Defects in Crystalline Solids (Part-1)
Prof. Shashank Shekhar
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur

Lecture - 10
Equilibrium Concentration using Defects Reactions

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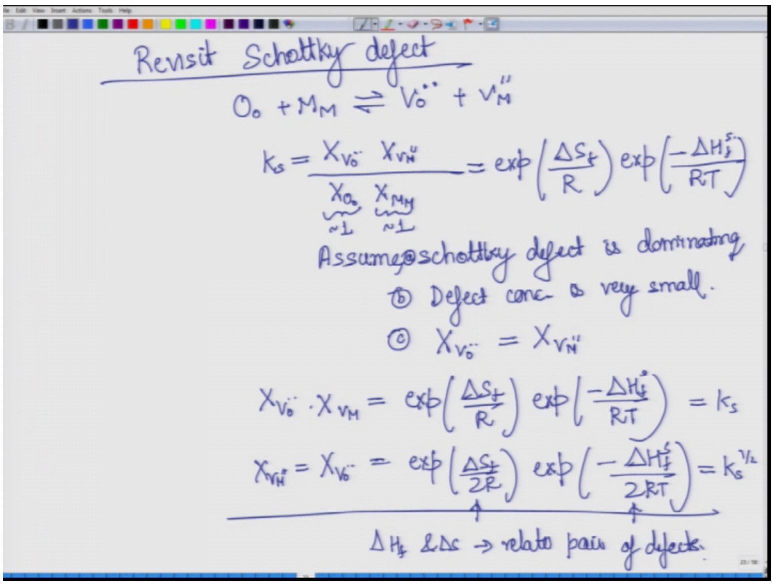

Revisit Schottky defect

$$O_O + M_M \rightleftharpoons V_O^{\bullet\bullet} + V_M''$$

$$K_s = \frac{X_{V_O^{\bullet\bullet}} X_{V_M''}}{\underbrace{X_{O_O}}_{\sim 1} \underbrace{X_{M_M}}_{\sim 1}} = \exp\left(\frac{\Delta S_f}{R}\right) \exp\left(\frac{-\Delta H_f^s}{RT}\right)$$

Assume ⓐ Schottky defect is dominating

ⓑ Defect conc. is very small.

ⓒ $X_{V_O^{\bullet\bullet}} = X_{V_M''}$

$$X_{V_O^{\bullet\bullet}} \cdot X_{V_M} = \exp\left(\frac{\Delta S_f}{R}\right) \exp\left(\frac{-\Delta H_f^s}{RT}\right) = K_s$$

$$X_{V_M''} = X_{V_O^{\bullet\bullet}} = \exp\left(\frac{\Delta S_f}{2R}\right) \exp\left(-\frac{\Delta H_f^s}{2RT}\right) = K_s^{1/2}$$

ΔH_f & ΔS → relate pair of defects.

So, we left it at this point. We saw the equilibrium concentration. So, I will add one more thing over here that this is equal to K s and when you take this, this is equal to square root of K s which is 1 by 2 and that is why we get these terms two which also represents that we are that delta H f, it is and delta S are related to pair of defects. So, we get the factor 2 over here, ok. So, that is a Schottky defect; now we have looked at Schottky, now let us revisit the Frenkel defect.

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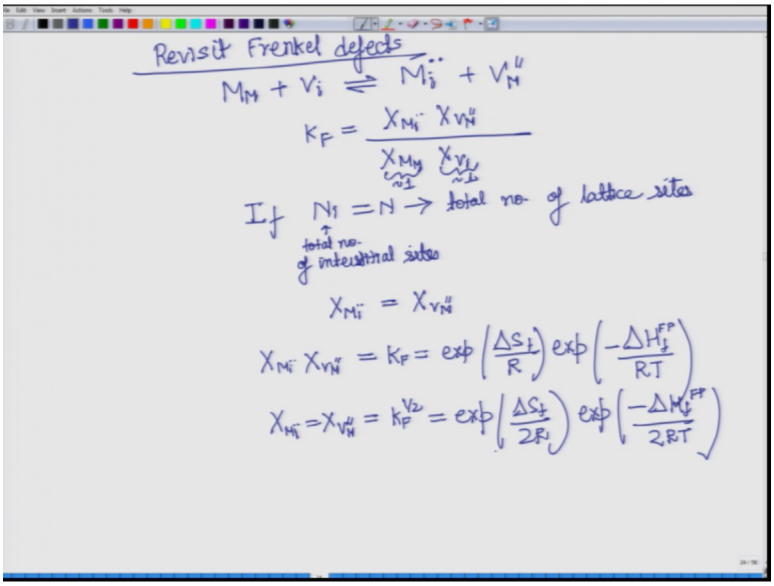

Revisit Frenkel defects

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

$$K_F = \frac{X_{M_i^{\bullet\bullet}} X_{V_M''}}{\underbrace{X_{M_M}}_{\sim 1} \underbrace{X_{V_i}}_{\sim 1}}$$

If $N_i = N \rightarrow$ total no. of lattice sites

$\uparrow$ total no. of interstitial sites

$$X_{M_i^{\bullet\bullet}} = X_{V_M''}$$

$$X_{M_i^{\bullet\bullet}} X_{V_M''} = K_F = \exp\left(\frac{\Delta S_f}{R}\right) \exp\left(-\frac{\Delta H_f^{FP}}{RT}\right)$$

$$X_{M_i^{\bullet\bullet}} = X_{V_M''} = K_F^{1/2} = \exp\left(\frac{\Delta S_f}{2R}\right) \exp\left(\frac{-\Delta H_f^{FP}}{2RT}\right)$$

Here we will make some more additional I will have to make some additional assumptions or simplifications you can say. So, what was Frenkel defect cation, I am going into vacancies. So, we can represent it as M m plus V i, V i as I said does not have to be there, this is just to keep a track of the interstitials that are being used. So, the metal iron has already moved to interstitial. So, this is something the no charges should have been. So, the whatever charge it is at the metal site is the additional charge. So, effectively it has two positive V m double prime.

Now, this rate constant for this now you should be able to predict this at this point. So, it will be equal to X M i dot dot X these are the fractions V m. So, we have like this, but here remember that the this fraction is with respect to the total number of interstitial sites, this fraction is with respect to the total number of lattice sites where the metals iron set.

So, therefore, there will be the denominator in both these cases are different and therefore, we can have two different cases. If N i is equal to N which is the most simpler case N i; you remember is the total number of interstitial sites, N is the total number of lattice sites and we have seen in the example of i steel F e carbon that there are two different kinds of interstitials that was the just two examples, there can be more type of interstitials.

So, the there the two examples that we discussed for tetrahedral and octahedral sites and depending on whether we are talking about BCC or FCC, there will be different relation between N i and N, but for the sake of simplicity first, let us assume that N i is equal to N. And therefore, K F and K i F is given like this and using the assumptions as before that this is the dominating defect; Frenkel defect is predominating defect in the system that we are talking about and the fraction of defects is small, we can say that this is approximately equal to 1. And therefore, and the another assumption or another understanding, we already have because this is the dominating defect.

We can also say that X M i dot dot is equal to X basically what we are seeing is number, but this translates to the fraction because N i is equal to N. And therefore, what we have is again first, we will take a look first will just take that product which is X V M is equal to K F is equal to exp, we will say Frenkel pair to represent that we are talking about this defect reaction, this enthalpy change cause of formation of Frenkel pair and divided by R T.

Now, when these two are equal which is again only possible when this is a dominating reaction and there are no other ways of generating these, if there are other ways then these two will not be equal. So, that assumption is important and when that is true we can say this each of them are equal therefore, this is square root. So, each of them will be equal to the square root of this quantity X N i dot dot is equal to X V m K F to the power 1 by 2 and when you take square root of this is equivalent to put a two factor over here.

So, this becomes exp delta S f by 2 R. So, for the case when we have N i equal to N, we get the relation like this. Now, this will be a little different when we have if you remember already from the earlier derivation for equilibrium concentration that this is different when we have N i not equal to N.

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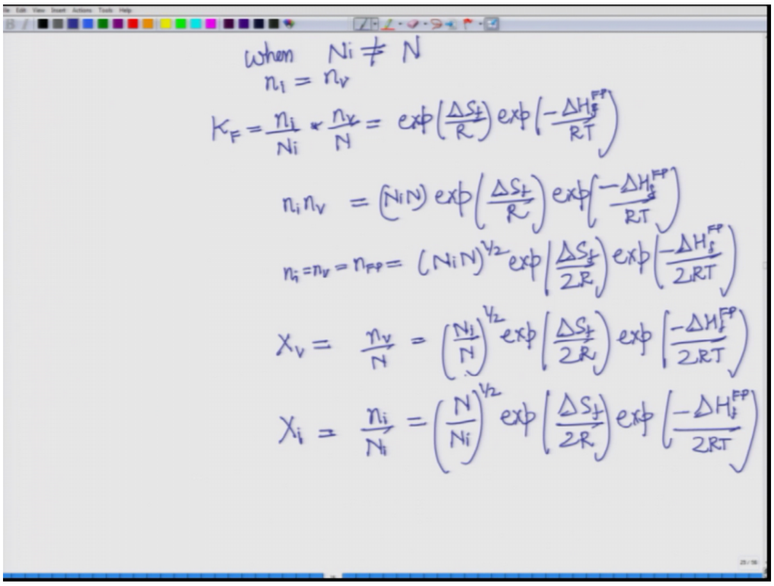

when $N_i \neq N$

$n_i = n_v$

$$K_F = \frac{n_i}{N_i} * \frac{n_v}{N} = \exp\left(\frac{\Delta S_f}{R}\right)\exp\left(-\frac{\Delta H_f^{FP}}{RT}\right)$$

$$n_i n_v = (N_i N)\exp\left(\frac{\Delta S_f}{R}\right)\exp\left(-\frac{\Delta H_f^{FP}}{RT}\right)$$

$$n_i = n_v = n_{FP} = (N_i N)^{1/2}\exp\left(\frac{\Delta S_f}{2R}\right)\exp\left(\frac{-\Delta H_f}{2RT}\right)$$

$$X_v = \frac{n_v}{N} = \left(\frac{N_i}{N}\right)^{1/2}\exp\left(\frac{\Delta S_f}{2R}\right)\exp\left(\frac{-\Delta H_f^{FP}}{2RT}\right)$$

$$X_i = \frac{n_i}{N_i} = \left(\frac{N}{N_i}\right)^{1/2}\exp\left(\frac{\Delta S_f}{2R}\right)\exp\left(\frac{-\Delta H_f^{FP}}{2RT}\right)$$

So, let us consider when N i is not equal to N, but what we still have is that n i is equal to n v that is number of interstitial sites is equal to number of vacancies sites. Why? Because, we this is the dominating defects. So, which means this is the largest in concentration and therefore, whenever a metals cation sites goes into the interstitial there will concomitantly up vacancy created and interstitial site created. Therefore, what we can write is something like this n i by N i where N i at the upper case N i as you know is the total number of interstitial sites; smaller case n i is the actual number of interstitial sites which have being used in to n v by N. Again now, the right hand side is similar that we have already used earlier which is delta S f by R.

So, what is thus this become n i n v is equal to N i N. So, there is a factor here and since n i is equal to n v this whole thing will have to be taken a square root. So, n i equal to n v equal to n FP. So, we will call it Frenkel pair defect. So, this is are not representing actually pair, but only one of this defect where, then it will become N i N 1 by 2. So, this we have to take a square root and therefore, it will also again have a factor 2 over here or you can say that n FP if you want to if you are talking about the let us say n v then you can say n v by N is equal to N i by N to the power 1 by 2 and this whole thing or you can say n i by N i equal to N by N i to the power 1 by 2.

So, we are now able to get fraction of interstitial as well as fraction of vacancies. So, you see that even for the case when N i is not equal to N we can get a relation and the relation has symmetry unit when you are talking X v then it is n i by N, when you talk about X i the fact the pre exponential factor is N by N i. And, presumably you will be knowing what is N total number of sites and N i where it is the total number of interstitial sites given what type of interstitial you are talking about and what type of crystal system you are talking about.

So, we will be able to find these fractions. So, again you can see that the whole derivation that we look at over here it becomes so much simpler if we know, if you put it in the form of a defect reaction. Now, we will look at; next we will move on to intrinsic ionization of electrons.

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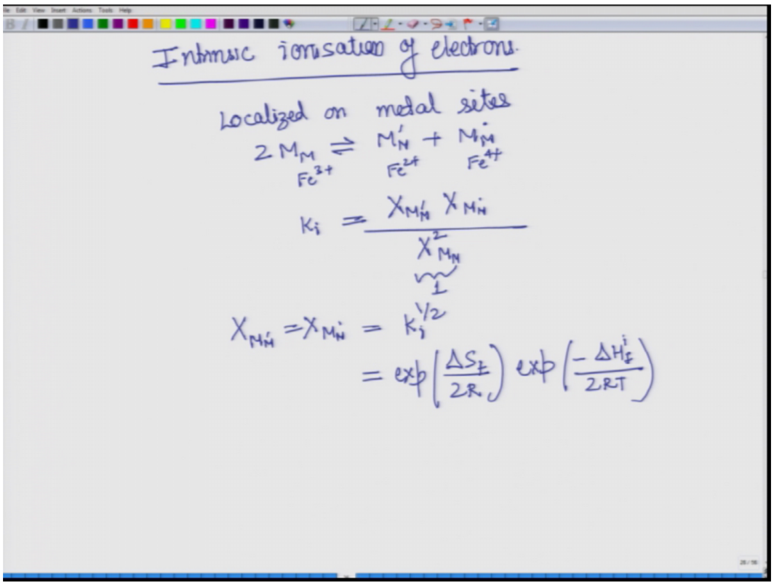

Intrinsic ionisation of electrons.

Localized on metal sites

$$\underset{Fe^{3+}}{2M_M} \rightleftharpoons \underset{Fe^{2+}}{M'_M} + \underset{Fe^{4+}}{M^{\bullet}_M}$$

$$K_i = \frac{X_{M'_M} X_{M^{\bullet}_M}}{\underbrace{X^2_{M_M}}_{1}}$$

$$X_{M'_M} = X_{M^{\bullet}_M} = K_i^{1/2}$$

$$= \exp\left(\frac{\Delta S_f}{2R}\right) \exp\left(\frac{-\Delta H^i_f}{2RT}\right)$$

So, we will try to find and first what we will do is when it is localized. So, localized on metal sites and for that we had seen instead of F e, we will just simply use M. So, it is something like M m electron going on to one of the metal site. So, it has a negative charge whole going onto the other ones so, it has a positive charge and it is nothing, but saying that something like F e 3 plus going to F e 2 plus and F e 4 plus like this in told you earlier. And now, in this particular case we I am representing at the rate constant by K i; this K i is equal to X again.

So, we have to write it like this, X M m this is prime X M m dot by X M m square. So, this 2 is coming from this two and like we said earlier the assumptions would be that this is the dominating defect and that would mean that these numbers been Frenched by any other factor and the total concentration is very small. So, the total concentration being very small this is approximately equal to one which is one square. So, it still remains one and since this is the dominating defect we can again say that X M m prime is equal to X M m dot.

So, we will this time we directly go and say this is square root of k i which is the rate constant and therefore, this is 1 by 2, well manifest itself inside exponential factor exponential which will be delta S formation 2 R exponential minus delta h formation for intrinsic ionization by 2 R T. So, we get the equilibrium concentration of metal with the negative charge and metal with the effective positive charge which are already equal which are equal and if we know the enthalpy change for this and the entropy change for this reaction, we will be able to calculate the equilibrium concentration.

So, this is when we are assuming that it is localized, now the other cases when it is delocalized. Now, here we will have to move on to next level meaning some more understanding and simplification will have to be done. So, now, we will say this is delocalized electrons while it will be different ok.

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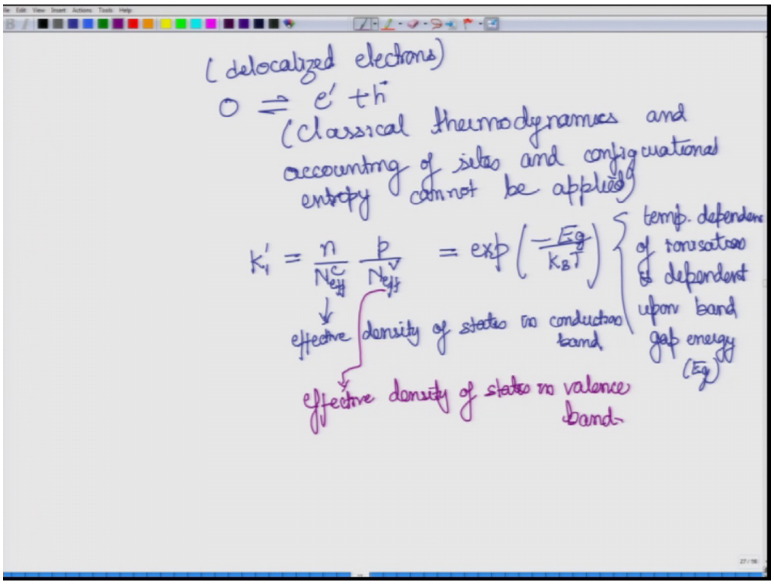

(delocalized electrons)

$0 \rightleftharpoons e' + h^{\bullet}$

(classical thermodynamics and accounting of sites and configurational entropy cannot be applied)

$$K_1' = \frac{n}{N_{eff}^{C}} \frac{p}{N_{eff}^{V}} = \exp\left(\frac{-E_g}{k_B T}\right)$$

temp. dependen of ionisation is dependent upon band gap energy (E_g)

effective density of states in conduction band

effective density of states in valence band

So, let us will see that in the moment. So, let us say that this is a perfect crystal giving out electron plus hole, right. Now, this is not localized on any site. Now, classical thermodynamics in the sense that we cannot apply number of sites etcetera, we cannot have with respect to number of sites density over here the fraction cannot be calculated like that.

So, classical thermodynamics and accounting of sites and configurational entropy when we say a classical thermodynamics we actually mean configurational entropy cannot be applied. So, this is a caution when you are using it for some relation like this; however, now it is are defect reaction. So, we can write it like this we will we have put a prime to designate it is different from it will be used differentially than the earlier rate constants.

So, here this e prime which is the electron with negative charge is given by N and since we are talking about concentration, but here on the denominator we will have an effective c meaning effective density of states in the conduction band similarly for p which is the whole this is N effective V or the effective density of states in the valence bands this will be given by exp minus E g by k BT depending on whether you are using per electron per mole as I said, you will have to use RR KB respectively and why g because temperature dependence of n n p or the ionization is given by the band gap energy.

So, this E g is nothing, but the band gap energy. So, the temperature dependence of ionization is dependent upon band gap energy which is E g and so, we get some relation like this which is very similar to what we obtain like for the earlier. So, just making it clear that this n effective is effective density of states in conduction band this is effective density of states in valence band. So, we have a relation very similar to the relation that we use for defect reaction then there are lattice sites invert. So, this is in the form of the equation and it as you can see it is very much similar to what we have been using. So, that gives us handle to be able to write down equation when both of them are involved which is what we will do in the next example which is non stoichiometric oxides.

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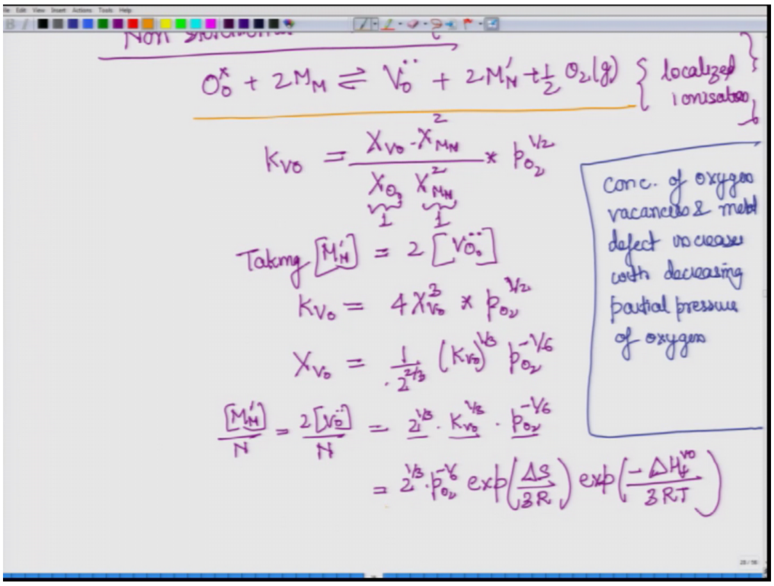

Non

$$O_O^x + 2M_M \rightleftharpoons V_O^{\cdot\cdot} + 2M_N' + \frac{1}{2}O_2(g)$$

localized ionisation

$$K_{V_O} = \frac{X_{V_O} \cdot X_{M_N}^2}{\underbrace{X_{O_O}}_{1} \underbrace{X_{M_N}^2}_{1}} * p_{O_2}^{1/2}$$

Taking $[M_N'] = 2[V_O^{\cdot\cdot}]$

$$K_{V_O} = 4X_{V_O}^3 * p_{O_2}^{1/2}$$

$$X_{V_O} = \frac{1}{2^{2/3}}(K_{V_O})^{1/3} p_{O_2}^{-1/6}$$

$$\frac{[M_N']}{N} = \frac{2[V_O^{\cdot\cdot}]}{N} = 2^{1/3} \cdot K_{V_O}^{1/3} \cdot p_{O_2}^{-1/6}$$

$$= 2^{1/3} \cdot p_{O_2}^{-1/6} \exp\left(\frac{\Delta S}{3R}\right) \exp\left(\frac{-\Delta H_f^{V_O}}{3RT}\right)$$

Conc. of oxygen vacancies & metal defect increases with decreasing partial pressure of oxygen

So, the relation if you remember we are talking about when oxygen escapes into as oxygen gas. So, let us say we have O o at its site plus and we are over here talking about metal oxide. So, it will form vacancy at oxygen site and initially you can say that it is positively charged. So, something it will have charges like this effective charges like this. So, the first case for non stoichiometric, we are not yet involving the free electrons or delocalized electrons, we are talking about localized ionization.

So, here K V o would be given as and apart from these we also need activity for o 2 and that activity for o 2 is given by pressure partial pressure partial pressure of o 2. So, these reaction become something like this. So, far so already we have added one complication here or you can say next level of difficulty. So, we have o 2 goes activity is measured in a different way, these activity can be directly measured as fraction and this for a activity of this gas it has to be measured in partial pressure which is given like this.

Now, taking; so, again the two assumptions would hold the assumptions that this is the dominating defect meaning these are not being generated by any other mechanism primarily only mechanism that is operative will creating these defects are this non-stoichiometric escaping of gas and that the defect concentration is small. So, when the defect concentration is small the first thing that we can do is make this it approximately equal to 1.

So because, they are so small the defects that these are the majority of real that is covering the real lattice sites now taking; so, each oxygen vacancy site is creating 2 electrons and each of those 2 electrons are going moving on to two different metal sites. So, the defect the metal sites with an additional negative charge that number would be equal to twice the number of vacancy sites that have been oxygen vacancy sites that have been created.

So, our relation would become something like this and it would mean that if you want to have the rate constant for K V o, it will now this is equal to 1, this is equal to 1 and this sense this number is equal to twice this number and that would also translate to since it is a M o type of metal therefore, it will also translate to X m equal to 2 X V o and therefore, we will have if you convert this 2 X V o it becomes 4 X V o square and therefore, it becomes 4 X o V q. So, 4 X V o q into p o 2 1 by 2.

So, you say that this relation again, we have M m prime equal to 2 times V 2 times V o o meaning each vacancy at oxygen site is leading to defect effect of a negative charge and two metals sites. And therefore, the concentration of metal sites would be twice the vacancy concentration and therefore, the number fraction it being M o type of solid would be also twice. Therefore, X M m is equal to 2 V o 2 X o and therefore, this is. So, we have taking the square of this will come 4 X v o square and into X V o is become 4 X V o q and therefore, what we have over here we can write it as X V o.

Now, this is this comes to the LHS. So, it is 1 by 4 which is equal to 1 by 2 square, but we have to take cube roots it becomes 1 by 2; 2 to the power 2 by 3 K V o, we have to take 1 by 3 of this, we also have to take this on to this side which means it is on minus 1 by 2 and then again cube root this. So, it is equal to minus 1 by 6. Now, like I said M m prime by n which is the fraction is equal to 2 V o dot i n this equal to what we are doing here is we have taken multiplied it by a factor of 2. So, this is into 2. So, this 2 to the power 1 minus 2 by 3 is equal to the power 1 by 3 and therefore, it becomes 2 to the power 1 by 3 into K V o to the power 1 by 3 into p o 2 to the power minus 1 by 6.

Now, these two terms remain and we can expand this term. So, this will become. So, this is K V o which will if you can expand as delta S and delta h therefore, we will have exp delta S and since it is cube roots. So, there will be a factor of 3 over here into exp exponential minus delta h formation for vacancy oxygen by 3 R T. So, this gives you the ratio or the fraction of metals site as well as the vacancy site. So, if you are talking about the metal site this is the metal site defect that is one electron localized on to it, this is how the relation is and if you are talking about vacancy oxygen oxygen vacancy sites you will have to divided by 2.

So, we are able to obtain a relation for metal sites as well as vacancy at the oxygen site and what we understand from here is that concentration of these oxygen vacancies and also these metal defects these increase as the p o 2 decreases. So, when you decrease this you would see that thus whole quantity increases. So, if you reduce the value of p o 2, this whole value increases and which means the concentration of V o and M m increases therefore, we have a important understanding gained from this reaction or from this equilibrium concentration and that is that concentration of oxygen vacancies and metal defects, I mean with localized electron increases with decreasing partial pressure of oxygen.

Now, this is something we can also actually directly see from this relation now if you go back to this relation equation over here what we see is that on the left hand side this is the reaction on the right hand side you have this reaction was not reaction, but these components. So, if you decrease this; what it means is that the reaction will have to go forward to maintain the reaction constant and therefore, the concentration of these two have to be increased.

So, whenever you decrease the partial pressure of oxygen the concentration of vacancy and the concentration of metal with the electron localized onto it has to increase. So, what we are obtaining or understanding or what we understand from the defect reaction over here is confirmed by the equation which gives you the direct concentration of these defects the vacancy oxygen vacancy defect concentration and metal with electron localized defect. So, this is the relation reaction when we have localized ionization.

Next we will look at the same reaction, but in this in the second case, we will assume that charges are non localized meaning instead of 2 M m, we will take two electrons which have free electrons and you remember that the classical thermodynamics is like we said we will not or we cannot take the site ratios similar to that we take for vacancy and interstitials.

So, and for as in the case of n and p; so, it the relation will be little bit different. Now will be mixing the two electrons will also be there, lattice sites will also be there, vacancies will also be there. So, you will see how that relation comes out in the next lecture.

So, see you next time.