Defects in Crystalline Solids (Part-I)
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Lecture – 09
Defect Reaction and its Thermodynamics

So, let us come back to where we left, so we, whether using Kroger Vink notation and we started writing different defects as a reaction using this Kroger Vink notation. So, this one was that we discussed last lecture Schotty defects.

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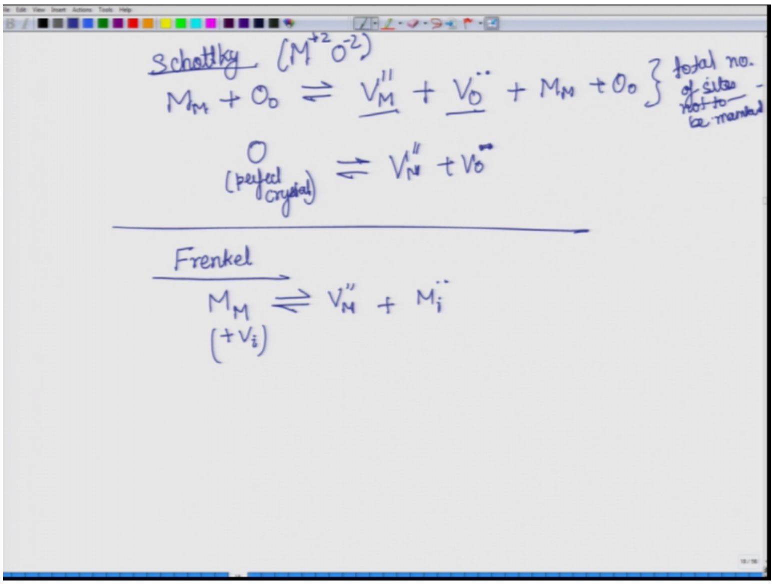

Schottky $(M^{+2}O^{-2})$

$$M_M + O_O \rightleftharpoons \underline{V_M''} + \underline{V_O^{\cdot\cdot}} + M_M + O_O \Big\}$$

total no. of sites ~~not to~~ be maintained

$$\underset{\text{(perfect crystal)}}{0} \rightleftharpoons V_M'' + V_O^{\cdot\cdot}$$

Frenkel

$$\underset{(+V_i)}{M_M} \rightleftharpoons V_M'' + M_i^{\cdot\cdot}$$

So, as you can see its reaction it can be written as a reaction. Next is Frenkel defect. So, now, we will try to right Frenkel defect as a reaction.

So, you remember in Frenkel defect what we have is a cation moves on into interstitial. So, we can write something M, which is a metal which will be the cation, it will move into a vacancy, these are interstitial. So, it will create a vacancy and this vacancy will not have a recharge where it should have recharge and assuming that the original charge of the metal was 2 units.

So, it will become too negative charges and interstitial metal will be in the interstitial and therefore, in the interstitial there should not have been any charge and therefore, it will be presented at 2 additional positive charges and to trace the interstitial site you can add here vacancy interstitial, it will not make any difference to the overall reaction and when we look into the thermodynamics, but this will only help us understand number of interstitial that have being used created and so on. So, this is the Frenkel relation or the Frenkel defect or which can be represented as the reaction.

Now, we will also look at, so far we have looked only at atomic defects; now let us look at if electrons and holes are generated, so the advantage of this defect reaction is that even electron and holes can be represented by these relations by these reaction and hence the thermodynamic equilibrium concentration can be obtain. So, next let us look at intrinsic ionisation of electrons.

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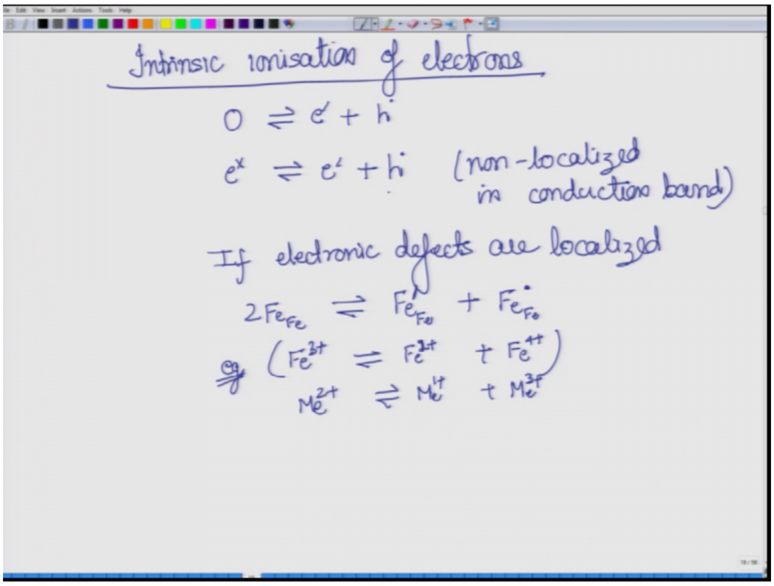

Intrinsic ionisation of electrons

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

$e^{x} \rightleftharpoons e' + h^{\bullet}$ (non-localized in conduction band)

If electronic defects are localized

$2Fe_{Fe} \rightleftharpoons Fe'_{Fe} + Fe^{\bullet}_{Fe}$

eg $(Fe^{3+} \rightleftharpoons Fe^{2+} + Fe^{4+})$

$Me^{2+} \rightleftharpoons Me^{1+} + Me^{3+}$

So, from nowhere or basically from perfect crystal, you can have one electron and one hole created, but remember in a defect reaction we also wanted to maintain mass. So, you can represent it something like this. So, electron with no charge effectively is moving on to create on electron which has a negative charge and hole which has a positive charge.

Now, these electrons and holes here you will realize a non-localized. It and basically it means that this electron is not present at any particular site they are in the conduction band. So, this is non-localized; not one any particular site cannot be said to be processing these electrons. So, in that since it is non-localized in the conduction band.

Now, on the other hand if we assume if these charges or electronic defects are localized which would mean that this electron has to be at a particular site and therefore, it can be represented by something let us say metal and let us put iron over here, so since this iron has to this electron as well as a hole has to go somewhere, so we can say that one of the iron atoms is taking the negative charge and one of the iron atoms is taking as taking the positive charge; effective, remember it is effective negative or effective positive charge.

What does that mean? That from whatever it was supposed to have it is 1 less and over here it is 1 more; which means that if we are talking about Fe, this Fe 3 plus sin is getting converted to Fe 2 plus and Fe 4 plus. So, you see that in the matrix Fe was in 3 plus valance a state, but because of the presence of extra electron and extra hole basically creation of electron and hole and which are getting localized on to this metal atom. This charge from 3 plus has been reduced to 2 plus.

So, it is 1 less than 3 plus. So, it is one represented as one negative and this is one more than this is 4 plus which is one more than 3 plus. So, it is represented as one dot. So, this is the intrinsic ionisation of electrons, when that is this is not localized and when it is localized was on an in particular atom. So, it could be anything something it could also be something like let us say metal 2 plus going to metal 1 plus 3 plus.

So, even this will be represented by something like this. So, here they have basically one at accepting one electron here it is accepting one hole. So, all these are examples of electronic defects which are localized. Now, let us look at how to write the defect reaction for a non stoichiometric system.

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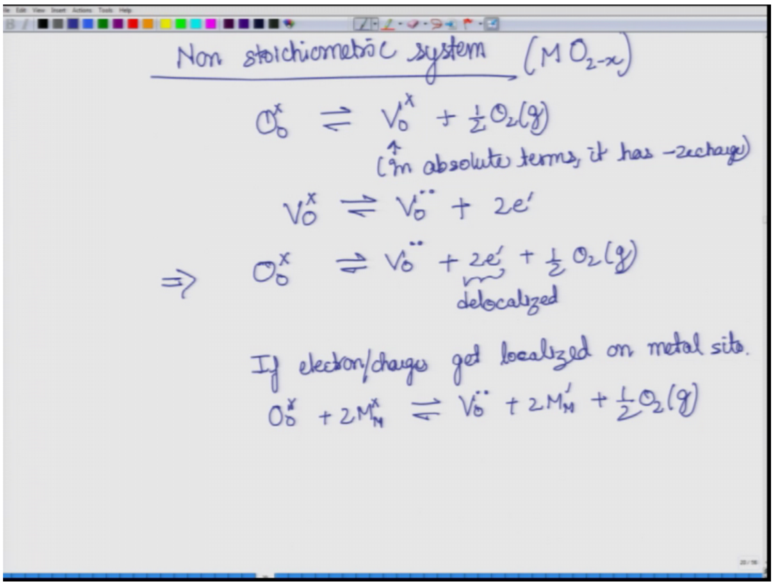

Non stoichiometric system (MO_{2-x})

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

(in absolute terms, it has −2e charge)

$$V_O^x \rightleftharpoons V_O^{\bullet\bullet} + 2e'$$

$$\Rightarrow \quad O_O^x \rightleftharpoons V_O^{\bullet\bullet} + \underbrace{2e'}_{\text{delocalized}} + \frac{1}{2}O_2(g)$$

If electron/charges get localized on metal site.

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

Even if it is a non stoichiometric system, remember that site number of sites present in the system would still maintain the stoichiometric ok. So, non stoichiometric can be occurring because let us say in a system like MO, a part of the oxygen escapes in and forms goes into the atmosphere as oxygen gas.

So, it will become so let us say it was MO 2 minus x. So, some part of the oxygen elements have left the system and into the atmosphere. How do we represent? So, basically oxygen that is oxygen site which can be shall neutral charge it forms vacancy at oxygen site and let us assume that it leaves in a neutral state meaning that it remains with the charges remain with the site where it was there because that we have to maintain charge neutrality. Therefore, the vacancy site will have 0 charge; effective 0 charge, but enough, but an absolute terms there is a minus 2 charge over here.

So, in absolute terms, it has minus 2 charge and where does oxygen atom actually go it escapes as gas. So, 1 by 2 O2 gas; this right now the charge over here is localized onto vacancy. Now this vacancy can delocalized the charge meaning it can let go the charge and therefore, it can happen something like this. It may further go on and it will have no absolute charge meaning in effective terms it is positively charged, the electrons have left it in a relative term it is 2 positive and where do the electrons go? It has got delocalized. So, this is 2 electron with negative charges and it has gone into the conduction band of the system.

So, overall this reaction can be written as vacancy at oxygen site with 2 positive effective charge with 2 electrons which are delocalized plus 1 by 2 O2 gas. So, the 2 electron is delocalized, now if let us say again like the previous case this electron is not delocalized, but it gets if electron or charges to get localized on a metal site because mostly metal will have variable valency.

So, this can be represented, so this 2 electron you will have to move on to some metal site. So, it will be represented by something like this, let us say that there is electron to there are 2 electron and they have moving to two different sites. So, each. So, each of the metal sites get reduced by one charge therefore, to begin with they are neutral oxygen site is neutral and it forms vacancy, which has effective positive charge to positive charge plus 2 M M negative charge plus 1 by 2 O2 gas, we see that we are now able to represent this kind of defect as a reaction.

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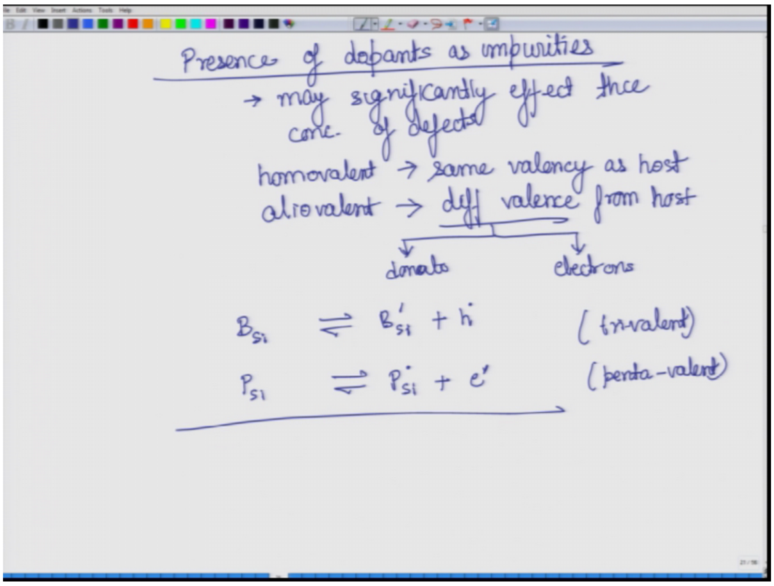

Presence of dopants as impurities

→ may significantly effect thce conc. of defects

homovalent → same valency as host

aliovalent → diff valence from host

donats

electrons

$B_{Si} \rightleftharpoons B'_{Si} + h^{\cdot}$ (trivalent)

$P_{Si} \rightleftharpoons P^{\cdot}_{Si} + e'$ (penta-valent)

Let us talk about still another defect which is presence of dopants. So, mostly in semiconductors you would know that dopants are added because they create charge with defects which lead to increase in electrons or in increase in holes. So, presence of dopants as impurities, let us look at that, so what do we know that whenever dopants are added it missing if you can lead effect the concentration it can significantly affect the concentration of defects may significantly affect the concentration of defects, now these dopants that have been added they can have a valency is similar to silicon or it can have a valency different from silicon.

So, first let us distributed into these 2 categories when it has similar valency as silicon which is which are the valency of 4 then it is called homovalent meaning same valency as host in case of silicon it means plus 4 it means 4 and if it is different in valancy than the host with in particular case silicon if it is different from 4 like plus it is 3 of 5 then it is called aliovalent.

Now, this aliovalent are the once which are of interest two people in semiconductors why because they can either donate electrons or they can accept the electrons and therefore, they can change the concentration relative concentration of n and p, the number of electron and number of holes.

So, let us look at example this boron, boron, if it is present at a silicon site silicon which should have 4 valence, but boron has three. So, it is trivalent and when boron is there it means that it has effectively one negative charge and therefore, it will emit one hole because it has effectively one charge and if you look at the charge neutrality for this reaction then you would realize that there should be a whole generated.

So, they you can see that this equation can so easily predict that hole has to be generated when have for each and every boron atom that sits at the silicon site. Now let us look at the other type of example as dopant which is phosphorus which is pentavalent. So, if phosphorus is setting at silicon site it has effectively one extra positive charge compare to boron which are extra negative charge it as one extra positive charge which means that there should be electron generated for this now this can also be represented by other broken one models that it has one extra electron has which is not satisfied.

So, this extra electron will move on to the conduction band, but in terms of reaction also you can show the same thing that phosphorus sitting at silicon will can be presented as one with effective positive charge and therefore, to maintain charge neutrality there will be a electron generated over here.

So, again you see that this defect reaction can be a very useful method to understand what is going on what will be generated even in terms of holes and electrons not only in terms of defect lattice type of defects. Now that we have looked at the defect reactions let us look at the usefulness of it in predicting the equilibrium concentration.

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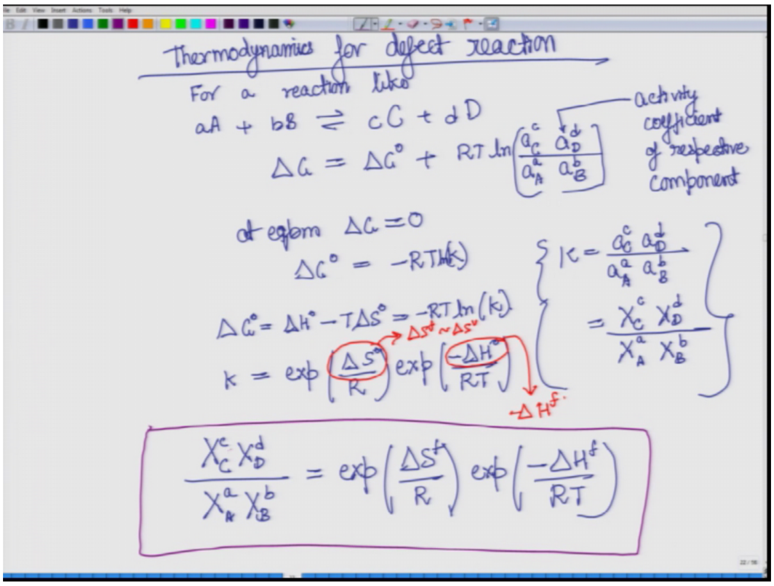

Thermodynamics for defect reaction

For a reaction like

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

$$\Delta G = \Delta G^\circ + RT \ln\left(\frac{a_C^c\, a_D^d}{a_A^a\, a_B^b}\right)$$

— activity coefficient of respective component

at eqbm $\Delta G = 0$

$$\Delta G^\circ = -RT\ln(K)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ln(K)$$

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

$\Delta S^f \sim \Delta S^v$

$-\Delta H^f$

$$K = \frac{a_C^c\, a_D^d}{a_A^a\, a_B^b} = \frac{X_C^c\, X_D^d}{X_A^a\, X_B^b}$$

$$\boxed{\frac{X_C^c\, X_D^d}{X_A^a\, X_B^b} = \exp\left(\frac{\Delta S^f}{R}\right)\exp\left(\frac{-\Delta H^f}{RT}\right)}$$

So, what is the basic thermodynamics when we are using a defect reaction; what it says what we know is that for a reaction which goes like this; a moles of A component b moles of B component if they react and form under equilibrium they form some c moles of C component and d moles of D component.

Then what we know is that the delta G the free energy change for this reaction can be given as this the delta G naught is at the standard state plus RT ln a. So, what we have here is a c which means activity coefficient of c component and to the power small c which is the number of moles. So, you have to be careful on what which c we are writing here.

So, let me we are try to be a little bit more clear. So, this is the capital C mean c the element or the c component activity coefficient of c component to the power c which is the this small c. Similarly, activity coefficient of D component to the power small d that is how many number of moles of d is activity coefficient of a component to the power a, activity coefficient of b component to the power is small b which is how many number of moles of b are there.

So, what is a? a is activity for respective component. Now at equilibrium we will have delta G equal to 0 meaning the reaction has come to an equilibrium the reaction is not moving we have equilibrium number of a component b component equilibrium component of c and d.

So, at that condition delta G is equal to zero and therefore, what we have is a relation like this if we represent this by k meaning k is equal to this quantity, now this quantity can be approximately said to be equal to the relative fractions. So, if there equilibrium fraction of c component is X c to the power small c. So, again let me, so here also it is not very clear I will just. So, we have equilibrium concentration of c to the power c equilibrium concentration of component d to the power of d that is how many moles there are equilibrium concentration of a to the power small a, which is the number of number of moles.

So, now we have a relation similar to that that we had derived earlier actually there is one more step before that. So, what is that step we know that delta G naught is equal to here is ln missing or in other words we have K equal to exp which is the exponent because this is log.

So, we are now taking the exponent of everything and dividing by dividing it by RT. So, what we are doing here is taking exponent on both side and hence we get rid of the log term and we get equation for k. So, first thing that you should note is that here this equation here we are using R meaning whatever energy terms we are using delta S. So, delta h it has be it has to be per mole term if we again translate it to per electron term then you can use k b.

Now, here delta S naught is nothing, but what we had earlier called as the delta S formation. So, that is equal to delta S vibration that is the same and similarly delta minus delta H naught here is nothing, but delta H, but minus since you are talking about minus delta S minus delta H formation. So, whatever it is about one vacancy or it is one Frenkel pair or one Schottky pair it can also relate to those formation energies also in this particular case it is talking about the change in enthalpy when this reaction goes from here to here, now this is the equation that is very similar to what we had obtained earlier, so, here now we can write it like this.

So, now when they whenever you write or defect as a reaction you would know all this quantities a, b, c, d the upper case A, B, C, D and the smaller case a, b, c, d and therefore, you would also know these quantities and related to that thermodynamic quantities delta S of and delta H of also would be known and therefore, from this if you know the right hand side you can get the left hand side and the left hand side if there is 1 or 2 particular component that you don't know then you can find that 1 or 2 component and are at least the relative ratio between the two.

So, that is the usefulness of writing defect as a reaction. So, instead of going through all the entropy are the configuration entropy and all those terms we can see that we can directly reach over here. So, another thing to understand is that when we write this equation because we have already seen derived the similar equation using configurational entropy.

So, we know that this is not the configurational entropy, this is the vibrational entropy. So, we have to be aware of that; that means, we write this equation like this is not a configuration entropy all that has been taken into account over here when we get this relation.

So, instead of going through all that process of configuration entropy we can just directly use this defect reaction and get the equilibrium concentration ok. So, now, let us apply this knowledge to some of the some of these reaction that we just talked about.

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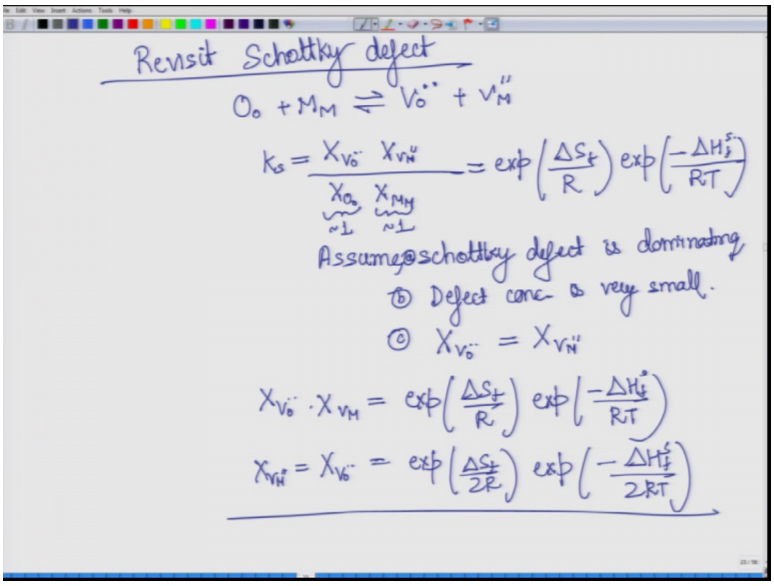

Revisit Schottky defect

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

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

Assume ⓐ schottky defect is dominating

ⓑ Defect conc. is very small.

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

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

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

So, let us say we go to, let us revisit Schottky defect, now how did we write Schottky defect reaction. So, we wrote it something like this. So, Schottky defect is what do what is Schottky defect, it is the vacancy at cation and vacancy at anion in that particular ratio and here we are assuming it is MO. So, M plus 2 O minus 2 and therefore, vacancy at O site will be equivalent to 2 positive charges and vacancy at metal site would be equal to 2 negative charges and therefore, this rate constant K s would be equal to X v o dot X v m prime double prime X o at o into X M at M.

And this we know is equal to the thermodynamic quantity which is delta S f by R times e x p minus delta H f Schottky defect. Now over here what has to be know over here what we know here is that what is the fraction of O on o first what is the fraction of a distraction M on M similarly what we also want to know is the fraction X V o X V M.

So there are certain essentials we will have to make here one is that this particular defect is the dominating defect, let us say if the vacancy were being produced by some other mechanism also then this then we will not be able to say that this relation is the final one or the vacancy concentration would also be influenced by the other reaction. So, we have to assume that this is the dominating defect.

So, one thing that we have to assume is that Schottky defect is dominating this is one assumption, second assumption is that defect concentration is very small why do we want to say that, why we want to say that is because in that particular case you will be able to say that fraction of oxygen site on oxygen is approximately equal to 1, if there were too many vacancies let us say 20 percent defects many oxygen has there are 20 percent vacancies of oxygen then O and O will not be equal to 1 and then it will we will have to evaluate it will be a lot more complicated and difficult to evaluate the fractions of V o and V M M.

So, the one of the defect one of the assumptions is the defect concentration is this is also to ensure that activity coefficient which has been related to X, which is the mole of fraction the mole of fraction of the defects. So, these this equation this a quality is also true and defect concentration is small, similarly the concert of fraction X M M is also approximately equal to 1. So, we have these 2 assumptions.

Because of this we get this relation and another assumption in these particular cases all its not really assumption, but it is derivation from this is that when you have all these conditions true, but it also means is that X V o actually then should be the number of number of vacancies it is also equal to X V M this is getting derived from the fact that number of vacancies is equal to number of metal sorry the number of vacancy at oxygen site is equal to the number of vacancy at the metal sites.

So, this equation can also be represented as fraction of X v o equal to fraction of X v m, now when we have this we can say that X V o dot into X V M is equal to e x p now since this is equal. So, we can take a square root and therefore, X V o dot X V M is equal to square root means 1 over 2 factor over here. So, this is a relation that we had derived earlier and you see that we have been able to derive it here to. So, this is one example, we will continue with more examples in the next class.

Thank you.