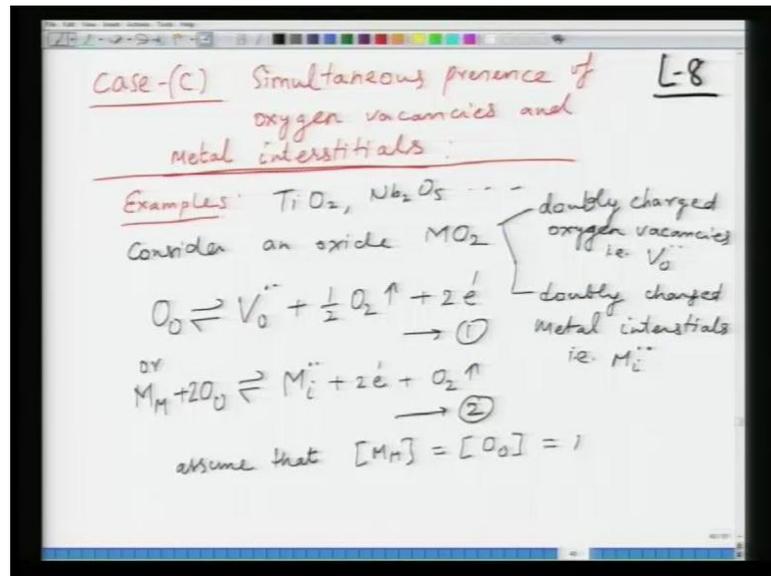


**Electroceramics**  
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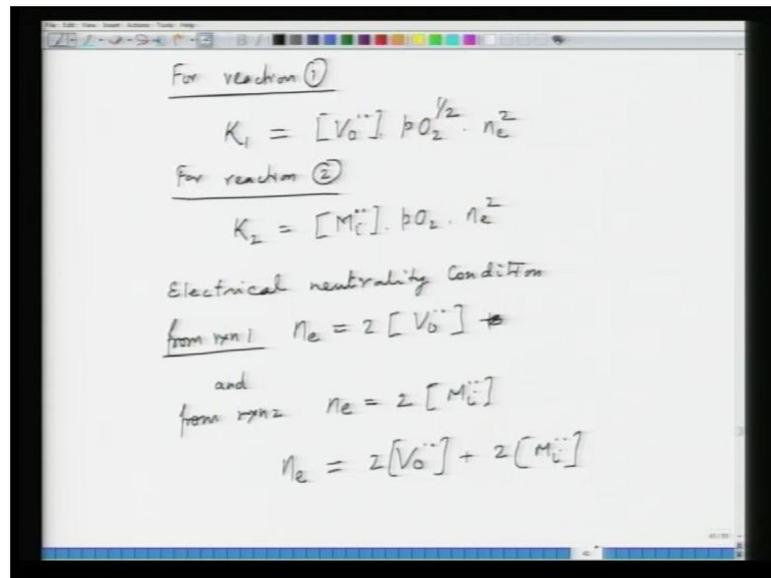
**Lecture - 9**

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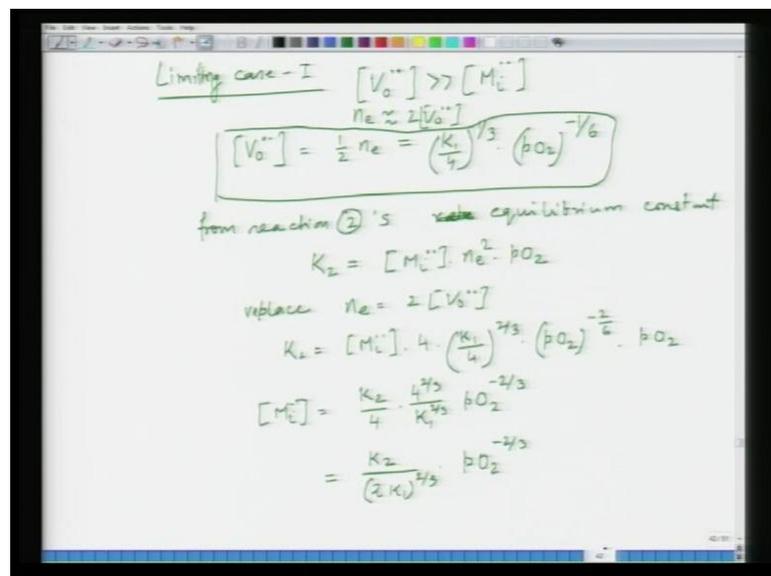
So, welcome to this new lecture. So, I will just briefly review what we did last time. So, basically we were continuing our discussion on defect equilibria in non stoichiometric materials, and following from what we discussed in lecture 7. We discussed for example, in case of oxygen deficient oxide when you have presence simultaneous presence of oxygen vacancies, as well as metal interstitials in that case what happens.

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Then we have worked out expressions of reaction constants for the reaction for vacancy formation and reaction format and interstitial formation; and then looked at the electrical neutrality conditions.

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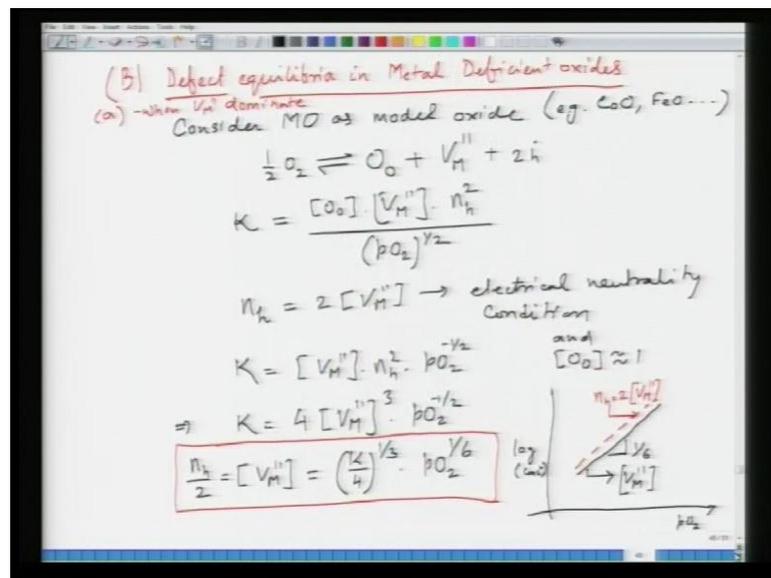


Followed by, for two limiting cases; case one when oxygen vacancy concentration is much larger than interstitial concentration, metal interstitial concentration in such a case we worked out what is the concentration of V o, and in such a case the since V o is much larger than M i, the electron concentration is now dependent upon V o concentration, it is



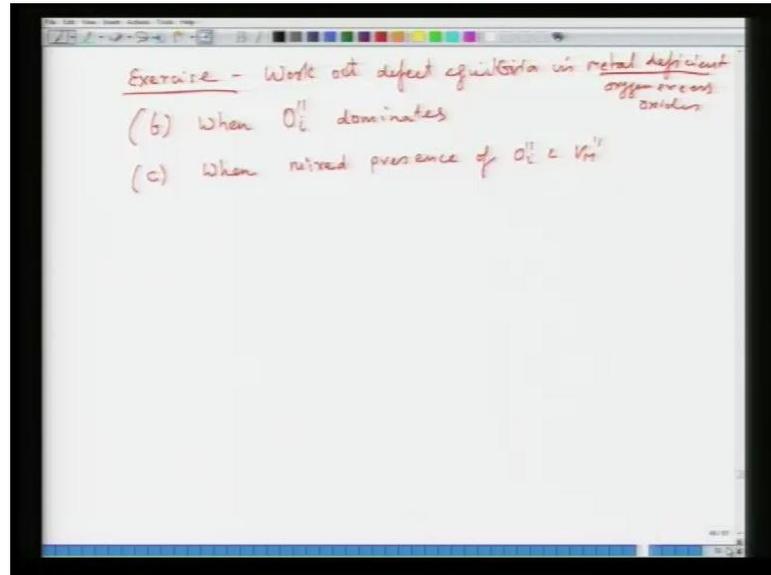
We worked out the  $V_o$  and  $M_i$  concentrations which have dependence of minus, which have dependence of minus 1 by 3 and plus 1 by 6. Of course, the boundary of partial pressure remains same which and which means that partial pressure of oxygen has to be much smaller than  $k_2$  by  $k_1$  square for this region. So, we constructed on the on this basis diagram, a plot of concentration of defects versus partial pressure of oxygen, where we clearly see how the defect concentrations vary as a function of oxygen partial pressure.

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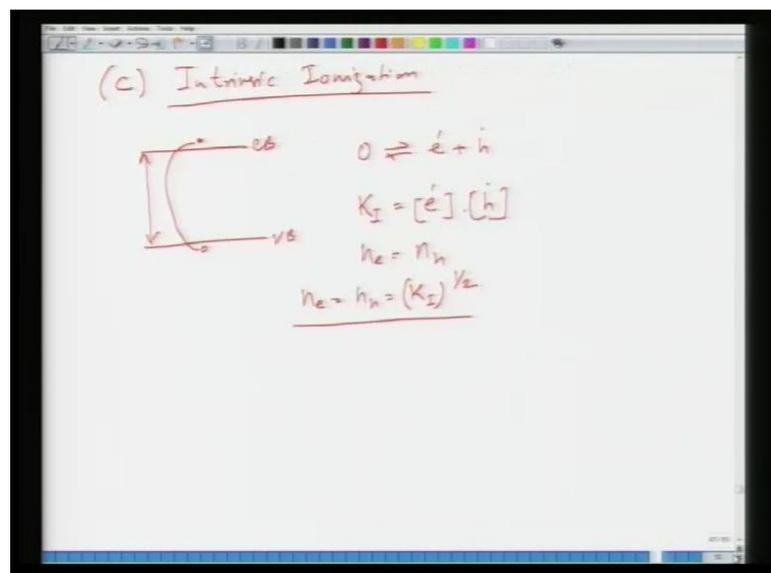
Then we looked at the defect equilibria and metal deficient oxides, when metal vacancies dominate and following the similar protocol as we have followed in case of oxygen deficient oxides. We worked out, what is the relation of metal vacancies and resulting holes with respect to partial pressure oxygen.

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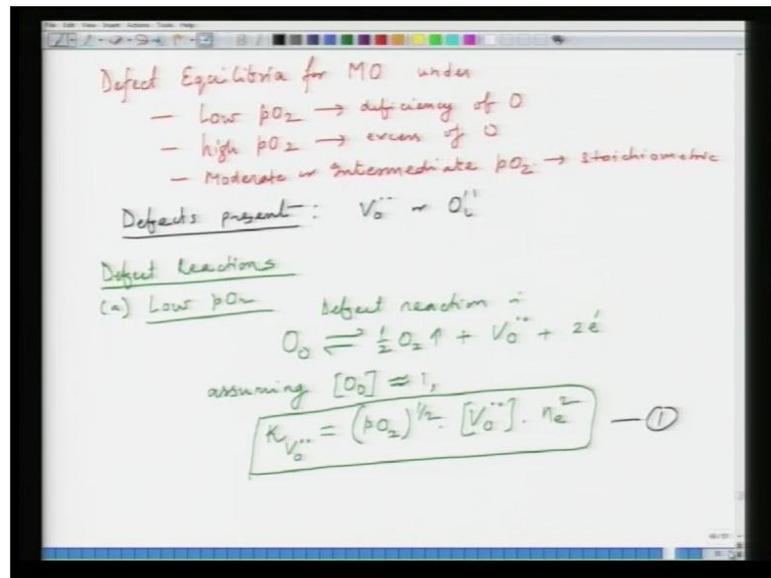
I left it to you as an exercise to work out this defect equilibria, when oxygen interstitials dominate and what happens when you have mixed presence of oxygen interstitials and metal vacancies. The derivation would be similar to what we did in case of oxygen deficient oxide.

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Then finally we looked at, what is the equilibria in case of intrinsic ionisation and in intrinsic ionisation the  $K$  value is equal to electron and hole concentration product, which is independent of partial pressure of oxygen.

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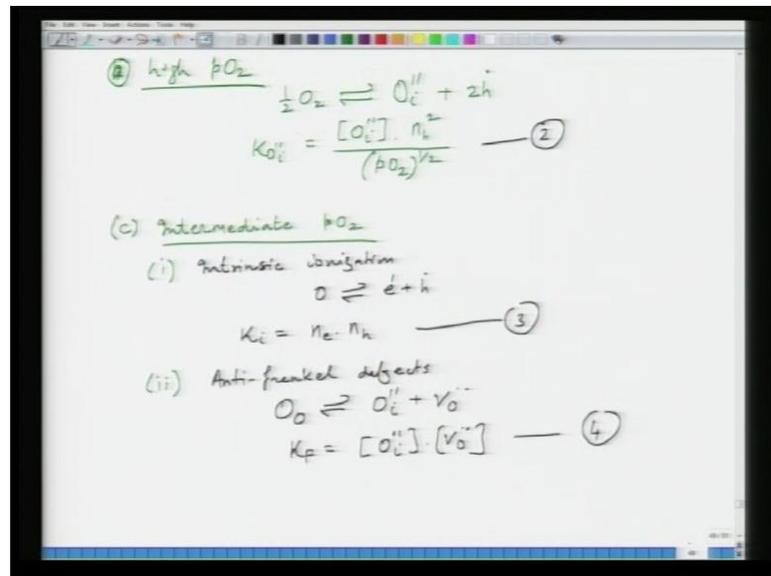
And then we started working on developing an equilibrium concentration diagram as a function of partial pressure of oxygen. There are three conditions which we are considering; one is low partial pressure of oxygen, which means you have deficiency of oxygen; another is high of partial pressure of oxygen, which means excess of oxygen and then you have moderate or intermediate oxygen partial pressures when oxide happens to be stoichiometric. The defects which are present as under these conditions are either oxygen vacancies or oxygen interstitials.

The type of defects that are present will depend upon things like, what is the crystal structure of materials etcetera, and what sort of a stoichiometric defect does the material prefer? Suppose you have a material which prefers Schottky defect in the stoichiometric condition, which means you have vacancies of metal and oxygen. Which means these are that the concentration of these defects also follow in higher and lower pressure of regime. In that case you will not have you will not have interstitials, but you will have vacancies as dominant defects.

So, in this case we have taken material to have Frenkel defect. So, this is MO having Frenkel defects, Frenkel defects of anion which means it would be anti Frenkel disorder, as a result the dominating defects that would be present at if the pressures would be  $V_o$  or  $O_i$ . So, now we write the defect reactions for low  $p_{O_2}$  it is a familiar defect reaction

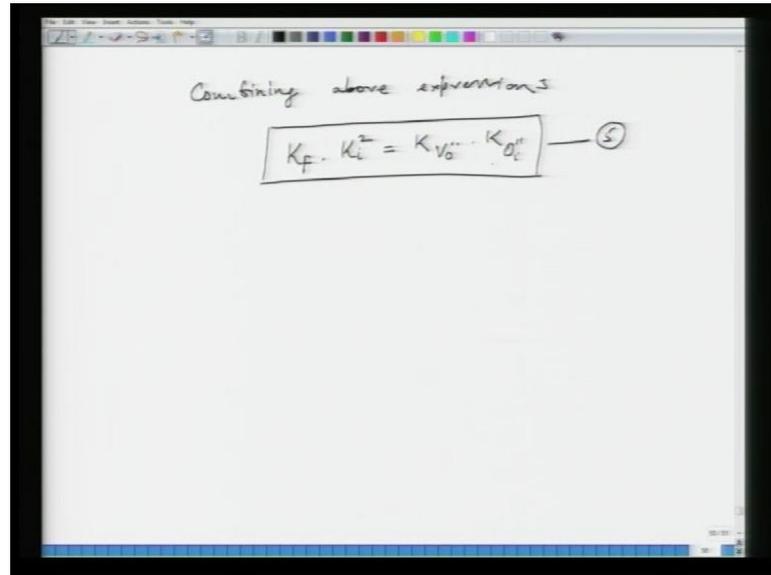
that oxygen goes out of the system giving rise to oxygen vacancy and then we worked out the, what is the equilibrium constant for this reaction.

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Then we looked that the high  $p_{O_2}$  case, similarly forming oxygen interstitials and then we looked at the conditions for intermediate  $p_{O_2}$ . In the case of a intermediate partial pressure of oxygen you can have two conditions. First condition is when you have a intrinsic ionisation which is the dominant factor, which means you have intrinsic formation of, which means you have formation of electrons and holes. Here  $k_i$  is equal to product of  $n_e$  and  $n_h$  independent of  $p_{O_2}$  or second scenario is when you have anti Frenkel disorder dominates, as a result you form oxygen interstitial and the oxygen vacancies, and  $k_F$  is product of these 2 defects concentrations and again independent of  $p_{O_2}$ , which we know.

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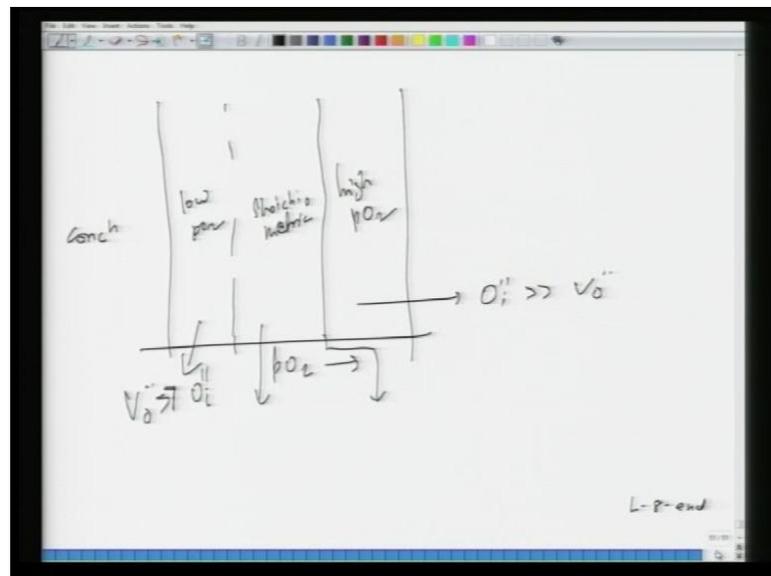


Combining above expressions

$$K_F \cdot K_i^2 = K_{V_o} \cdot K_{O_i}^2 \quad \text{--- (5)}$$

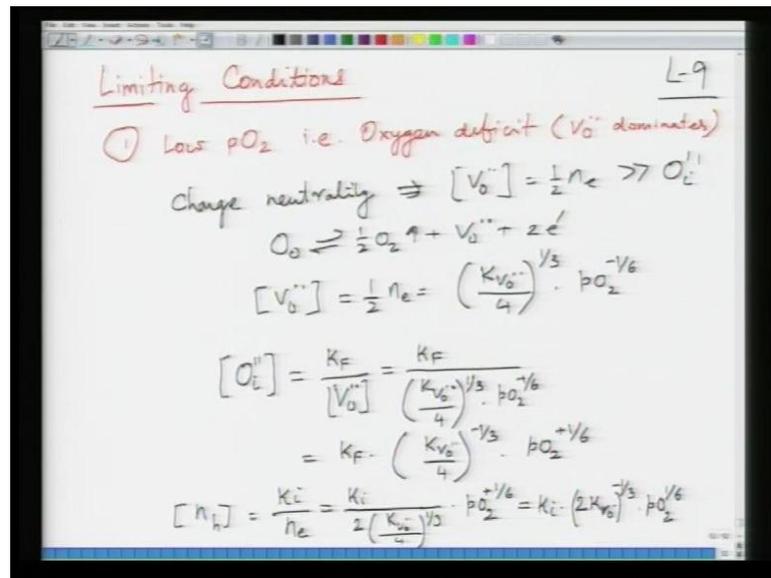
Then if you combine these expressions you can get an equality which is  $k_F \cdot k_i^2$  is equal to  $k_{V_o} \cdot k_{O_i}^2$  just as a point of interest.

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Now, we are going to look at the limiting conditions for each of these regions. So, that we can work out the defect concentration profiles in each of these three regions, which is low  $p_{O_2}$  is stoichiometry, intermediate  $p_{O_2}$  or high  $p_{O_2}$ .

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So, we will start discussion for this lecture. So, we will take limiting conditions. So, we will take the first limiting condition, which is the first condition is when you have low  $pO_2$  conditions. That is according to our particular oxide you have oxygen deficit that is  $V_o$  dominates.

So, in such a situation if you look at the defect reaction, defect reaction was  $O_o$  going out to giving rise to  $V_o$  and 2 electrons. So, as a result of the charge neutrality, means  $V_o$  is equal to half  $n_e$  and these two are much bigger than  $O_i$ . So, this is the situation. So, now we can write, we know that what is what, and this reaction would be, I can just write the reaction, now  $O_o$  was equal to half  $O_2$ ,  $V_o$  plus 2  $e^-$ . So,  $V_o$  for this reaction you can work out yourself, half  $n_e$  will be equal to  $k_{V_o}$  divided by 4 to the power 1 by 3 into  $pO_2$  the power minus 1 by 6. So, this was the expression for  $v_o$ .

Now, since  $V_o$  is the dominating defect as a result, what is the concentration of  $O_i$  now? The concentration  $O_i$  will be governed by the reaction which by the Frenkel disorder reaction. So, now,  $O_i$  will be,  $k_F$  divided by  $V_o$ . So, this as a result becomes  $k_F$  divided by  $k_{V_o}$  to the power 1 by 3 into  $pO_2$  to the power minus 1 by 6, and this becomes to, equal to  $k_F$  into  $k_{V_o}$  divided by 4 to the power minus 1 by 3 into  $pO_2$  to the power plus 1 by 6. From the intrinsic ionisation reaction you can work out the concentration of holes. So,  $n_h$  would be  $k_i$  divided by  $n_e$ , now  $n_e$  concentration is given by this reaction, which is this particular equation that we worked out. So,  $k_i$

divided by 2 into  $k V_o$  divided by 4 to the power 1 by 3 multiplied by  $p O_2$  to the power minus 1 by 3.

This would be the expression for your whole concentration and which can be further modify into, you can write it as  $k_i$  into  $2 k V_o$  to the power minus 1 by 3 because these go up and multiplied by  $p_o$  to the power 1 by 6. We have got the expressions for  $V_o$ ,  $O_i$ ,  $n_e$  and  $n_h$  and the region of low partial pressure of oxygen. So, what it happen, what happens here is, again to retreat, that here  $V_o$  and  $n_e$  concentration which is oxygen vacancy and electron concentration is given by this reaction, which is the dominant reaction. Now,  $O_i$  and  $n_h$  concentration are given by the intrinsic disorder conditions, which is  $k_F$  by  $V_o$  or  $k_i$  by  $n_e$ . So, these are the conditions for low  $p O_2$  region.

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Since  $[V_o^{\bullet}] \gg [O_i^{\bullet}]$

$$\left(\frac{k_{V_o^{\bullet}}}{4}\right)^{1/3} \cdot pO_2^{-1/6} \gg k_F \left(\frac{k_{V_o^{\bullet}}}{4}\right)^{2/3} \cdot pO_2^{1/6}$$

$$k_F^{-1} \cdot \left(\frac{k_{V_o^{\bullet}}}{4}\right)^{2/3} \gg pO_2^{1/3}$$

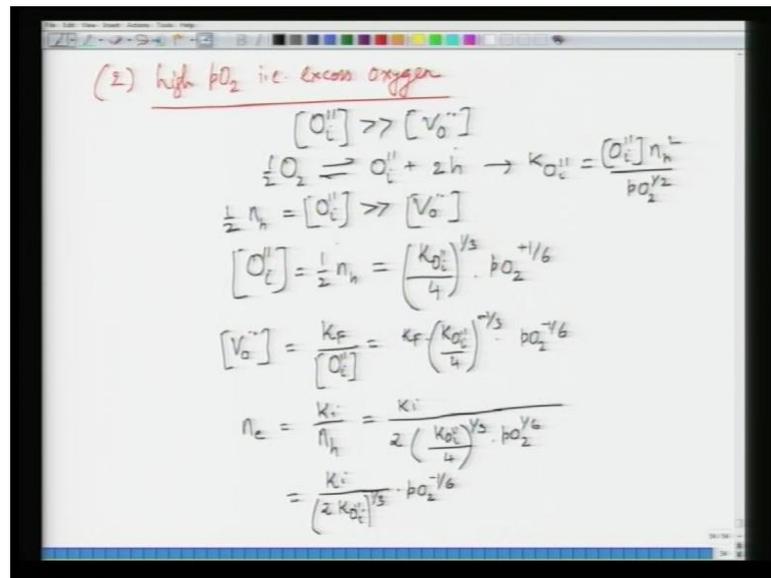
$$pO_2 \ll \left(\frac{k_{V_o^{\bullet}}}{4}\right)^2 \cdot k_F^{-3}$$

$$\rightarrow pO_2 \ll \frac{k_{V_o^{\bullet}}^2}{16 k_F^3}$$

Now, we have to work out what is the condition of partial pressure of oxygen that will allow this to happen, below which this will happen. So, for that since  $V_o$  is much larger than  $O_i$ . So, if you now replace the  $V_o$  value, which is  $k V_o$  divided by 4 to the power minus 1 by 3 into  $p O_2$  the power minus, plus 1 by 3 into, this should be plus not minus, much greater than  $O_i$  and which is  $k_F$  multiplied by  $k V_o$  divided by 4 to the power minus 1 by 3 into  $p O_2$  to the power, plus 1 by 6. So, what you do is that, you take this on that side. So, basically it becomes  $k_F$  to the power minus 1 into  $k V_o$  divided by 4 to the power 2 by 3, greater than  $p_o$  to the power 2 by 6 which is 1 by 3.

So, which means basically  $p_{O_2}$  is less than your, so you just cube that everything. So, if this becomes  $k_{V_o}$  divided by 4 square, multiplied by  $k_F$  to the power minus 3 or alternatively it becomes  $p_{O_2}$  is much lesser than  $k_{V_o}$  square divided by 16  $k_F$  cube. So, this is the partial pressure of oxygen, which is smaller than this particular ratio. At these pressures your conditions  $V_o$  much larger than  $O_i$  is going to be valid. So, this is the first limiting condition.

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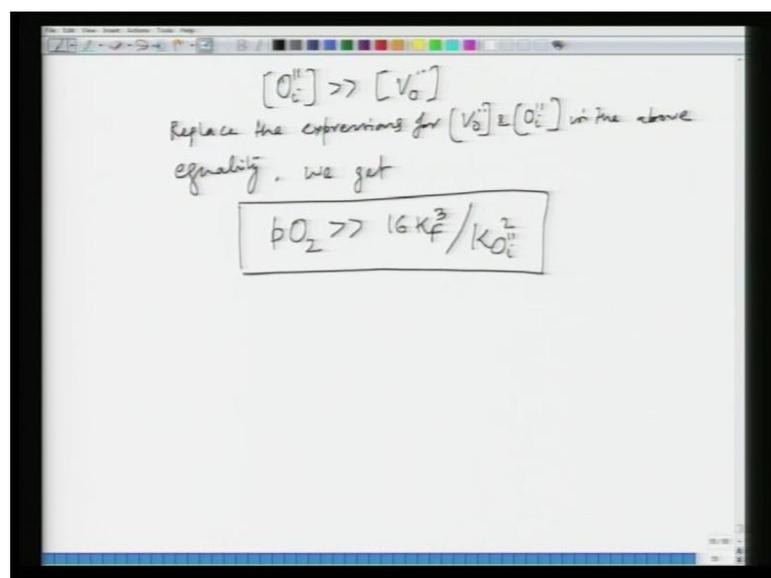
Now, to work out the second limiting condition let us take high  $p_{O_2}$ . That is excess oxygen under, these conditions the requirement is  $O_i$  is greater than  $V_o$ . So, the dominant reaction in such a case was half  $O_2$ ,  $O_2$ ,  $O_i$  plus 2  $h$  and the electrical neutrality condition was  $n_h$ , half  $n_h$  is equal to  $O_i$  is much larger than  $V_o$ .

So, now how do we work out  $O_i$ , again you follow the similar procedures we have done it many times now. So, I will just write the expression. So,  $O_i$  is equal to, so reaction constant for this would be  $k_{O_i}$ . So,  $O_i$  is equal to half  $n_h$ , would be equal to  $k_{O_i}$  would be equal to  $O_i$  multiplied by  $n_h$  square divided by  $p_{O_2}$  the power half, and you make the replacement for  $n_h$ , in terms of  $O_i$  is equal to 2  $O_i$ . So, that will become  $O_i$  square. So, what you get? So, basically what you get is, so this will be  $O_i$ ,  $n_h$  square divided by  $p_{O_2}$  to the power half. So,  $O_i$  would be your  $k_{O_i}$  divided by 4 to the power 1 by 3 multiplied  $p_{O_2}$  to the power plus 1 by 6. So, this would be the expression for your  $O_i$  and  $O_i$  and  $n_h$ .

So, similarly as compared to the previous case now,  $V_o$  concentration is now determined by Frenkel reaction. So, which is  $k_F$  divided by because if it is a dominating condition when  $p_{O_2}$  are the, when  $V_o$ ,  $O_i$  is the dominating defect and  $V_o$  cannot be created by any other means other than Frenkel defect. So, but Frenkel defect also gives rise to both  $V_o$  and  $O_i$ . So, the  $V_o$  concentration will depend upon  $O_i$  concentration. So,  $k_F$  divided by  $O_i$ , and this would be equal to  $k_F$  into  $k_{V_o}$ , sorry  $k_F$  into  $k_{O_i}$  divided by 4 to the power minus 1 by 3 into  $p_{O_2}$  the power minus 1 by 6.

Similarly,  $n_e$  will be equal to  $k_i$  divided by  $n_e$  and  $n_e$  would be equal to  $k_i$  divided by  $n_e$ . We can write  $k_i$  divided, sorry by  $k_i$  divided by  $n_h$ , just slipping out a little bit. So, this should be  $n_h$ . So,  $k_i$  divided by  $2 k_{O_i}$  divided by 4 to the power 1 by 3 into  $p_{O_2}$  to the power 1 by 6, which means  $n_e$  would be now, you can either take lesser side. So, you can make it. So, this will become  $k_i$  divided by  $2 k_{O_i}$  to the power 1 by 3 into  $p_{O_2}$  the power minus 1 by 6. So, we have got the expressions for  $O_i$  and  $n_h$  from the defect reaction and we have got the concentrations of oxygen vacancy and electron from the Frenkel and an intrinsic ionisation reaction, because that is the only mechanism by which these defects can be created. But the concentration of these will depend upon the concentration of other defects, which is oxygen interstitial and holes.

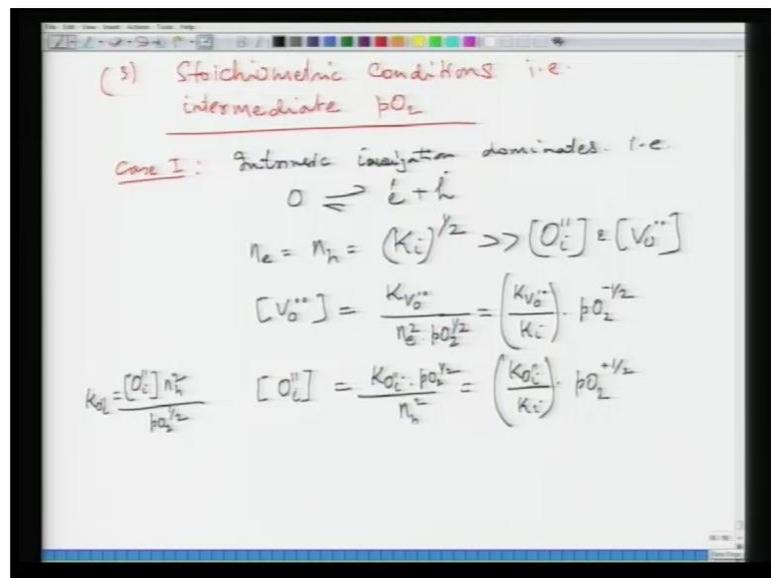
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So, now what we need do is that, we need to work out what is the limiting condition and the limiting condition has to be worked out by the condition that,  $O_i$  is much larger than

V o. So, you just now replace the concentration of O i and V o here and I will just write the final expression now. So, what you will get is, so the place the expressions for V o and O i in the above equality or inequality, we look at its we get p O 2 much bigger than 16 k F cube divided by k O i square. So, which means the on the higher pressure side p O 2 must be larger than this particular value. Now, we will look at the conditions, limiting conditions for the or the defect concentrations in the stoichiometric region. So in the stoichiometric region we have two cases which are possible.

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So, we can have, so we will just write number 3. So, in this we will first take case one, case one is the, is the condition when intrinsic ionisation intrinsic, this internal disorder or intrinsic ionisation dominates. That is electron hole creation. So, corresponding concentrations would be, here n e is equal to n h will be equal to k i to the power half, and these two in this case since you have this is the dominating phenomena these two are much larger than both O i and V o.

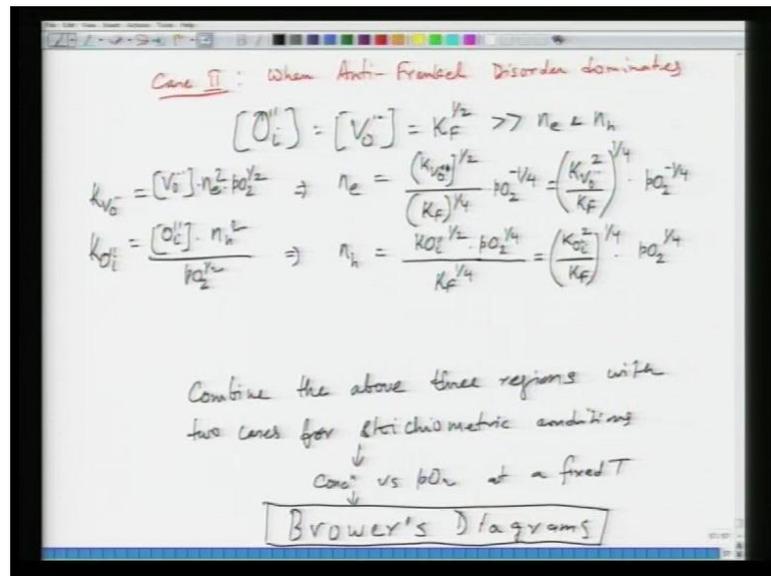
So, how do you find the concentration? But, you still have some O i and V o present. So, how do we find out the concentration of O i and V o? So, in this case now the concentration of O i and V o are given by now, what are the instances where n h, n e, O i and V o are related. They are related only in the relations when oxygen vacancy is formed or the oxygen interstitial is formed. So, for V o concentration, V o will be equal to k V o divided by k i, now we know that, let me just write the complete thing. So, in

the  $V_o$  reaction we knew that  $V_o$  was equal to  $\frac{1}{2} O_2$  multiplied by  $\frac{1}{2} O_2$  plus  $V_o$  plus 2 electrons.

Now in case of less partial pressure of oxygen, since oxygen vacancy dominates the defect, which means electron concentrations automatically fixed by vacancy concentration. Now, here what we are saying is that  $n_e$  and  $n_h$  concentrations are much larger than  $O_i$  and  $V_o$ , which means in this expression now which is the reaction for formation of vacancy of oxygen any concentration is no longer governed by  $V_o$  concentration, rather  $V_o$  concentration is now governed by  $n_e$  concentration. So, what we will do is that, so this expression was  $V_o$  was equal to  $k V_o$  divided by  $n_e$  square multiplied by  $p O_2$  to the power half.

So, this would become  $k V_o$  divided by  $k_i$ . Now,  $n_e$  is given as  $k_i$  to the power half, which means  $n_e$  squares become  $k_i$  into  $p O_2$  to the power minus half. So, this is the vacancy concentration in this region, which is the stoichiometric region. Similarly,  $O_i$  concentration will be given by  $k O_i$  divided by  $p O_2$  to the power half multiplied by, just a second because we had  $k O_i$  was equal to  $p O_2$  to the power half divided by  $O_i$  into  $n_h$  square. So,  $O_i$  will be equal to, no it is  $k O_i$  was equal to  $O_i$  into  $n_h$  divided by  $n_h$  square. So,  $O_i$  now will be equal to  $k O_i$  divided multiplied by  $p O_2$  to the power half divided by  $n_h$  square. So, this becomes  $k O_i$  divided by  $k_i$  into  $p O_2$  the power plus half. So, in this region the  $V_o$  and  $O_i$  concentration will be lower than  $n_e$  and  $n_h$  concentrations, but they will change as  $p O_2$  the power half in case of  $V_o$  oxygen vacancy or  $p O_2$  to the power of plus half in case of oxygen interstitials.

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So, this is the case one, when your internal ionisation dominates. Now, case two can be when anti Frenkel disorder dominates, which means  $O_i$  is equal to  $V_o$  is equal to  $k_F$  to the power half, much larger than both  $n_e$  and  $n_h$ . So, that is the case under stoichiometric condition.

Now, since  $O_i$  and  $V_o$  are independent of partial pressure of oxygen, which means in the defect reactions. So, now, I have to work out what is  $n_e$  and  $n_h$ . So, I know that for that for  $k_{V_O}$ , I had  $V_o$  multiplied by  $n_e$  square multiplied by  $p_{O_2}$  to the power half, for  $k_{O_i}$  had  $O_i$  multiplied by  $n_h$  square divided by  $p_{O_2}$  to the power half. So now, since  $O_i$  and  $V_o$  are independent of partial pressure of oxygen, but  $n_e$  now is much smaller than or  $n_h$  is much smaller than these two, these two will be dependent on. So, as a result now  $n_e$  will be equal to  $k_{V_O}$  to the power half divided by concentration of  $V_o$ , which is  $k_F$  to the power half and this will now become  $k_F$  to the power 1 by 4, and this will be  $p_{O_2}$  to the power minus 1 by 4.

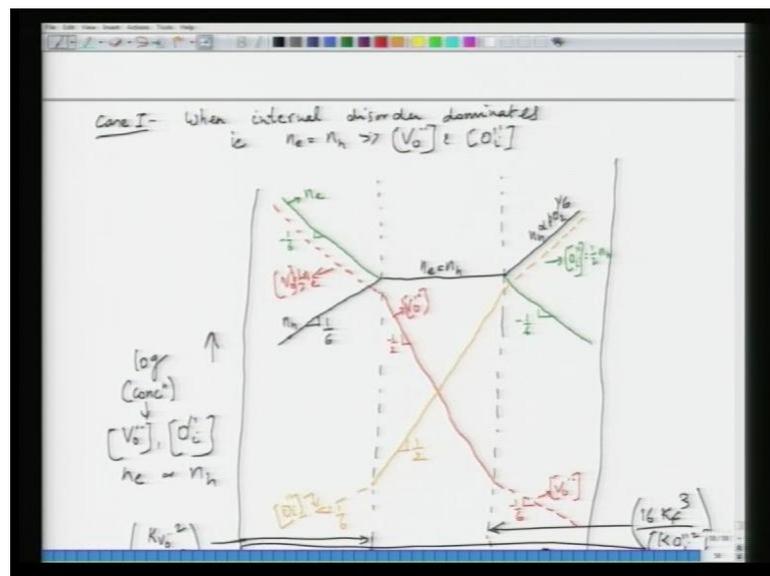
So, this becomes  $k_{V_O}$  to the power half divide by  $k_F$  to the power 1 by 4 or  $k_{V_O}$  square divided by  $k_F$  to the power 1 by 4, that can also be written. So, basically you write it as  $k_{V_O}$  divided by  $k_F$ . So, this becomes sorry to the power 1 by 4 into  $p_{O_2}$  to the power minus 1 by 4 and similarly,  $n_h$  will be equal to  $k_{O_i}$  to the power 1 by 2 divided by into  $p_{O_2}$  to the power 1 by 4 divided by concentration of  $O_i$ , which is  $k_F$  to

the power 1 by 4. So, this becomes  $k O_i^2$  divided by  $k F$  to the power 1 by 4 into  $O_2$  to the power 1 by 4.

So, we have established these two conditions for stoichiometric condition. So, now we have complete picture, we have determined the concentration of defects for the region when partial pressure of oxygen is low, we have and we have also determined the limiting condition of oxygen partial pressure, below which this is going to happen. We have also established the condition of concentrations for the region, when oxygen partial pressure is high as well as we have also worked out what is the limiting condition of that high partial pressure of oxygen. And between those two ends of partial pressure of oxygen we will have a stoichiometric region, in which case one, an internal disorder dominates and case two when anti Frenkel disorder dominates.

Now, what we will do is that, we will we will now combine these and make the plots. So, now combine the above three regions with two cases for stoichiometric condition and this will give rise to concentration versus  $p O_2$  diagram, at a fixed temperature. This will give you what is called as B r o w e r s, Brower's diagrams, these are very important diagrams in case of ceramics, to work out what is the defect concentration as a function of partial pressure of oxygen.

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So, we will we will look at the first case. So, we will look at the first case. Case one; when internal disorder dominates, that is  $n_e$  is equal to  $n_h$  much bigger than  $V_o$  and  $O_i$ . So, what we will do that? We will just make these lines, let us say this is  $\log$  of  $p_{O_2}$  and this is  $\log$  of concentration and that would mean  $V_o$ ,  $O_i$ ,  $n_e$  or  $n_h$ . So, first I will mark, what are the limiting conditions? So, this this is the boundary condition, this is the limiting condition. So, this would be low  $p_{O_2}$ , this would be high and this would be intermediate  $p_{O_2}$ . So, the conditions that we worked out were oxygen partial pressure. So, if I go to some earlier slides. So, this was the first condition  $k V_o$  divided by  $16 k V_o^2$  divided by  $16 k F^3$ . So, this boundary we will mark, this boundary would be  $k V_o^2$  divided by  $16 k F^3$ . Now, since  $k$  depends upon the temperature this boundary will shift as a function of temperature. So, we are considering this exercise at a constant temperature and now we will look at what is the condition further which is  $16 k F^3$  divided by  $k O_i^2$ . So, this would be  $16 k F^3$  divided by  $k O_i^2$ . So, these are the two boundary conditions.

Now, in the first region we knew when we had this internal disorder which dominates, we know that in this condition in the centre  $n_e$  was equal to  $n_h$ . Let us start at some arbitrary concentrations, which will be dependent now on only temperature, that we can calculate by just knowing, what is the band gap of the material? Now, we know that  $n_h$  varies at higher pressures if you now go back to pervious slides what we can see is that  $n_h$  varies as a function of  $p_{O_2}$  to the power. So, this is  $n_h$  is proportional to  $p_{O_2}$  to the power plus 1 by 6, and how it varies? In the lower pressure side it varies as minus 1 by 6. So, this is again  $n_h$ .

Now, in the, what about  $n_e$ ? So,  $n_e$  goes as in the higher pressure side as as again minus 1 by 6, this would sorry plus 1 by 6, I am sorry. So,  $n_e$  in this region would be vary as minus 1 by 6, it would also vary as minus 1 by 6 in this region. This would be  $n_e$ , what about  $V_o$  and  $O_i$ ? We know that  $O_i$  is half of  $n_h$  in this region. So, this would be  $O_i$  is equal to half of  $n_h$  and let me use a different colour here, I do not want to confuse it. So, I will choose a different colour. So, this would be  $O_i$ , in the lower pressure region I will have  $V_o$  is equal to, in we will use a different colour here as well. So, this would be my  $c$  half of  $n_e$ .

So, now we have drawn the concentrations of three defects on each side. Now, what about how do they vary? Now, now we know that in the centre region both  $V_o$  the  $V_o$

decreases at minus half  $p O_2$ ,  $p O_2$  to the power minus half and  $O_i$  increases as  $p O_2$  to the power plus half. So, the slope will change here. So, this will become like this. So, this will be your  $V_o$  and this will vary at minus half and again it continues to vary as minus 1 by 6 in the higher pressure region. So,  $V_o$  varies as minus 1 by  $p O_2$  to the power minus 1 by 6 in the high pressure region, I will just draw this line which somehow got erased.

So, now we will see what happens with  $O_i$ ,  $O_i$  again varies in the intermediate pressure range as plus half. So, this point of intersection would be parallel somewhere here. So, this goes as plus half and again it goes as minus plus 1 by 6 in the in the low pressure region. So, I am just putting the right square brackets around everything. So, that everything is correct. So, this is how you will plot the concentrations of each of them because the moment you draw one of them, then you get the lead to draw others into other regions. So, first we do  $n_e$  is equal to  $n_h$  in the central region, it is the stoichiometric region because we knew that it is like this, and then from the ends of  $n_e$  and  $n_h$  you follow  $n_e$  and  $n_h$  plots according to the equations that you have worked out in the, in this in the previous previous slides and then  $V_o$ .