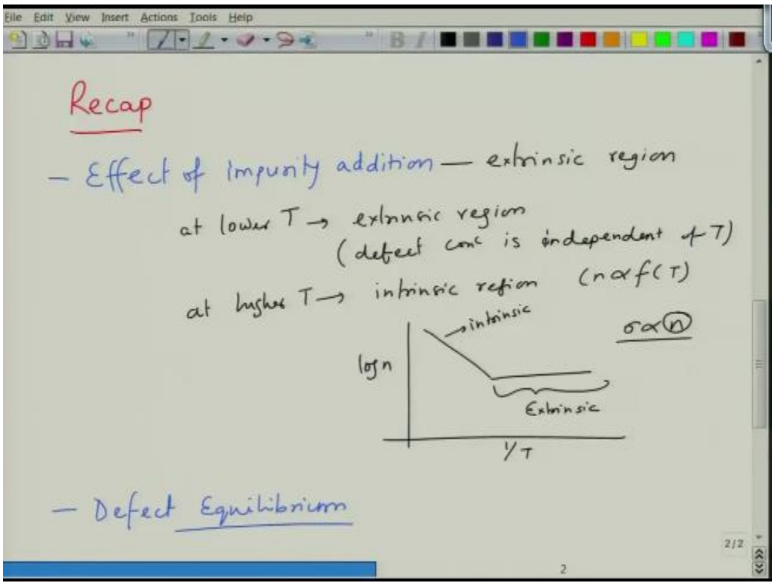
Fundamentals and Applications of Dielectric Ceramics
Prof. Ashish Garg
Department of Materials Science and Engineering
Indian Institute of Technology – Kanpur

Lecture - 12
Defect Concentration: Non Stoichiometric Oxides

So, welcome again to the new lecture of this course fundamentals and applications of dielectric ceramics. So, we will just briefly do a recap of what we did in the last lecture.

(Refer Slide Time: 00:23)



Recap

— Effect of impurity addition — extrinsic region

at lower T → extrinsic region
(defect conc is independent of T)

at higher T → intrinsic region $(n \propto f(T))$

$\sigma \propto n$

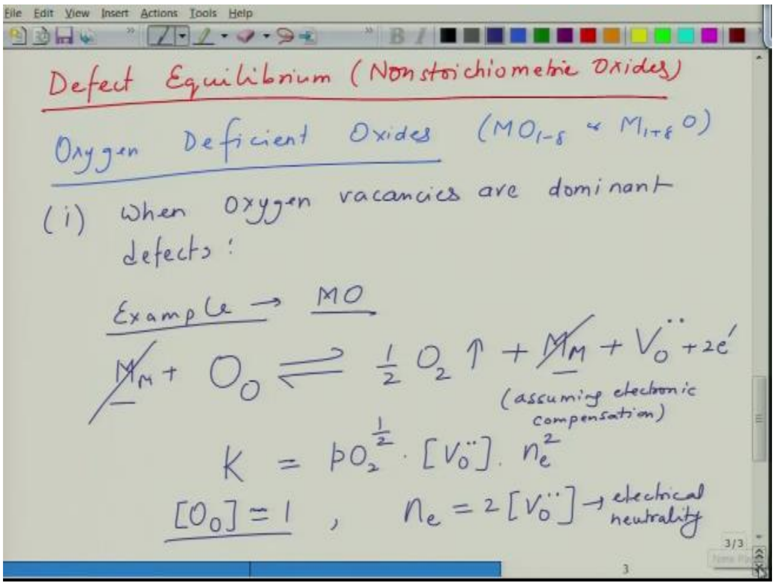
— Defect Equilibrium

So, in the last lecture, we looked at effect of impurity addition. So, effect of impurity addition leads to formation of extrinsic region when you plot concentration versus temperature. So, generally at lower temperature, you will have extrinsic region where defect concentration is independent of temperature okay, and at higher temperature, you will have intrinsic region where n will be a function of temperature and generally the plot will look like this. So, if you have login as a function of 1 over T.

So, this is the higher temperature region, this is a lower temperature region, so this would be your extrinsic region and this would be intrinsic region okay and this is also reflected in properties such as conductivity and diffusivities and things like that, where you will see that because of constant defect concentration, the conductivity also remains constant as a function of temperature because conductivity is proportional to n. So, as a result despite having some dependence on temperature, it virtually remains constant up to certain temperature because of constant defect concentration which is high and then we looked at the defect equilibrium.

So basically, we wanted to establish conditions as a function of ambient conditions. So, in the case of stoichiometric solids or stoichiometric defects, the concentration of defects is basically dependent upon temperature only, it does not depend upon the conditions like partial pressure, oxygen, etc and the denominator whether you will have $2kT$ or whether you will have 3 kT, 4 kT or whatever, it will depend upon the stoichiometry of oxides. For MO, it would be 2 kT, for M_2O_3 and MO_2, it could be different.

(Refer Slide Time: 02:57)



Defect Equilibrium (Nonstoichiometric Oxides)

Oxygen Deficient Oxides ($MO_{1-\delta}$ & $M_{1+\delta}O$)

(i) When oxygen vacancies are dominant defects:

Example → MO

$$\cancel{M_M} + O_O \rightleftharpoons \frac{1}{2}O_2 \uparrow + \cancel{M_M} + V_O^{\cdot\cdot} + 2e'$$

(assuming electronic compensation)

$$K = pO_2^{\frac{1}{2}} \cdot [V_O^{\cdot\cdot}] \cdot n_e^2$$

$[O_O] \simeq 1$, $n_e = 2[V_O^{\cdot\cdot}]$ → electrical neutrality

So, let us now further develop on the same thing. We were looking at the defect equilibrium in non-stoichiometric, so we are looking at the case of oxygen deficient oxides okay. So basically, it is a case of either $MO_{1-\delta}$ or $M_{1+\delta}O$ okay. So, let us say the first case which is when oxygen vacancies are dominant defects. So, if example is of MO, then the defect reaction can be written as

$$M_M + O_O \leftrightarrow \frac{1}{2}O_2 \uparrow + M_M + V_O^{\cdot\cdot} + 2e'$$

so, oxygen at oxygen site goes out okay, leaving at, so metal at metal site will remain, so if you just write so metal at metal site remains at metal at metal site, which means metal sites are conserved.

Oxygen site to maintain the site conservancy will become empty. So, this will become V_O and the compensating defects will be 2 electrons if you consider electronic compensation okay. So, this is assuming electronic compensation. If you consider ionic compensation, you will not form electrons, rather you will have a reduction of metal ions okay. So, that is what is going to happen. So, basically now, if you want to write down the defect, so you can basically write down that reaction constant.

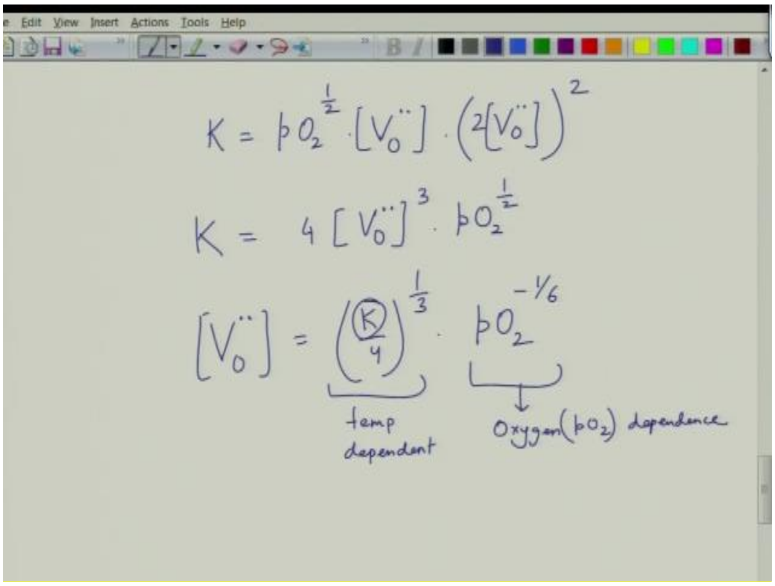
$$K = pO_2^{1/2}.[V_{\ddot{O}}].n_e^2$$

,we can ignore M_M because M_M is canceled on both sides, if I say electron concentration as n_e, it becomes n_e square okay. So, it becomes a product of vacancy oxygen, vacancy concentration multiplied by electron concentration square multiplied by pO_2 to the power half and here we are assuming that O_O is equal to 1 okay.

$$[O_O] = 1\,,\ \ n_e = 2[V_{\ddot{O}}]$$

So, we assume that O_O is equal to 1, which is basically the case of ideality and to maintain the electrical neutrality, what is the electrical neutrality condition, the electrical neutrality condition is that for every oxygen we can see we are creating 2 electrons, which means n_e is equal to twice of okay, this is electrical neutrality alright.

(Refer Slide Time: 06:43)



$$K = pO_2^{\frac{1}{2}} \cdot [V_O^{\cdot\cdot}] \cdot (2[V_O^{\cdot\cdot}])^2$$

$$K = 4[V_O^{\cdot\cdot}]^3 \cdot pO_2^{\frac{1}{2}}$$

$$[V_O^{\cdot\cdot}] = \underbrace{\left(\frac{\boxed{K}}{4}\right)^{\frac{1}{3}}}_{\text{temp dependent}} \cdot \underbrace{pO_2^{-1/6}}_{\text{Oxygen}(pO_2)\text{ dependence}}$$

So, when you write this and if you substitute this in the above equation, it becomes,

$$K = pO_2^{1/2}.[V_{\ddot{O}}].(2[V_{\ddot{O}}])^2$$

So, if you now just rearrange it, this K will become.

$$K = 4[V_{\ddot{O}}]^3.pO_2^{1/2}$$

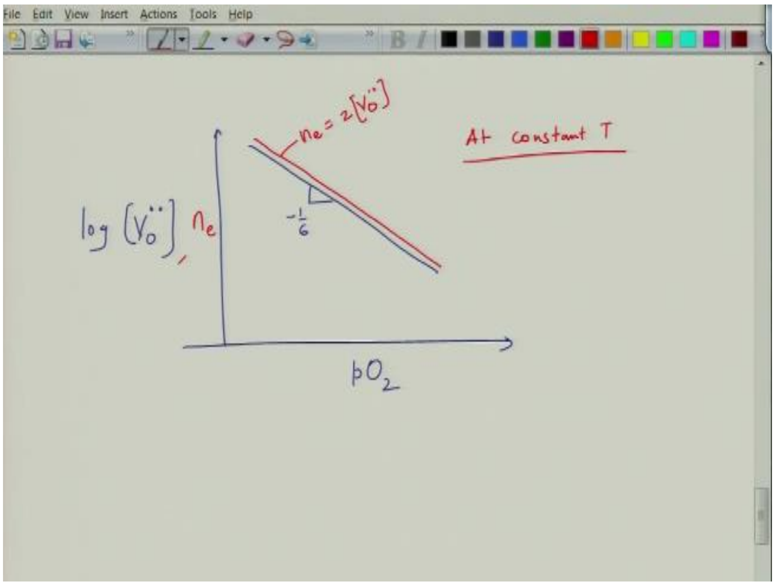
So, I can write this as now Vo being if I just want to express Vo now, so this becomes.

$$[V_{\ddot{O}}] = \left(\frac{K}{4}\right)^{1/3}.pO_2^{-1/6}$$

So, of course K can be written from the usual free energy reaction and this will become some K_1 into exponential of minus delta H by kT.

So, temperature dependence will be in-built here, but what is important here is in addition to dependence upon temperature, so this is temperature dependent because K will show the temperature dependence, but this is additionally what we see is oxygen, partial pressure of oxygen dependence. So, what this shows you is that as you increase the partial pressure of oxygen, the vacancy concentration will go down, and as you decrease the partial pressure of oxygen, the vacancy concentration will go up.

(Refer Slide Time: 08:36)



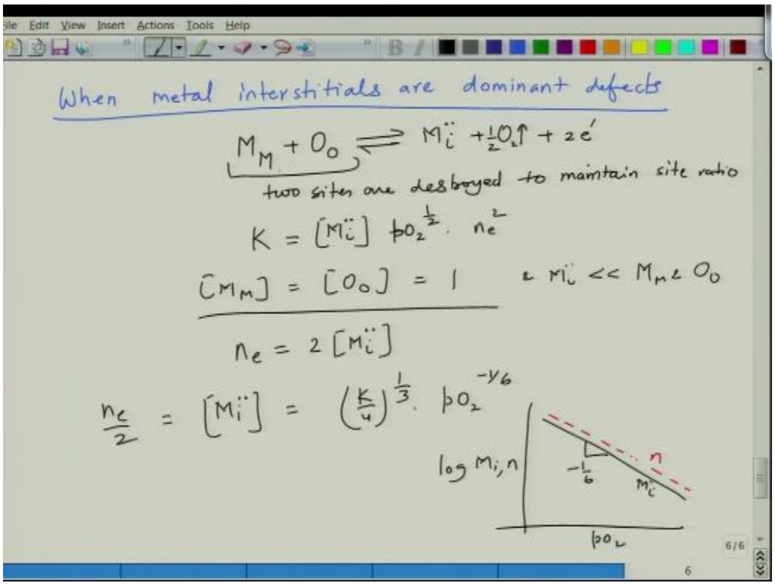
So, when you plot this, when you plot Vo, so you can plot this as a function of you know for log plot, semi log plot okay. So, let us say logVo, pO_2. So, the vacancy concentration will decrease as a function of pO_2 and this will we have a slope of $-\frac{1}{6}$. You can also plot on the same plot by electron concentration, n_e, which is twice of Vo, so basically this line would be, it will run parallel right. So, this is n_e, which is twice of Vo.

So, this is what we see that in case of non-stoichiometric oxides in addition to temperature dependence which will be similar to what you have. So, this is at constant temperature okay. So, at a constant temperature, the vacancy of, oxygen vacancy and electron concentration will go down as you increase the partial pressure of oxygen. So, basically as you reduce the partial pressure of oxygen, you will make oxygen more and more oxygen deficient and you will create more and more vacancies and consequently electrons in the system, that is how you make a defect prone oxide okay, right.

Now, why should n_e be constant, n_e is twice of V_O. So, for every vacancy you create, you are creating 2 electrons. So,

as you increase the vacancy concentration, the electron concentration will also increase or decrease as depending upon the condition okay. So, this is the condition when you have oxygen vacancies present.

(Refer Slide Time: 10:36)



When metal interstitials are dominant defects

$$\underbrace{M_M + O_O}_{} \rightleftharpoons M_i^{\cdot\cdot} + \tfrac{1}{2}O_2\uparrow + 2e'$$

two sites are destroyed to maintain site ratio

$$K = [M_i^{\cdot\cdot}]\ pO_2^{\frac{1}{2}} \cdot n_e^2$$

$$[M_M] = [O_O] = 1 \qquad \& \ M_i^{\cdot\cdot} << M_M \ \& \ O_O$$

$$n_e = 2[M_i^{\cdot\cdot}]$$

$$\frac{n_e}{2} = [M_i^{\cdot\cdot}] = \left(\frac{K}{4}\right)^{\frac{1}{3}} \cdot pO_2^{-1/6}$$

Now, let us see what will happen when metal interstitials are dominant. So, when metal interstitials are dominant defects, then we can write it

$$M_M + O_O \leftrightarrow M_i^{\cdot\cdot} + \frac{1}{2}O_2 \uparrow +2e'$$

So, we have site valence the metal has lost its site and gone to interstitial site, oxygen has lost its site, gone out. So, these 2 sites are destroyed right to maintain site ratio right okay. So, for one oxygen site destroyed, you will have altered destroy the metal site, that is why it becomes metal interstitial.

So, now when you write the defect reaction for this,

$$K = [M_i^{\cdot\cdot}].pO_2^{1/2}.n_e^2$$

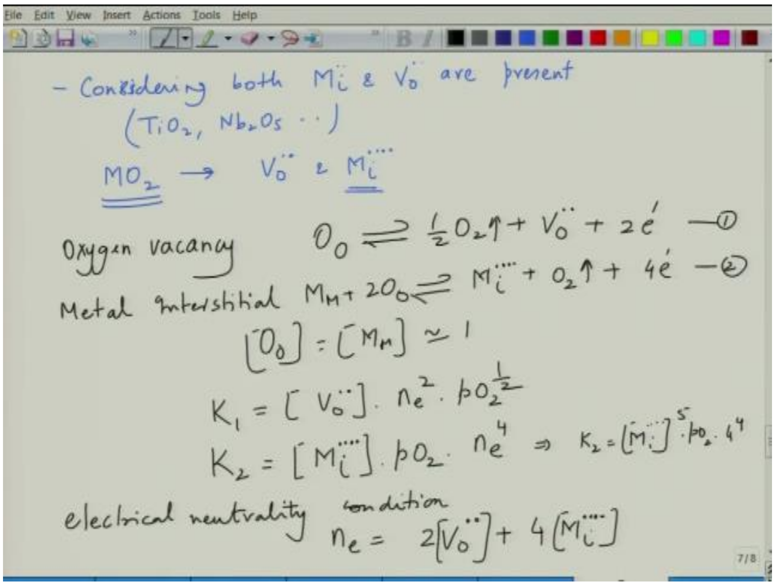
, and we can take these M_M okay considering ideal situation, especially when M_i is very small as compared to M_M and O_O okay because there are more metals and oxygens, then interstitial, and what is the electrical neutrality condition, that says that $n_e = 2\ M_i$ okay, you are creating 2 electrons for every metal interstitial.

So, now you can do the math yourself, so if you do this substitution, you will have

$$\frac{n_e}{2} = [M_i^{\cdot\cdot}] = \left(\frac{K}{4}\right)^{1/3} . pO_2^{-1/6}$$

So, again you can make the plot and the plot will be similar to the previous plot where you did plot M_i, n_e both on log scale as a function of pO_2 and as you increase the pO_2, the metal interstitial concentration will decrease and this is the electron concentration, this is n and this is M_i right.

(Refer Slide Time: 13:56)



- Considering both $M_i^{\cdot\cdot}$ & $V_O^{\cdot\cdot}$ are present
(TiO₂, Nb₂O₅ ..)

$MO_2 \rightarrow V_O^{\cdot\cdot}$ & $M_i^{\cdot\cdot\cdot\cdot}$

Oxygen vacancy $O_O \rightleftharpoons \frac{1}{2}O_2\uparrow + V_O^{\cdot\cdot} + 2e' \quad — ①$

Metal interstitial $M_M + 2O_O \rightleftharpoons M_i^{\cdot\cdot\cdot\cdot} + O_2\uparrow + 4e' \quad — ②$

$[O_O] = [M_M] \simeq 1$

$K_1 = [V_O^{\cdot\cdot}] . n_e^2 . pO_2^{\frac{1}{2}}$

$K_2 = [M_i^{\cdot\cdot\cdot\cdot}] . pO_2 . n_e^4 \Rightarrow K_2 = [M_i^{\cdot\cdot}]^5 . pO_2 . 4^4$

electrical neutrality condition
$n_e = 2[V_O^{\cdot\cdot}] + 4[M_i^{\cdot\cdot\cdot\cdot}]$

Now, a little tricky one, the tricky one is what happens when both of them are present. Now, the previous cases could be when vacancy formation energy is very low as compared to metal interstitial forming energy or metal interstitials form very easily as compared to vacancies. Now, there could be situations where both energies are sort of comparable okay, then there is a possibility that both of them could be present and this is for example in TiO_2 or even in niobium oxide, these are scenarios.

So, lets say we take a case of MO_2 okay, we do not take a case of just to reflect the oxide, we take a case of MO_2. So, if we take a case of MO_2, in case of MO_2**,** we will have oxygen vacancies as vacancy defects and we will have metal interstitial which will be 4 positive charges interstitials okay. So, for every metals interstitial, so you will consider for charge valence for every metal interstitial, you will have 2 oxygen vacancies right. So, let us say we have defect reactions.

So, we write the defect creation for oxygen vacancy okay, let me just use a different color. So, for oxygen vacancy, we first write as oxygen and oxygen site, goes out of system, this creates a vacant oxygen site plus this gives rise to 2 electrons.

$$O_O \leftrightarrow \frac{1}{2} O_2 \uparrow + V_O^{\cdot\cdot} + 2e'$$

For metal interstitial, I can write this as,

$$M_M + 2O_O \leftrightarrow M_i^{\cdot\cdot\cdot\cdot} + O_2 \uparrow + 4e'$$

You can write the same thing for MO also, and considering that O_O = M_M = 1, they are very large number as compared to defects.

We can write the defect reactions as, so if I take this as 1, this as 2, for 1, I can write K1 as

$$K_1 = [V_O^{\cdot\cdot}].n_e^2.pO_2^{1/2}$$

K_2, I can write as

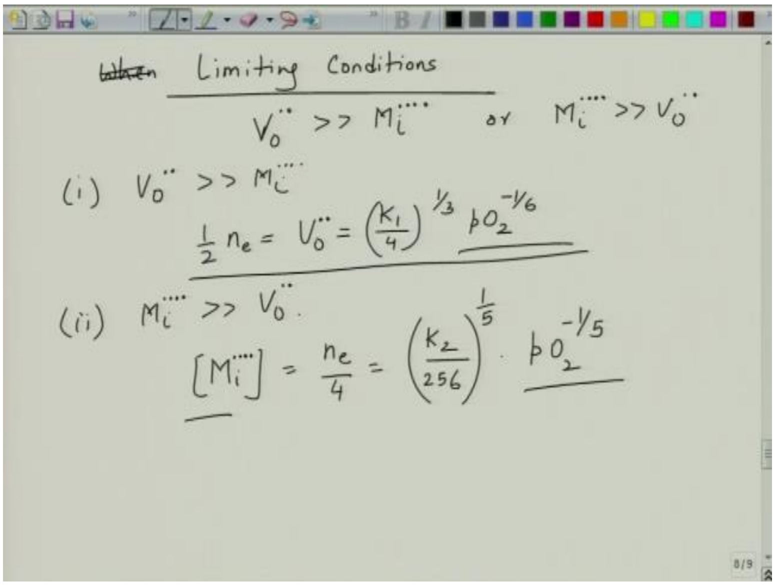
$$K_2 = [M_i^{\cdot\cdot\cdot\cdot}].pO_2.n_e^4$$

Now, what is the electrical neutrality condition,

$$n_e = 2[V_O^{\cdot\cdot}] + 4[M_i^{\cdot\cdot\cdot\cdot}]$$

, depending on which one dominates, or it has to be balanced right. So, this will be the electrical neutrality condition. So, you can consider cases.

(Refer Slide Time: 17:37)



~~When~~ Limiting Conditions

$$V_O^{\cdot\cdot} >> M_i^{\cdot\cdot\cdot\cdot} \quad \text{or} \quad M_i^{\cdot\cdot\cdot\cdot} >> V_O^{\cdot\cdot}$$

(i) $V_O^{\cdot\cdot} >> M_i^{\cdot\cdot\cdot\cdot}$

$$\frac{1}{2} n_e = V_O^{\cdot\cdot} = \left(\frac{K_1}{4}\right)^{1/3} \underline{pO_2^{-1/6}}$$

(ii) $M_i^{\cdot\cdot\cdot\cdot} >> V_O^{\cdot\cdot}$.

$$\underline{[M_i^{\cdot\cdot\cdot\cdot}]} = \frac{n_e}{4} = \left(\frac{K_2}{256}\right)^{\frac{1}{5}} \cdot \underline{pO_2^{-1/5}}$$

So, the first case is when, so limiting cases, we consider limiting cases right. Limiting conditions will be when Vo is very large as compared to Mi or it could be when Mi is very large as compared to Vo okay. So, we consider these limiting conditions. The limiting condition let us say,

(i) $V_O^{\cdot\cdot} \gg M_i^{\cdot\cdot\cdot\cdot}$

$$\frac{1}{2}n_e = V_O^{\cdot\cdot} = \left(\frac{K_1}{4}\right)^{1/3} .pO_2^{-1/6}$$

This is straightforward. This you will have to work out a little when M_i is greater than V_O.

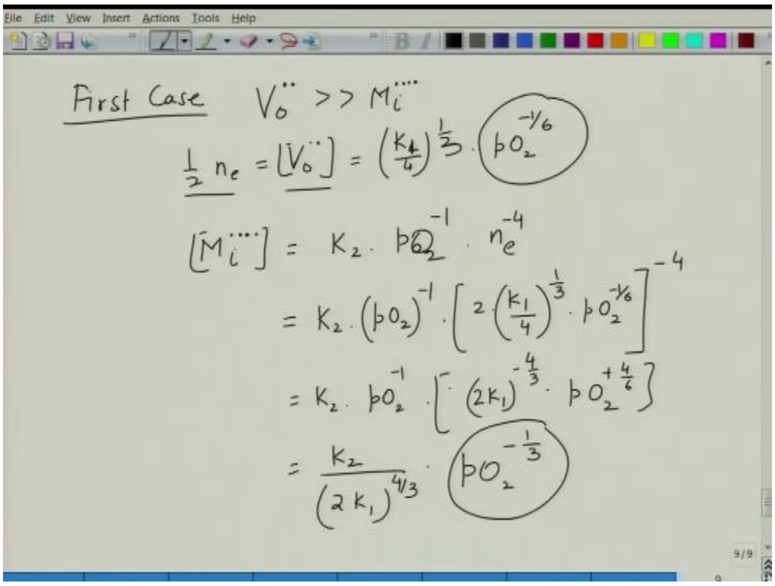
(ii) $M_i^{\cdot\cdot\cdot\cdot} \gg V_O^{\cdot\cdot}$

then ne = 4Mi okay. So ne = 4Mi, you will have to substitute it there. So, it will become 4 to the power 4 into Mi to the power 4 right. So, basically it will become Mi to the power 5, if you multiply by this Mi. So, Mi will be equal

$$[M_i^{\cdot\cdot\cdot\cdot}] = \frac{n_e}{4} = \left(\frac{K_2}{256}\right)^{1/5} .pO_2^{-1/5}$$

So, this is what you will have situations like. So, you will have M_i showing a dependence of $(-1/5)$ and oxygen showing a dependence of $(-1/6)$. So, now in both of these regimes, you would like to calculate what is the corresponding metal interstitial concentration and what is the corresponding oxygen vacancy concentration.

(Refer Slide Time: 20:48)



First Case $V_o^{\cdot\cdot} >> M_i^{\cdot\cdot\cdot\cdot}$

$$\frac{1}{2} n_e = [V_o^{\cdot\cdot}] = \left(\frac{K_1}{4}\right)^{\frac{1}{3}} \cdot \boxed{pO_2^{-1/6}}$$

$$[M_i^{\cdot\cdot\cdot\cdot}] = K_2 \cdot pO_2^{-1} \cdot n_e^{-4}$$

$$= K_2 \cdot (pO_2)^{-1} \cdot \left[2 \left(\frac{K_1}{4}\right)^{\frac{1}{3}} \cdot pO_2^{-1/6}\right]^{-4}$$

$$= K_2 \cdot pO_2^{-1} \cdot \left[(2K_1)^{-\frac{4}{3}} \cdot pO_2^{+\frac{4}{6}}\right]$$

$$= \frac{K_2}{(2K_1)^{4/3}} \cdot \boxed{pO_2^{-\frac{1}{3}}}$$

So, let us say the first case, the first case was when Vo was much greater than Mi okay. So, in the first case, we can calculate,

$$\frac{1}{2}n_e = [V_O^{\cdot\cdot}] = \left(\frac{K_1}{4}\right)^{1/3} .pO_2^{-1/6}$$

So, we have got the expressions for n_e and V_O, but we do not know how the M_i is going to vary in this regime. So M_i is written using the M_i formula, so M_i formula is basically the second equation, which is simplified as,

$$[M_i^{\cdot\cdot\cdot\cdot}] = K_2 . pO_2^{-1} . n_e^{-4}$$

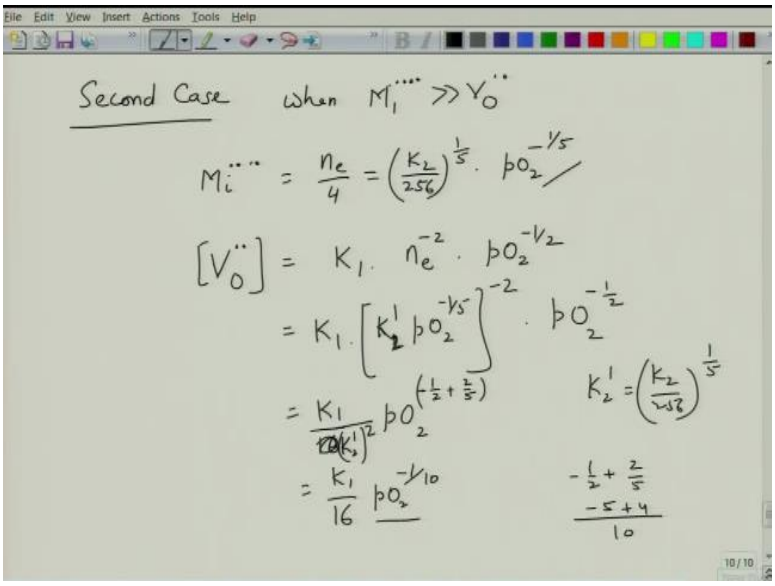
$$[M_i^{\cdot\cdot\cdot\cdot}] = K_2 . pO_2^{-1} . \left[2\left(\frac{K_1}{4}\right)^{1/3} . pO_2^{-1/6}\right]^{-4}$$

$$[M_i^{\cdot\cdot\cdot\cdot}] = K_2 . pO_2^{-1} . \left[(2K_1)^{-4/3} . pO_2^{4/6}\right]$$

$$[M_i^{\cdot\cdot\cdot\cdot}] = \frac{K_2}{(2K_1)^{4/3}} . pO_2^{-1/3}$$

So, for the first case when oxygen vacancies dominate over metal interstitials, then your M_i goes as pO_2 to the power $-1/3$ and an oxygen vacancies go as $-1/6$.

(Refer Slide Time: 23:58)



Second Case when $M_i^{\cdot\cdot\cdot\cdot} \gg V_O^{\cdot\cdot}$

$$M_i^{\cdot\cdot\cdot\cdot} = \frac{n_e}{4} = \left(\frac{K_2}{256}\right)^{\frac{1}{5}} . pO_2^{-1/5}$$

$$[V_O^{\cdot\cdot}] = K_1 . n_e^{-2} . pO_2^{-1/2}$$

$$= K_1 . \left[K_2' \, pO_2^{-1/5}\right]^{-2} . pO_2^{-\frac{1}{2}}$$

$$K_2' = \left(\frac{K_2}{256}\right)^{\frac{1}{5}}$$

$$= \frac{K_1}{(K_2')^2} pO_2^{\left(-\frac{1}{2}+\frac{2}{5}\right)}$$

$$-\frac{1}{2}+\frac{2}{5}$$

$$\frac{-5+4}{10}$$

$$= \frac{K_1}{16} pO_2^{-1/10}$$

For the second case when M_i dominance over V_O okay, when $M_i \gg V_O$, we calculated the expression for M_i. So,

$$M_i^{\cdot\cdot\cdot\cdot} = \frac{n_e}{4} = \left(\frac{K_2}{256}\right)^{1/5} . pO_2^{-1/5}$$

Now, we would like to calculate what is Vo in this case. So, Vo in this case can be calculated using the first equation, the first equation says that

$$[V_O^{\cdot\cdot}] = K_1 . n_e^{-2} . pO_2^{-1/2}$$

So, you replace n_e from there,

$$[V_O^{\cdot\cdot}] = K_1.\left[K_2' pO_2^{-1/5}\right]^{-2}.pO_2^{-1/2}$$

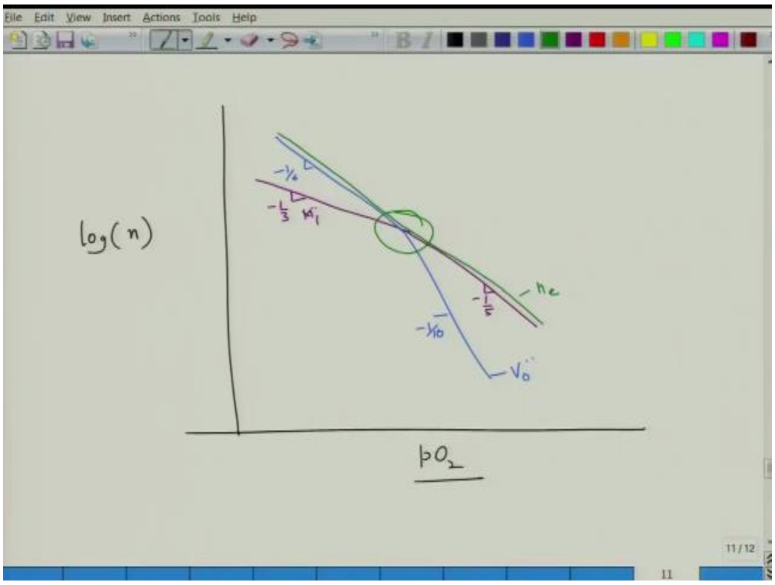
$$[V_O^{\cdot\cdot}] = K_1.\left[K_2' pO_2^{-1/5}\right]^{-2}.pO_2^{-1/2}$$

$$[V_O^{\cdot\cdot}] = \frac{K_1}{(K_2')^2}.pO_2^{-1/2+2/5}$$

$$[V_O^{\cdot\cdot}] = \frac{K_1}{16}.pO_2^{-1/10}$$

So, in this regime, oxygen vacancy has a dependence of $-1/_{10}$ and M_i has a dependence or $-1/_{5}$. So, this is how now when you want to make a plot of these and n will follow basically the dominant defect, whether it will follow V_O, it will follow M_i.

(Refer Slide Time: 27:45)



So, if you now want to plot this log of let us say defect concentration I just write as n okay and then I write it as pO_2 okay. So, I see that defect concentration. So, let us first plot the vacancy concentration, oxygen vacancy concentration goes as pO_2 to the power $-1/_{6}$ okay and then it goes as pO_2 to the power $-1/_{10}$ okay. So, pO_2 to the power $-1/_{10}$ is obviously, so let us first draw this when oxygen vacancy dominates, then let us say $-1/_{6}$ the first case.

So, the magnitudes will of course depend upon the value of K_1 and K_2 and so on and so forth, but generally the trend would be something like this. So, we saw that in certain regime, the oxygen vacancy concentration goes as $^{-1}/_{6}$ okay, then the oxygen vacancy concentration is $^{-1}/_{10}$. So, initially it is minus $^{-1}/_{6}$ and then becomes $^{-1}/_{10}$. So, this is $^{-1}/_{6}$, this is $^{-1}/_{10}$. So, this is for let us say V_O okay. The M_i if you look at the variation of M_i, the M_i in this case goes as $^{-1}/_{3}$ okay.

So, when oxygen vacancy goes as $^{-1}/_{6}$, M_i goes as $^{-1}/_{3}$. So, M_i would be something like, if I use a different color, this would be M_i Okay. So, this will go as $^{-1}/_{3}$. So, this is M_i, and if you look at the second region, the second region the M_i goes as $^{-1}/_{5}$. So, it will go sort of in this fashion $^{-1}/_{5}$ and the electron concentration in the first case to follow this line, in the second case to follow this line. In the first case, it will go as $^{-1}/_{6}$, in the second case it will go as $^{-1}/_{5}$ okay.

So, this will be the line of ne okay. So, that is how the electron impurity concentrations will vary when you have mixed effects, there will be crossover regime and it is not perfect, there may be this region can be even more complex okay, the crossover region, but this is how roughly the variation of defect concentration will be as a function of partial pressure of oxygen when you have mixed presence okay.

So, what we have done in this class is we have looked at the variation of defect concentration as a function of partial pressure of oxygen when one particular defect dominates and what happens when two defects coexist together. So, we elaborate up on this further in the next lecture. Thank you.