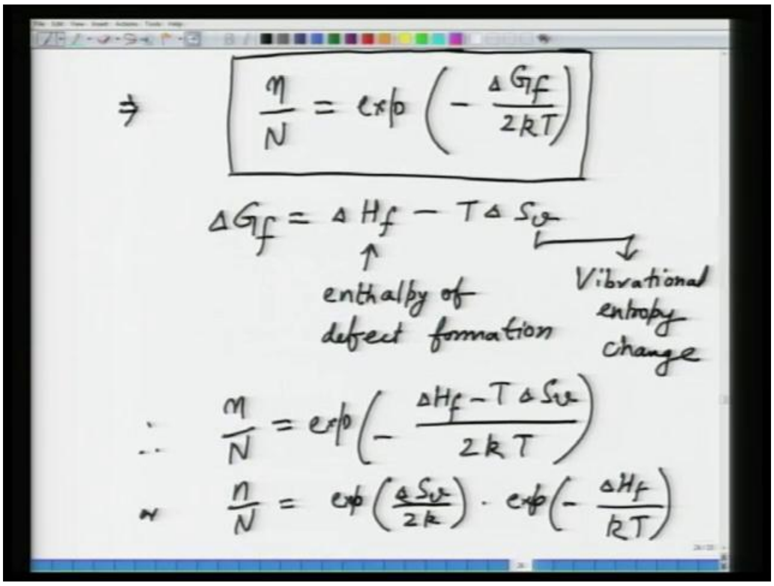

$$\Rightarrow \boxed{\frac{n}{N} = \exp\left(-\frac{\Delta G_f}{2kT}\right)}$$

$$\Delta G_f = \Delta H_f - T\Delta S_v$$

$\uparrow$ enthalpy of defect formation

$\downarrow$ Vibrational entropy change

$$\therefore \frac{n}{N} = \exp\left(-\frac{\Delta H_f - T\Delta S_v}{2kT}\right)$$

$$\text{or} \quad \frac{n}{N} = \exp\left(\frac{\Delta S_v}{2k}\right) \cdot \exp\left(-\frac{\Delta H_f}{kT}\right)$$

So, Delta H f in the case of Frenkel defect, it could be delta H s in case of Schottky defects. So, naturally as you see as delta H f increases, which means as the energy expense formation per pair of defects increases. Then in the formation of defects increases, then the number of defects go down and as the temperature increases number of defects go up.

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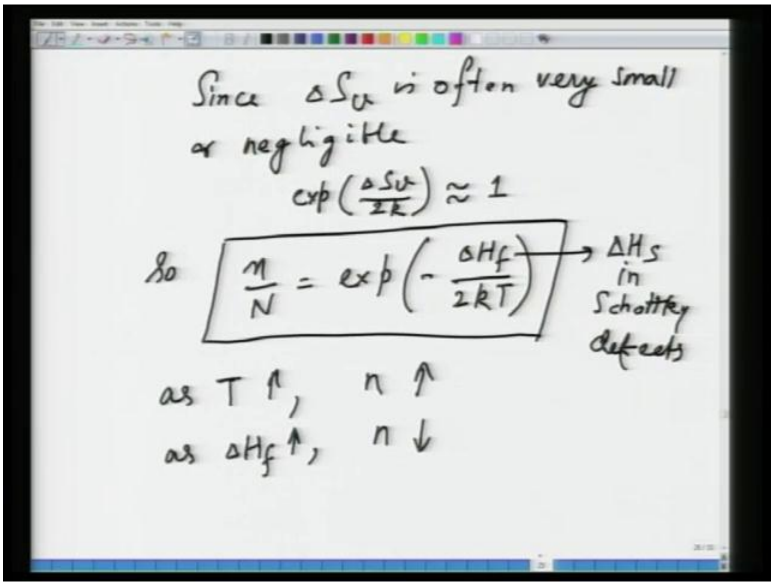

Since ΔS_v is often very small or negligible

$$\exp\left(\frac{\Delta S_v}{2k}\right) \approx 1$$

So $$\boxed{\frac{n}{N} = \exp\left(-\frac{\Delta H_f}{2kT}\right)} \rightarrow \Delta H_s \text{ in Schottky defects}$$

as $T \uparrow$, $n \uparrow$

as $\Delta H_f \uparrow$, $n \downarrow$

This is this is something which you can looked at look at the formula. Then you can try putting various numbers. So, for an instance you can you can try putting delta H f.

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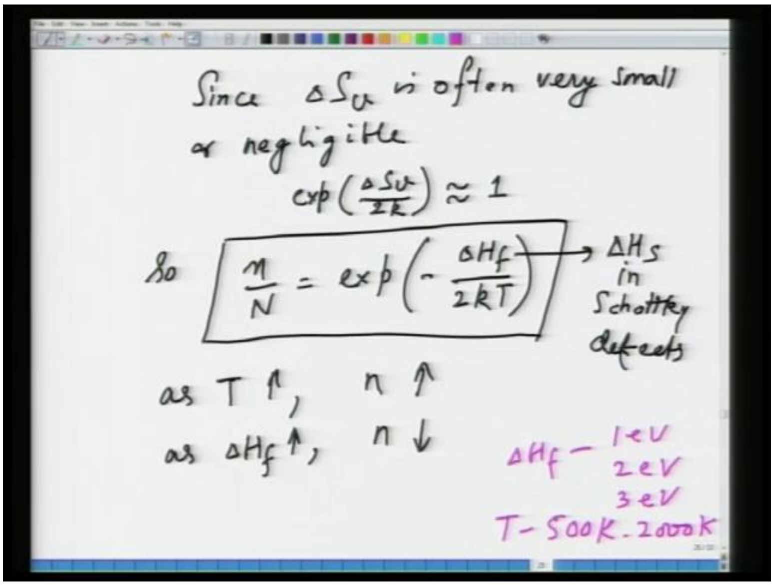

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as $T \uparrow$, $n \uparrow$

as $\Delta H_f \uparrow$, $n \downarrow$

ΔH_f – 1eV
2eV
3eV

T – 500K - 2000K

Delta H f can be something like 1 electron volt, 2 electron volt, 3 electron volt per atom. Then you can look at temperatures at various temperatures from 500 K to 2000 K, just hypothetical cases. You can work out, what is n? Then you can see how how there is small n, that is the number of defects change as the function of these variables.

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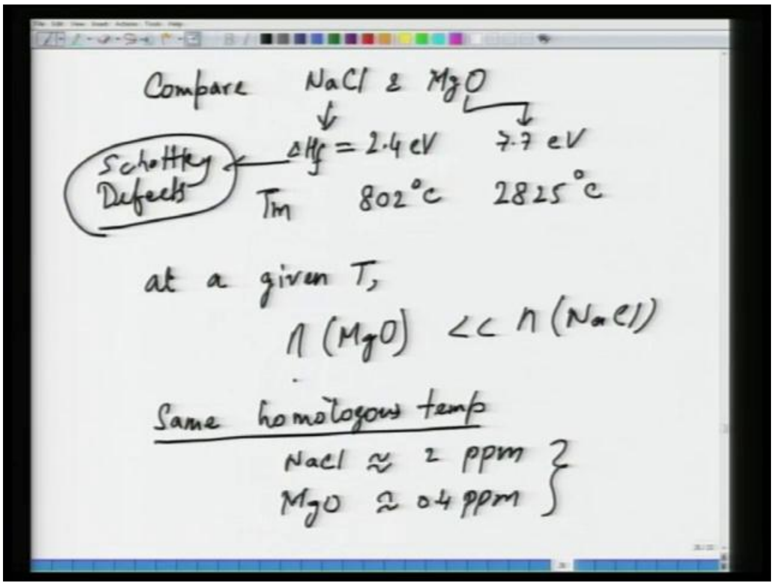

Compare NaCl & MgO

Schottky Defects ← $\Delta H_f = 2.4\ eV$ $7.7\ eV$

T_m 802 °C   2825 °C

at a given T,

$n(MgO) << n(NaCl)$

Same homologous temp

NaCl ≈ 2 ppm

MgO ≈ 0.4 ppm

Then we looked at the case of comparison of Na Cl and Mg O. We see that Na Cl has very large defect formation energy as compared to sorry magnesium oxide has very large defect formation energy as compared to Na Cl. This is because of high melting point, which is because of high bond energy or stronger bonds as compared to NaCl. So, at any given temperature, the number of defects in MgO are much smaller in number as compared to NaCl. However, if you take the same homologous temperature, in that case their defect concentration works out to be roughly equal.

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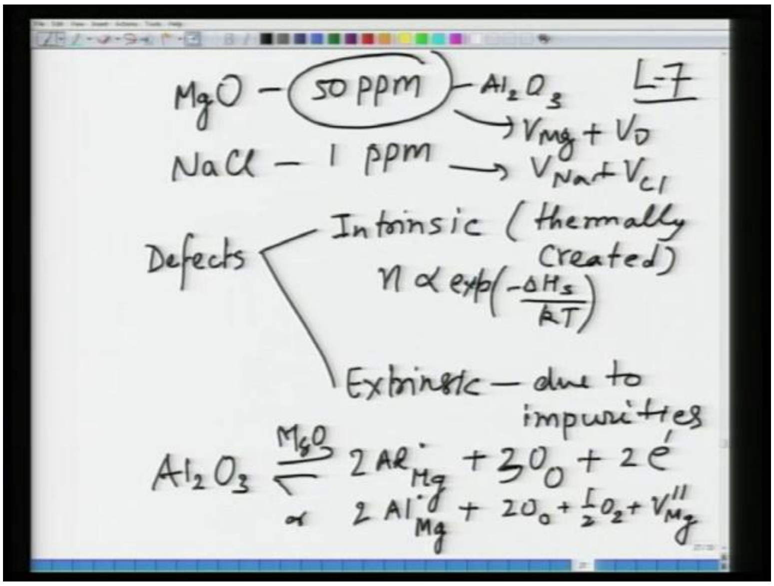

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MgO – 50 ppm – Al_2O_3 → $V_{Mg} + V_O$

NaCl – 1 ppm → $V_{Na} + V_{Cl}$

Defects

Intrinsic (thermally created)

$n \propto \exp\left(-\frac{\Delta H_s}{kT}\right)$

Extrinsic – due to impurities

$$Al_2O_3 \xrightarrow{MgO} 2Al^{\bullet}_{Mg} + 3O_O + 2e'$$

$$\text{or } 2Al^{\bullet}_{Mg} + 2O_O + \frac{1}{2}O_2 + V''_{Mg}$$

So, in this lecture we will just extend that a little bit. So, for now what happens is that in case of Mg O, Mg O it is very difficult to make it completely pure. So, in case of Mg O the impurity tolerance is about 50 PPM where as in case of sodium chloride the impurity tolerance is about 1 PPM. Now, as a result when you have 50 PPM impurities and these impurities could be for example, Al2 O3, so as a result the defects which are created in Mg O. Now, they are due to Al2 O3 because there are two kinds of defects, defects could be intrinsic. Intrinsic means thermally created, so here n will be proportional to exponential of minus delta H. Let us say Schottky defect divide it by k T, so at given temperature n will be determined by the magnitude of temperature. Then you have extrinsic. Extrinsic are due to impurities, impurities which are a aliovalent.

So, when you put Al2 O3 in Mg O, you know that Al2 O3 when you put in Mg O. Let us say, both aluminium go to magnesium site carrying 1 positive charge. Both the oxygen’s, let us say all 3 oxygen’s go to oxygen side. In that case it will give rise to another 2 electrons or so any of these two reactions is possible. So, the bottom one is most likely, now magnesium oxide is a material as well as sodium chloride is a material. Both of them are prone to having Schottky defects. Schottky defects will be in this case, it would be V Mg plus V O. In this case it would be V Na plus V Cl. I am not I am not put the charges on top, there will be charged defects. Now, in in Mg O the thermally created defects would be will be Schottky defects. So, as a result you have magnesium vacancy and oxygen vacancy. Since, cations are usually smaller than anions, these are more mobile as compared to oxygen vacancies.

Now, similarly now when you put to Al2 O3, then also you create magnesium vacancies. So, what happens is that at lower temperatures in Mg O, the defect creation in Mg O is governed by the proportion of Al2 O3. Normally you have at least about 50 PPM, above 50 PPM of Al2 O3, the concentration of vacancies is roughly similar to 50 PPM. You can see that for 1 mole of Al2 O3 you create 1 vacancy. So, if you put 50 PPM Al 2O3, you have 50 PPM of vacancies, which are not thermally created. And and if you look at the previous number, in the previous slide the the the concentrations are of the order of 2 to 3 PPM, which means of few PPMs. Let us say so, which means the number of impurities created by number of defects created by impurities are much more larger and this is extremely significant at lower temperatures than at high temperatures, whereas Na Cl it has only 1 PPM tolerance. So, at least even at the same homologous temperature, that the the impurities create the defects created by impurities in Mg O is about 50 times higher than in Na Cl, which is contrary to just thermally created defects. So, what happens is that in case of Na Cl?

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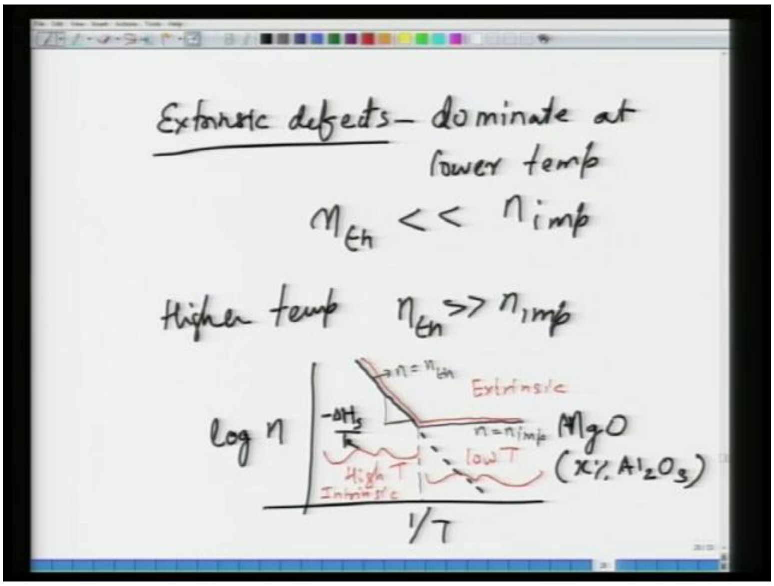

Extrinsic defects – dominate at lower temp

$n_{th} << n_{imp}$

Higher temp $n_{th} >> n_{imp}$

So, extrinsic defects, these defects which are created due to impurities dominate at at lower temperatures, because n thermal is a smaller than n impurity, where n is the number of defects created by either impurity or thermal means, whereas at higher temperatures n thermal tends to dominate over n impurity. So, as a result in in defects you see two behaviors, one is extrinsic behavior, one is intrinsic behavior. Extrinsic behavior, this this replicates itself in the properties specially like diffusivity and conductivity as we will see later. We will see that intrinsic behavior is more predominant at higher temperatures, whereas extrinsic behavior is more predominant at lower temperatures, where defect concentration is independent of temperature. It is dependent it, so what you see is that if you plot defect concentration, let us say, log n verses 1 by T.

So, for example, this is Mg O containing some Al2 O3 x percent Al2 O3. So, what you will see is that the concentration varies like this. So, this your minus delta H f or H s in case of Schottky defects H s. Delta H s by k. So, this goes like this and beyond this. Let us say critical temperature, what dominates is… So, this is n is equal to n impurity and this is n equal to n thermal. So, this is how the behavior is? So, overall behavior is something like this. This is so up to this temperature, it is all thermal of this is 1 by T. So, this is low temperature regime and this is high temperature regime.

So, this behavior is called as extrinsic behavior and this behavior is called as intrinsic behavior. Whereas, for Na Cl since, the impurity concentration is very small, the the domination of impurities in terms of defect concentration is limited to a very small temperature. So, this is the relevance of impurities in creating the defects. Now, the before we move on to defect equilibria into thermodynamics of defect, defects in oxides, we will just see what are the units for units for defect concentration? Here n by N is nothing but fraction, so you can of course relate the defect concentration in terms of fraction.

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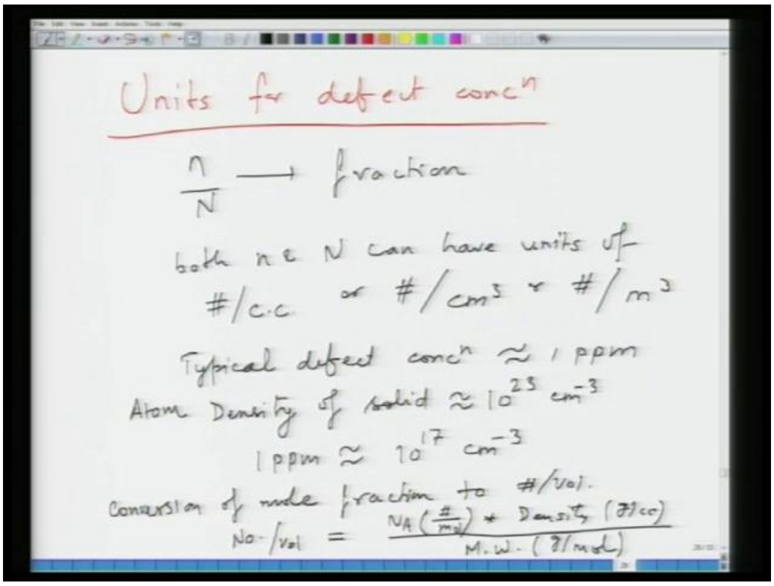

Units for defect conc^n

$\frac{n}{N} \longrightarrow$ fraction

both n & N can have units of

#/c.c or #/cm^3 or #/m^3

Typical defect conc^n $\approx$ 1 ppm

Atom Density of solid $\approx 10^{23}$ cm^{-3}

1 ppm $\approx 10^{17}$ cm^{-3}

Conversion of mole fraction to #/vol.

$$\text{No./vol} = \frac{N_A\left(\frac{\#}{mol}\right) * \text{Density}\ (g/cc)}{\text{M.W.}\ (g/mol)}$$

So, which means ratio of number of defects to the ratio of to the number of let lattice sites, however both n and N can have units of number per c c or number per centimeter cube or number per meter cube. So, you can have this or you can have… So, this is numbers basically number per unit volume. So, so for instance a typical defect concentration is ceramics is is about 1 PPM. Let us say the density of solid is is about atomic density of solids, atom density of solid is equal to about 10 to the power 23 per centimeter cube. In that case 1 PPM is almost equivalent to 10 raise to power 17 per centimeter cube. So, if you want to calculate now, if you want to convert the mole fraction to a number per unit volume.

So, to number per unit volume, then you can. So, you can, this will be so number per unit volume would be equal to NA, which is avogadro number; number per mole multiplied by density, which is gram per c c divided by molecular weight, which is gram per mole. So, this will give you number per unit volume. So, this is how you can calculate number of formula units, number of defects per unit, number per unit volume, okay?

So, now the next topic that we will consider is, so far we have seen how to calculate the defect concentration? What are the different kinds of defects and what are the defect units? Now, we will see what is the thermodynamic basis of writing these defect reactions? How we can then extend this thermodynamic approach into calculating this defect concentration as a function of parameters, such as pressure and temperature? So, now we will look at the, this is an important topic called as defect, defect equilibria.

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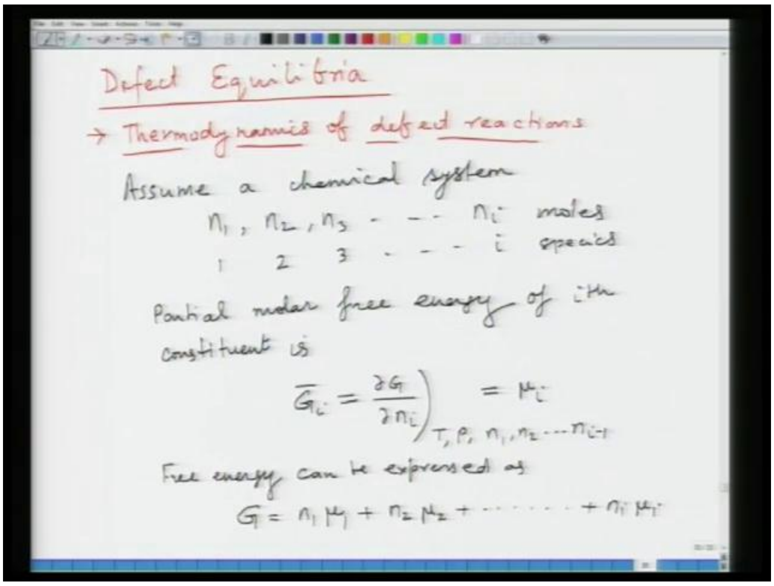

Defect Equilibria

→ Thermodynamics of defect reactions

Assume a chemical system

$n_1, n_2, n_3 - - - n_i$ moles

$1 \quad 2 \quad 3 - - - i$ species

Partial molar free energy of ith constituent is

$$\bar{G}_i = \left.\frac{\partial G}{\partial n_i}\right)_{T, P, n_1, n_2 \cdots n_{i-1}} = \mu_i$$

Free energy can be expressed as

$$G = n_1 \mu_1 + n_2 \mu_2 + \cdots\cdots + n_i \mu_i$$

So, first in so defect equilibria is nothing but a equilibrium. What happens to defects under equilibrium? How can we represent this defect? We said that we can write these defects formation of these defects in a solid as a defect reaction, in a similar fashion as a chemical reaction. So, for that we need to establish a thermodynamic basis. How can we do that? So, first we will discuss is, what is called as the topic is thermodynamics of of defect reactions? So, basically a defect when a when a chemical reaction takes place, there is a change in free energy, right?

That change in free energy is related to some thermodynamic parameters, such as your reaction constant. This reaction constant is related to the activities or the concentrations of various species. They take part in the completion of that reaction and the knowledge of equilibrium concentration. With respect to parameters is a required to work out a complete defect equilibrium diagram from which we can work out any given temperature, at any given temperature, at any given pressure. What is the defect concentration of each type in a given material? So, for instance the most important thing is to work out in oxides is calculation of defect concentration, as a function of partial pressure of oxygen because these oxide materials are typically used at various pressures.

For example, as a sensors, so gas sensor in gas sensing application. So, in that case you can look at at different oxygen partial pressures, which defect will dominate in a in in a particular material. So, if you want to really go into, so for this we will take the approach of… So, what is called as chemical thermodynamics or metallurgical thermodynamics especially in solutions? So, well solution means you have a solid solid containing various species 1 to n let us say. What happens to thermodynamic free energy in that solid and what happens to that equilibrium?

So, if you want to go into details of thermodynamics, if you want to understand the basics of thermodynamics you should go to, you should to refer to any book on basic thermodynamics, such as a thermodynamics Craig Haskell. It is a very nice book or Darken and Gurry, I will list some of these website some of these. I have listed some of these website books in in the webliography of this course, in the beginning of in the possibly in the first lecture. You can just look through the internet and find some basic books on the metallurgical thermodynamics or chemical thermodynamics.

So, we will start for example, with the chemical system consisting of so, so assume so, assume a chemical system. This consists of n 1 n 2 n 3 to n i moles and species are 1 2 3 i species. The partial mole of free energy free energy of a particular constituent, let us say of i th constituent is given as, so partial molar free energy is equal to chemical potential, which is so let us say G i is expressed as del G which is the overall free energy divided by del n i at constant temperature, constant pressure; n 1 n 2 n i minus 1 except n i everything else is constant. This is also equal to mu i or chemical potential of species or entity i.

Now, we can write the total the net free energy, free energy can be expressed as… So, G is equal to n 1 mu 1 in terms of chemical potential of each of these species. So, n 1 n 1 mu 1 plus n 2 mu 2 and so on and so forth, plus n i mu I. This is the chemical, this is the free energy now. So, suppose the now assume the system is open, so for an open system considering the system as open system. Now, for the definition of closed system, I assume that you know the definition of open and closed systems from the basics of thermodynamics.

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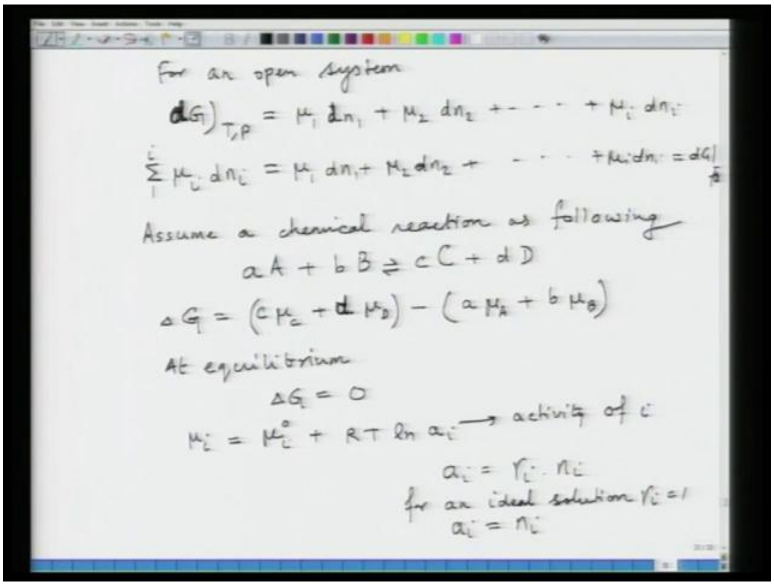

For an open system

$$dG)_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 + \cdots + \mu_i dn_i$$

$$\sum_1^i \mu_i dn_i = \mu_1 dn_1 + \mu_2 dn_2 + \cdots + \mu_i dn_i = dG|_{T,P}$$

Assume a chemical reaction as following

$$aA + bB \rightleftharpoons cC + dD$$

$$\Delta G = (c\mu_C + d\mu_D) - (a\mu_A + b\mu_B)$$

At equilibrium

$$\Delta G = 0$$

$$\mu_i = \mu_i^o + RT \ln a_i \longrightarrow \text{activity of } i$$

$$a_i = \gamma_i \cdot n_i$$

for an ideal solution $\gamma_i = 1$

$$a_i = n_i$$

So, from of an open system, now I can write del G at constant temperature and constant pressure to be equal to mu 1 d n 1 plus mu 2 d n 2 mu i d n I, I can write d g. So, let us not make it confusion, so d g constant that temperature and pressure is equal to mu 1 d n 1 plus mu 2 d n 2 up to mu i d n i. There mu is the chemical potential of each entity and n is the n n 1 n 2 n 3 n i are the concentrations. Now, now from this I can write this as from 1 to i is equal to d G at T n p constant temperature and pressure. Now, del now assume a chemical reaction, so we are taking a system where many species are present to react and then some products formed.

So, assume a chemical reaction as as following. So, let us say a moles of a capital A plus b moles of capital B react together to form c moles of capital C plus d moles of capital D. So, the free energy change that you write delta G. Delta G can be written as c of mu C plus d of D of mu D. This is the product minus the reactant a of mu A plus b of mu B.

So, this is the net free energy change. Now, at equilibrium what happens? So, at equilibrium delta G is equal to 0, so this we know. Now, we can write as and we know that mu i is equal to mu i naught plus R T l n a I, where a i is the activity of i th species.

So, now what is the activity we know that a i is equal to gamma i multiplied by n i or c i depending upon what is the convention. So, gamma i into n i where for an ideal solution I, where gamma i is is the you can say activity co-efficient. So, for an ideal solution gamma i is equal to 1. So, a i is equal to n i and delta G naught, so for ideal solution gamma i is equal to 1. We can take then a i to be equal to n i. So, now let us move to the next slide. So, when a when a system contains several phases in that case the condition of equilibrium basically means, that that if you if you draw the free energy composition diagram, which I am not going to draw. But what it means is that the, I can well draw it for instance.

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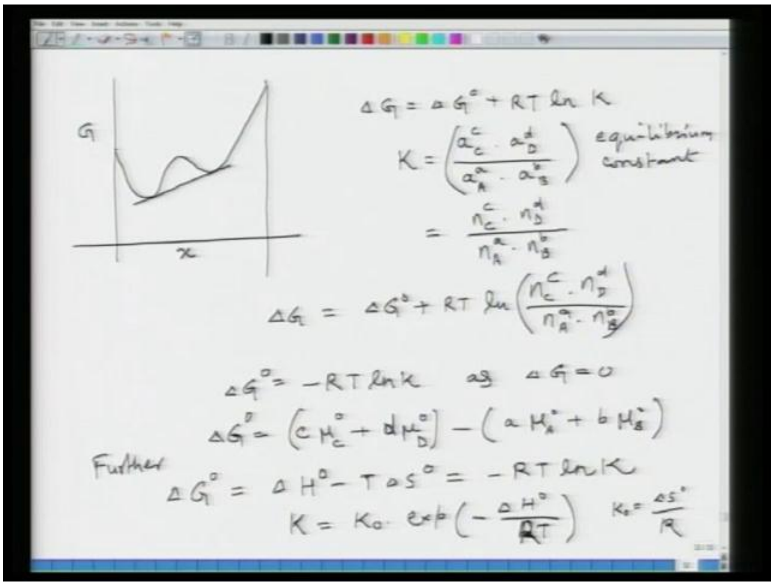

$$\Delta G = \Delta G^{\circ} + RT \ln K$$

$$K = \left(\frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}\right) \text{ equilibrium constant}$$

$$= \frac{n_C^c \cdot n_D^d}{n_A^a \cdot n_B^b}$$

$$\Delta G = \Delta G^{\circ} + RT \ln\left(\frac{n_C^c \cdot n_D^d}{n_A^a \cdot n_B^b}\right)$$

$$\Delta G^{\circ} = -RT \ln K \quad \text{as} \quad \Delta G = 0$$

$$\Delta G^{\circ} = (c\mu_C^{\circ} + d\mu_D^{\circ}] - (a\mu_A^{\circ} + b\mu_B^{\circ})$$

Further

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = -RT \ln K$$

$$K = K_0 \cdot \exp\left(-\frac{\Delta H^{\circ}}{RT}\right) \quad K_0 = \frac{\Delta S^{\circ}}{R}$$

So, these are the 2 phases. So, what did basically means is? This is free energy composition diagram and what it means that, when 2 phases are in equilibrium the chemical potential of 2 phases or several phases is same. So, if you have 2 phases, then chemical potential of each constituent in both phases is same. If you have more than 2 phases, 3 phases, 4 phases then also chemical potential of each constituent tend to in all the phases is same. Now, we know what chemical potential is? So, we can write this delta G, which is the net free energy change to be equal to delta G naught, which is the free energy change in a standard state plus R T l n k.

Now, what is k? k as we know is a activity of a to the power A into activity of b to the sorry we have to write product on top, activity of the c to the power C into activity of d to the power D divided by activity of a a to the power A multiplied by activity of b to the power B. Assuming that it was a ideal solution, this is equal to n C to the power c into n D to the power d divided by n A to the power a into n B to the power b. So, this is your k, so delta G is now equal to delta G naught plus R T l n and C to the power c and D to the power d divided by n A to the power a n B to the power b.

Now, what is delta G naught? Delta G naught is the free energy change in the standard state, that is at unit activities, all right? So, and delta G naught is a is a constant under specified standard states. At equilibrium we can write delta G naught as delta G naught as minus of R T l n k because delta G is equal to 0 and delta G naught expression is basically c mu C naught plus d. Sorry d mu D naught minus same as the free energy change for a reaction. We have a delta G naught in which is the free energy change of in the standard state is equal to a mu A naught plus b mu B naught. So, I so basically you have written what k is.

So, now k, k as you know is nothing but equilibrium constant or often referred as reaction constant, which relates the activities of products to the reactants under a given conditions. So, now I can write what is delta G naught? Delta G naught can be written in the terms of delta, so further delta G naught can be expressed in terms of delta H naught minus T delta S naught, which is the enthalpy change in the standard state minus temperature multiplied by the entropy change in the standard state. This is given as minus R T l n k. So, I can write now this as, so basically what it means is that k is equal to k naught into exponential of minus delta H naught divided by k T. What is k naught? k naught is your delta S naught divided by R. So, this is very clear, you can just divide by R T or k T here. So, I will just make it R, let us not big use there so it R everywhere or you make it k everywhere. So, it depends whether you take it per atom or per mole?

So, this is what is k is equal to expression of k. So, k also is a temperature dependent entity. How can you show it in a more elegant manner? The temperature I can I can show it in a more elegant manner, that temperature dependence of k as d l n k divided by d 1 by T to be equal to minus of delta H naught by R.

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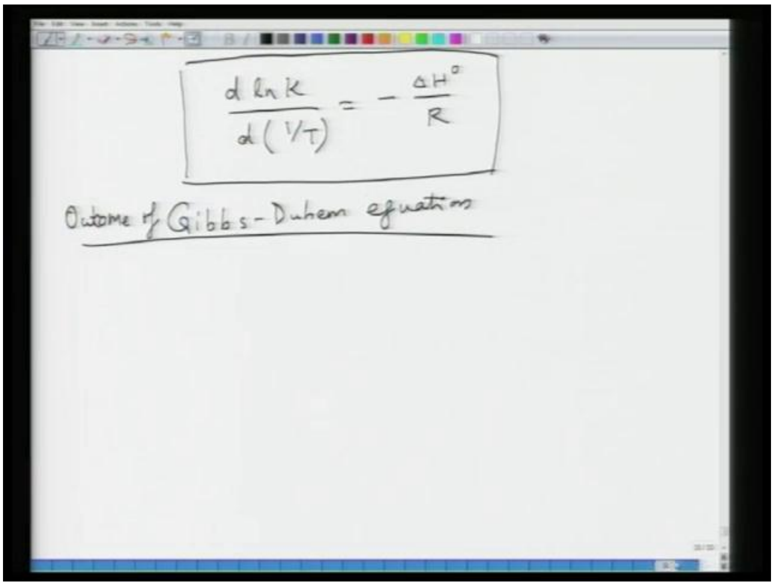

$$\boxed{\frac{d \ln K}{d(1/T)} = -\frac{\Delta H^0}{R}}$$

Outcome of Gibbs-Duhem equations

So, this shows that the k is dependent on temperature, which is equal to minus delta H naught by R. This is called as your, this is basically a very important. This is an outcome of of Gibbs Duhem equation and what was the Gibbs Duhem equation? If you go to the previous slides…

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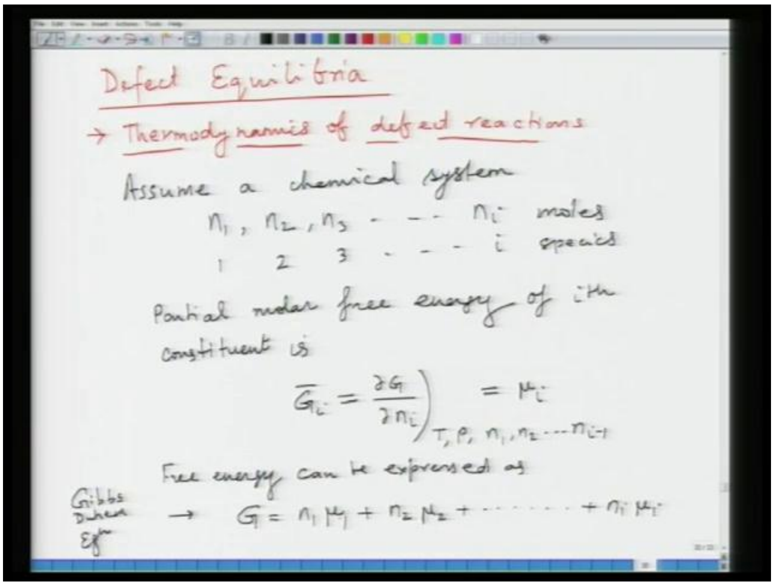

Defect Equilibria

→ Thermodynamics of defect reactions

Assume a chemical system

$n_1, n_2, n_3 \ldots n_i$ moles

$1 \quad 2 \quad 3 \ldots i$ species

Partial molar free energy of ith constituent is

$$\bar{G_i} = \left.\frac{\partial G}{\partial n_i}\right)_{T, P, n_1, n_2 \ldots n_{i-1}} = \mu_i$$

Free energy can be expressed as

Gibbs Duhem Eqn → $G = n_1 \mu_1 + n_2 \mu_2 + \ldots\ldots + n_i \mu_i$

So, this was your… It is a it is a fundamental thermodynamic relation, where you relate the free energy with respect to, free energy to the concentration of species and and chemical potential. So, what basically this tells you is that, this is an this basically tells you that, just like we treat solute in a solvent in a proper in a normal material, we can treat defects in a solid as solute in the solvent.

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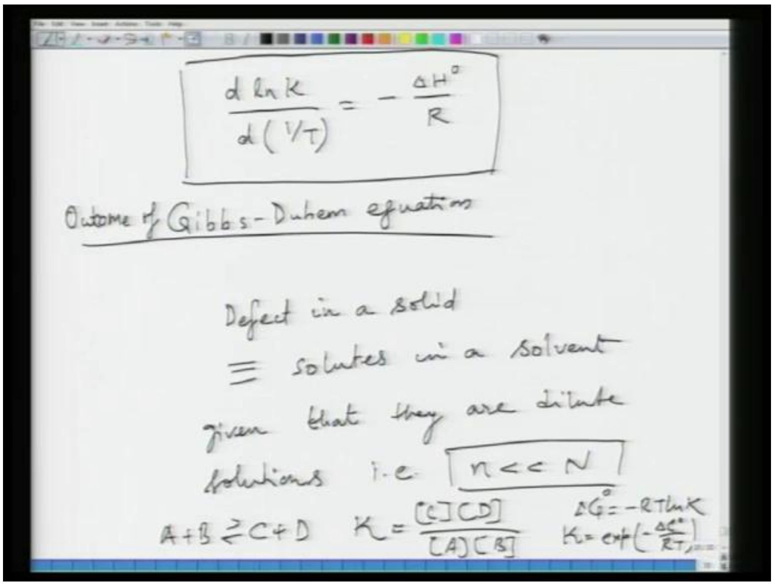

$$\boxed{\frac{d \ln K}{d(1/T)} = -\frac{\Delta H^{0}}{R}}$$

Outcome of Gibbs-Duhem equations

Defect in a solid

$\equiv$ solutes in a solvent

given that they are dilute

solutions i.e. $\boxed{n << N}$

$A + B \rightleftarrows C + D \quad K = \frac{[C][D]}{[A][B]} \quad \Delta G^{0} = -RT \ln K \quad K = \exp\left(-\frac{\Delta G^{0}}{RT}\right)$

So, defects in a solid are equivalent to solutes in a solvent given that, they are they are dilute dilute solutions. That is n, which is a number of defects is smaller as compared to capital N. So, this thermodynamics basis which is established for solids or solvents containing dilute concentration of solids solutes can be extended to defects because defects are also present in small very present in the solid, in very small numbers. The presence of these defects in the small numbers can be treated the other equivalent to solutes in a solvent or in a given solid.

So, the further, so basically the the formulism that we have established here that, you you write a chemical reaction. So, A plus B is equal to C plus D and you write k, which is so you write concentration of C concentration of D multiplied by a multiplied by B. Delta G is equal to minus R T l n k, so basically k is equal to exponential of minus delta G naught divided by R T. So, we are going to calculate k for all the defects considering defects formation as a in in the form of a defect defect reaction. Relate it to thermodynamic parameter such as delta G naught, which can be related to delta S H naught and and temperature. So,, this is how we are going to treat all the defect formation in in the solids. So, now what we are going to do is, that we are going to establish this defect equilibrium, which we have so far understood now in oxides.

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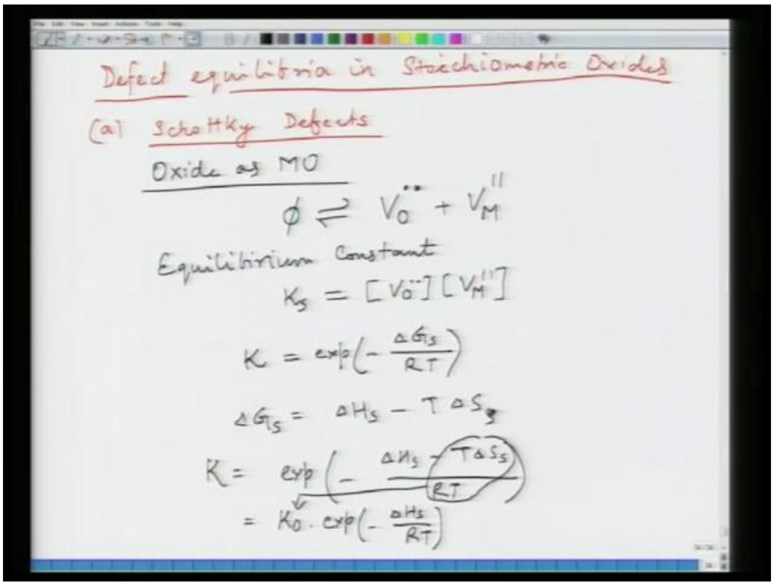

Defect equilibria in Stoichiometric Oxides

(a) Schottky Defects

Oxide as MO

$$\phi \rightleftharpoons V_O^{\bullet\bullet} + V_M^{''}$$

Equilibrium Constant

$$K_S = [V_O^{\bullet\bullet}][V_M^{''}]$$

$$K = \exp\left(-\frac{\Delta G_S}{RT}\right)$$

$$\Delta G_S = \Delta H_S - T\Delta S_S$$

$$K = \exp\left(-\frac{\Delta H_S - T\Delta S_S}{RT}\right)$$

$$= K_0 \cdot \exp\left(-\frac{\Delta H_S}{RT}\right)$$

So, let us take so first the case of defect in stoichiometric oxides. So, let us let us take first the case of Schottky defects. So, defect reaction for a so consider the oxide as M O so, what is the defect reaction in this oxide M O? I can write 0 or null to be equal to V O plus V M dash dash, okay? Now so, V O is doubly charged vacancy and V M is doubly charged metal vacancy or sorry V O is doubly charged oxygen vacancy an V M is doubly charged an a cation vacancy. So, what is the equilibrium constant for this reaction? Now, treat this as a chemical reaction, so equilibrium constant let us say k s. k s is given as concentration of V O multiplied by concentration of V M. So, we are treating it as a normal chemical reaction. We also knew that k s is also equal to exponential of minus delta G s divided by R T just from the previous slide.

We we know that the there is a temperature dependence of k so, we have written now k in the form of free energy change. Delta G s was equal to delta H s minus T delta S s s. So, where delta H s is the enthalpy change for Schottky defect formation and delta S s is the entropy change, which is mainly a vibrational entropy change. It is and this can be further written as, so you can write k as exponential of delta H s minus T delta S s divided by R T is equal to, let us say… So, T T will cancel here we will make that at k naught exponential minus of delta H s by R T. So, this particular thing is k naught, okay?

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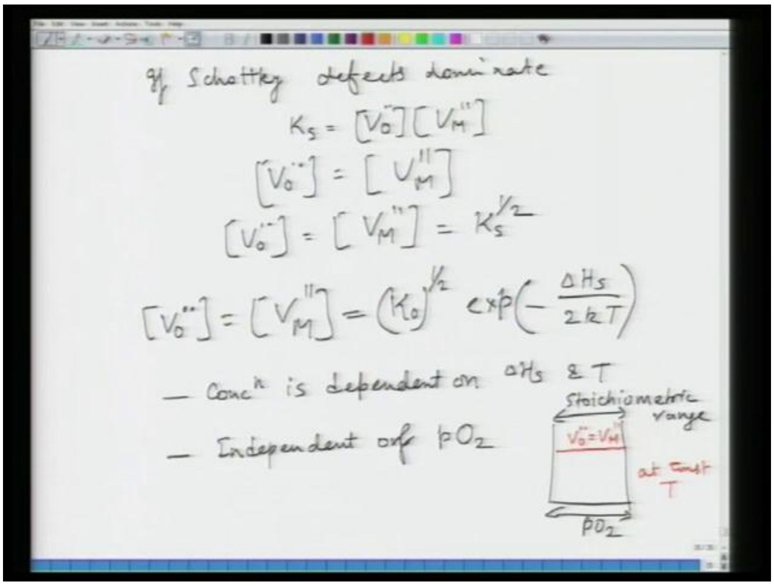

If Schottky defects dominate

$$K_S = [V_O^{\bullet\bullet}][V_M^{''}]$$

$$[V_O^{\bullet\bullet}] = [V_M^{''}]$$

$$[V_O^{\bullet\bullet}] = [V_M^{''}] = K_S^{1/2}$$

$$[V_O^{\bullet\bullet}] = [V_M^{''}] = (K_0)^{1/2} \exp\left(-\frac{\Delta H_S}{2kT}\right)$$

— Conc^n is dependent on ΔH_S & T

— Independent of pO_2

So, so having done this, so let us say if the Schottky defects is that other, if Schottky defects dominate or are the are the defects in in majority present, in that case I can write. So, in that case k s was equal to V O multiplied by V M. We know that v O is equal to V M, right? So, which means V O is equal to V M is equal to k s to the power half. So, in a such a solid V O is equal to V M is equal to k naught to the power half into exponential minus delta H s divided by 2 k T. So, this V O is equal to V M is equal to k naught to the power half exponential minus delta H s by 2 k T.

Now, one you can see many things from this first V O and V M has same dependence on delta H s and T as we calculated, when we calculated the concentration of intrinsic defects in the solid. So, first we verify the correctness of that derivation. Two there is no so, although it is an oxide M O there is no dependence on partial pressure of oxygen. So, one concentration is dependent on delta H s and T and the increase or decrease is in the same fashion as we discussed in the concentration part. Two, independent on independent of p O 2, which means wherever possible, wherever this defects are wherever the oxide, whatever the regime in which oxide is in the stoichiometric state. When Schottky defects dominate the defect concentration is independent of partial pressure of oxygen, so which means in the stoichiometric range.

So, let us say if this was the stoichiometric range of p O 2. So, this was the stoichiometric range and if Schottky defect dominates in that case the concentration would be like this. This would be within this particular range of p O 2, it would not be too large. It would be around one atmosphere and this would be V O is equal to V M and independent of partial pressure of oxygen. This is at constant constant temperature, okay? So, in the next part we will look at the same exercise for Frenkel defect.

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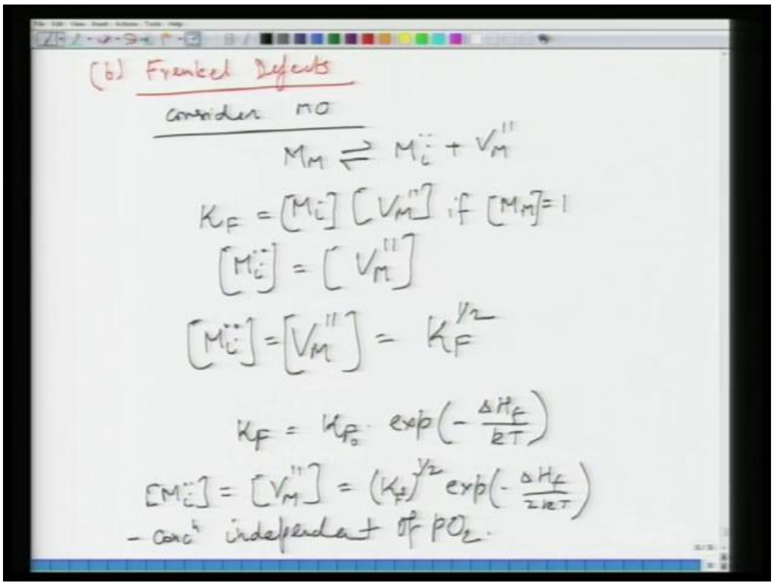

(b) Frenkel Defects

consider MO

$$M_M \rightleftharpoons M_i^{\bullet\bullet} + V_M^{''}$$

$$K_F = [M_i^{\bullet\bullet}][V_M^{''}] \text{ if } [M_M] = 1$$

$$[M_i^{\bullet\bullet}] = [V_M^{''}]$$

$$[M_i^{\bullet\bullet}] = [V_M^{''}] = K_F^{1/2}$$

$$K_F = K_{F_0} \cdot \exp\left(-\frac{\Delta H_F}{kT}\right)$$

$$[M_i^{\bullet\bullet}] = [V_M^{''}] = (K_F)^{1/2} \exp\left(-\frac{\Delta H_F}{2kT}\right)$$

- concn independent of pO_2.

So, we will quickly go through that. So, thermodynamic equilibrium in Frenkel defects. So, again consider on oxide, consider M O. Frenkel defect reaction can be written as metal site goes to interstitial site forming 2 having 2 positive charges followed by metal vacancy having 2 negative charges. The reaction constant k F can be written as M i into V M assuming M M to be equal to 1. And and if M M works in very large number, which means M i and V M are very small as compared to concentration of M M.

We know that M i is also equal to V M, so as a result you can write M i is equal to V M is equal to k f to the power half. So, again you apply the same formulism with the same formulism was that, I can write k f to be equal to k f naught exponential minus delta H f by k T. So, I just equate it there, so as a result M i is equal to V M is equal to k f naught to the power k f naught into exponential minus delta H f by 2 2 k T. So, again you see similar sort of expression where, concentration is related to exponential minus delta H f by 2 k T similar to expression that we derived earlier. Again there is no dependence on partial pressure of oxygen.

So, concentration independent of p O 2, so depending upon which defect dominate in the stoichiometric state. In both cases the defect concentration is independent of partial pressure of oxygen. Now, let us say what happened in the non-stoichiometric states these, so these stoichiometric states are common at around 1 atmosphere. Non-stoichiometric states, non-stoichiometric either oxygen deficient state or oxygen excess state or metal deficient or metal excess, otherwise would be possible, when so, oxygen deficient would be possible. When oxygen pressure partial pressure is very low, and oxygen excess would be possible, when oxygen partial pressure is very high. So, we will now look at the equilibria in these non-stoichiometric states.

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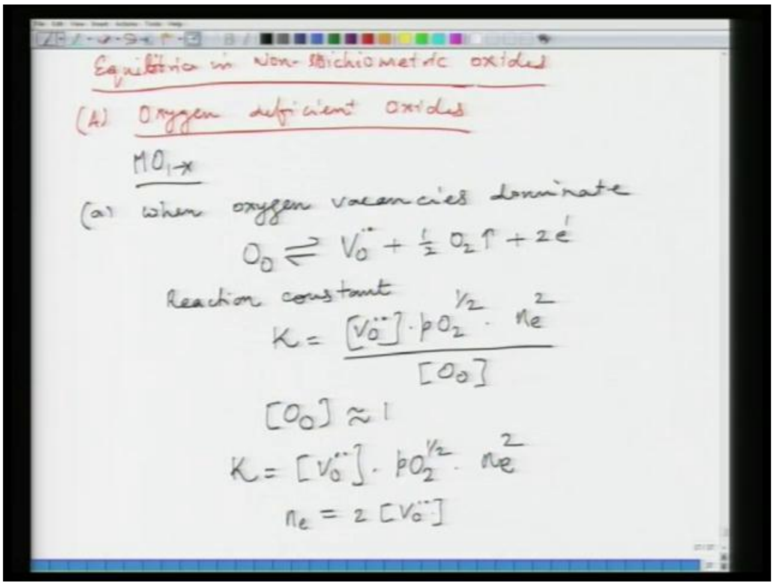

Equilibria in Non-Stoichiometric oxides

(A) Oxygen deficient oxides

MO_{1-x}

(a) when oxygen vacancies dominate

$$O_O \rightleftharpoons V_O^{\bullet\bullet} + \frac{1}{2} O_2 \uparrow + 2e'$$

Reaction constant

$$K = \frac{[V_O^{\bullet\bullet}] \cdot pO_2^{1/2} \cdot n_e^2}{[O_O]}$$

$$[O_O] \approx 1$$

$$K = [V_O^{\bullet\bullet}] \cdot pO_2^{1/2} \cdot n_e^2$$

$$n_e = 2[V_O^{\bullet\bullet}]$$

So, so first we will take the case of oxygen deficient oxides. So, oxygen deficient is oxides means M O 1 minus x. So, we will take first case when oxygen vacancies dominate. So, when we take that in that case again I write the defect reaction the writing of defect reaction is similar to what we did earlier, so formation of vacancy of oxygen plus formation of 2 electrons. So, the reaction constant would be, so let us say or equilibrium constant k would be equal to V O into p O 2 to the power half into n e square divided by O O.

Now, again assuming that defect are in very small concentration as compared to O O. So, we take O O to be equal to 1. So, hence k is equal to V O multiplied by p O 2 to the power half multiplied by n e square. So, so this is the expression you get now. From this expression you can see that for each vacancy, each oxygen vacancy created you have 2 electrons. So, the eventually the concentration of electrons is two times the concentration of vacancies. So, I can write this expression n e to be equal to 2 of V O. So, this is because of to maintain the electrical neutrality.

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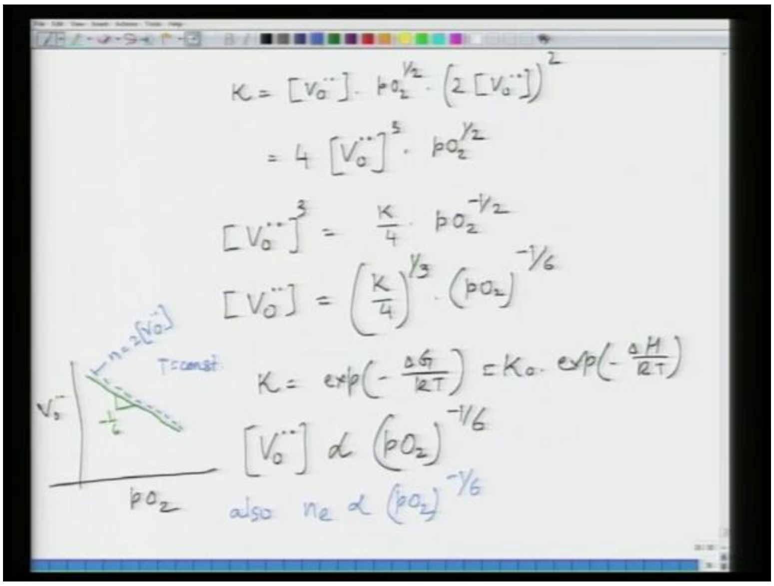

$$K = [V_O^{\cdot\cdot}] \cdot pO_2^{1/2} \cdot (2[V_O^{\cdot\cdot}])^2$$

$$= 4 [V_O^{\cdot\cdot}]^3 \cdot pO_2^{1/2}$$

$$[V_O^{\cdot\cdot}]^3 = \frac{K}{4} \cdot pO_2^{-1/2}$$

$$[V_O^{\cdot\cdot}] = \left(\frac{K}{4}\right)^{1/3} \cdot (pO_2)^{-1/6}$$

$$K = \exp\left(-\frac{\Delta G}{RT}\right) = K_o \cdot \exp\left(-\frac{\Delta H}{RT}\right)$$

$$[V_O^{\cdot\cdot}] \propto (pO_2)^{-1/6}$$

also $n_e \propto (pO_2)^{-1/6}$

So, I can write k to be as k was equal to V O into p O 2 to the power half multiplied by n e square. So, I can write that as 2 V O square. So, this could be equal to 4 V O cube into p O to the power half. Now, what it means is that V O is equal to k by 4 into p O 2 to the power minus half V O cube or V O is equal to k by 4 to the power 1 by 3 into p O 2 to the power minus 1 by 6. So, assuming that k k you know is again equal to exponential of minus delta G y k T. So, again it is it is nothing but you know k naught into exponential of minus delta H s by H by k T. This delta H can be determined experimentally, so which means you can determine the k experimentally. So, k will be at a constant temperature are known quantity.

So, which means what it tells you is that, V O is proportional to p O to the power minus 1 by 6. So, when you plot this concentration of, so if u take just as log scale and this is V O so, in that case you get the relation decreases like this and this would be your minus 1 by 6. So, the the the concentration of oxygen vacancies decreases as you increase the partial pressure oxygen, which is intuitively understandable because as you are increasing the partial pressure of oxygen. Basically you are more pumping in more oxygen into the system, as a result you are reducing the concentration of oxygen vacancies. So, this this is the dependence of partial oxygen vacancy concentration on partial pressure of oxygen in the defect in in a non stoichiometric oxide, which is oxygen deficient and where oxygen vacancies are dominating defects.

So, what would be the concentration of electrons? The electron concentration would be simply this. So, just a straight line parallel to this previous line, so this could be n which is equal to 2 V O. So, you have this so the the only difference now here is, so and also n e is proportional to p O 2 to the power minus 1 by 6. The only difference that you see with respect to previous case of stoichiometric oxide is, in case of stoichiometric oxide. There was only temperature dependence, there was no partial pressure of there was no dependence on partial pressure of oxygen. Here, not only you have a dependence on temperature which is as a result of k being dependent on temperature, you also have a dependence on partial pressure oxygen.

So, if you take this, if you plot this concentration as a function of partial pressure of oxygen, at constant temperature and pressure a constant temperature not pressure. Sorry so, at constant temperature then you see this kind of trend the oxygen vacancy concentration reduces as you increase the as you increase the partial pressure of oxygen. So, this is for the case when your oxygen vacancies are dominant. What happens when your metal is an excess?

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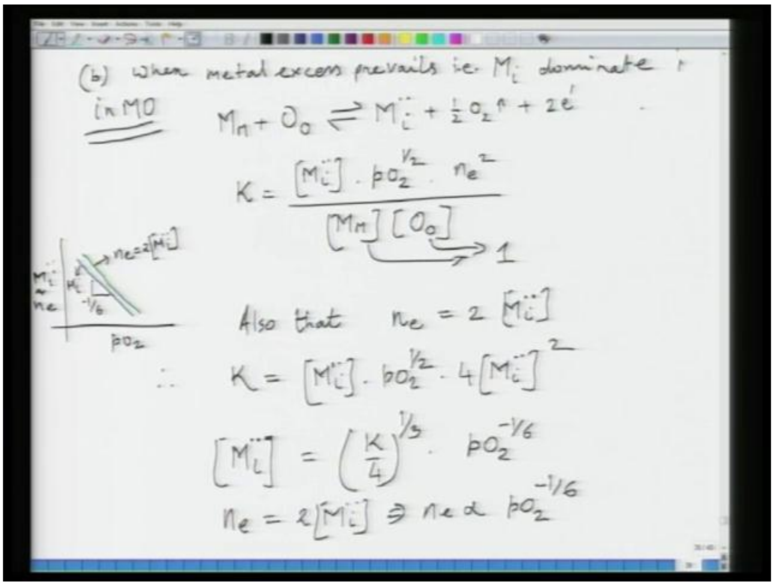

(b) when metal excess prevails i.e. M_i dominate in MO

$$M_M + O_O \rightleftharpoons M_i^{\cdot\cdot} + \frac{1}{2}O_2\uparrow + 2e'$$

$$K = \frac{[M_i^{\cdot\cdot}] \cdot pO_2^{1/2} \cdot n_e^2}{\underbrace{[M_M][O_O]}_{\to 1}}$$

Also that $n_e = 2[M_i^{\cdot\cdot}]$

$$\therefore K = [M_i^{\cdot\cdot}] \cdot pO_2^{1/2} \cdot 4[M_i^{\cdot\cdot}]^2$$

$$[M_i^{\cdot\cdot}] = \left(\frac{K}{4}\right)^{1/3} \cdot pO_2^{-1/6}$$

$$n_e = 2[M_i^{\cdot\cdot}] \Rightarrow n_e \propto pO_2^{-1/6}$$

So, second case is, so case b is when V M dominate, in such a case the reaction can be M M. So, we will not spend too much time in writing reactions. Now, because we have already understood, how to write a reaction? So, here your metal now here sorry sorry I am little wrong here here M i dominates metal excess would M i not V M. So, apologies for that, so M M plus O O M i plus oxygen goes out because to maintain the side balance. Otherwise you will have a vacant side plus you will form 2 electrons or alternatively you could have M i plus O O, but that would be nothing but Frenkel defect.

So, so this is the non-Stoichiometric defect. So, equilibrium constant for this reaction k is equal to M i p O 2 to the power half into n e square divided by M M concentration into O O. Assume that these to be equal to 1. So, k is and also also to maintain the charging in neutrality you have n e to be equal to 2 times of M i. So, I can write now k as M i into p O 2 to the power half into 4 M i square. Again you can write this as M i is equal to k divided by 4 to the power 1 by 3 into p O 2 to the power minus 1 by 6.

So, here whether it is oxygen vacancies or whether it is a metal interstitials in if the oxide is M o. So, excuse me, so we can take in M O, so whether it is oxygen vacancies or metal interstitial both of them depend upon p O 2 to the power minus 1 by 6. As a result the electron concentration n e will be equal to 2 M I, which will so, n e is also proportional to p O 2 to the power minus 1 by 6. So, again when you plot these 2 p O 2 M i or n e so, if your, this is your, this will be your 1 by 6. So, this will be M i and this would be n e is equal to twice of M i.

So, this is the case when you have a oxygen deficiency, which means either oxygen vacancies is prevailed or metal interstitials prevail. In the next class, we will look at we will look at some other cases to work out the defect equilibria in and these non-stoichiometric oxides.

Thank you.