Electroceramics
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Lecture - 6

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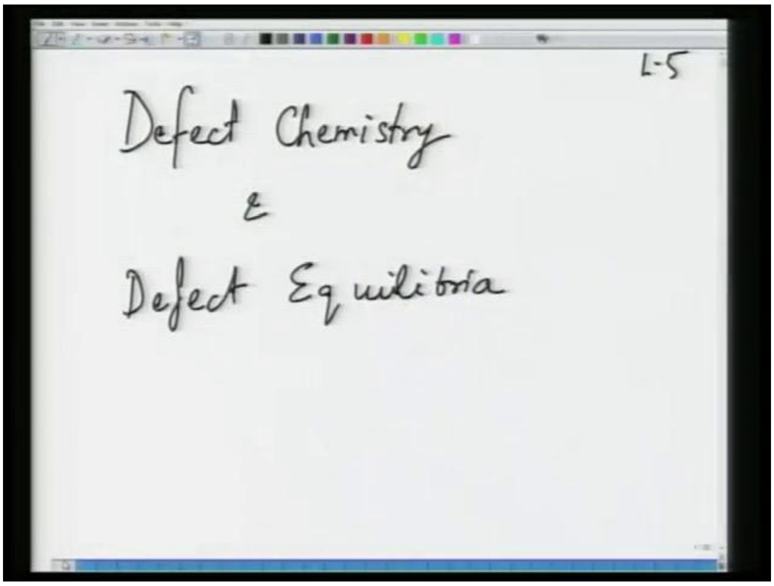

L-5

Defect Chemistry

&

Defect Equilibria

So, welcome to this new lecture. In the last lecture we started with the defect chemistry and defect equilibria and ionic solids or in electro ceramics.

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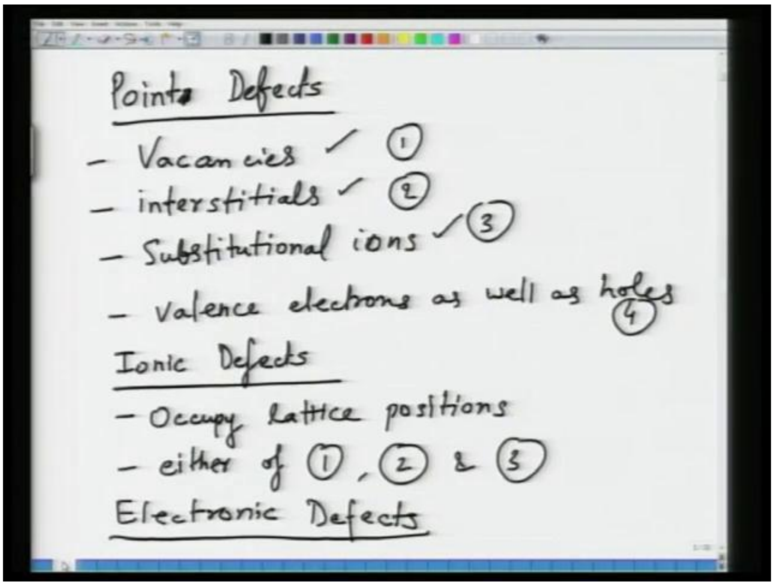

Points Defects

- Vacancies ✓ ①
- interstitials ✓ ②
- Substitutional ions ✓ ③
- valence electrons as well as holes ④

Ionic Defects

- Occupy lattice positions
- either of ①, ② & ③

Electronic Defects

So, there we introduced the concept of defects, there are various kind of point defects such as vacancies, interstitials, substitutional ions, etcetera.

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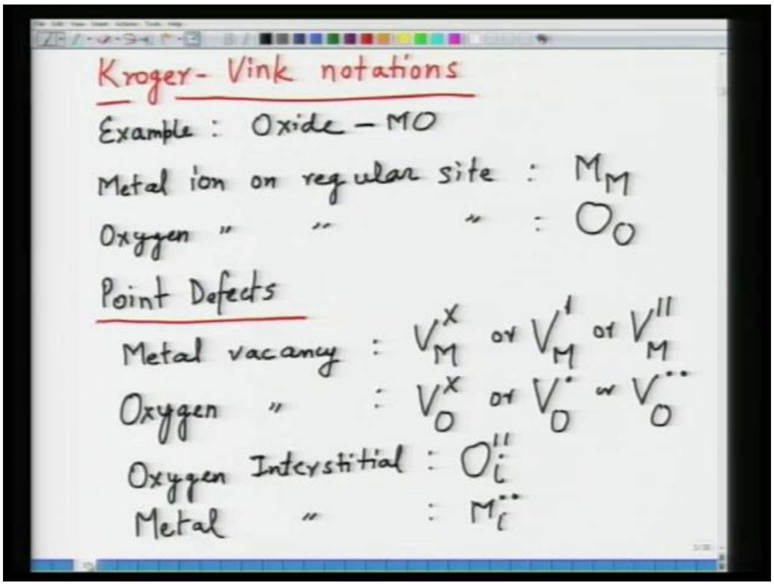

Kroger- Vink notations

Example : Oxide – MO

Metal ion on regular site : M_M

Oxygen " " " : O_O

Point Defects

Metal vacancy : V_M^x or $V_M^{'}$ or $V_M^{''}$

Oxygen " : V_O^x or $V_O^{\bullet}$ or $V_O^{\bullet\bullet}$

Oxygen Interstitial : $O_i^{''}$

Metal " : $M_i^{\bullet\bullet}$

And then we introduced the Kroger Vink notations where each defect whether charged or uncharged has a particular notation by which it is denoted.

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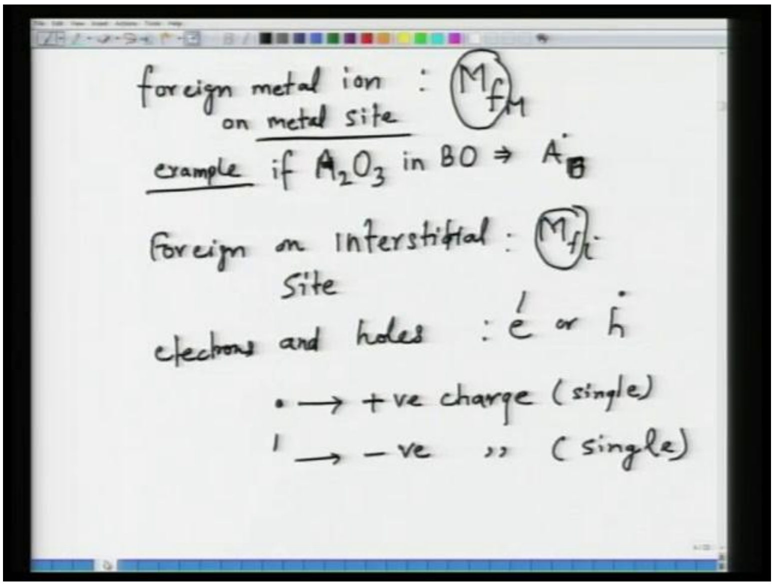

foreign metal ion on metal site : $\boxed{M_f}_M$

example if A_2O_3 in BO ⇒ $A_B^{\bullet}$

Foreign on interstitial site : $\boxed{M_f}_i$

electrons and holes : $e^{'}$ or $h^{\bullet}$

$\bullet \rightarrow$ +ve charge (single)

$' \rightarrow$ –ve " (single)

In the nut shell if a defect is positively charged then it is determined by, then it is denoted by a dot on top of it. So, for example, if in case of oxygen vacancy you write it V O double dot if it is completely ionized, and we will in this course we will assume that all the defects are completely ionized. And if it is a negatively charged defect such as metal vacancy then it would have a dash - one dash would mean single charge and two dash would mean double charge and so on and so forth.

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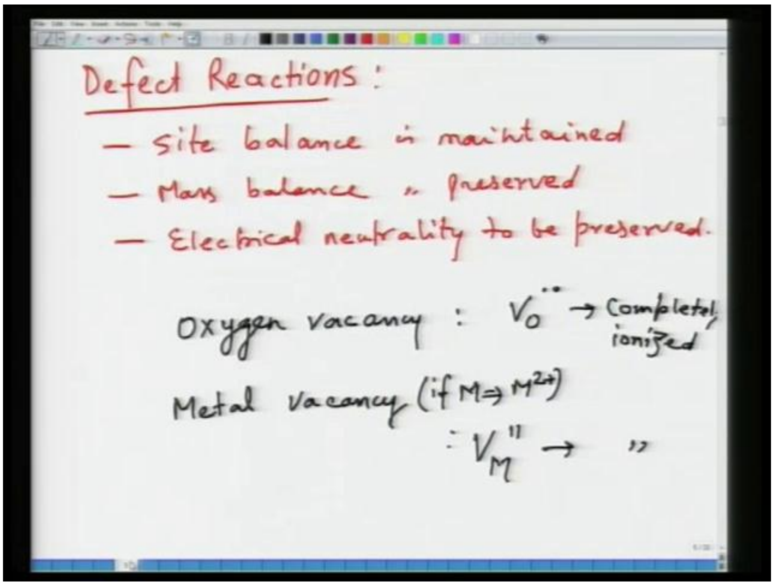

Defect Reactions :

— site balance is maintained

— Mass balance " preserved

— Electrical neutrality to be preserved.

Oxygen vacancy : $V_O^{\bullet\bullet}$ → Completely ionized

Metal vacancy (if $M \Rightarrow M^{2+}$)

: V_M'' → "

And then we looked at various defect reactions first of all the rules which govern the formation of defect reactions. So, formation basically what it means is that formation of defects can be interpreted via a reaction just like a chemical reaction. The thermodynamic bases we will establish a little later, but so you, if you write them like a chemical reaction then what you have to do is that you have to maintain the site balance, mass balance has to be preserved and also since the solid is electrically neutral, the electrical neutrality has to be preserved.

And in this case if since we are treating oxides as the main materials in this defect chemistry module, we will treat oxygen vacancy as V O double dot assuming that it is completely ionized and a metal vacancy if metal was M 2 plus then it would be V M double dash if it was completely ionized, if the if the valence of the metal is different then it would be V M single dash or triple dash or 4 dash depending upon the variance of the material.

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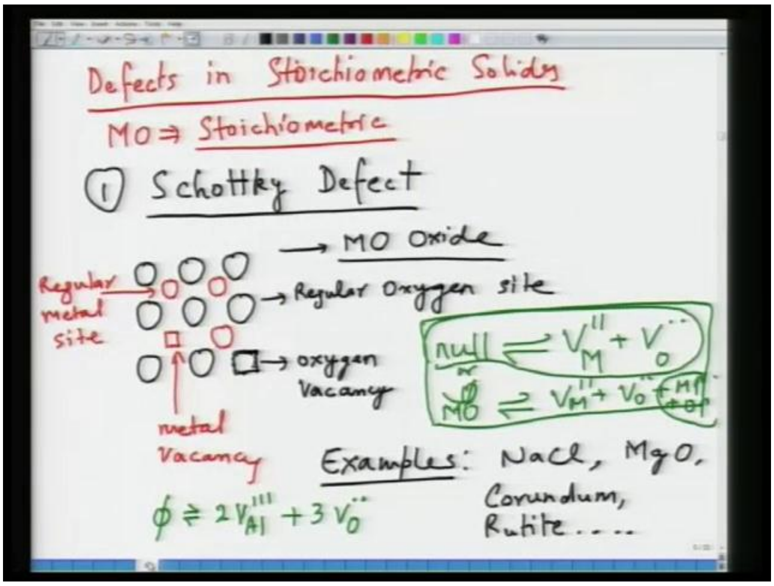
Defects in Stoichiometric Solids

MO ⇒ Stoichiometric

① Schottky Defect

$\text{null} \rightleftharpoons V_M'' + V_O^{\bullet\bullet}$

$\overset{\phi}{\cancel{MO}} \rightleftharpoons V_M'' + V_O^{\bullet\bullet} + M + O$

Examples: NaCl, MgO, Corundum, Rutile . . . .

$\phi \rightleftharpoons 2V_{Al}''' + 3V_O^{\bullet\bullet}$

And then we looked at what are defects in stoichiometric solids assuming the case of M O as a stoichiometric solid. So, the first important defect is Schottky defect. Schottky defect is nothing but formation of a metal and oxygen vacancy simultaneous formation. This does not disturb the stoichiometry of the material.

So, so basically you have a pair of two vacancies in a in a given solid. The, of course, the relative proportion of these vacancies will change if if you had materials like A l 2 O 3 or T i O 2 so that I would leave it to you to work out, but make sure that you maintain the charge and site balance there.

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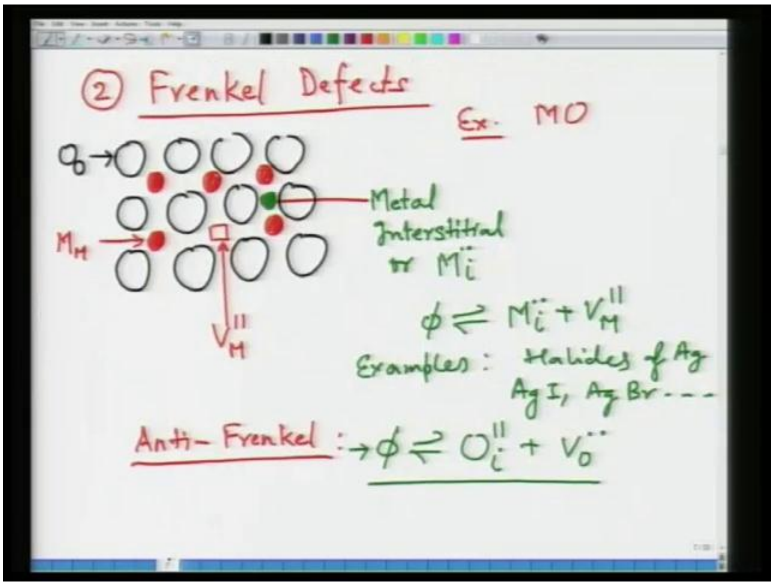

② Frenkel Defects

Ex. MO

$\phi \rightleftharpoons M_i^{\cdot\cdot} + V_M''$

Examples : Halides of Ag

AgI, AgBr - - -

Anti-Frenkel : $\rightarrow \phi \rightleftharpoons O_i'' + V_O^{\cdot\cdot}$

And another kind of important defect is Frenkel defect. Frenkel defect is formation of either a metal interstitial coupled with formation of metal vacancy, complimentary metal vacancy or in case of Anti-Frenkel it is formation of oxygen interstitial complemented by an oxygen vacancy. So, these are these are the two most common defects that occur in a stoichiometric solids.

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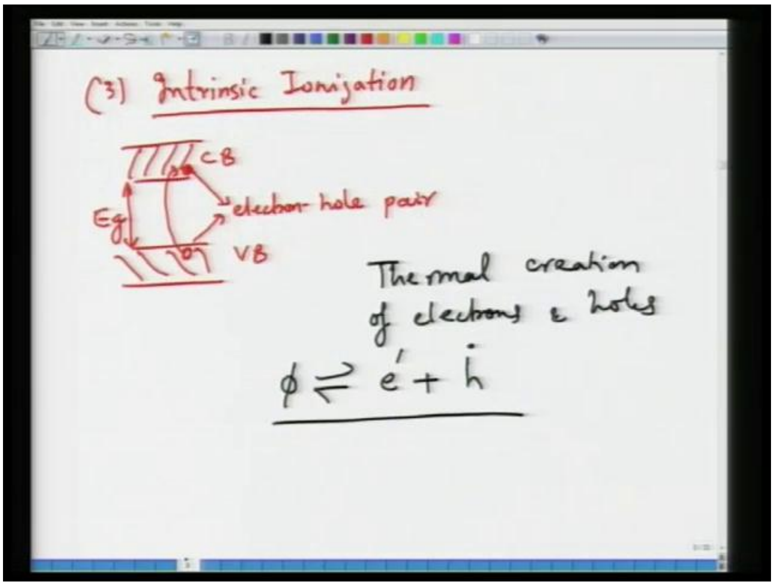

(3) Intrinsic Ionization

Thermal creation of electrons & holes

$\phi \rightleftharpoons e' + h^{\cdot}$

And third is an intrinsic ionisation which is nothing but excitation of electrons from the valence band to conduction band giving rise to a electron hole pair and this can occur in any material.

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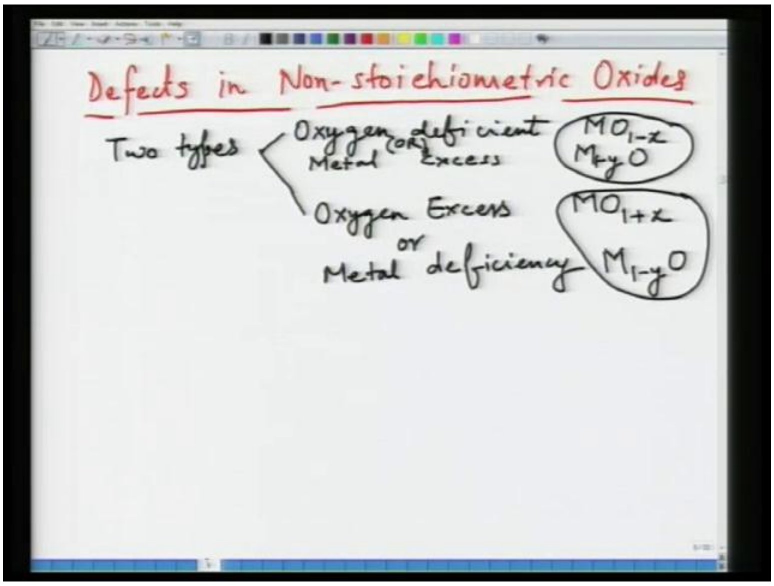

And then we looked at defect in the stoichiometric non-stoichiometric solids. In reality what happens is that most of these materials operate either at high oxygen pressure or low oxygen pressure and depending upon the operating conditions they may they are often non-stoichiometric. So, there are two basic types one is oxygen deficient or a metal excess which is which is denoted as M O 1 minus x or M 1 minus y O.

And second type is oxygen excess or metal deficient and this is written as either M O 1 plus x or M 1 minus y sorry it should in the in the previous case it should be M 1 plus y O and in the in in this case it would be M O 1 plus x or M 1 minus y O.

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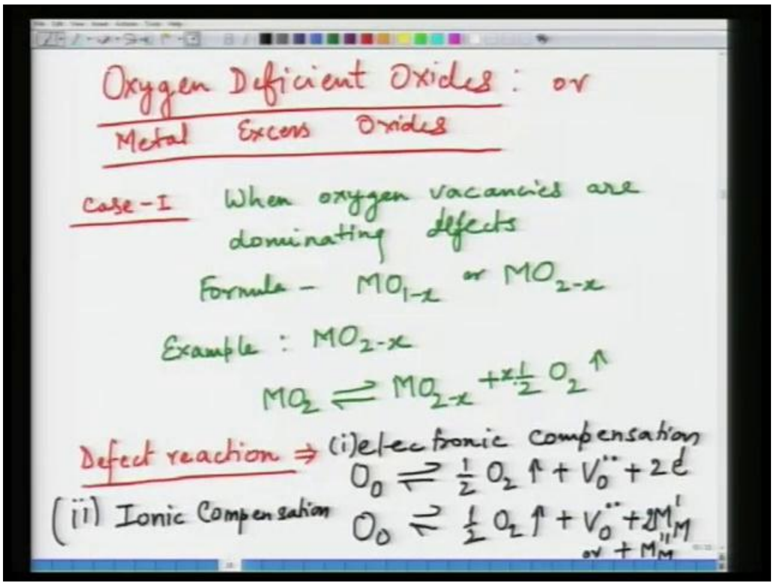

Oxygen Deficient Oxides : or Metal Excess Oxides

Case - I When oxygen vacancies are dominating defects

Formula - MO_{1-x} or MO_{2-x}

Example : MO_{2-x}

$$MO_2 \rightleftharpoons MO_{2-x} + x \cdot \frac{1}{2} O_2 \uparrow$$

Defect reaction ⇒ (i) electronic compensation

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

(ii) Ionic Compensation

$$O_O \rightleftharpoons \frac{1}{2} O_2 \uparrow + V_O^{\bullet\bullet} + 2M'_M \text{ or } + M''_M$$

And then we took various cases for starting with oxygen deficient or metal excess oxides and the case one was where we took oxygen vacancies as dominating defect and we established how the defects can be formed, you can have electronic compensation of defects or you can have ionic compensation. Basically in both of these cases you will have formation of oxygen vacancy coupled with either formation of electrons or say free electrons or reduction of metal vacancy, metal site, metal on metal site.

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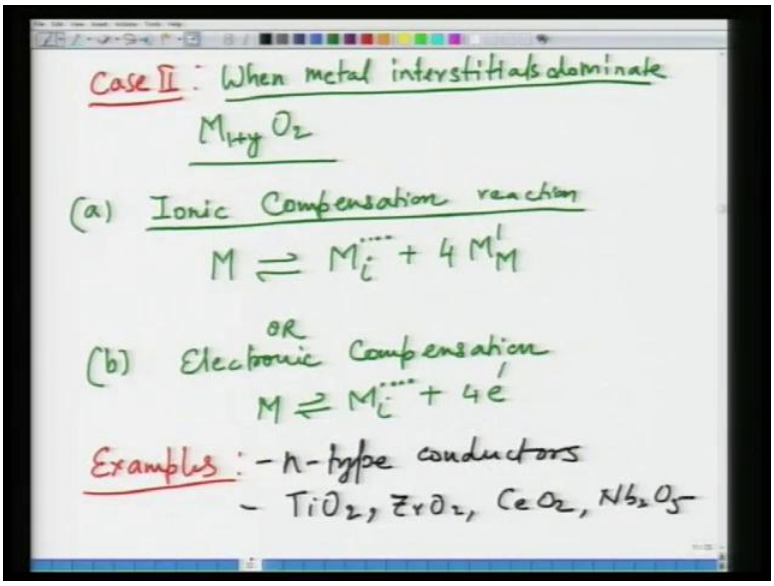

Case II : When metal interstitials dominate

$M_{1+y}O_2$

(a) Ionic Compensation reaction

$$M \rightleftharpoons M_i^{\bullet\bullet\bullet\bullet} + 4M'_M$$

OR

(b) Electronic Compensation

$$M \rightleftharpoons M_i^{\bullet\bullet\bullet\bullet} + 4e'$$

Examples : - n-type conductors

- TiO_2, ZrO_2, CeO_2, Nb_2O_5 -

And then we looked at the case when metal interstitials dominate and in that case the formula would be for example, in this case we have taken M O 2. So, here it would be M 1 plus y O 2 and as a result so here since metal is plus 4 vacancy, the metal will form an interstitial followed by, complimented by reduction of metal on the metal site or if it was electronic compensation then it would give rise to 4 electrons. So, that difference in two cases is number of electrons created, relative proportion of two defects and examples of such cases could be n type conductors materials such as T i O 2, zirconium oxide, cerium oxide, N b 2 O 5. So, now we will look at the case of metal deficient oxides.

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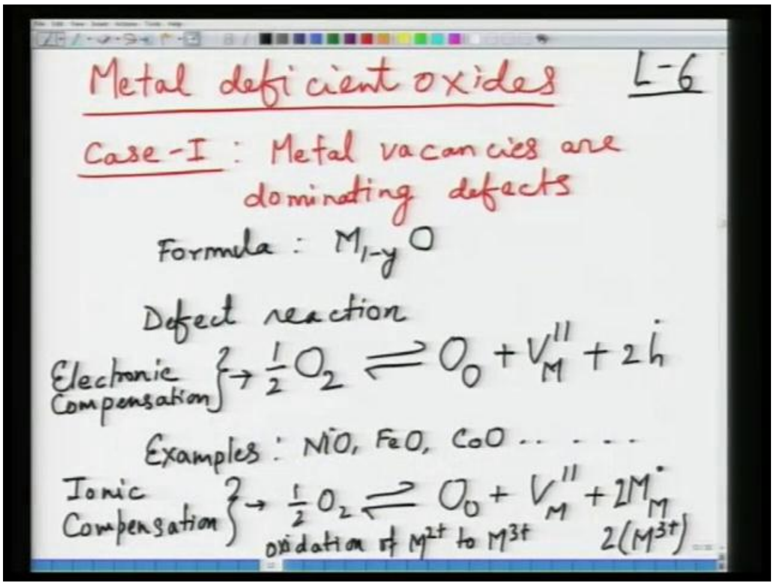

Metal deficient oxides L-6

Case-I : Metal vacancies are dominating defects

Formula : $M_{1-y}O$

Defect reaction

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

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

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

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

So, we will start with. So, in case of metal deficient oxides as you can guess intuitively it would be either metal vacancies or oxygen interstitial if it was excess oxygen in case of excess so metal deficient would in this case we another case of oxygen excess and formation in this case typically happens at the surface. We will deal with two cases. The first case is case one is when metal deficiency, metal vacancies are dominating defects.

So, in this case we represent the oxide. We write the material as a formula is M 1 minus y O as we have seen earlier and if it was M O if it was M 2 O or M O 2 then it would be different of course, and where y represents the extent of non-stoichiometry and the possible defect reaction that would occur is, so, defect reaction would be, so, you have since it is a case of metal deficiency so you have oxygen coming out, oxygen coming in oxygen goes to oxygen site, but if it was so we are taking the case of M O type which means for.

Now, you have to maintain the site balance so you create one oxygen site where the oxygen goes complimenting that you have to have a metal site, but since this is a metal deficient oxide you will have vacancy of metal. Now this vacancy of metals since it is a M O form it would be doubly negatively charged, double negative charges. Now, this can be complemented in this case for for example, by formation of two holes. So, this is your electronic compensation. So, basically you have creation of holes and as a result of creation of holes just like in the previous case this forms a p type conductor and examples of materials which show this characteristic could be your materials like N i O, F e O, C o O etcetera. So, most of these transition metal oxides they show this characteristic.

Now, this is electronic compensation right? If you have ionic compensation this would mean half O 2 O o complimentary metal site which is vacant. Now, unlike in the previous case where the metal reduction occurred here you may have metal oxidation oxidation. So, metal on metal site if it was oxidising to plus extra plus 1 state and this would be 2 M M dash. So, basically what a defectively means is that this is equal to 2 of M 3 plus. So, metals so basically what it means is is that oxidation of M 2 plus to M 3 plus. Now, you can have also from M 2 plus to M 4 plus in that case only one site will be oxidized. So, this is the basis of any compensation of electronic compensation and these materials. Now, typically what you will find these materials are susceptible to having extra holes so metal vacancies often complemented by creation of extra holes giving rise to a p type conduction behaviour in these materials.

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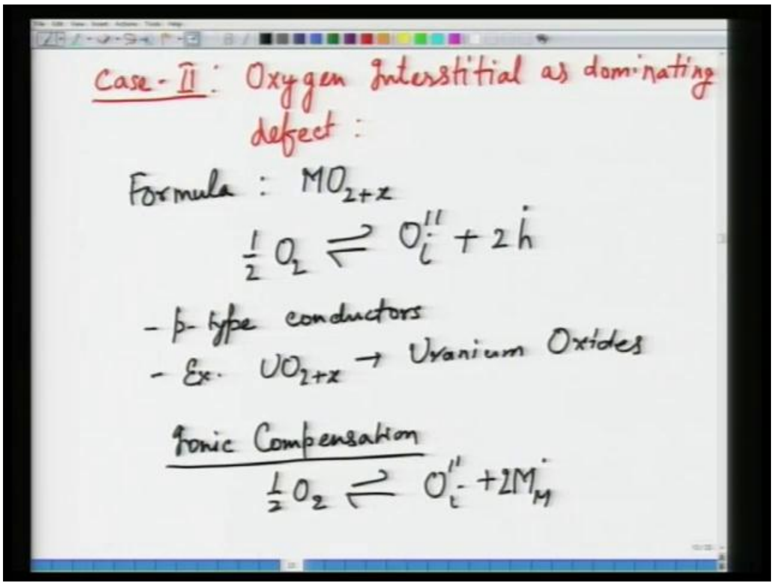

Case - II : Oxygen Interstitial as dominating defect :

Formula : MO_{2+x}

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

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

Ionic Compensation

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

Now, we will take the second case. Second case is when you can have oxygen interstitial as dominating defect. So, in this case what happens is that now how do you represent these materials. So, formula would be M O 2 plus x since you have extra oxygen and so extra oxygen in another way means you have deficiency of metal and the way these this happens is half O 2 so here the oxygen does not go to oxygen site rather it goes to interstitial site. So, it goes, if it goes to interstitial site you do not need to create any kind of vacancy if it goes to interstitial site and if it is completely ionised it will have two double dashes O i double dash plus formation of 2 holes.

This would be your again this would give rise to p type conductors. I am choosing whether it is M O or M O 2 based on the cases in which each of these defects are observed. So, the choice of the basis of choosing whether M O or M O 2 for particular case is entirely based upon type of materials which show this behaviour. An example is like U O 2 plus x which is uranium oxide. So, again this is your electronic compensation, ionic compensation would again mean oxidation of metal. So, in principle it is also possible so so ionic compensation would mean plus M M dot. So, two of the metal sites will be oxidized, but again as I said in these in both of these cases the materials prefer to have p in the prefer to be in the form of p type conductors by creation of extra holes. So, this is the basis for formation of defects in non-stoichiometric oxides. So, we have discussed two of these cases and looked at the examples whether it is oxygen excess or oxygen deficient.

Now, not only you can have defects created by as a as a result of Schottky or Frenkel defect formation or electronic disorder formation, you can also have and as we saw because of deficiency or excess of oxygen or metal. You can also form defects by dissolving impurities in these materials, most of these materials, most of these ceramic materials they tend to contain some amount of impurity in them depending upon their nature and their structure. Impurity incorporation often is governed by the size of interstitials that you might have, the size of ion which coming inside the host lattice etcetera. But if you look at for example, most of the reflective oxides none of them is available in extremely pure form and also it is very difficult to, it is commercially economically very expensive to fabricate these materials in ultra pure form. So, as a result they tend to have some sort of impurities in them. So, most of these impurities when they are present in the host lattice they also give rise to complementary defects.

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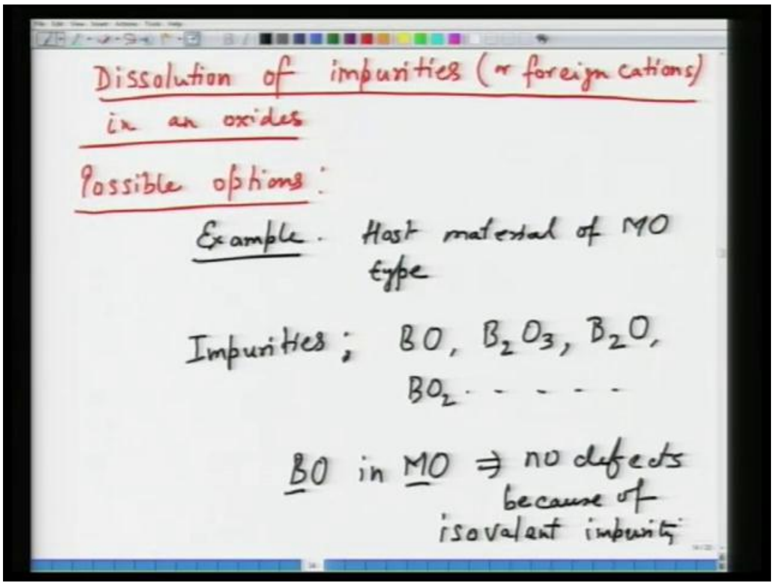

Dissolution of impurities (or foreign cations) in an oxides

Possible options:

Example. Host material of MO type

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

BO in MO ⇒ no defects because of isovalent impurity

So, we will discuss this as this part as dissolution of you can say impurities whether intentional or unintentional or foreign cations, assuming that most of these impurities are oxides as well in an oxide. So, here we will so you can have various kinds of so possibilities are various. For example, host material would be of M O type. Now, if you have impurities, a impurities can be B O or B 2 O 3 or B 2 O or B O 2 and so on and so forth.

Now, if it was in substitution impurity which means B replaces M on the metal site in that case you do not have any problem. Oxygen occupies oxygen site and B occupies the metal site given that if their sizes are not too different, if the sizes were too different then the host lattice does not accept the impurity that readily, as a result the impurity is present as a solid chunk of impurity inside the material than substituting because it gives rise to massive strain in the lattice and it is, but however if the sizes were equivalent then B O in M O, no defects because the valence of B and valence of M are equal.

However, when you have replacement of a, if you have dissolution of impurities in the form of B 2 O 3 or B 2 O or B O 2. In this case the cation which is coming in to the host lattice has a different valence and these are called as aliovalent ions. In previous case it would be called as isovalent, in the previous case it would be aliovalent. So, no defects because in the previous case the you you will not form any defects because of isovalent impurity.

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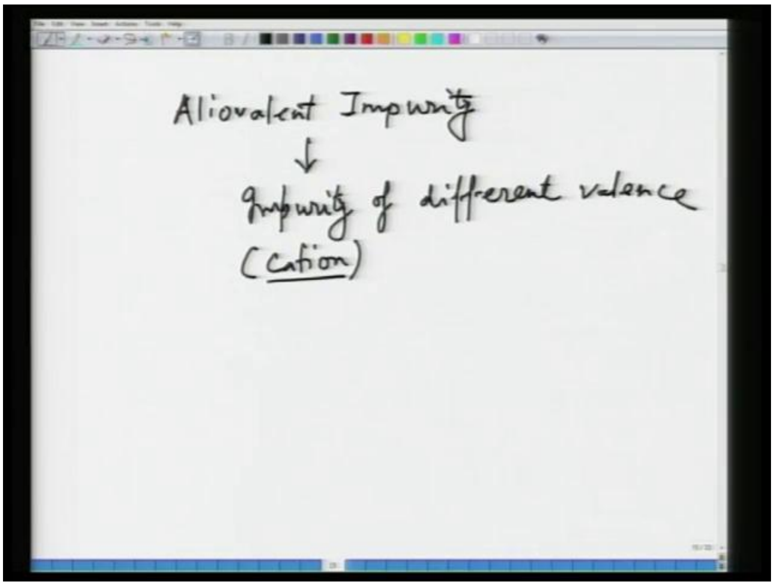

Aliovalent Impurity

↓

Impurity of different valence

(Cation)

However, when you have aliovalent aliovalent impurity what it means is that impurity of different valence and by which you basically mean cation because oxygen if you consider impurity as an oxide, oxygen has same valence of oxygen so there is no problem there, but cation has profound effect on the type of defects that you will create.

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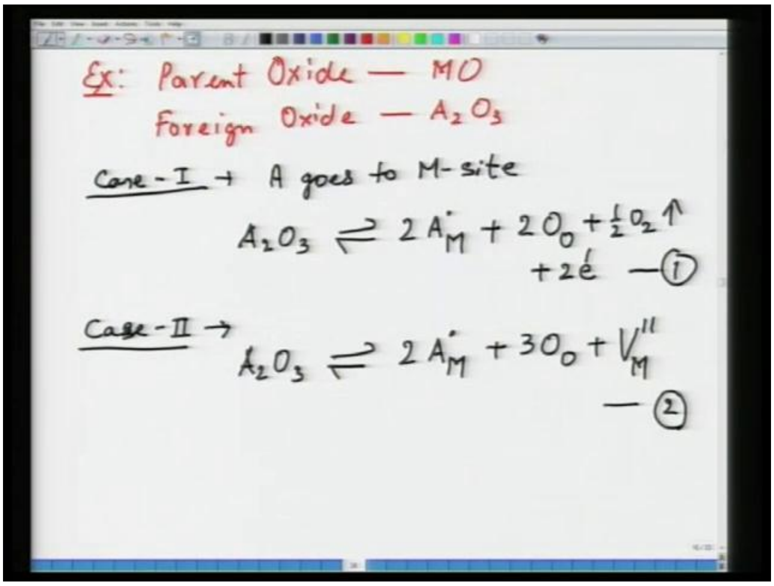

Ex: Parent Oxide — MO

Foreign Oxide — A_2O_3

Case-I → A goes to M-site

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

Case-II →

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

So, let us take the case of dissolution of so suppose here we take example. So, the host the parent oxide or the host oxide is, parent oxide is M O and the foreign oxide is let us say in this case A2O3. So, what are the scenarios which are possible? You can have various scenarios for example, if you if you have now in in these cases what will happen is A will typically go to M site. So, as a result you will have either creation of some of the metal vacant sites or you will have creation of some other charges. So, let us see what these things are. So, let us say first is case one. So, in this case the first case is let us say the impurity atom A goes to the metal site. So, what it do so you have dissolution of case one is A goes to M site M site and so let us say what it happens is here.

So, A2O3 going to going into M O lattice let us say both of A goes go to M site, both of the A's have gone to M site, what it means is that the valence of A is plus 3 valence of M is plus 2 as a result the A which is going to M site it is going to have extra plus 1 charge which is denoted by a dot. So, 2 A M dot plus let us say since two A's are going to two M sites, the two to maintain the site and mass balance two of the three oxygen's here go to oxygen site. So, which means they maintain the site balance of M O which is the parent lattice. Extra oxygen goes out half O 2. So, extra oxygen does not stay inside. So, this is balanced in terms of mass in site, but, how about the charges, the electrical neutrality. You have now plus two charges here, these plus two charges have to be compensated.

So, these two charges here are compensated by creation of two electrons. So, this is your electronic compensation and giving rise to quasi free electrons. So, this is case one. Case two here again you have A going to A site, but in this case all the three oxygens occupy oxygen site. So, let us see what happens here. So, A2O3 so both the A's go to M site having one positive charge at each site plus all three oxygen's go to oxygen site. Now, both the A's have gone to M site, all the three oxygens have gone to oxygen site. So, mass balance is fine, but what about the site balance? Parent lattice has one of one M site for O site.

Now, here you have created three O sites. So, for three three three of these O sites you need to have three of M sites and you are filling only two of them which means one of the O sites which is created as a result of three oxygens going to oxygen sites, you will have one metal site which would be vacant. So, you will have V M having two negative charges. Now, this is balanced site in mass wise as well as charge wise. So, this is another possibility that could happen in these when you when you put A2O3 impurity in M O solid. So, these are two cases when you have dissolution of foreign oxide into a host oxide of M O type let us say. Now, you can also have other scenarios.

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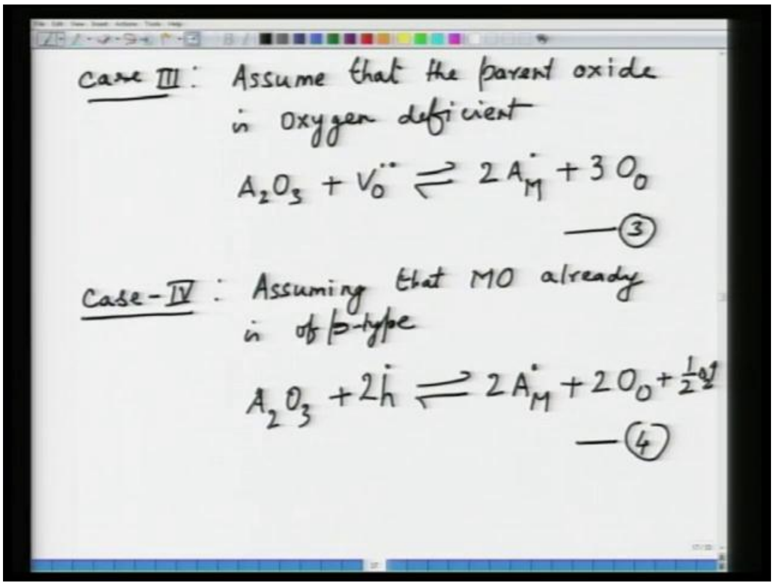

Case III: Assume that the parent oxide is oxygen deficient

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

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

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

Other scenario for example is, suppose the parent oxide was oxygen deficient to begin with so here assume that the parent oxide is oxygen deficient, it already had oxygen deficiency. So, then what you have you have A 2 O 3 going into the M O lattice plus you had V O’s present there. Now what is going to happen to these V O’s? So, both the metals so you had 2 A’s go to M site, now what? Since, you had one oxygen site already vacant and you are going to create two for these all the three oxygens occupy oxygen site. Now, what has happened is the oxygen vacancy which was present to, which was present in the solid to begin with has taken care for one extra oxygen. As a result you would not create any other defect in the material. So, this would be case three.

So, here it is balanced site wise as well as you have charge wise balance as well you have two positive charges on the left and two positive charges on the right. And you can take case four. Case four would be assuming that M O already had already is of p type which means it already has lot of holes inside it. So, how do you do, how do you do now. So, you have A 2 O 3 A 2 O 3 plus some holes for present let us say I am not going to, I am going to balance this reaction later on. So, both the A’s go to M site two positive charges. Now, here in this case what happens is since you had already holes present and let us say 2 O O’s and half O 2 one of the extra oxygen goes out since you have to maintain the site balance. So, here I do not create any defect on this side, all I do is that I make it 2 h plus just to balance it electronically and now you also have site balance and this is another kind of reaction that would be possible if the material was of p type to begin with.

So, in the previous slide we looked at when the material was a stoichiometric it did not have any defect to begin with, then what is the scenario? So, you can have creation of a metal vacancy or creation of two extra electrons or alternatively if the metal was already oxygen deficient or contained holes to begin with then these holes or oxygen vacancies could be compensated by presence of these impurities. So, as a as a home work you can do for example, as an exercise.

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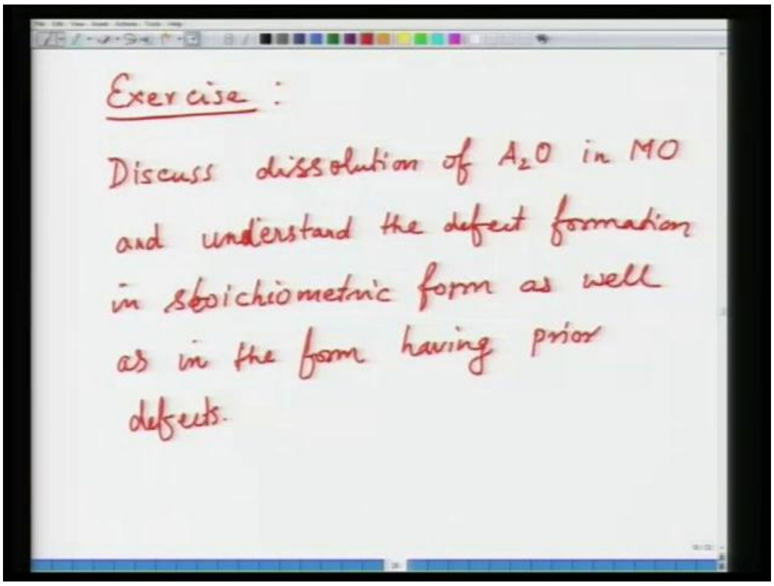

Exercise :

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

You can discuss dissolution of A 2 O in M O and understand the the defect formation So, this I will leave it to you to work out yourself and that will make it clear what happens when you put oxides of different valence and parent lattice. So, I will just leave it to you at the moment. The solution of this I will provide these will be provided in extra sheets or some reference will be provided for these if you want to go through them. So, so this has established so, so far what we have seen is how the defects, what kind of defects are there, how they are form in formed in a stoichiometric solids, how their defects are formed in non-stoichiometric solids where you have either metal deficiency or oxygen excess or metal excess or oxygen deficiency and what happens when you dissolve either intentionally or unintentionally an impurity which is typically an oxide in a parent lattice and this particular material impurity material has different valence cations as compared to the host lattice.

So, I hope that now it is clear how the defects are formed, but the question now is I said in the beginning of the lecture that these defects are present in the solid thermodynamically, but the question now arises how, what is the equilibrium concentration for these defects, how can we work it out? There is a thermodynamic basis by which we can work out the equilibrium concentration of these defects especially the intrinsic defects.

Now, here we are going to talk about intrinsic defects. You have two two kind of defect one is a intrinsic defect which is the defect which is created as a result of either non-stoichiometry of the solid or or Schottky or Frenkel defects, second type of defect is extrinsic defect which is created as a result of impurity incorporation in the material. So, these two are two different cases. So, here we will look at what is the equilibrium concentration of intrinsic defects in a given material?

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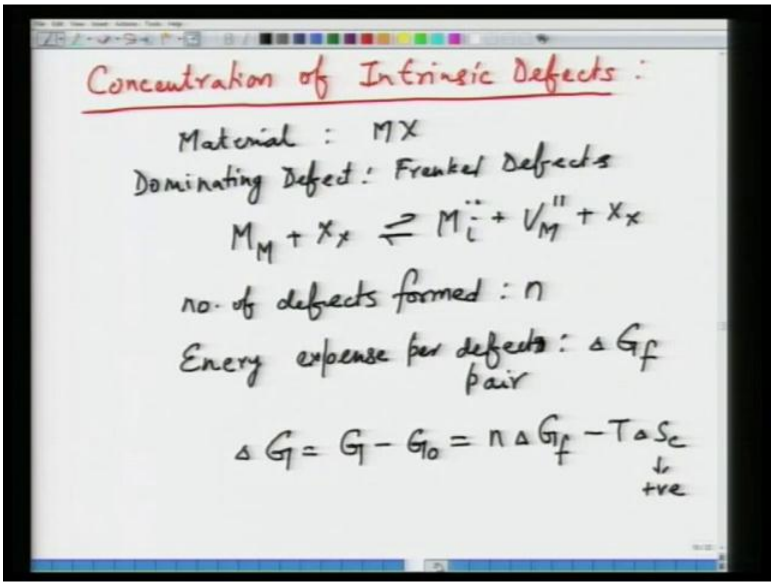

Concentration of Intrinsic Defects :

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

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

So, what we will do is that concentration of intrinsic defects. Let us consider with the for example, formation of let us say Frenkel defect in a in a material M X. So, the the material we take is is of M X type which means M and X valancies are same and let us say the dominating defect is is Frenkel defect. So, if it was a Frenkel defect then I can write this as M M plus X X as M i plus V M plus X X. So, you have site balance because you have one anion site and one cation site, you have charged valence the interstitial adding in two charges is balanced by two negative charges on the metal vacancy site. So, this is your defect reaction.

Now, when you form the defects what happens thermodynamically? Thermodynamically the system had a free energy before the defects were formed. Imagine the crystal having no defects, it has certain free energy. Now, defects want to form, once that defect form there is a free energy change associated with that, so and each defect is going to have its own energy formation or you need to spend some energy in forming that defect. So, what is that energy balance? Let us say if if you form number of defects that are formed are are n and the energy expense per defect let us say is delta G f. So, basically per defect per defect pair you can say because here you are, here you are going to form a pair. So, the moment you form metal interstitial you have metal vacancy.

So, energy expense per pair is per defect pair is delta G f. So, what is the net free energy change so delta G from a 0 defective state to let us say n defective state is equal to G minus G naught. G naught is the defect free state so this would be n delta G f. So, this is your enthalpy change minus at a given temperature at that particular temperature we are we are assuming that here temperature and pressure are constant.

At this particular temperature what is the change in the entropy because the moment you create the defects inside a material you are going to lead to, it is going to it is going to lead to change in the configurational entropy which is delta S c and which is going to be positive quantity because you are going to introduce defects which means you introduce a disorder inside the material and as the disorder increases the entropy change, entropy always increases. So, this is what is the basic thermodynamic free energy change that is going to happen when you form n Frenkel defect pairs, each defect pair having energy of formation of delta G f and and and minus of that entropy term which is a positive term because of increase in the entropy.

Now, when you plot this delta G which is going to happen with respect to n so how do you, why we are going to do this? We are going to do this because we want to find out what is the equilibrium concentration. Now, equilibrium concentration will be achieved when this free energy change will be minimum. You can keep forming defects, let us say you form n 1 defects n 2 defects n 3 defects n 4 defects etcetera etcetera now all these concentrations are not going to stable, only one particular concentration is going to be stable at which delta G is going to be minimum.

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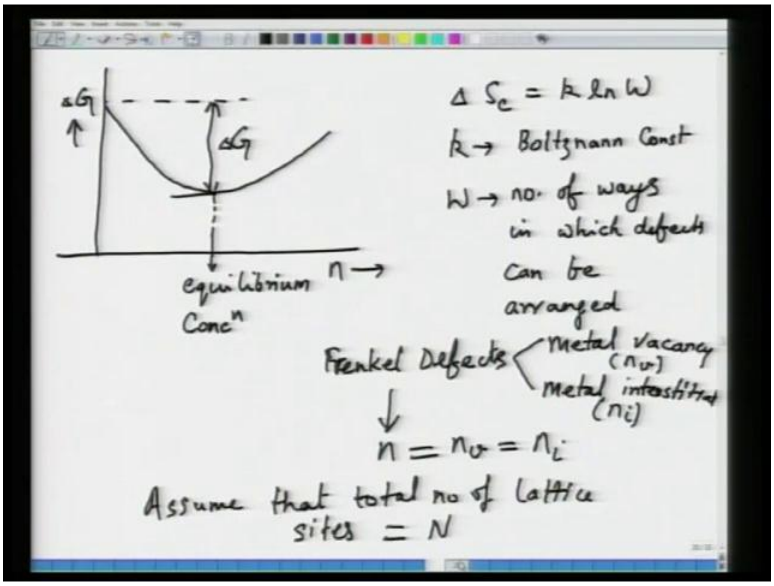

$\Delta S_c = k \ln W$

$k \rightarrow$ Boltzmann 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 $= N$

So, the plot of delta G if you plot delta G versus n let us say the n defects is going to be something like this. You can simulate this graph as well and this minima will correspond to equilibrium concentration because here this change in free energy would be maximum which means the free energy of the crystal after formation of these many defects will be minimum.

So, what we now need to do is that we need to differentiate that particular equation which we wrote in the previous slide with respect to n and find out what is the equilibrium concentration of defects. So, let us do that, now for to do that first we need to work out what is the change in entropy. Change in entropy can be written as delta S c can be written as k l n W where k is nothing but your Boltzmann constant and W is is W is nothing but number of ways in which defects can be arranged inside the solid on these lattice sites. So, the moment you put defects you you can, you can put defect in the way you want it, but what is the optimum way? So, and and of course, there are going to be many different possible ways.

So, let us work out what is the number of ways in which you can put these defects on the metal sites sorry on on the on the atomic sites or in the lattice. Let us say now when you form when you form these Frenkel defects. So, Frenkel defect would mean you have metal vacancy and you have metal interstitial. Now, let us say, we are saying total number of defect is equal to n this is going to be equal to number of vacancies n v and this is going to be equal to number of interstitial which is n i. So, just by equality and just by looking at the defect reaction itself this is very simple. So, number of the Frenkel defect pairs n is equal to number of metal vacancies and number of metal interstitials.

So, now now assume that total number of lattice sites is equal to capital n. So, in this case if if these are the numbers which you have what is the number of possible ways in which you can arrange the vacancies?

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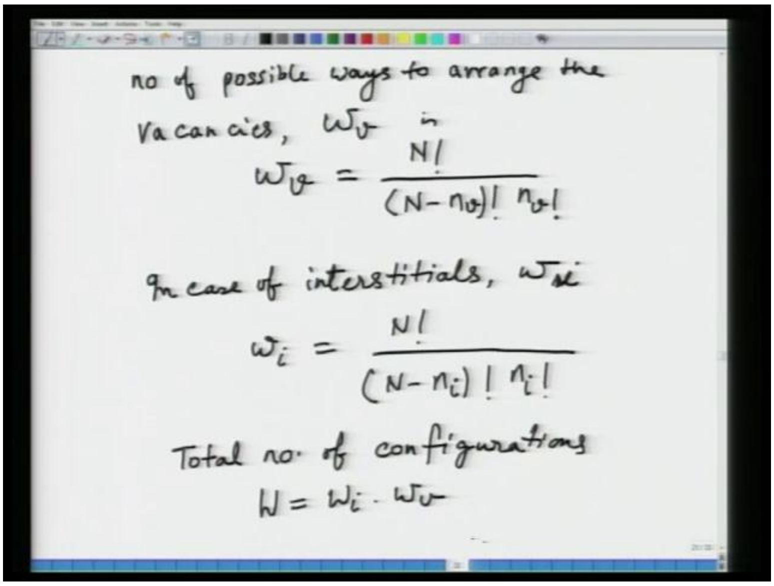

no of possible ways to arrange the
Vacancies, W_v is

$$W_v = \frac{N!}{(N-n_v)!\, n_v!}$$

In case of interstitials, W_i

$$W_i = \frac{N!}{(N-n_i)!\, n_i!}$$

Total no. of configurations

$$W = W_i \cdot W_v$$

So, so let us say number of possible ways to arrange the vacancies. Let us say that is written as W v. So, this so W v is given as factorial N divided by N minus n n v factorial multiplied by n v factorial. So, so this is your W v. Now similarly, what is the number of possible ways to arrange the interstitials? So, in case of interstitials we can define this as W n sorry W i and this W i is again given as since you have similar number of interstitials and vacancies this would be N factorial divided by capital N minus n i factorial multiplied by n i factorial.

So, this we have so far worked out individual ways for arranging vacancies as well as interstitial. So, what is the total number of configurations? We define that as W and this is nothing but product of W i into W v. So, as a result we can work out what is the entropy change.

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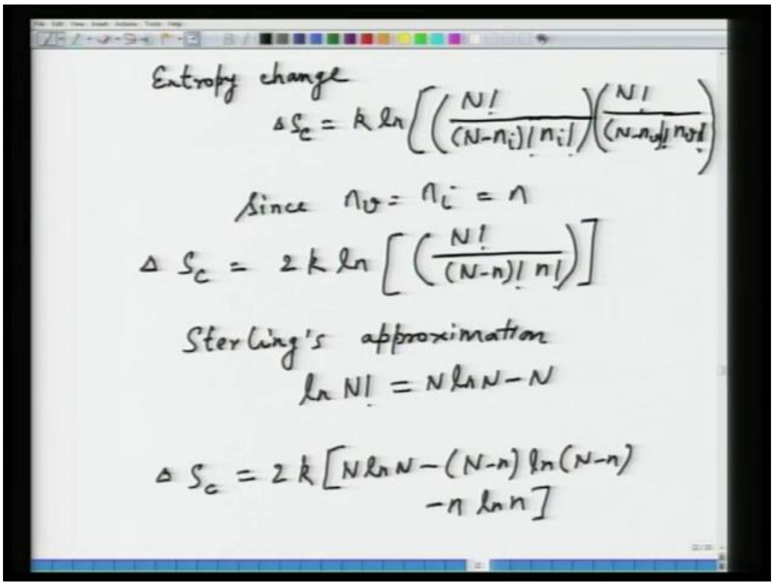

Entropy change

$$\Delta S_c = k \ln \left[\left(\frac{N!}{(N-n_i)!\, n_i!} \right) \left(\frac{N!}{(N-n_v)!\, n_v!} \right) \right]$$

Since $n_v = n_i = n$

$$\Delta S_c = 2k \ln \left[\left(\frac{N!}{(N-n)!\, n!} \right) \right]$$

Sterling's approximation

$$\ln N! = N \ln N - N$$

$$\Delta S_c = 2k \left[N \ln N - (N-n) \ln (N-n) - n \ln n \right]$$

Entropy change is entropy change is delta S c that is equal to k l n multiplied by N factorial divided by N minus n i factorial into n i factorial and again N minus n v factorial into n v factorial. Now, since we know that n v is equal to n i so we can write this as so it would be 2 k l n N factorial is equal to n, we can write this as N minus n factorial into n factorial.

Now, to solve this log of factorials you need to use Sterling’s approximation. So, which is Sterling’s approximation is nothing but if you have l n N factorial then this would be N l n, N l n N minus N. So, if you apply this this to our equation what you can work out is delta S c would be equal to 2 k N l n N minus of N minus n l n N minus n minus of a small n into l n small n. So, this is the expression that you work out after working out both W i and W v and then eventually W and substitute in the expression for change in the entropy.

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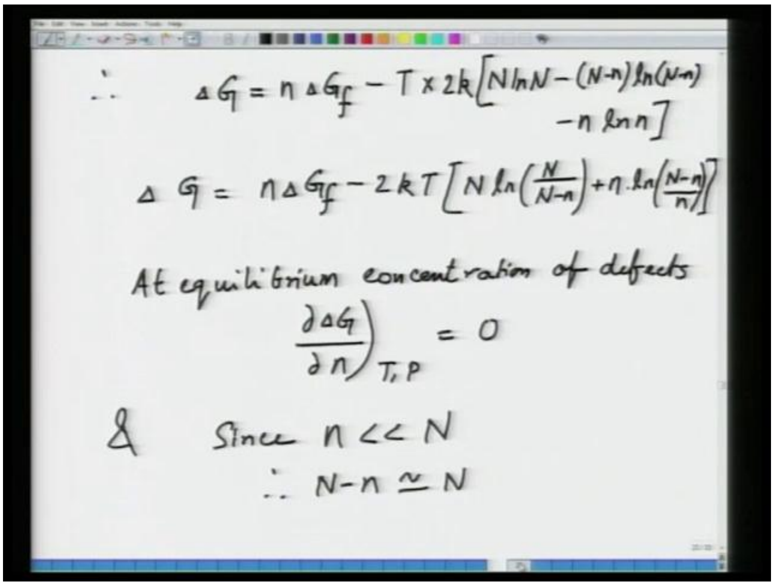

$$\therefore \quad \Delta G = n\Delta G_f - T \times 2k\left[N \ln N - (N-n)\ln(N-n) - n \ln n\right]$$

$$\Delta G = n\Delta G_f - 2kT\left[N \ln\left(\frac{N}{N-n}\right) + n \ln\left(\frac{N-n}{n}\right)\right]$$

At equilibrium concentration of defects

$$\left.\frac{\partial \Delta G}{\partial n}\right)_{T,P} = 0$$

& Since $n << N$

$\therefore \; N-n \simeq N$

So so the net free energy change so the total free energy change that we wrote earlier delta G that would now be equal to n delta G f this is the first term minus of T into 2 k into capital N l n N minus capital N minus small n l n capital N minus small n minus of small n l n n. So, this is your expression for free energy. So, this delta G now you can write it as n delta G f minus of 2 k T into N, if you can rearrange, if you rearrange these what you will get is N l n N divided by N minus small n plus small n into l n of N minus small n divided by small n.

This is what you are going to get if you do it, if you rearrange these. That is very simple you can just, you just need to open this up. So, that will give you the form so if you just do this N l n, N l n N minus N l n n minus n. So, you can take the N out you can make it l n N divided by N minus n and this would become plus. So, plus n l n N minus n minus small n l n small n. So, you take out small n and then this would become l n of N minus small n divided by small n.

So, this is very simple to do. Now, at equilibrium we have we have already talked about the equilibrium. At equilibrium at equilibrium concentration of defects we can say del of delta G del n at constant temperature and pressure is equal to 0 and we can also assume since number of defects in the solid are going to be much smaller than the number of lattice sites, we can say since and n is very small as compared to N so N minus small n is almost equal to capital N as I that you will see when we calculate these numbers. So, using these two formulisms now you can simplify this equation further. So, when you differentiate what you will find is this so if you do that exercise and replace capital N minus small n to be equal to, almost equal to capital N then you will find as small n so this would lead to.

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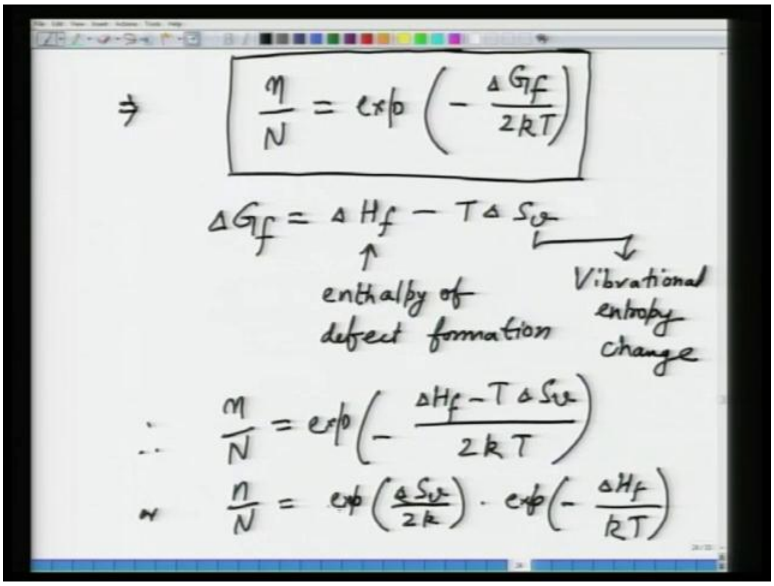

$$\Rightarrow \quad \boxed{\frac{n}{N} = \exp\left(-\frac{\Delta G_f}{2kT}\right)}$$

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

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

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

So, if you differentiate the free energy equation with respect to n this would lead to it is a very simple differentiation. So, this would lead to exponential of minus delta G f divided by 2 k T. So, so this is an important expression. So, what this, what this tells you is that so vacancies, formation of vacancies is exponential function of energy expense per pair and temperature and as you can see now here as the temperature increases this number will increase and as this number increases this number will decrease, it is going to be much harder to form defect when you have low temperature and higher energy expense. Now, this delta G f can further be broken into delta H f minus T delta S v.

So, this delta H H f is nothing but your enthalpy of defect formation and delta S v is nothing but so earlier we took the configuration entropy change this would be your vibrational entropy change.

So, if you do, if you if you plug this in above equation so as a result small so small n by T t delta S v divided by 2 k T and this can further be equal to exponential of delta S v by

2 k multiplied by exponential of minus delta H f by k T. Now, in most cases what happens is this entropy change is very small so this can so this term is often neglected.

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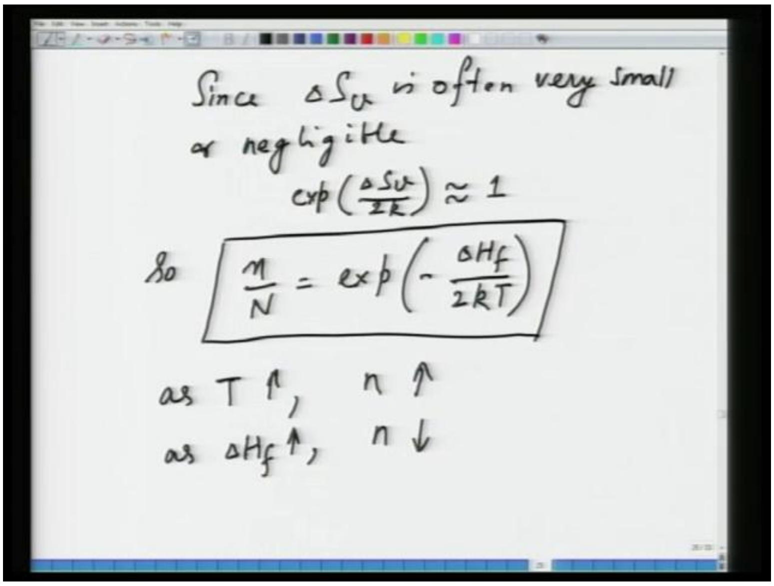

Since ΔS_v is often very small or negligible

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

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

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

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

So, since delta S v is often very small or negligible so exponential of delta S v divided by 2 k is almost equal to 1. So, n by N is equal to exponential of minus delta H f by 2 k T. So, this is your standard expression to calculate the equilibrium concentration of defect in an in a ceramic material or in an ionic solid.

Now, this expression tells you that n is an exponential function in temperature and enthalpy of formation. So, you can write so, as temperature increases n increases and as delta H f increases n decreases. So, what you will see is that most of these ceramic materials they have appreciable intrinsic concentrates, appreciable intrinsic defect concentration at higher temperatures. At lower temperatures they do not contain significantly larger number defects.

Similarly, delta H f, delta H f is enthalpy of defect formation so which you can guess that delta H f is nothing but ease of defect formation, represents the ease of defect formations. Of course, materials with higher bond distance are going to formed find it much more difficult to form defects and you will and similarly, materials with higher temperature they will have a higher melting points, they will have at one temperature lower defect concentration as compared to those with lower melting points because melting points are related to bond energies for example, you can make comparison between magnesium oxide and sodium chloride.

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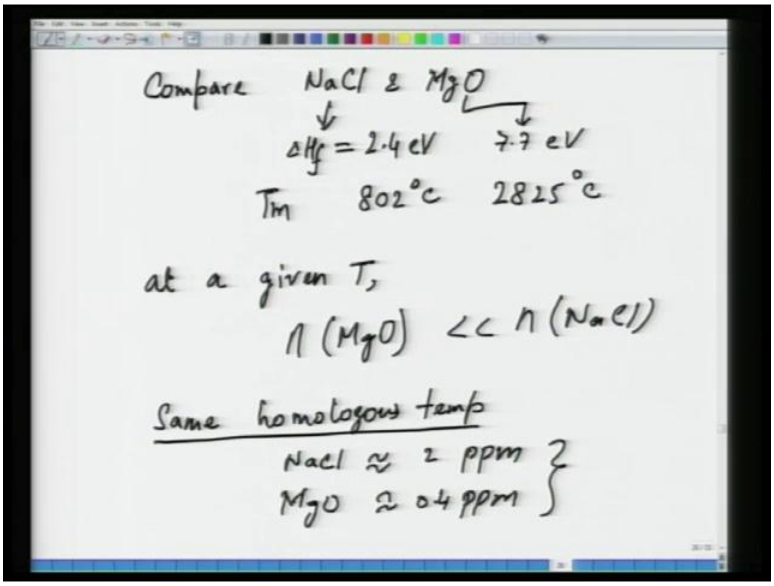

Compare NaCl & MgO

$\Delta H_f = 2.4\ eV$ $7.7\ eV$

T_m $802^\circ C$ $2825^\circ C$

at a given T,

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

Same homologous temp

Nacl ≈ 2 ppm

MgO ≈ 0.4 ppm

Sodium chloride is a material with so for instance you can make a compare N a C l and M g O. For M g O delta H f is almost equal to 2.4 electron volt and in this case it is 7.7 electron volt and this is directly related to T m. So, T m of N a C l is about 802 degree centigrade, in case of M g O it is about 2825 degree centigrade and these are so you can see that M g O being a larger melting point compound because of larger bond energy it has larger enthalpy of defect formations.

So, as a result intrinsic defect concentration in M g O so at a at a given temperature number of defects in M g O is much smaller than in N a C l and this is because of higher defect formation energy in M g O as a result of higher bond energy. So, however if you if you if you scale it to same homologous temperature then defect concentrations can be almost comparable so at same homologous temperature of course, below the melting point of N a C l. So, you can find that N a C l will have roughly 2 p p m defects and M g O will have approximately 0.4 p p m. So, they are more comparable when you talk about same homologous temperature, but the point here is the effect of bond energies and the temperature and however so these defects are this is intrinsic defects. Now, in the previous expression we worked out this expression for Frenkel defects. Similar expression can also be worked out for Schottky defects because there also you have pair of defects so there is no difference.

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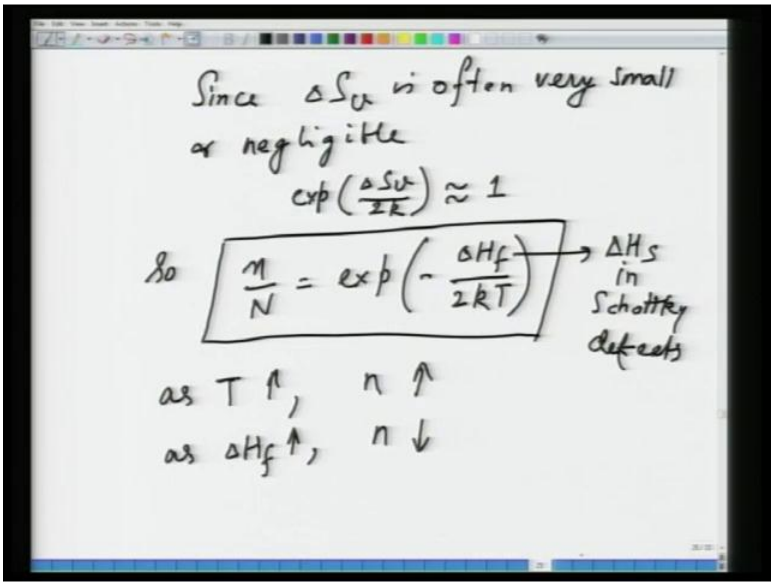

Since ΔS_v is often very small or negligible

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

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

So, the only thing is that this will become delta H s in Schottky defects.

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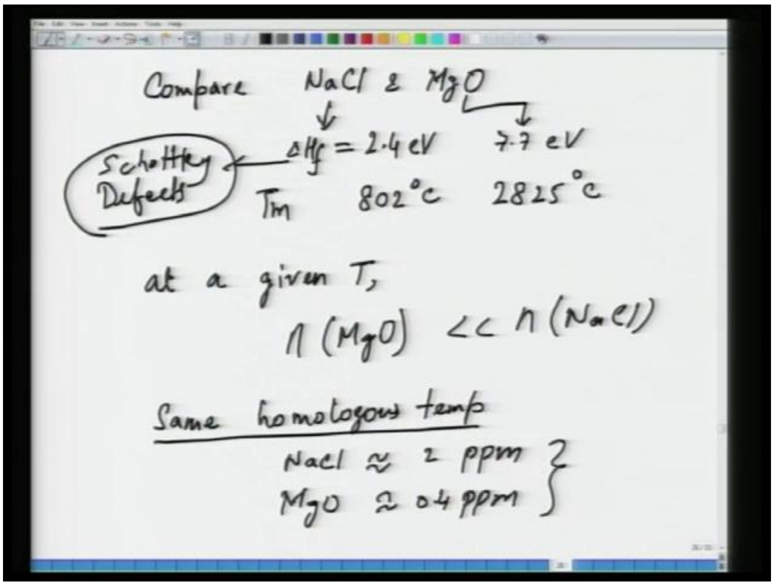

Compare NaCl & MgO

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

So, when we talk about N a C l and M g O it is delta H f is nothing but for Schottky defect because both of the materials are prone to having Schottky defects. However, the the derivation remains same and there is no change. So, we will we will take up the, we will we will we will finish here and we will take up the defect equilibria and what is the thermodynamic bases of treating defect reactions in the next class.

Thank you.