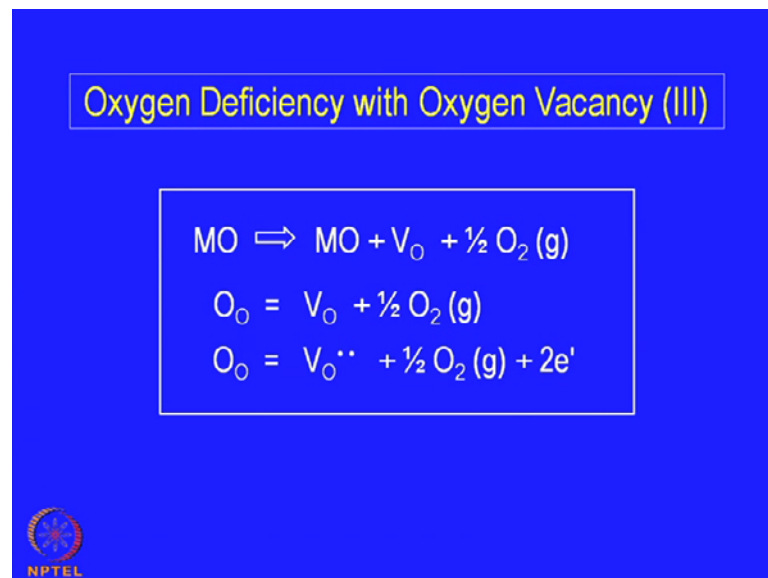**Advanced Ceramics for Strategic Applications**
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Lecture - 8
Defects in Crystalline Solids (Contd.)

In this class, let us continue our discussion on the Defects in the Crystalline Solids. Particularly you were discussing about the point defects, the different vacancies interstitials, short (()), front (()) and so on. We ended up in the earlier class discussing about the defect reactions and defect equations.
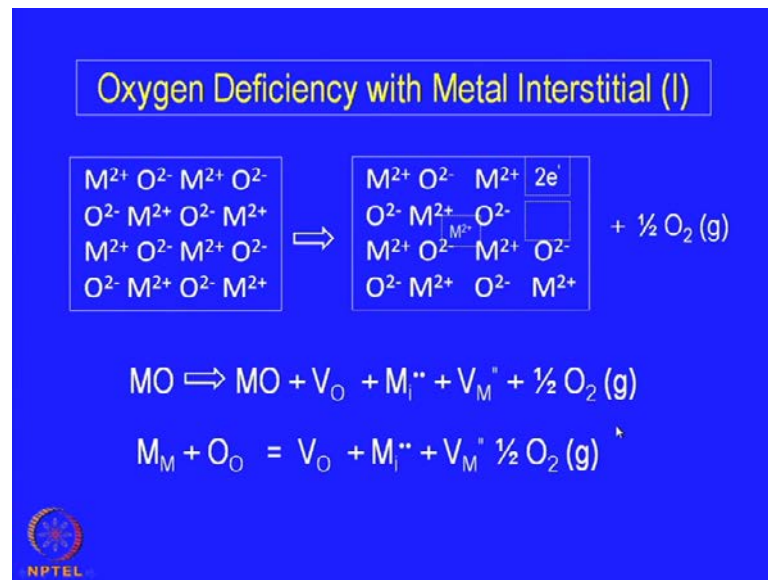
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We have started with one particular type of defect that is oxygen deficiency, and this oxygen deficiency is caused by oxygen vacancy. And so in that case, what would be the final equation and the reaction which is taking place; so this is the final equation step by step, so you have discussed this already.

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Let us go to another situation once again it is the oxygen vacancy, but not by oxygen sorry once again it is a oxygen deficiency, but created not by oxygen vacancy but metal interstitial right; so it is same thing either because we are talking about ratio. So, oxygen deficiency can be caused also by metal interstitial and in this in that case what should be the kind of reaction, what would the actual physical change what is taking place in the oxide. So, this is once again a oxide lattice and that is going to reactive oxygen a metal interstitial here.

Now, this metal interstitial will be created metal interstitial impact, this metal has come from there this metal was originally there and this surface and then it is come along with it is two positive charges. So, along with the two positive charges it is come there, so it has impact from regular lattice site. So, since the regular lattice site has been changed, so as you mentioned earlier one the lattice site is not there or it is been eliminated corresponding oxygen lattice site also have been eliminated.

So, that oxygen has actually gone out; so metal has gone there and the corresponding oxygen cannot sit there just like that. So, it has also to go out right that is how you create a metal interstitial. So, that how it has been return their and off course this in this case it is already a (()), because there is no charge here and metal has come along with this two positive charges.

So, it is in effectively positive site has been created and metal vacancy has been created there, a metal vacancy has been created there and then half O 2 has gone there right and leaving this metal electron over there. So, over all you can equate, now you are considering this is not a actually equation is not an equality sign and you cannot write here. But, (()) equality sign you have to consider the lattice one lattice both lattices are involved here, both oxygen lattices and metal lattices involved here. So, here oxygen vacancy is created metal interstitial is created, then oxygen metal vacancy has also been created, there will be plus there has to be a plus there has to be a plus right.

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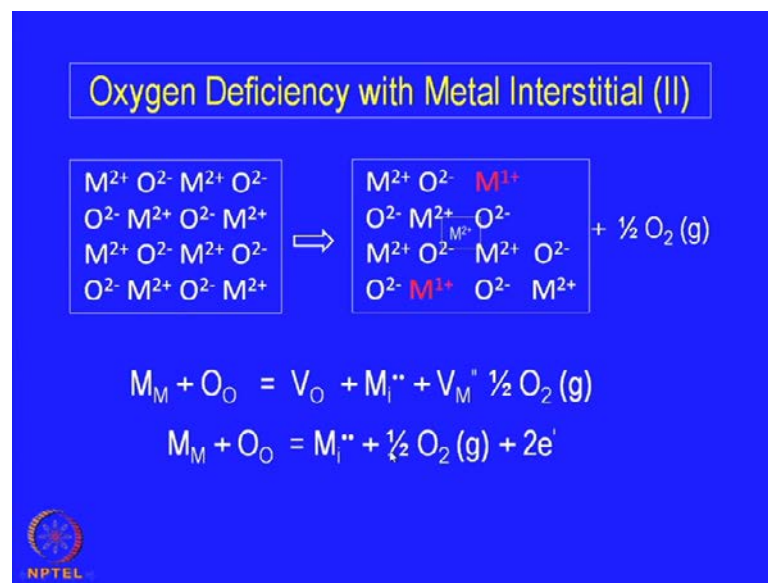
So, this is the reaction and then I am going little fast, because there are more less similar things one one's somebody looks that it and sure it will be quite clear. So, that same thing metal oxygen you electrons which were there is now been distributed to two metal ions. So two of them has changed over to 1 plus and 1 plus and that is how a actually this electron has been released and it is a free electron.

So, ultimately what you are getting is a metal interstitial oxygen gas in the form which is going out g in this case is a gas range; that means, that oxygen is not in the not in the lattice, but it is gone out of the atmosphere. So, that is why this g parenthesis has already been used. So, it is in the form of a gas a molecular gas right and that is why it is written although it is one atom of oxygen, but basically you are writing to designate that is it has gone out in the form of a molecule. So, a free electron has been two free electrons has

been generated and this has been positive charge effectively positive charge a metal interstitial has been generated.

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Oxygen Deficiency with Metal Interstitial (III)

$$MO \implies MO + V_O + M_i^{\bullet\bullet} + V_M'' \; \tfrac{1}{2} O_2 \,(g)$$

$$M_M + O_O = V_O + M_i^{\bullet\bullet} + V_M'' \; \tfrac{1}{2} O_2 \,(g)$$

$$M_M + O_O = M_i^{\bullet\bullet} + \tfrac{1}{2} O_2 \,(g) + 2e'$$

And the too over all reaction will be like this is the to denote what is happening physically in the lattice and then both charge and mass balances and finally, this is the equation on has to write for this reaction. So, this is, but in both cases it is oxygen deficient the ratio of metal to oxygen is more than one.

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Oxygen Deficient Oxide

Oxygen Vacancy

$$MO \implies MO + V_O + \tfrac{1}{2} O_2 \,(g)$$

$$O_O = V_O + \tfrac{1}{2} O_2 \,(g)$$

$$O_O = V_O^{\bullet\bullet} + \tfrac{1}{2} O_2 \,(g) + 2e'$$

Metal Interstitial

$$MO \implies MO + V_O + M_i^{\bullet\bullet} + V_M'' \; \tfrac{1}{2} O_2 \,(g)$$

$$M_M + O_O = V_O + M_i^{\bullet\bullet} + V_M'' \; \tfrac{1}{2} O_2 \,(g)$$

$$M_M + O_O = M_i^{\bullet\bullet} + \tfrac{1}{2} O_2 \,(g) + 2e'$$

In an identity this is the two things you have to consider, so far for the oxygen deficient oxide, two possibilities one is the oxygen deficiency, other is oxygen vacancy or metal interstitial both of them give rise to the same thing. And both in both these cases you are generating two electrons each, two electrons which are free; that means, if you are talking about impact. You will see later on in other classes when you consider the conductivity these are the space these are the charges or charge carriers.

And therefore these electrons are actually giving rise to semi conductivity in this material. So, all non stichomythic oxides, because of the related to the defect concentration the point defect concentration and depending on the point defect concentration and the nature of the point defect and the kind of non stichomythic. You are generating an electronic charge carrier free electronic charge carrier, which is much more mobile.

And you will give rise to a very large conductivity an impact they are the origin of the oxide semi conductivity or semi conductivity in some of these oxides particularly the transition metal oxides. So, oxygen deficiency can originate or can be caused either by oxygen deficiency oxygen vacancy or metal interstitial both of them are point defects are the crystalline defects.

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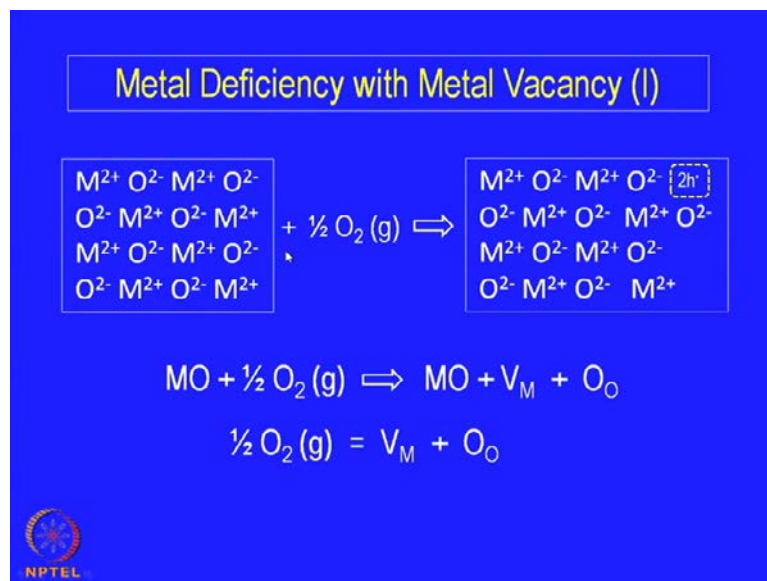
In the identical manner you can talk about metal deficiency, you have talked about oxygen deficiency now you are talking about metal deficiency is more or less than same

situation just in the reverse manner. Here you are adding oxygen earlier you have been releasing oxygen, if you remember in both these cases you are releasing oxygen right you are releasing oxygen, oxygen is on the right and now oxygen is on the left. So, you are adding oxygen and oxygen going into this lattice, in the form of a metal vacancy or if you add oxygen extra oxygen corresponding metal you are not adding.

So, metal vacancies are created again I am not going to the details of that you just anybody can go through it and find out the logic from this, how it is been written. So, half O 2 g once again, half O 2 gas is going in to the lattice as a lattice oxygen O subscript O; means oxygen at the sub at the oxygen site, oxygen is going at the oxygen site this one are M subscript M means a metal going at the original M site. So, that is how it is been denoted, so this is a original lattice site.
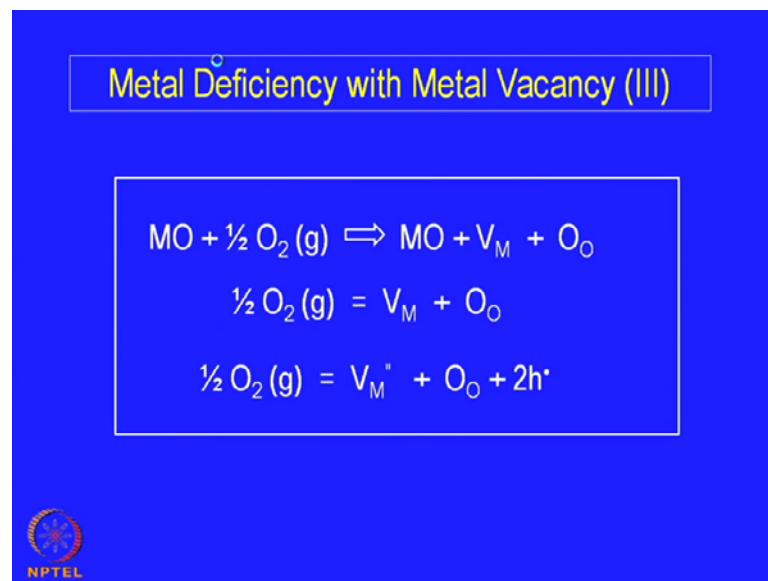
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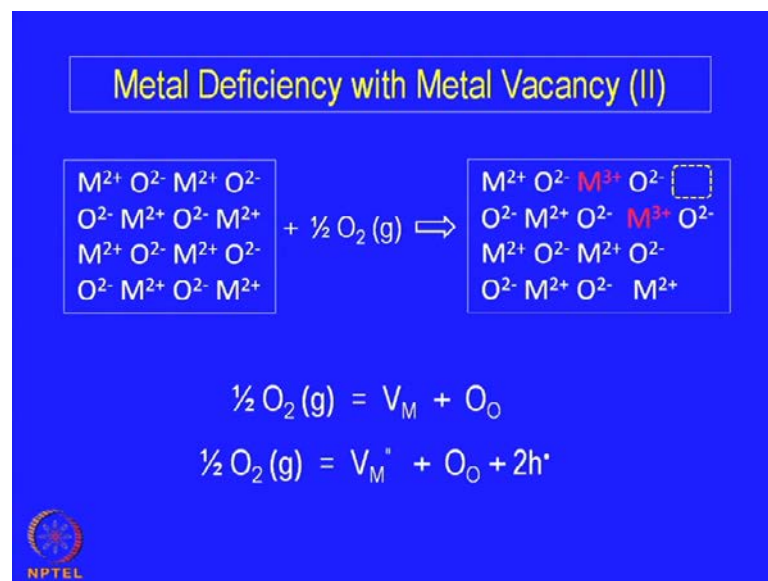
And finally, once again the difference here, is in this case the metal is increasing it is valance, earlier cases when the oxygen deficiency was there. Then the metal was decreasing it is valance from 2 plus it was going to 1 plus. In this particular case when metal deficiency is there, the metal is going from 2 plus to 3 plus and consequently you are generating two holes not electrons, they are also mobile species. So, for the electrical conduction is concern, but there holes deficiency of electrons and they are also offer all practical purposes they have.

They similar characteristics as electrons except that they have a positive charge while electron has negative charge. So, you have a positive charge and those positive charges actually getting added to the 2 plus sites. So, one each to two different metals and that is how you are creating 2 and 3 plus sites and there variable valance; they can change anytime impact, it is a kind of resonating valance; that means, for all the time they are not 3 plus and hole is mobile and these mobile species, when is getting attached to this, then it become 3 plus, next time it will be once again 2 plus.

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So, the final reaction is like this, once again half O 2 g going to metal vacancy and then a lattice site of oxygen and two holes that is what (()) and these are the different steps by which one can understand, why you are writing this.

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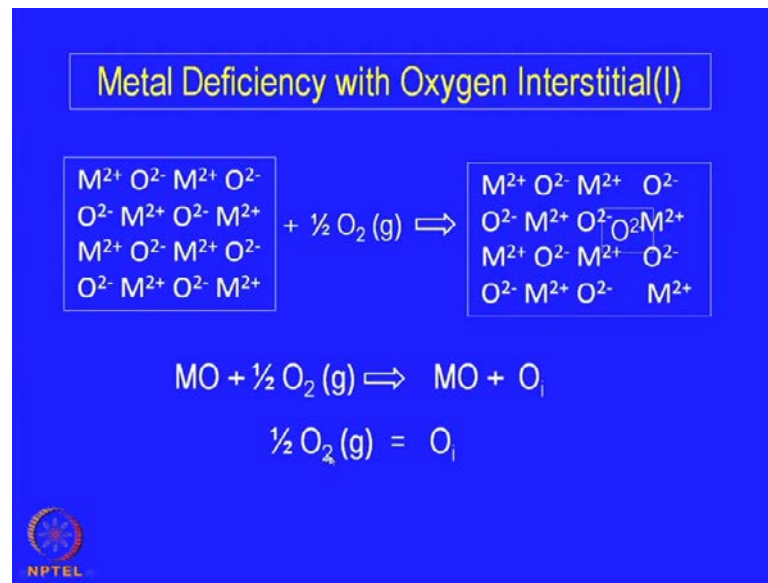
And the last possibility is metal deficiency once again, but with oxygen interstitial. Of course, one has to remember oxygen interstitial is difficult, because compare to metal ions oxygen ions are much larger. So, oxygen and going into a oxide lattice in the interstitial position is difficult job, I mean energetically is not that favorable. However, in certain cases it can still happen and has a imprinciple that possibility exist. So, will you write, that it is very simple half O 2 g just going to interstitial site.

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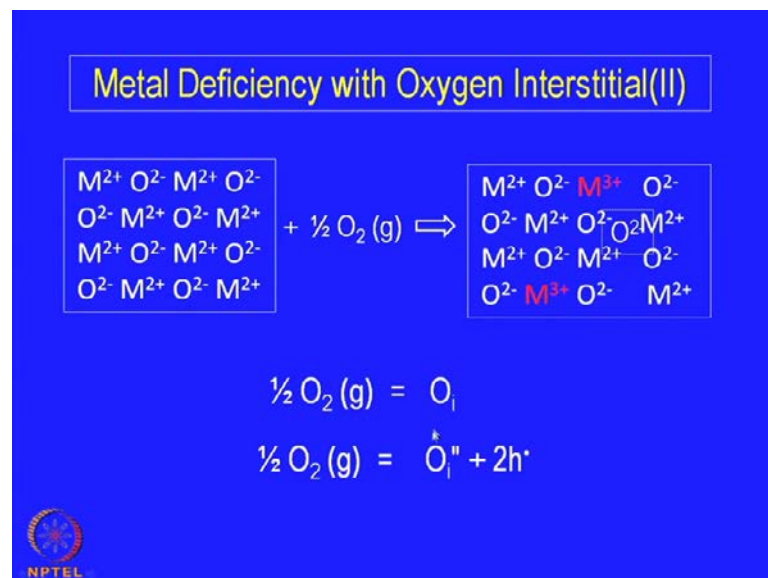
And finally, of course,, the same thing happens here also into 2 plus it change over to in 3 plus basically because, you have created this situation creates 2 holes. So, these holes are mobile, so that is what is happening here and these are the reactions one can write as a consequence of those reactions taking place.

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And finally, this is the resultant once again the same thing has repeated here the 3 equations has been given in two different slides has been combined here in the consulted manner; so you are creating two holes.

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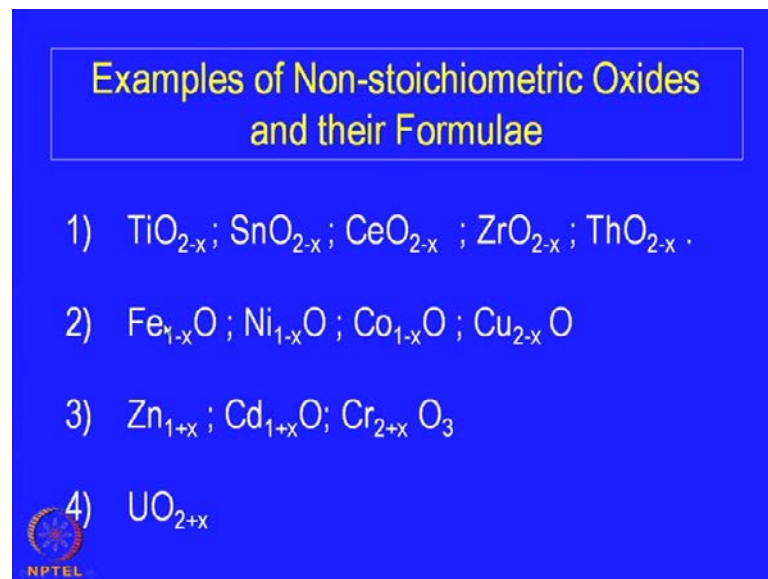
And the final consolidation is here either because of the metal deficient oxide can be created, either by metal vacancy here or oxygen interstitial both of them will result in the same thing. So, far as the charge balance is concern, you are basically interested in what kind of concentrations are different defects will be created as a result of this metal deficiency.

And you can see in both the cases weather the metal vacancy created by metal vacancy or oxygen interstitial, in both the cases actually you are generating two holes. Earlier case when you have oxygen deficient it was two electrons and metal deficient it is two holes and that is as a rule it is true. That means, you have to remember whenever there is a metal deficient oxide it will be a electron hole, which as the mobile species and they are actually, you will see later on which actually they are p type semiconductors.

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Examples of Non-stoichiometric Oxides and their Formulae

1) TiO_{2-x}; SnO_{2-x}; CeO_{2-x}; ZrO_{2-x}; ThO_{2-x}.

2) $Fe_{1-x}O$; $Ni_{1-x}O$; $Co_{1-x}O$; $Cu_{2-x}O$

3) Zn_{1+x}; $Cd_{1+x}O$; $Cr_{2+x}O_3$

4) UO_{2+x}

Now, these are some examples I have given you some list earlier a table what are the different kind of oxides, which can have non stoichiometric compound and non stoichiometric in them. They are the examples of non stoichiometric oxides and there formula and formula is also given, because this formula itself denotes which kind of defects they are having. For example, TiO 2 TiO 2 you have written as TiO 2 minus x and all these all these has been written as 2 minus x TiO 2 minus x, SnO 2 minus x, CeO 2 cilium oxide 2 minus x, ZrO 2 minus x, anthodium oxide 2 minus x.

All are 2 minus x, which means the notation of the formula itself indicates that, there is a oxygen vacancy. Oxygen vacancy is the predominant in defect and they are oxygen deficient oxides oxygen deficiency, because of oxygen vacancy. Here these are metal vacancies you have written these oxides in the form of Fe 1 minus x O naught a O x minus 1 a 1 minus x. First of all it is not 1 minus x it is not a oxygen deficient, it is a metal deficient no metal deficiency can be either by metal vacancy or oxygen interstitial. So, but in this case it has been absorbed or it has been found that they are all metal deficiency is because of metal vacancy.

So, you have written 1 minus x not 1 plus x on that side, 1 plus x will right by the mistake once again there is I will come back. So, these are FeO NiO CeO all of them of that oxides and 2 minus x 1 minus x denotes that there are metal deficient and metal vacancy are the, so there are two aspects one is the metal deficiency, other is the metal vacancy. So, metal deficiency is created by metal vacancy or oxygen interstitials, but which one is correct the formula itself tells you about that.

So, next one is Zn 1 plus x O, it should be 1 plus x O Zn O Cd O cadmium oxide, chromium oxide all of them is written as 2 plus x 1 plus x it means that a metal interstitial. These are oxygen deficient oxides like this one, the first one first category there oxygen deficient less oxygen is there. But, in this case the oxygen deficiency is because of oxygen vacancy and in this case the same thing oxygen deficiency, because of metal interstitial.

So, they are very specific they are specific one is to understand which particular point defect is given rise to what kind of non stoichiometric and that tells us a lot about it is properties about it is behavior. So, for as the conductor conduction process is concern there are many other aspects one can understand from this information. And the last loop is only one compound is there UO 2 plus x, UO 2 plus x which is uranium dioxide and it has an oxygen interstitial as I mention 2 minutes back.

That oxygen interstitials having oxygen interstitials in any oxide structure is very difficult, because metal ions are much smaller, metal can go easily to the interstitial site, but oxygen for oxygen it going to be interstitial site is very energetically is not, so favorable. So, but even then you have one example for oxygen do go oxygen does go into the interstitial site.

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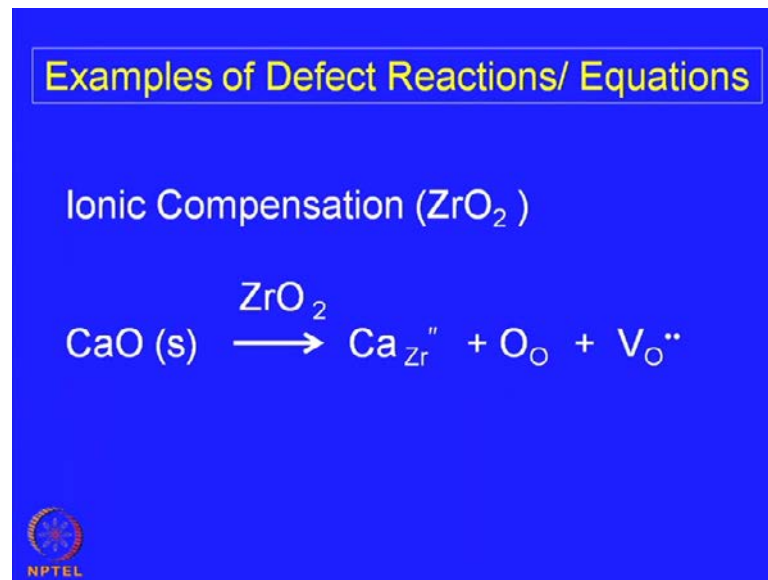
Now, we are coming to you have already seen some we have already seen some reactions how light reactions this is another few examples slightly different way. There are two possibility you know one is what you call the ionic compensation, because you are talking about non stoichiometric oxides. So, there is the right kind of ratio is not there and both the species are charge species. So, if one of them is not there or available less quantity then the other, then that charge imbalance.

So, you know impact to maintain that charge imbalance the to utilize the charge imbalance there has to be some charge compensation. Now, this you have already seen that the metal ions are getting either decrease in their valance or increase in there valance depending on the nature of the non stoichiometric and (()) the defect. So, that always continues.

So, that is what you call the electronic compensation; that means, the electronic charge has been what is charge compensation has been taken care of by electronically. Electronically that means, the charge on the particular site or charge on that particular metal the valance of that metal had changed, so that is what we called the electronic charge compensation. There is another charge compensation what do you call the ionic charge compensation; that means, the ions itself is missing or an ion has been added the valance is not changing, the valance of the metal valance of the ion is not changing.

Whether it is metal ion or the oxygen ion, but the ion itself may be missing. So, the charge has gone out or an added together. So, the valance is not changing, but the metal itself metal are than oxygen ion may be the concentration will changing, so that is what we call ionic compensation. And this in some of compounds where some of the important compounds where such things happen one of the very important example is zirconium dioxide or stabilizer zircon.

Zircon you know it as three different polymers and to stabilize the highest polymer (()) you have to add some other divalent metal oxides like calcium oxide. Some time treble and metal oxides are also added like (()) oxide, but anyway by adding the here is what is called the (()) substitution; that means, zirconium 4 plus has been substituted by calcium calcium 2 plus. So, there is the charging balance the in the lattice in the cationic side there is a charging balance.

So, calcium goes to the zirconium side and there is a deficiency of two positive charges this was 4 tetravalent this is divalent. So, there is a deficiency of two positive charges. Now, this charge has to be balanced then only calcium can go into the solid solution right. Otherwise if charge cannot be balance, then it cannot go into the solid solution it cannot form a solid solution fortunately the charge has been balanced in this passion. So, you remove some oxygen as a bodily some oxygen ions are completely removed, here there is no change of valance. Because all these ions are very stable valiant ions, whether it is oxygen whether it is zirconium, whether it is a calcium. So, zirconium valance change is very difficult it is energetically not possible calcium is also the same thing. So, what can happen that some of the ions (()) been removed from the lattice.

So, that is what happens oxygen vacancy created oxygen goes out, oxygen is fortunately all oxides it can happen because oxygen is available in the atmosphere and after slightly elevated temperature all these reactions can take place there is a gas solid reaction. So, oxygen can exchange between the solid and the environment. So, or it can go in or it can go out quite easily, because oxygen is available in the atmosphere also oxygen is same oxygen is also available within the matter.

So, if the kinetics is true or kinetics is favorable oxygen can interchange or exchange between the atmosphere and the (()). So, that is what happens here the oxygen goes out as soon as you push calcium into the zirconium lattice zirconium dioxide lattice some

oxygen from this will go out in the form of oxygen vacancy and that is what we call the ionic compensation. There is no change of valance here there is absolutely no change in valance only change, but still you have to maintain charge balance, because you are adding only 2 plus instead of 4 plus.

So, some negative ion has to go out that is what happens and it creates huge amount of oxygen vacancy and that is advantages for many properties. We will find later on that this oxygen vacancy give rise to huge amount of very easy oxygen mobility oxygen can diffuse through the lattice very easily and that gives rise to what you call the ionic conductivity. Instead of electronic conductivity, we get ionic conductivity in the solid and this is a very, very good ionic conductor and there huge amount of technological applications.

For that you will see later on how ionic conductivity can be used one can use make a electro chemical cell and it is becomes an electrolyte. So, if you maintain two different oxygen (()) on the other side of the zirconium plates when can get E M F and that E M F even one can use that E M F for power generation. So, that is a big advantage just buy considering the point defects. So, the defects are actually, so important in understanding the properties and then exploiting that properties for our benefit.

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Examples of Defect Reactions/ Equations

Electronic Compensation ($Fe_{1-x}O$)

$$2\,Fe_{Fe} + \tfrac{1}{2}\,O_2\,(g) = 2\,Fe_{Fe}^{\bullet} + V_{Fe}''$$

$$\tfrac{1}{2}\,O_2\,(g) \quad = \quad O_O + V_{Fe}'' + 2h^{\bullet}$$

Well this is the next one same thing examples of defective reactions and equations, here it is an electronic compensation you have discussed already. But, just one or two

examples one additional example may be this is a specific oxide not (()) or anything the specific oxide iron oxide ferrous oxide a Fe O a Fe O 1 minus x. So, if the formula itself indicate you have a iron vacancy and that is the reaction that is the that is the equation you can write that is 2 Fe Fe; that means, Fe goes to the Fe side half oxygen is added to the system.

And then you have oxygen vacancy a iron vacancy doubly charged iron vacancy and this is a singly positive charge singly positive charge iron atom or an ion which means the Fe 2 plus or Fe 2 plus has changed over to Fe 3 plus. So, Fe 3 plus this is what it means, this symbol means the iron has gone to the Fe side with a double with positive effective positive charge; that means, it is increases vacancy. And that is possible because it has generated some holes 2 h means holes and these are negative effective negative charge these are effective positive charge and holes positive charge any way.

So, final equation is half O 2 g oxygen lattice it goes to the oxygen lattice where adding oxygen from the outside and putting in into the regular lattice side corresponding oxygen vacancy a corresponding iron you are not adding. So, iron vacancy is created and that iron vacancy is effective negative charge and that is being compensated by two holes generated holes which means these holes as such will not be there it will be attached to a particular metal sides.

And that is why this will actually happen, either you proceed from this end and take this or you can right this end to that actually this is the final thing happens. So, this is a electronic compensation in case of Fe 1 minus x O.

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This is another together with that you like to find out what is the concentration, what is the partial pressure dependence of this concentration. And for that you consider a equilibrium constant for this defect equation, whatever defect equation you have written the same question is written here. And you can define a equilibrium constant at the particular temperature which is temperature dependent of course. So, it is this is the square brackets actually concentration.

So, it is the concentration multiplied by this concentration and multiplied by this concentration, this concentration is h square (()) because here coefficient is two and on the left side you have a O 2. And so, half of that this coefficient is half. So, it is actually partial pressure concentration here can be converted to partial pressure, because it is in the gas form, so P o 2 to the power one form half. So, the equilibrium constant is the consternation product of the consternations of the products to the reactance.

So, and the neutrality condition here is that from this equation itself, you will find for each oxygen vacancy a sorry each metal vacancy or iron vacancy you are generating two holes. So, the concentration of holes is double than this, that is what is written the concentration of the holes is twice that of this. Remember this is sometimes confusing most of the time mistake is to goes the two sides, on the other side right you have to see the two is on the right side.

So, the concentration of holes is actually two times this because for each iron vacancy two holes have been written that. Now, this concentration of holes the actually known as p it is denoted by p the p positive, this comes from the semi conductor physics. So, this is this p ultimately if you replace that in this equation that this is replace by p and this is p square anywhere. So, it becomes p q and finally, this becomes proportional the p proportional to the this is of occurs constant at particular temperature.

So, it becomes a proportional to P o 2 to the power 1 6th. So, that is a very important derivation an information that. In this kind of oxides the concentration of the holes the concentration of holes and also the concentration of this vacancy because this is related by this number of holes is equal to twice number of oxygen iron vacancy. So, both the number holes as well as iron vacancy is proportional to p O to the power of 1 6th.

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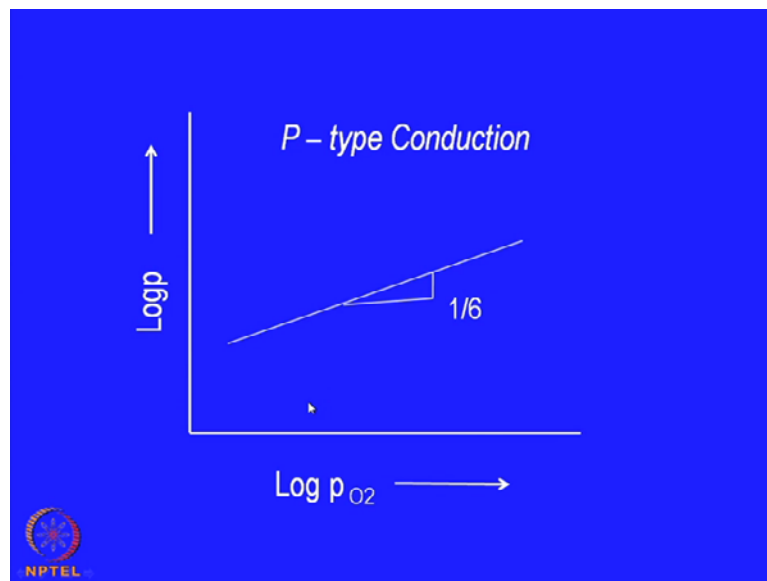
So, higher is the potential a higher is the P o 2, higher will be in the concentration and that can be soon here if you plot log make a log log plot I am sorry this will be N again this is P. So, this is a log P, log p against log P o 2 you will get a positive slope of 1 6th and as a rule impact, whenever there is a positive slope you will get a P type conductivity.

So, this is a P type conduction and of course, this slope may change some times this is 1 6th, sometimes it is 1 4rth, sometimes it is 1 8 and so on. But, positive means it is P type

as the conductivity or the log P or the log concentration of the defend defects increases as P o 2 increases, which indicates that it may be a P type semiconductor.

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$$TiO_{2-x}$$

$$2\,Ti_{Ti} + O_O = 2\,Ti_{Ti}{}' + V_O{}^{\bullet\bullet} + \tfrac{1}{2}\,O_2\,(g)$$

This is equivalent to:: $O_O = \tfrac{1}{2}\,O_2\,(g) + V_O{}^{\bullet\bullet} + 2\,e'$

$$K = \frac{[V_O{}^{\bullet\bullet}]\cdot[e']^2\cdot p_{O2}{}^{1/2}}{[O_O]\,p_{O2}{}^{1/2}}$$

Neutrality Condition: $2\,[V_O{}^{\bullet\bullet}] = [e'] = n$

$$[e'] = n \propto p_{O_2}^{-1/6}$$

Another example TiO 2 minus x the only difference here in find that it is a oxygen vacancy that earlier it was iron vacancy, here it is a oxygen vacancy. And if you go through this the similar processes this equation impact it can be written as here once again 2 Ti Ti oxygen. And then ultimately two oxygen a half O 2 gas goes out of the system and so, it clear oxygen vacancy there and once again you can this is the final equation is this one only on the metal oxygen sub lattice.

This is the regular oxygen site this is half O 2 g, which is going out and as a result you are creating oxygen vacancy. And for charge compensation you have to create to electrons not holes in this time, at this time it will be two electrons. Otherwise the relationship exactly same, instead of metal vacancy, you have oxygen vacancy and twice the number of oxygen vacancy is equal to the electron consternation, which is again not p n in this time. And you will get the concentration of electron or in other words in is proportional to P o 2 for minus 1 6th.

So, this is the reverse and the inverse of that, so it is minus 1 6th and it is becoming electrons, so whenever there is a negative slope.
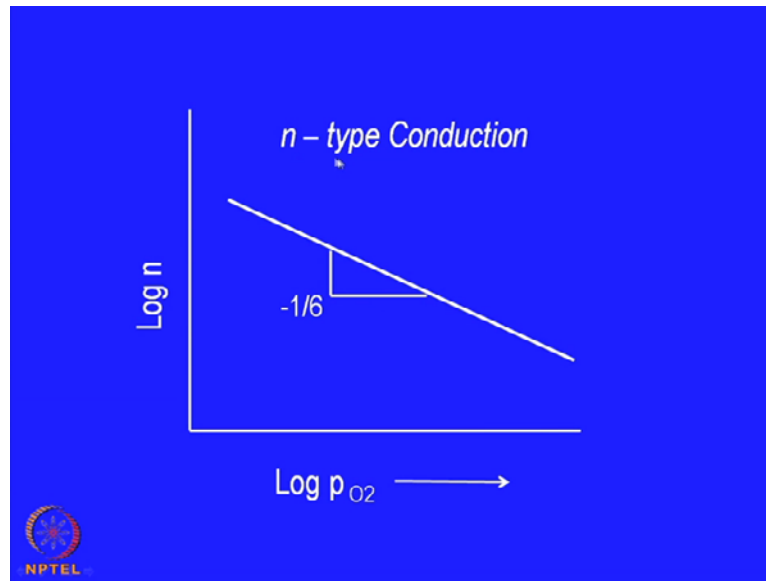
So, you plot this would be end, so log n that is concentration of the electron as a function of P o 2. So, it will be a negative slope, a negative slope means an n type conductor, so that is also as a rule.

Generalize oxygen to should be dependents of defect concentration and oxide with Anti Frenkel defect, you are talking about a little bit generalized things, we are considering, we are considering we are already consider what happens when the metal vacancy or oxygen vacancy. And in some cases you will get p type conductor or electronic

compensation another case ionic compensation all those things we have disused. Here you are taking a very generalized situation and considering that defects are getting created in a particular oxide.

In a particular oxide let us say you know once again, the defects are generated only at the oxygen sub lattice, metal sub lattice you are not including. So, in oxygen sub lattice two types of defects can take place or can be created, one is oxygen vacancy and oxygen interstitial right. This is oxygen vacancy this oxygen intestinal, so that why it is called anti Frenkel defect, if you remember from original definition. So, whenever there is a presence of oxygen vacancy and oxygen interstitial, you call anti Frenkel defect.

Now, that is one of our assumptions for considering what you are going to do now oxygen concentration varies over a wide range. Well oxygen concentration you did not known exactly what is the oxygen pressure range, but you are saying it varies over a very, very wide range you do not know exactly is that right, but you will see you will see when you come to the final results.

Non stoichiometries of both oxygen deficiency and oxygen excess are possible at extreme limits of oxygen pressures low and high pressures respectively. You have seen in some cases oxygen vacancies are there, in some cases metal vacancies are there, but you have not seen any situation, where oxygen vacancy an oxygen interstitial are present in the same system.

Normally it is not a very usual system in most cases you will find either oxygen interstitial is predominate or oxygen vacancies predominate or metal vacancies is predominate or metal interstitial is predominate. Two of them predominate all the time is not almost impossible, almost impossible here also you as taking about you have consider to different defects oxygen vacancy an oxygen interstitials. But, you are saying that they are predominate and two different consequential ranges same material, but it two different anti Frenkel values.

One is predominate at very high (( )) which is possibly the oxygen interstitial, because you are trying to equilibrate the system at with very high concentration of oxygen, so more oxygen can go into the system. Whereas if you take very low oxygen concentration then oxygen will come out from the system from this oxide, so you can expect may oxygen vacancy to be generated.

So, basically you have a taking trying to see how the concentration different, defect concentration can change as a function of P o 2 based on these two consideration that there are only oxygen vacancy and oxygen interstitial, no other metal sub lattice defects.

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Following defect reactions and corresponding equilibrium constants may be written:

1) $O_O = O_i'' + V_O^{\cdot\cdot}$ $\Rightarrow$ $[O_i''][V_O^{\cdot\cdot}] = K_F$

2) $O_O = \frac{1}{2} O_2(g) + [V_O^{\cdot\cdot}] + 2e$ $\Rightarrow$ $[V_O^{\cdot\cdot}] \cdot p_{O2}^{\frac{1}{2}} \cdot [e]^2 = K_1$

3) $Null = e' + h^{\cdot}$ $\Rightarrow$ $[e'] \cdot [h^{\cdot}] = K_e$

4) $\frac{1}{2} O_2(g) = O_i'' + 2h^{\cdot}$ $\Rightarrow$ $\dfrac{[O_i''] \cdot [h^{\cdot}]^2}{[p_{O2}]^{1/2}} = K_2$

Well you have some interest why you are doing that that will be clear in the minute you can write following 4 equations following defect reactions and corresponding equilibrium constants may be written. What you are writing they are different equilibrium situations, because you have talked about oxygen vacancy an oxygen interstitial. And if they are both of them are charged oxygen interstitial will be negatively charged effectively negatively charged, because you have two negative ions of oxygen ion and deficiency of that will be two positive ions or positive charges.

So, this is one kind of equilibrium; that means, a lattice site oxygen at oxygen site can go to an oxygen interstitial side and once it leaves the lattices side these becomes a vacancy. So, oxygen lattice side goes to the physically the mass will go to the interstitial side and consequently there will be oxygen vacancy. So, that is one kind of equilibrium we are considering and that will give rise to a equilibrium constant of this nature. This occurs is always one this concentration is, so high in the lattice that this as to be taken as activity or concentration is one.

So, only the concentration of this multiplier by concentration of this will be an equilibrium constant of this particular reaction for this particular equilibrium. You can

also have of course, they may not be taking place simultaneously, but under different conditions you can also have this equation or this kind of reaction. That means, it is basically they oxygen deficient region, this is an oxygen deficient region which you have consider in case of TiO 2, TiO 2 here oxygen deficient because of the oxygen vacancy and you wrote very similar exactly the same equation.

So, whenever there is a oxygen vacancy is generated as a result of the reaction between the atmospheric oxygen and the oxygen within the solid, then you write this equation oxygen again the oxygen at the oxygen site, the lattice site an it goes out as oxygen vacancy a oxygen gas. Result of that oxygen vacancies created and two electrons get released. Now, this is the equilibrium constant for this, again concentration of this concentration of this, concentration of this, divided by concentration of that, this concentration is always one.

So, you define another equilibrium constant K 1 this is K F, this K 1 impact F stands for Frenkel although it is anti Frenkel. But, actually we are taking about K stands for Frenkel and this is K 1 and then you can have, well before that you can also consider this here you are considering oxygen vacancy at very low P o 2. But, at a very high P o 2 this oxygen from outside can go into the solid in the form an oxygen interstitial, because you are already assume that oxygen vacancy an oxygen interstitial are the predominate defect here.

So, based on that assumption, if more oxygen gas is available outside in the atmosphere and part of it will certainly (()) the system in side to go into this system as oxygen interstitial. And once oxygen interstitial goes in then oxygen a whole will be created it will created hole. So, here it was electron, because oxygen vacancy where created here oxygen interstitial has been created. So, holes are been created and this set the fourth or third impact I am not consider that the number, this is the another equation equilibrium constant.
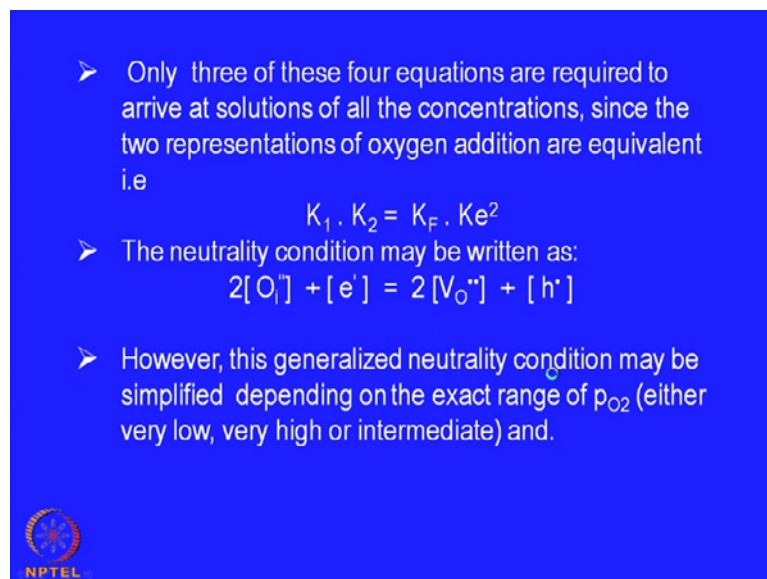
Once again it is the concentration of this, it is the concentration of that, multiplied are divided by concentration of this. Now, this time this concentration is no long a one this partial pressure of an oxygen. So, this partial pressure oxygen as be written here the partial pressure of oxygen is appose on this side on the numerator here is on the

denominator. On the fourth one checks will be because you have created electrons you have created holes.

So, they will also maintain certain amount of balance, so there will be a fourth equation which will say that (()) null means this electron and this hole may put together an relate each other. So, that means, a zero charge is getting generated that sort has been written as null. So, this also I will have a this also will have a what happened this cursor will not moving. So, this is also another equilibrium constant. So, that are four equilibrium constant for corresponding to four different reactions K F, K 1, K e and K 2.

K 1 and K 2 are this, one is at a very high of actually it will happened only at very high partial pressure, K 1 will have a very low partial pressure oxygen. And this will continue to happen whenever there is reactions and holes are there and this is just a ionic compensation. This ionic compensation this is electronic compensation and then these are happing at two different partial pressure like this.

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> Only three of these four equations are required to arrive at solutions of all the concentrations, since the two representations of oxygen addition are equivalent i.e
> $$K_1 . K_2 = K_F . Ke^2$$
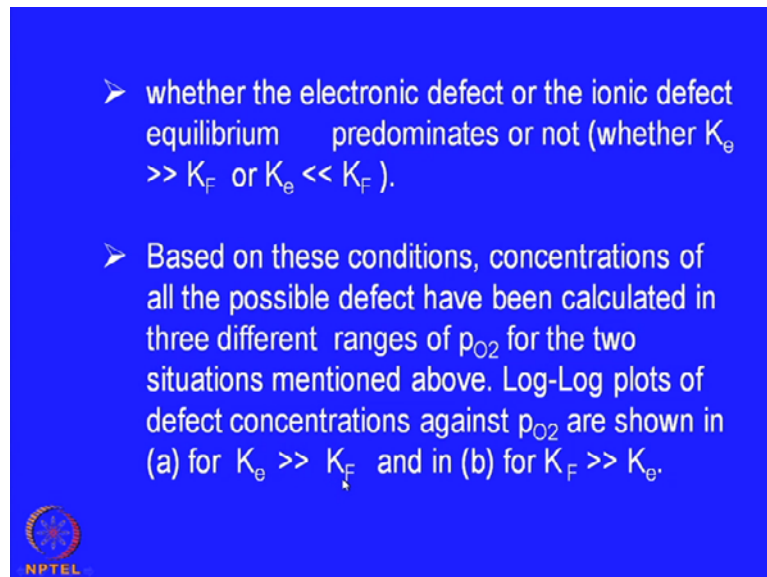> The neutrality condition may be written as:
> $$2[O_i''] + [e'] = 2[V_O^{..}] + [h^.]$$
>
> However, this generalized neutrality condition may be simplified depending on the exact range of p_{O2} (either very low, very high or intermediate) and.

While only three of this four equations are equal to arrive at solutions of all the concentrations. Says that two representations of oxygen addition are equivalent that is K 1 into K 2 equal to K F into K e square into K F, no K F will not be there this K F will not be there. Because you can see from here this equation K 1 into K 1 K 2 actually P o 2 basically canceling out and it is this square of this is there an oxygen vacancy an oxygen

interstitial of there. And then this and this is also there, so you will find K 1, K 2 multiplication actually K e into multiple square of this.

That is why this has been written like that and the neutrality condition you written as these are negative terms are negative charges, oxygen interstitial as well as electrons negative charges, oxygen interstitial has two charges. And this is a one charge and this also positive charge positive charges on the one side and negative charge on the side that will be the neutrality condition these must be maintain all that time because material is electrically neutral. So, these must be maintained; however, this generalized neutrality conditions may be simplified depending on the exact range of P o 2 either very low or very high or intermediate.

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> whether the electronic defect or the ionic defect equilibrium predominates or not (whether K_e >> K_F or K_e << K_F).

> Based on these conditions, concentrations of all the possible defect have been calculated in three different ranges of p_{O2} for the two situations mentioned above. Log-Log plots of defect concentrations against p_{O2} are shown in (a) for K_e >> K_F and in (b) for K_F >> K_e.

And whether the electronic defect or the ionic defect equilibrium predominates or not that is whether K e is greater than or K F or K e is greater than should be greater than or less than. So, is all that fine whether K e is greater than K F for K e is less than K F depending on that this situation may slightly change will be clear, when you go to that diagram. Based on these conditions concentrations of all the possible defect have been calculated in three different ranges of P o 2 for the two situations mentioned above. Log, log plots of defect concentrations against P o 2 are shown for in a diagram a for K e greater than the K F and in (b) K F greater than K e; now this may not be very clear just now.
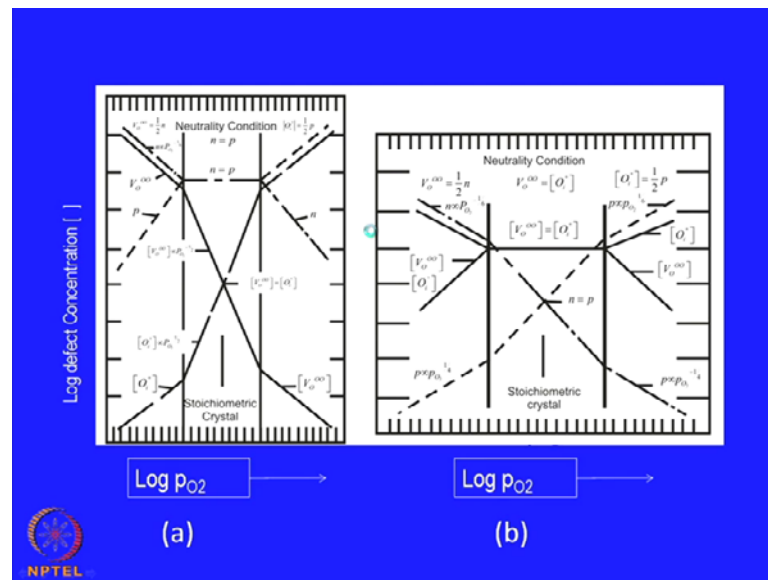
But, when you go to the diagram when go the diagram it will be quite clear, what exactly you need in this diagram you have plotted P o 2 log P o 2. And then these are the different concentrations there are different concentrations had been plotted for example, this one is actually in the concentration of the electrons this is very low P o 2, very low p O 2 this is very P o 2 you are not mentioned exactly what is the range. But, this is what this is the concentration of in that is the electronic concentration, this is on the concentration of P.

On right side the highest one is concentration of P and this is the concentration of n and this is here concentration of p and on this side concentration of n. So, all this four different defects have been calculated has a function of P P o 2 and this is the variation n varies number of holes a number of electrons varies in this manner with a with a slope of minus point minus 1 by 6 this is 1 by 6. And then it goes there becomes constant at a intermediate due to n becomes P and then on this side is p and n becomes lower.

So, on this side n dominates p is very low other values of these are oxygen vacancy, this oxygen interstitials changes from this manner and becomes very comparable to the concentration of holes on the right side. And oxygen vacancy is very low on the side and then goes like that and it becomes comparable to the electronic concentration. But, electron concentration is higher still higher than the oxygen vacancy or oxygen interstitial on this side it is hole concentration is higher.

And there is a intermediate temperature range where n is equal p; that means, number of electrons and number holes are same. So, this means and these intersections this is a intersection of actually K 1 this one no this a K F sorry I will tell you this is intersection is K F this is oxygen vacancy and oxygen into interstitial that was the equilibrium constant for that.

And here it is the K e, this is K e where the concentration of n and p is same the difference between the, this diagram and this diagram is you can see the here the, this oxygen vacancy an oxygen interstitial are same in this flat region. This is P o 2 in dependent region this P o 2 independent region where they compensation is ionic compensation, where here due to independent there is also P o 2 independent also a small region, but the compensation is electronic compensation right.

So, what did the basically means that this is the stoichiometric crystal is written here, this is stoichiometric crystal, this also stoichiometric crystal. So, in this region you have an electronic conductivity, although in fact, it as an electronic conductivity it depending on which is this value. Here you can see this is K e, K e is less than this value this is K K K 1 into K 2 a K F this is K F and this is K e. So, here K e is much smaller than K F for here K F is smaller than K e.

So, this is this corresponding to K e the electronic compensation and this is ionic compensation. So, ionic compensation is less important here, electronic is important here, electronic is less important ionic is important. Now this of course, depends on the particular solid, which particular solid, but this a very generalized situation or any oxide, better oxide you take.

Whatever oxide you take you will get this kind of variation and at very low here to electronic conductor at very high p 2 is p type conductor, hole conductor or it can be and there will be a there will be a intermediate region, why there where it will be either a intrinsic conductivity. That means, in equal to p means in semiconductor terminology you call it an intrinsic conductivity or a completely ionic conductor.

So, this is possible are any this is a very generalized situation, the whole range is not applicable to all the oxides. Some of the oxide resides here mostly stoichiometric for example, (()) like things which as ionic compensation is more important thing. So, they

you are not given here any particular value of P o 2, so that is also variable from material to material.

So, in some cases the materials will behave in this manner or all in this range in some cases material will fall, an another material fall in this range. So, there are materials where are oxides which are normally ionic conductors. So, they fallow this kind of a situation, there are other oxide which are normally hole type conductor, they will be falling in this range. And there will be a another category of oxides which are normally are mostly negative are electronic conductor they will for carry fall in this category.

So, if you have a material of this nature basically a electronic conductor, if go on increasing the P o 2 at some point you will reach this, is not known at what partial pressure or what high pressure or not you may an experimentally may or may not reach. But, theoretically you are suppose to go to this; similarly if you have ionic conductor like this and then expose it to very, very low P o 2 at some point of time it will become n type conductor electronic conductor.

The same material if you ha take it two a very high P o 2 very high partial pressure may be several atmospheres of partial pressure then it will become p type conductor. So, is not that all the materials will have permanently, ionic conductor or a electronic conductor or a hole conductor they can be changed depending on the P o 2 depending on the temperature and so on. But, although those things to as a large extended as to be determine experimentally, so this is the sense of this kind of a calculation and this kind of a diagram.

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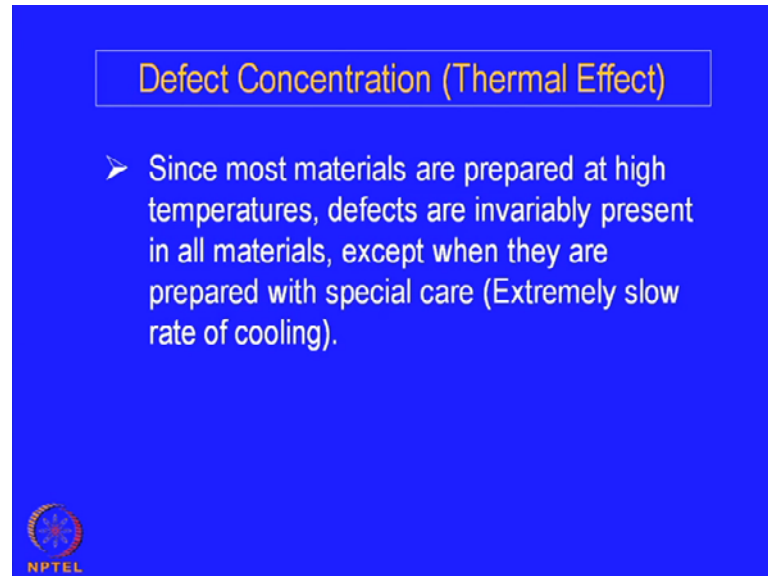

Finally, I think there is only couple of slides defect concentration thermal effect what do you have discuses, so far the defect concentration changes with the partial pressure. Because, it equilibrates with a moment and depending on it is preparation condition depending on the environmental condition to partial pressure the defect concentration will change. And accordingly, it is conductivity, it is mobility, it is diffusion coefficient all of them will change whatever is related to the defect concentration.

Why there ionic defects or electronic defect it will certainly change right, but there is another very important parameter which also as a great in influence on a defect concentration that is thermal effect a temperature. And that is what it is written here the generation of point defects increases structural energy of a crystal, at the same time it increases the entropy randomness of the atomic position of the system. Dominance of the entropy term particularly at higher temperatures results in lowering of free energy of the system.

So, formation of defect is a preferred phenomenon particularly at high temperatures. So, it is not that defects are not allowed, defects are actually preferred because by generating this kind of point defects. Actually you change you reduce the free energy of the system because the entropy term increase, by increasing entropy term you have actually reduce the energy; and therefore, defects will automatically form at high temperature. So, where

depending on the temperature defects automatically going to come and it is a preferred thing from thermionic point of you.

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I think that is what since most materials are prepared at high temperatures defects are invariably present in all materials, except when they are prepared with special care extremely slow rate of cooling. If they somebody once a very pure material or not only pure an a defect free material then it has to take a very special care, so that defects are not generated,, but on the normal circumstance defect you will be generated. And there they actually tend to minimize the free energy of the system and free energy of the system minimization means the it more stable thermo dynamically.

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Finally, this is equation which is a very simple arrhenius kind of equation mathematically the defect concentration is expressed as n by N, this is basically concentration term exponential minus delta H by 2 k T delta is a enthalpy, enthalpy of formation of defect. So, for formation of each defect, there is a enthalpy term and associated with each defect in have a enthalpy term. So that depends on the particular type of defect of the structure of material in, which it is generated and so on.

So, where n by N is the concentration of concentration of any particular defect delta h is the heat of formation one defect, k is the Boltzmann's constant and T is the temperature in degree Kelvin. The value of delta h is usually 1 to 10 electron volt at a typical a typical temperature of 1000 degrees centigrade, the concentration may vary from 10 power minus 2 to around 10 to the power of minus 7 depending the value of delta H which may vary from 1 to 8 electron volt.

Well that is all I think about our discussion on the defects in crystals, point defect in crystals, and as you can see, there is enormous importance of the point defects. When you try to discuss try to understand some diffusible properties like the electrical conductivity as well as diffusion coefficient. Particularly these two properties very, very critical for understanding that you must a good idea, have a defect characteristics, and how it generated and conditions influenced and so on so forth. So with this we have come to end of this discussion and.

Thank you very much for you kind attention.