Fundamentals and Applications of Dielectric Ceramics
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Lecture - 11
Intrinsic and Extrinsic Defects

Okay, so welcome again to this new lecture of fundamentals and applications of dielectric ceramics. So, we will just briefly recap the previous lecture.

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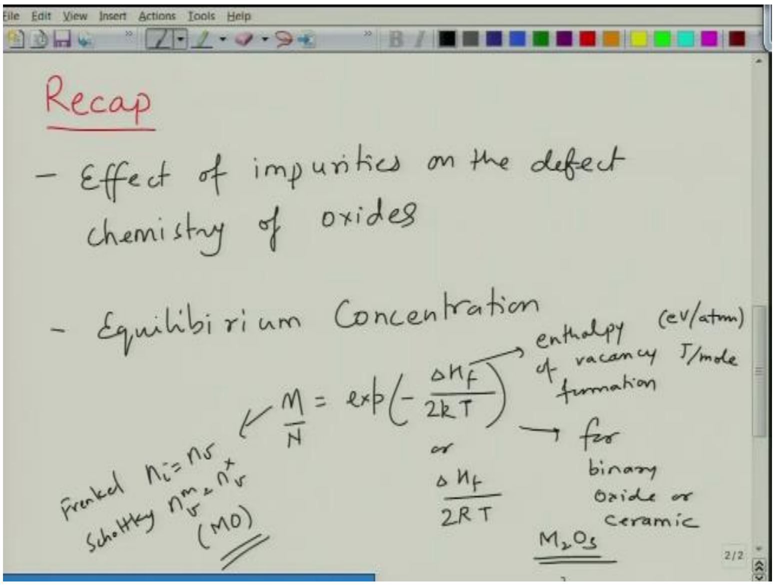

Recap

- Effect of impurities on the defect chemistry of oxides

- Equilibirium Concentration

$$\frac{M}{N} = \exp\left(-\frac{\Delta H_F}{2kT}\right)$$

enthalpy of vacancy formation (eV/atom) J/mole

or $\frac{\Delta H_F}{2RT}$

→ for binary oxide or ceramic

M_2O_3

Frenkel $n_i = n_v$

Schottky $n_v^m = n_v^+$ (MO)

So in the previous lecture, we learnt about effect of impurities, whether you know impurities can be intentional, they could be unintentional on the defect chemistry of oxides. So when you have oxide MO, when you put an N2O3 in it, then you bring in extra oxygen into the system. So, this extra oxygen coming into the system will give rise to what we call as electrons or it can also give rise to metal vacancies and if you bring in oxide which is N2O, then it does the opposite.

So, you could also use these impurities to tailor the defect chemistry. So suppose some oxide is to begin with oxygen deficient or metal deficient and it has electronic charges, then you can control the defect chemistry by bringing in appropriate dopant or impurity atom to control the defect chemistry and this is something which is very prevalent in oxide dielectrics and then second thing that we looked at was equilibrium concentration of defects.

So, we just took a very basic thermodynamic route of to calculate the impurity concentration, so we just looked at the change in the free energy when you consider vacancies and host atoms as 2 different entities, and just depending upon the configuration entropy and the enthalpy, balance of between 2 things will give rise to changes in the free energy and then if you have a equilibrium concentration at a certain temperature, which means the free energy must be minimum at that concentration.

So we just took the minimum of, we just took the derivative of free energy as a function of composition, made it equal to 0, and we got the equilibrium concentration, which is,

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

So this $\Delta H_f$is basically enthalpy of a vacancy formation and this could be in you know eV per atom or it could be also in you know Joule per mole and so on and so forth.

You can write this as ΔH_f divided by kT or it can also be written as $\Delta H_f/RT$, but then you will have to adjust the units accordingly where k is the Boltzmann constant, R is the gas constant, and you can see from this that as the temperature increases, the number of vacant, so in this case it will be $2kT$, I am sorry, because you are dealing with pair of defects, so as a result it becomes $2kT$, but in case of metallic systems, it will be just $1kT$.

So whether it is, so this n could be equal to n_i is equal to n_v for Frenkel defects and for Schottky it could be and n_v^m and this could be n_v^x okay because cation anion vacancies there. So, this is for MO or MX, but if it is M_2O_3, then equality will change accordingly okay. So, you will have to do that analysis again. So, this is basically for binary oxide or ceramic, but if you do the analysis for something like M_2O_3, then it would be different. If you do it for M_2O_5, it would be different.

The denominator will not remain same because the number of vacancies that you create as a result defect formation will be different for every cation we can see or cation interstitial. So what we will do is that we will look at the defect chemistry in 2 systems, one is the stoichiometric oxides. So now we look at the defect equilibrium. So, we have seen how the defects form. Now, we will look at defect equilibrium as a function of temperature and partial pressure and these 2 types of systems.

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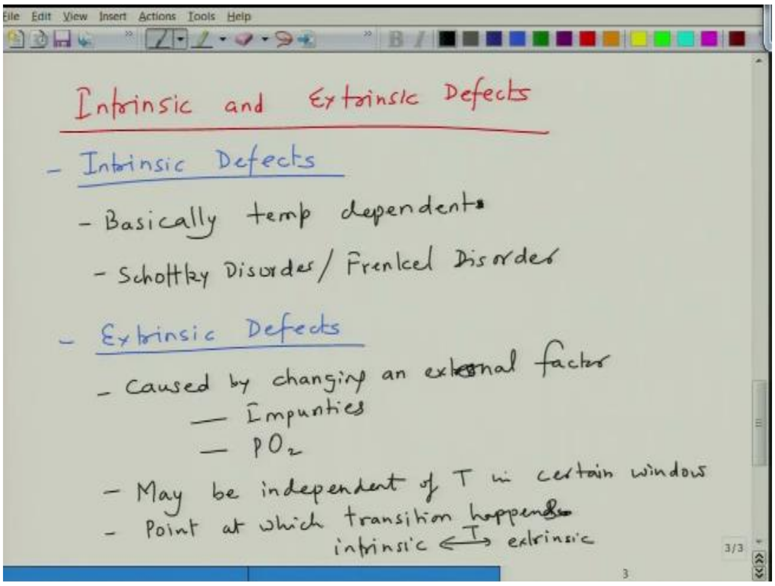

Intrinsic and Extrinsic Defects

- Intrinsic Defects
  - Basically temp dependents
  - Schottky Disorder / Frenkel Disorder
- Extrinsic Defects
  - Caused by changing an external factor
    - Impurities
    - pO_2
  - May be independent of T in certain window
  - Point at which transition happens

$$\text{intrinsic} \xleftrightarrow{T} \text{extrinsic}$$

So, when you consider the defects, there are 2 kinds of defects we can say, intrinsic and extrinsic defects. So here, we can say that intrinsic defects are those, so what are intrinsic defects? The intrinsic defects are the ones which are basically temperature dependent and which form in the solid intrinsically, there is no external variable such as you know oxygen efficiency, oxygen deficiency, oxygen excess or impurity or whatever.

So basically, it is temperature dependent, so defects like Schottky disorder, Frenkel disorder these are all intrinsic defects, they do not change the stoichiometry of the system and they can be determined from the intrinsic defect equation. Then we have extrinsic defects and these defects are created as a means of, so they are caused by you can say external factor and what could this external factor be, it could be impurities, it could also be partial pressure of oxygen, ambient pressure and so on and so forth.

So, this defect concentration may be independent of temperature in certain cases right or at least there is a certain window when this is independent. So basically, and generally what happens is that there is a crossover. So, there is a point at which transition occurs from intrinsic so extrinsic or extrinsic to intrinsic depending upon how you look at it at which transition happens. So basically, you say that intrinsic to extrinsic and this could be for example temperature okay, the temperature at which a solid will show behavior like intrinsic, and below a certain temperature, it will show extrinsic behavior.

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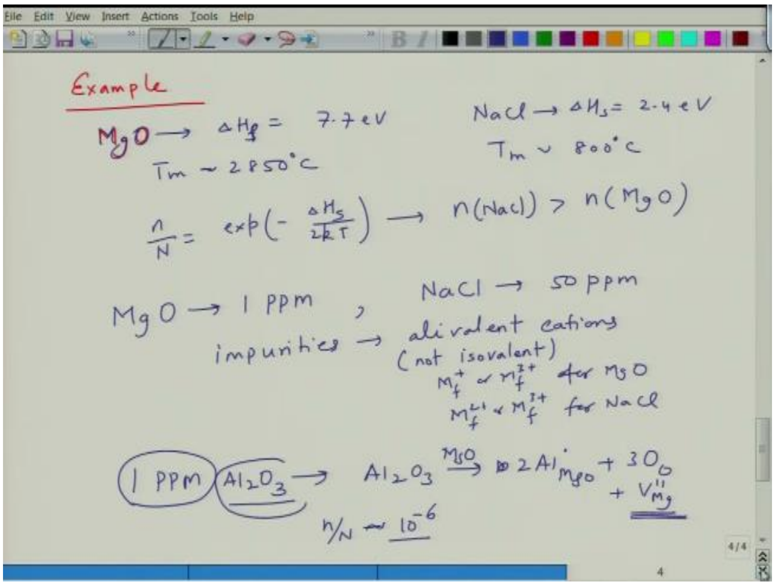

Example

MgO → $\Delta H_f = 7.7\ eV$

$T_m \sim 2850^\circ C$

NaCl → $\Delta H_s = 2.4\ eV$

$T_m \sim 800^\circ C$

$$\frac{n}{N} = \exp\left(-\frac{\Delta H_s}{2kT}\right) \longrightarrow n(NaCl) > n(MgO)$$

MgO → 1 ppm , NaCl → 50 ppm

impurities → alivalent cations (not isovalent)

M_f^{+} or M_f^{3+} for MgO

M_f^{2+} or M_f^{3+} for NaCl

$\boxed{1\ ppm}$ $\boxed{Al_2O_3}$ → $Al_2O_3 \xrightarrow{MgO} 2Al_{Mg}^{\bullet} + 3O_O + V_{Mg}''$

$n/N \sim 10^{-6}$

So, for example if we take case of let us say we take a case of 2 oxides okay. So, let us say we take a case of MgO. MgO has Schottky defect formation energy of 7.7 eV. On the other hand if you look at the case of NaCl, so this is MgO, if you look at NaCl, then ΔH_s is approximately 2.4 eV. So as a result, the melting point of MgO is about 2850℃ approximately and for sodium chloride it is about 800℃ okay.

Now you can see that we saw that,

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

So, at any given temperature above 0 K, the defect concentration in NaCl will be larger than defect in MgO okay, but so NaCl because of its lower melting point and lower defect formation energy will have more number of defects. However, in case of MgO, so these oxides are all you know prone to having certain impurities.

So let us say we can put certain impurities in MgO and that MgO impurity level is 1 ppm, whereas in case of sodium chloride, the impurity level is 50 ppm, and generally these impurities are basically a aliovalent, aliovalent means different valence cations okay, aliovalents means not isovalent, so both of these are M^{2+}, so it could be M_f^{+} or M_f^{3+} okay for MgO okay and for NaCl it could be M_f^{2+} or M_f^{3+} because Na is $^{2+}$.

So, as a result, the concentration, the extrinsic defects is much higher than that defect, so in case of MgO when we put in 1 ppm of let us say Al_2O_3 okay. So, when you put in1 ppm of

Al_2O_3, what will you create. So Al_2O_3 will go to MgO. So here, both the aluminum atoms go to oxygen site sorry magnesium site, all the 3 oxygens will go to oxygen site let us say and then we create, let us say we can see off magnesium, so this will be positively charged, this will be negatively charged.

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

So, we create this vacancy of magnesium. So, for every ppm of, so you can see that 1 mole of Al_2O_3 creates 1 mole of oxygen vacancies okay. So, if you have 1 ppm of Al_2O_3 present, which means that you will have 1 ppm of vacancies and this 1 ppm is a very large number, it is 10^{-6}. So basically, we are saying n/N is equal to 10^{-6}.

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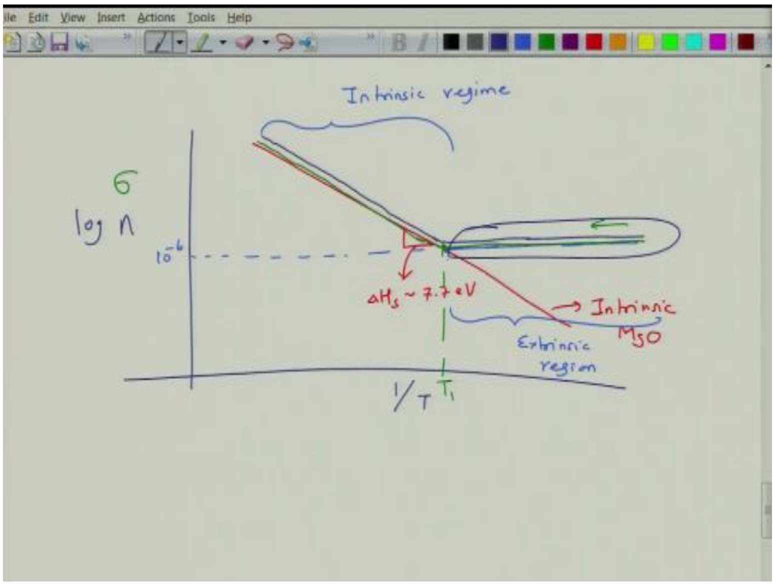

So, when you plot this as a function of temperature, so when you plot the impurity concentration as a function of, so we will have to plot in this fashion. So, let us say this is *log n*. So, for an intrinsic solid, we see that there is an exponential relationship. So, as you increase the temperature, the concentration will increase and this is in an exponential manner, this is for intrinsic MgO and the energy will be given by this slope. So, this gives me $\Delta H_S \sim 7.7\ eV$

Now at very low temperature, this concentration will be extremely low, it will be 10^{-15}, 10^{-16}, 10^{-10}. Now that I have put in an impurity of 10^{-6} concentration, I can draw a line of -6 concentration at certain point. So, this corresponds to 10^{-6}, so which means up to this temperature, no matter what the temperature is, the impurity, the vacancy concentration will always be 10^{-6}, okay.

The intrinsic vacancy concentration is very low as compared to extrinsic vacancy concentration, so this region will become what we call as extrinsic region, it is only at this point the intrinsic concentration takes over extrinsic concentration and then we reach in a regime which is called as intrinsic regime. So, basically if you want to plot now the final concentration plot, the final concentration plot would be something like this, it would be like this and then it follows for an impure MgO.

So up to a certain temperature, let us say T_1, so as you increase the temperature from this side up to a certain temperature, the concentration of vacancy remains constant at 1 ppm and only after T_1 when the intrinsic vacancy concentration increases, then it becomes intrinsic, and this is also manifested in conductivity, the conductivity in these systems is also proportional to the concentration of vacancies. So, the conductivity, if you plot conductivity here, we have not seen the expression of conductivity, but conductivity will also show similar behavior.

The conductivity will show a behavior like this up to this point and then conductivity will show a constant value up to this point. This is true for sodium chloride, it is also true for silicon, it is also true for many doped systems in which there is extrinsic region, there is an intrinsic region, and extrinsic so intrinsic region crossover happens at a particular temperature when intrinsic defects start increasing in number exponentially and they take over the extrinsic different concentration okay.

So, this is also a way of controlling the carrier concentration. So, when you dope something with something else, then you can create sufficient number of carriers in them so that solid becomes conducting up to a certain temperature and determined by the impurity concentration primarily. So within this region, this constant behavior is basically the extrinsic behavior, is this constancy of concentration as well as the properties. So, this is what I wanted to convey.

So even though sodium chloride, even though magnesium oxide has lower number of defects, if you put impurities in that, it can become conducting by putting sufficient number of impurities.

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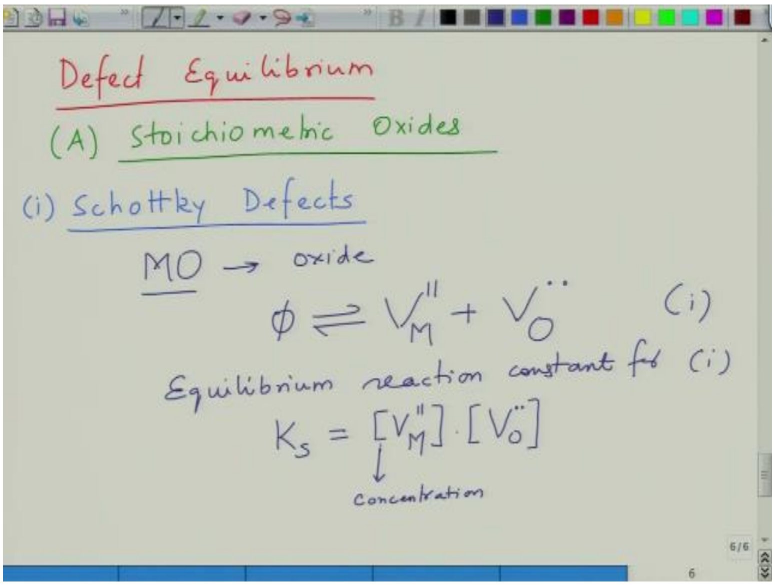

Defect Equilibrium

(A) Stoichiometric Oxides

(i) Schottky Defects

MO → oxide

$$\phi \rightleftharpoons V_M'' + V_O^{\cdot\cdot} \qquad (i)$$

Equilibrium reaction constant for (i)

$$K_S = \underset{\substack{\downarrow \\ \text{concentration}}}{[V_M'']} \cdot [V_O^{\cdot\cdot}]$$

So now, let us move to defect equilibrium in these oxides. So, we move to defect equilibrium, and this defect equilibrium basically first we will take example of stoichiometric. So basically, what will be the equilibrium concentration of defects under given set of conditions, that is what a defect equilibrium. So, in this case, we consider first Schottky defects, so we first look at Schottky defects. So, let us say the oxide is MO, so the binary oxide. So how do you write the defect reaction?

The defect reaction is basically 0, so this will be,

$$\emptyset \leftrightarrow V_M'' + V_O^{\cdot\cdot}$$

so Schottky defect will have vacancy of metal plus vacancy of oxygen, this is negatively charged, this is positively charged. So, we can write an equilibrium constant. So, equilibrium reaction constant for this

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

let us say this is 1, for 1 would be K_S is equal to V_O multiplied by, V_M multiplied by V_O. We could have written in terms of activity, but let us say it is 100% activity kind of system. So basically, square brackets denote concentration right, the brackets alright.

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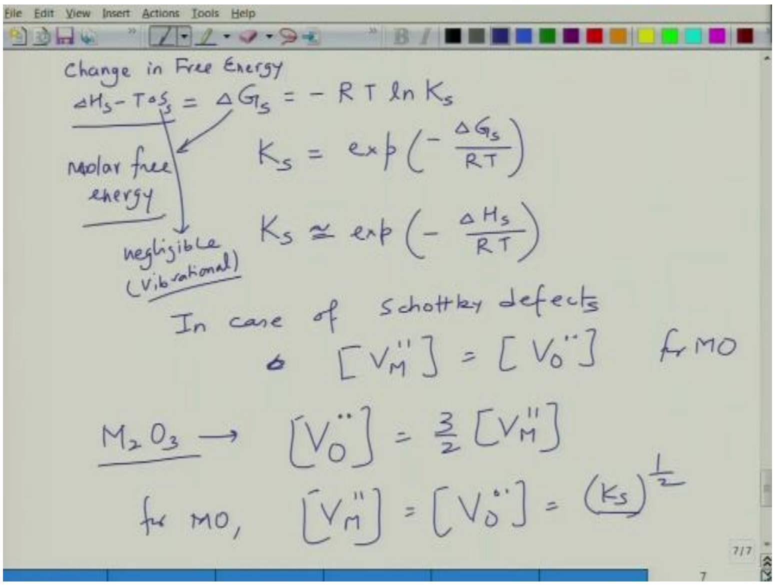

Change in Free Energy

$\Delta H_S - T\Delta S_S = \Delta G_S = -RT \ln K_S$

Molar free energy

negligible (Vibrational)

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

$K_S \simeq \exp\left(-\frac{\Delta H_S}{RT}\right)$

In case of Schottky defects

$[V_M''] = [V_O^{\cdot\cdot}]$ for MO

$M_2O_3 \longrightarrow [V_O^{\cdot\cdot}] = \frac{3}{2}[V_M'']$

for MO, $[V_M''] = [V_O^{\cdot\cdot}] = (K_S)^{\frac{1}{2}}$

So, the equilibrium constant, but equilibrium constant for a given reaction can also be expressed as we can write

$$\Delta G_S = -RT \ln K_S$$

okay, the change in, so when we say free energy by definition it means Gibbs free energy in this system. So, we can write this Ks as

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

we can write RT or KT, but let us say we write in terms of RT.

So here, ΔG_S is basically the molar free energy of defect formation and basically this will be equal to $\Delta H_S - T\Delta S_S$, you can say this is molar free energy okay and ΔH_S would be the enthalpy of defect formation and ΔS_S would be that change in the entropy which is mainly vibrational in nature and we ignore that for most cases. So, we can approximate this as ΔK_S to be equal to, so if let us say this is negligible, basically it is vibrational in nature, then we can approximate,

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

RT or KT depending upon the unit you can write.

So, if Schottky defects were to dominate, so now from this equation you can write now in case of Schottky defects, we know that

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

for MO, but if it is not for MO, if it is for M_2O_3, then it would be different. What would it be for M_2O_3? For M_2O_3, you will have 2V$_M$ and 3V$_O$, which means for every 2 metal, we can see you are forming 3 oxygen vacancies, which means

$$[V_M''] = \frac{3}{2}[V_O^{\cdot\cdot}]$$

, this is for M_2O_3. So accordingly, the defect constant will change, the reaction constant will change.

So if this is 2 for MO, we are taking for MO, then for MO, I can write

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

right, that is right because we say that K$_S$ is equal to product of these two, so when you put in, substitute one of them, then it becomes $K_S^{1/2}$.

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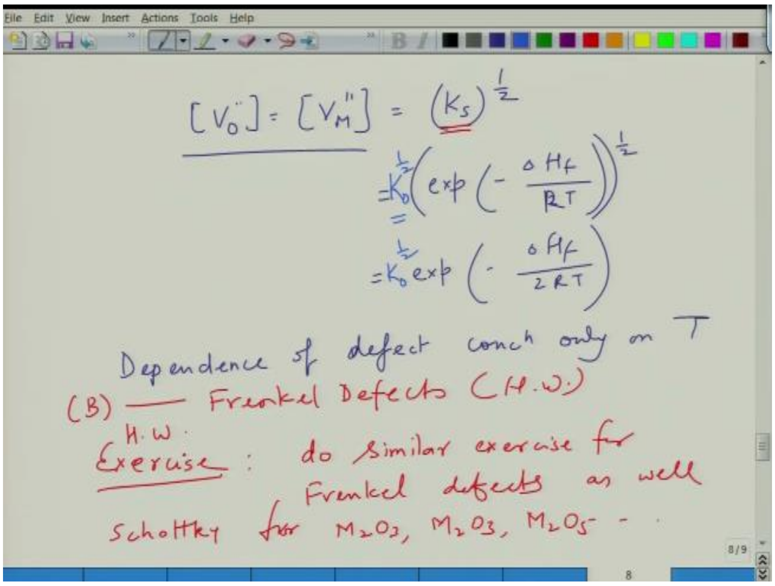

$$[V_O^{\cdot\cdot}] = [V_M''] = (K_S)^{\frac{1}{2}}$$
$$= K_0^{\frac{1}{2}}\left(\exp\left(-\frac{\Delta H_f}{RT}\right)\right)^{\frac{1}{2}}$$
$$= K_0^{\frac{1}{2}}\exp\left(-\frac{\Delta H_f}{2RT}\right)$$

Dependence of defect conc^n only on T

(B) —— Frenkel Defects (H.W.)

H.W. Exercise : do similar exercise for Frenkel defects as well

Schottky for M_2O_3, M_2O_3, M_2O_5 - .

So, then you can write this as basically

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

and what was K$_S$,

$$K_S = \left[exp\left(-\frac{\Delta H_S}{RT}\right)\right]^{1/2}$$

So, this becomes

$$K_S = exp\left(-\frac{\Delta H_S}{2RT}\right)$$

, so this is what we got from thermodynamics as well when we calculated the concentration right. So, this is $\frac{\Delta H_f}{2RT}$. So, we can see in this case that V$_M$ and V$_O$ are dependent only on, dependence of defects only on temperature, despite being an oxide, it does not depend upon partial pressure of oxygen.

There is no partial pressure of oxygen that is playing a role here. So, you can do as an exercise, do similar exercise for Frenkel defects as well as Schottky for you can say M_2O_3, what will happen for M_2O_3, what will happen for M_2O_3, what will happen for M_2O, what will happen for M_2O_5 and so on and so forth okay. So, this is homework exercise for okay. So, this is fairly straightforward and you will see the same thing in case of Frenkel defects as well, that defect concentration will remain independent of partial pressure of oxygen, it will depend only upon temperature.

Next thing that we see is defect equilibrium in non-stoichiometric solids. So this is about the stoichiometry oxides, so this we have taken for Schottky defect and you can do the same exercise for, so B, can B for Frenkel defect, this is basically your homework okay and the answer in this in that case would be, let me give you the hint.

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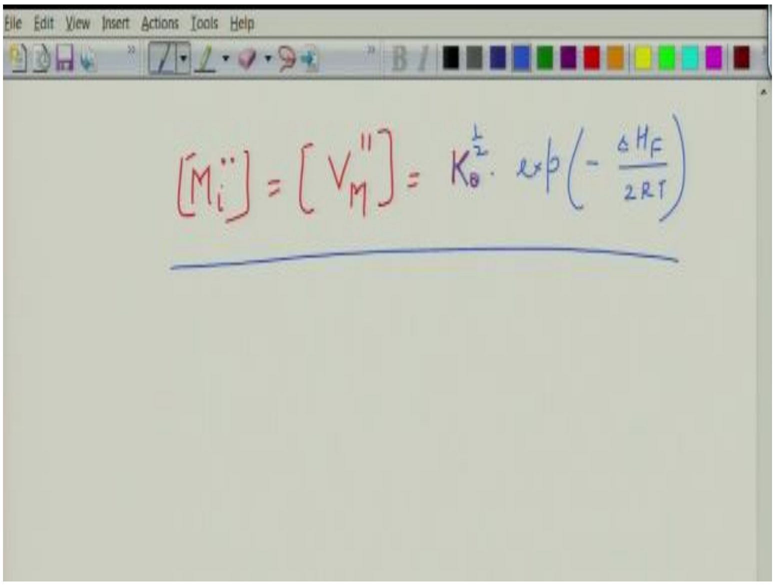

$$[M_i^{\cdot\cdot}] = [V_M''] = K_0^{\frac{1}{2}} \cdot exp\left(-\frac{\Delta H_F}{2RT}\right)$$

You will get

$$[M_i^{\cdot\cdot}] = [V_M''] = K_0^{1/2} exp\left(-\frac{\Delta H_F}{2RT}\right)$$

, so you can also write these if you take K_S to be G_S, in the form of G_S, then sometimes what people do is that everything which is constant comes out as K_0, so this will become $K_0^{1/2}$, but even if you do not write K_0**,** it is you should understand expression.

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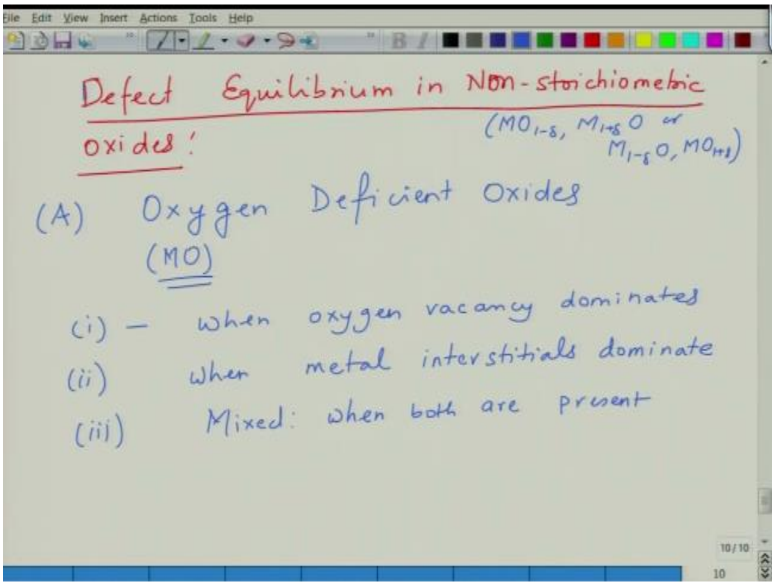

Defect Equilibrium in Non-stoichiometric oxides!

($MO_{1-\delta}$, $M_{1+\delta}O$ or $M_{1-\delta}O$, $MO_{1+\delta}$)

(A) Oxygen Deficient Oxides
(MO)

(i) – when oxygen vacancy dominates
(ii) when metal interstitials dominate
(iii) Mixed: when both are present

Now let us move on to the next thing which is defect equilibria in non-stoichiometric okay. So, let us take the first case of let us say oxygen deficient oxides, so which means that we consider case of MO let us say. So, what are the possibilities? The possibilities are when oxygen vacancy dominates, so what kind of defects will be present will depend upon the defect formation energy.

So whichever defect, see when you form that defect, then defects are formed in a lattice and every lattice has certain energy with respect to formation of defects, so very closed packed lattice generally putting in interstitials is more difficult as compared to creating vacancies because for putting in something you need to expand and dilate the lattice whereas creating vacancies is just removing an atom. So especially, anion vacancies are far more difficult because anions are bigger, on the other hand, cation vacancies are easier to form.

So, it depends upon the defect formation energy what defects will dominate. So, there could be multiple scenarios. The first scenario is when oxygen vacancies dominate, in this so if you have oxygen vacancies, we can also have metal interstitial and third scenario could be mixed when both are present. So, these are the three scenarios that we will look at that we take the case of defective non-stoichiometric will mean you will have either MO_1-δ or you will have $M_{1+\delta}O$ or you can have M_1-δO or you can have $MO_{1+\delta}$, these are the non-stoichiometric cases.

So, these are the 3 cases that we will see. We first take the case of oxygen deficient oxides, in case of MO most likely, in most cases and then first case is when oxygen vacancy dominates, the second case is when metal interstitials dominate and third case is when both of them could be simultaneously present. So, we will do the analysis of this in the next class and we will stop here today. So, what we have done is we have basically today looked at we have moved beyond the impurity concentration.

We also looked at how when you put in impurity, you can tailor the concentrations and giving rise to two regions, one is extrinsic, second is intrinsic, and generally you will see for example phosphorus and silicon and even some other higher impurity oxide and in the pure oxide will give rise to extrinsic region at over temperature which is dominated by presence of appropriate defect which could be vacancy or interstitial followed by at high temperature intrinsic region when intrinsic defect concentration takes over the extrinsic concentration.

So, we will stop here today. We will expand upon this defect equilibrium in non-stoichiometric oxides in the next lecture. Thank you.