Defects in Crystalline Solids (Part-I)
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Lecture – 11
Effects on Defect Reaction

So, let us continue our discussion where we left last time. So, we were looking at this defect reaction.

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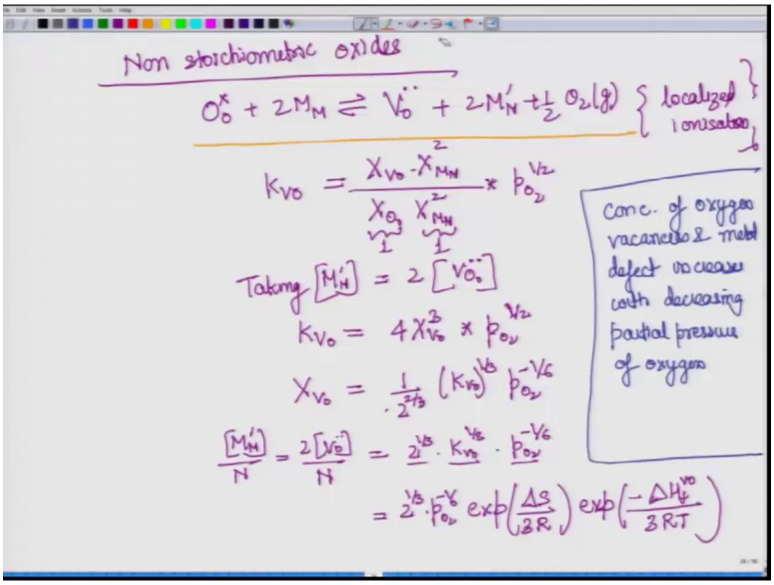

Non stoichiometric oxides

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

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

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

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

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

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

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

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

So, here it is a non stoichiometric oxide basically oxide where basically oxygen going or escaping into atmosphere and living behind vacancy. However, like I said earlier that number of sites would remain fixed that sorry, the ratio of sites would remain fixed the number of sites need not remain fixed, but the ratio of sites which basically is proportional to the M and O that will remain as it is. And, for writing that defect as a reaction, this is the reaction and for that we get concentration of oxygen vacancy and we also get concentration of M M prime basically where the electrons are localized.

So, here we had assumed localized ionization like I said last time that next what we will do is delocalize the electrons over here and then see how we can look at the equation and get a equilibrium concentration. Because, now we will have two different kind of a species; one which is electron and whole kind of species and the other would be vacancy kind of species. Vacancies which are related to lattice sites, but, but electrons and wholes they are not related to or they do not have a on the denominator the lattice number of lattice sites what they have is the N effective, the density of states.

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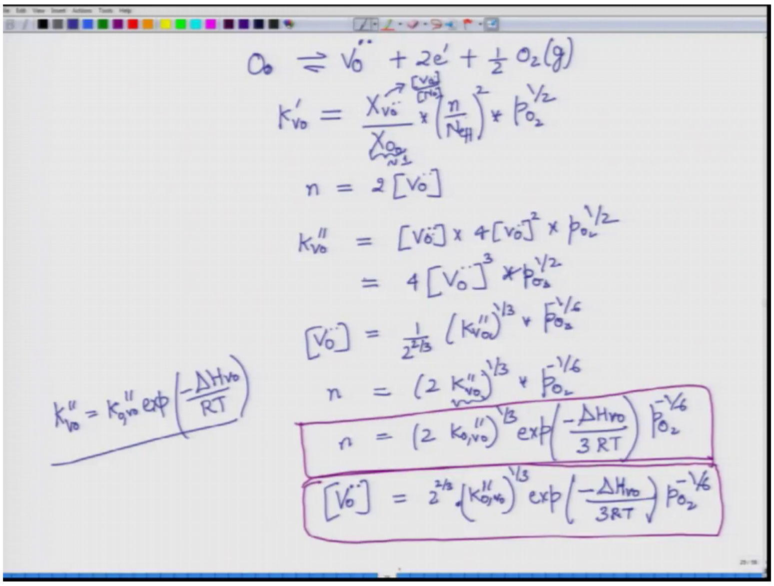

$$O_O \rightleftharpoons V_O^{\bullet\bullet} + 2e' + \frac{1}{2} O_2(g)$$

$$K'_{V_O} = \frac{\overset{\frac{[V_O]}{[N_O]}}{X_{V_O^{\bullet\bullet}}}}{\underbrace{X_{O_O}}_{\sim 1}} \times \left(\frac{n}{N_{eff}}\right)^2 \times p_{O_2}^{1/2}$$

$$n = 2[V_O^{\bullet\bullet}]$$

$$K''_{V_O} = [V_O^{\bullet\bullet}] \times 4[V_O^{\bullet\bullet}]^2 \times p_{O_2}^{1/2}$$

$$= 4[V_O^{\bullet\bullet}]^3 \times p_{O_2}^{1/2}$$

$$[V_O^{\bullet\bullet}] = \frac{1}{2^{2/3}} (K''_{V_O})^{1/3} \times p_{O_2}^{-1/6}$$

$$n = (2\underbrace{K''_{V_O}}_{})^{1/3} \times p_{O_2}^{-1/6}$$

$$K''_{V_O} = K''_{0,V_O} \exp\left(\frac{-\Delta H_{V_O}}{RT}\right)$$

$$\boxed{n = (2K''_{0,V_O})^{1/3} \exp\left(\frac{-\Delta H_{V_O}}{3RT}\right) p_{O_2}^{-1/6}}$$

$$\boxed{[V_O^{\bullet\bullet}] = 2^{2/3} (K''_{0,V_O})^{1/3} \exp\left(\frac{-\Delta H_{V_O}}{3RT}\right) p_{O_2}^{-1/6}}$$

So, let us write down this equation when similar equation however, this time what we are doing is delocalizing. So, oxygen at oxygen site lives behind vacancy and since it was supposed to be negative with so, no actual absolute charge it remains effectively positive and it means two electrons have been left or have escaped. So, these two electrons remain as electrons not localized on any metal site and plus 1 by 2 O 2. So, now, we have three different kind of species actually, not even two. We have lattice related sites we have electrons and we have oxygen whose activity is given not in fraction or not in fraction concentration, but in partial pressure.

So, now how do we write the equilibrium constant? So, let us see we will write it like this, K Vo prime for vacancy we can still the activity can be still related to the concentration fraction and therefore, it will remain X for the oxygen we can still write X o. Now, for the electron the concentration ratio would be given as n by N effective density of states and since there is a factor of 2; so, there will be a power of 2 and then for oxygen like we said that the activity will be expressed as partial pressure of O 2 and since there is a power of 1 by 2 sorry the factor of 1 by 2 it translates to factor of the power of 1 by 2.

Now, another thing that we know is that, n number of electrons would be equal to twice the number of vacancy at oxygen sites because the each oxygen atom that escapes lives behind one vacancy and each of those oxygen atoms were associated with 2 electrons. So, their 2 electrons and one the number of electrons will be equal to 2 times of vacancy of at oxygen site.

So, now here we have different denominators which are constant and we need to club them together and therefore, what we can do is pull them together and combine them into this is again a constant. So, we can combine them into this factor and name it a new constant as K Vo double prime. So, we can make it K v double o prime that is not the only thing we will also do what we have always been doing which is assuming that this is the dominant defect and oxygen the defect concentration is very small so, assuming that this can be taken approximately as one.

So, the denominator of this meaning this will become with this we will translate to V o by N o. N o is a number of oxygen sites. Now, this a constant, this is a constant so, we will plug them together we will pull it to the left hand side and club into together and so, now, we have K Vo double prime. So, this prime here is not for negative sign remember it is just to show that it is different from K Vo prime and K Vo prime is different from K Vo. So, do not confuse this prime with a negative sign those will be associated with the components in the reaction, this is a rate constant.

Now, we will use this over here. So, what you have here is n will be replaced by 2 V o. So, it will take a square it will become 4 V o square and this is V o. So, 4 V o square into V o is 4 V o cube. So, we will first write it like this which is equal to. So, now, we will rewrite this equation. So, as to get the concentration of V o and this is nothing, but and n is twice of this.

So, if we write n in this similar formalism it will come out to. So, this will be multiplied by 2 and this is minus 2 by 3. So, it becomes 2 1 by 3 we can pull them together and it becomes ok. So, there is one mistake that I committed here we have to take cube root because it is V cube. So, this one becomes minus 1 by 6 because it is also going to the (Refer Time: 07:53) and then we are taking cube roots and it becomes minus 1 by 6. So, note that this is minus 1 by 6 and similarly here it will be minus 1 by 6.

Now, this is a constant, but this constant is also related to the formation energy and entropy and therefore, it has something like this. So, some standard constant and with respect to that this will be. So, if you want to convert it or if you want to or get it into the similar formation or similar formalism as earlier in terms of delta H exponential of delta H, then we will convert this using this relation. And therefore, this n will be equal to and to take into account cube root. So, there will be a factor of 1 by 3 and since it is R we are assuming that this quantity is given in per mole and this is also o 2, this is also o 2 and if you also if you like you can also write for the V o in a similar form.

Remember, this double prime is not for minus it is just to show that this is a different constant. And, this constant has consumed in it these constants the denominator here over here and this denominator when we were using just a fraction then you do not have a denominator and therefore, we did not have this have been worked this kind of formation earlier, this kind of equation form earlier. So, these are two similar relations and this is not very clear. So, let me rewrite this part. So, these are two similar relation the only thing is that n is twice of V naught and everything else in the quantity remains the same.

Now, we have once we have this equation we can do something more which is plot it as a equation of p o 2 and as we stated in the previous lecture that concentration of oxygen vacancy and your defect increases with decreasing partial pressure.

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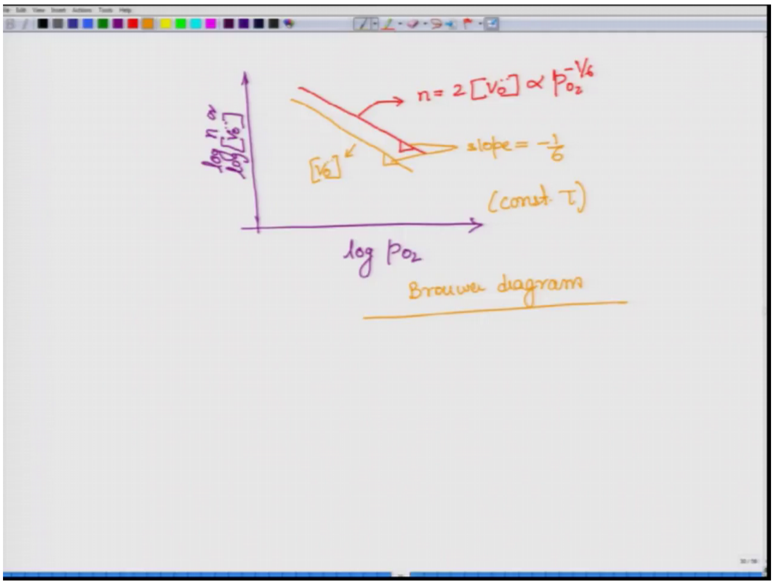

So, when you plot it this would become even obvious. So, here on the x axis we have log partial pressure of oxygen and on the y axis you can have log n or log vacancy oxygen concentration. So, how would this look like? If you look at the equation behind it everything over here assuming temperature is constant. If temperature is constant then all these things are constant the only thing is changing is p, but now, if you take it in log then this is again a linear form of relation and therefore, what you will have.

If let us first draw the V o so, it will be a straight line like this. So, this is our V o log V o concentration actually and similarly if you want to plot n n is nothing, but twice of this. So, it will come out like this n is equal to 2 times and this is proportional to p o 2 to the power minus 1 by 6. So, the slope here the slope that that is exists over here both these slopes is equal to minus 1 by 6 and the assumption here is constant temperature this kind of plot is called Brouwer diagram.

And, now, you can see what the equation is saying and what the reaction is saying as your partial pressure decreases which are going in this direction concentration of n and concentration of vacancy increases. And, what you also can now see from this plot is that if when you take the log plot then it is a linear relation and you can predict the slope which is equal to minus 1 by 6. So, you can get to know how much pressure if you know the pressure predict what will be the n or if you know what is the n you desire then you know what pressure to partial pressure of oxygen should be. So, this is a very useful diagram and it is very important with respect to defect chemistry.

So, now that we have looked at different kinds of defects we looked at different ways of writing them, first different ways of getting the equilibrium concentration. First we used the entropy configuration, configurational entropy; second formation second formalism was using it as a defect reaction. So, when you use it as a defect reaction then using the defect reaction you can again get equilibrium concentration using the rate constant and the equilibrium constant. So, using both of these we saw there are that wide variety of defects that can be written as a reaction and you can get equilibrium concentration for them and in fact, in the defect reaction I believe it is much more straight forward to get the concentration or relation for concentration.

Now, let us solve some problem. Now, that we have looked at all the basics of course, there can be more combinations and permutations of different kinds of defects and now, if you know the fundamentals you can understand and you can take this understanding forward.

Now, let us try to solve some simple problems on these defects.

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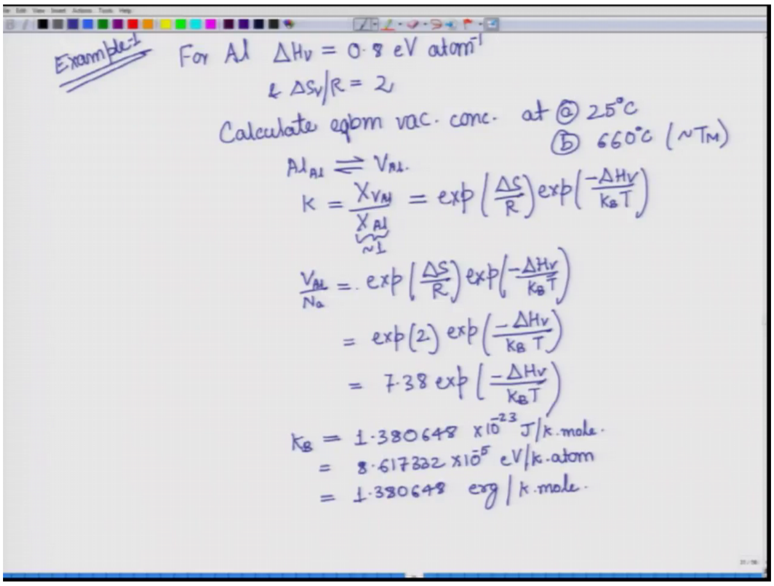

Example-1

For Al $\Delta H_v = 0.8$ eV atom^{-1}

& $\Delta S_v / R = 2$

Calculate eqbm vac. conc. at ⓐ 25°C

ⓑ 660°C ($\sim T_M$)

$$Al_{Al} \rightleftharpoons V_{Al}.$$

$$K = \frac{X_{V_{Al}}}{\underbrace{X_{Al}}_{\sim 1}} = \exp\left(\frac{\Delta S}{R}\right)\exp\left(\frac{-\Delta H_V}{K_B T}\right)$$

$$\frac{V_{Al}}{N_a} = \exp\left(\frac{\Delta S}{R}\right)\exp\left(-\frac{\Delta H_v}{K_B T}\right)$$

$$= \exp(2)\exp\left(\frac{-\Delta H_v}{K_B T}\right)$$

$$= 7.38 \exp\left(\frac{-\Delta H_v}{K_B T}\right)$$

$$K_B = 1.380648 \times 10^{-23} \text{ J/K.mole.}$$

$$= 8.617332 \times 10^{-5} \text{ eV/K.atom}$$

$$= 1.380648 \text{ erg/K.mole.}$$

Let us say you have given that for aluminium delta H v is equal to 0.8 electron volt per atom and delta S v by R is equal to 2. You are so, this is example one and what you need to do is calculate equilibrium vacancy concentration at a, 25 degree Celsius and b, 660 degree Celsius. For aluminium 660 is close to melting point. So, you are being asked that at a room temperature what will be the equilibrium vacancy concentration and at near the melting point what will be the vacancy equilibrium vacancy concentration. So, what we have is something like this aluminium to vacancy aluminium, that will be the defect reaction for this and in the simple terms in this defect reaction the equilibrium constant would be given by X V Al by X Al and this will be equal to delta S by R.

So, we are assuming that this delta S by R delta was in per mole and therefore, delta S by R is given. So, it does not matter whether we are what is the final unit of delta S because once you know delta S by R it is equal to delta S by k if delta s for given in per atom and exp minus delta H v by K B T. Here we are using K because delta H v is given in electron volt per atom sorry the unit should have been per atom.

So, now this is the equation and assuming that this is the dominating defect and the defect concentration is small first approximation that we can do is we can take this approximately equal to 1. Now, we have X V Al. So, what we can write X V Al is as vacancy aluminium by N a. So, this will give you the vacancy concentration in per mole. So, this can this will become X V Al is equal to, delta S by R is given as 2. So, it is exp 2 this will be cause this is this remains the same and exp 2 will translate to 7.38. So, we have simplified our equation a little bit.

Now, what we have here is delta H v. So, what we need now K B. So, there are K B value is a usually given, but if it is not given then you must actually this is the quantity that you should remember and this has you can write it in different units. So, if you write it like this actually it should be per mole, we do not need so many decimals. This is just to let you know this is up to this extent this is known. So, this is in joule per Kelvin per mole this is in electron volt per atom per Kelvin and there is also another unit erg per Kelvin per mole.

So, now, when we know this, now we are we know this quantity we know this temperatures is are given this is given. So, we can quickly calculate this and we will multiply it with N a to get number of vacancy per mole.

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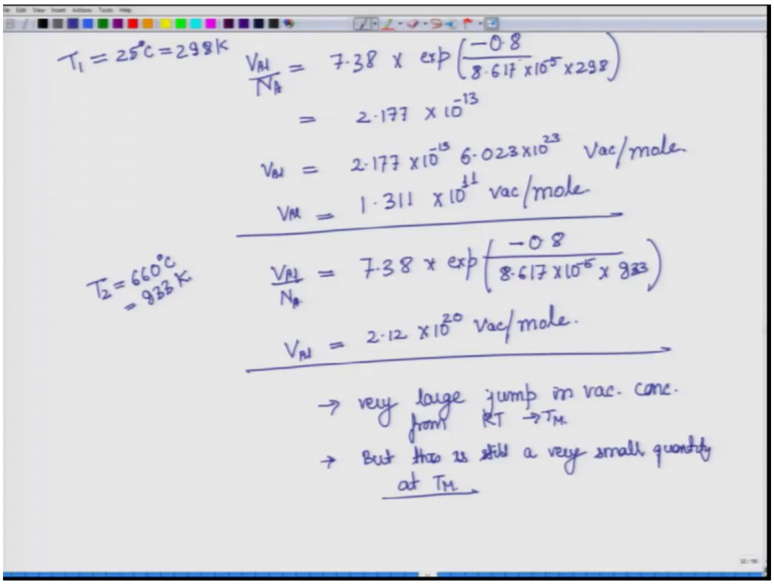

$T_1 = 25°C = 298 K$

$$\frac{V_{Al}}{N_A} = 7.38 \times \exp\left(\frac{-0.8}{8.617 \times 10^{-5} \times 298}\right)$$

$$= 2.177 \times 10^{-13}$$

$$V_{Al} = 2.177 \times 10^{-13}\ 6.023 \times 10^{23} \text{ Vac/mole}$$

$$V_{Al} = 1.311 \times 10^{11} \text{ vac/mole}$$

$T_2 = 660°C = 933 K$

$$\frac{V_{Al}}{N_A} = 7.38 \times \exp\left(\frac{-0.8}{8.617 \times 10^{-5} \times 933}\right)$$

$$V_{Al} = 2.12 \times 10^{20} \text{ Vac/mole.}$$

→ very large jump in vac. conc. from RT → T_M.

→ But this is still a very small quantity at T_M.

So, first let us solve it for T one equal to 25 degree Celsius which is equal to 298 K. So, first you have to convert it to Kelvin, now this. So, we are calculating at T 1 equal to 25 degree Celsius which in Kelvin is 298 Kelvin. So, V Al by N a is equal to 7.38 into minus 0.8 because delta H v is given at 0.8 and we will use the K b in electron volt per Kelvin. So, it is 8.6 we will go only up to 617 into 10 to the power minus 5 and temperature as you said is 298. So, this will translate to 10 to the power minus 13. So, this is the fraction. Now, we will multiply it by Avogadro number which is now this is also Avogadro number is also something that you should know is equal to.

So, when we have multiplied by this then it is. So, many vacancies per mole and it will translate to 1.311 into 10 to the power 11. Now, this looks like a very large number, but see it is you have to note that it is per unit mole and mole is 6.023 into 10 to the power 23. So, it is if you look at it in terms of fraction it is 10 to the power minus 12 twelfth fraction that is for each 10 to the power 12 atom there is one vacancy. So, this is a very small quantity.

Now, let us do this calculation for 660 degree Celsius which is equal to 933 Kelvin. So, V Al by Na actually I should have denoted N a by upper case is. So, let me write it like this is 7.38 into exp minus 0.8 delta H v is same and K b value remains same 8.617 into 10 to the power minus 5 and temperature is different which is 933 and when you multiply it with then what you get is 2.12 into 10 to the power 20 vacancy per mole.

So, what are the few things that you observe here there is a very large jump in vacancy concentration from room temperature to T M and this is expected, but even at if you look at this number 10 to the power 20 this is still a very small fraction. No, of course, it is much larger than this number, but if you look at it as per mole then it is still a very very small number like 0.001 approximately less than 0.001. So, but this is still a very small quantity at T M.

So, this is a big jump from room temperature to melting point, but this is still as you can realize is a very small fraction 0.001. So, we have not even reaching point 1 percent we are not reaching 1 percent this is less than 0.1 percent of the number of all the number of sites are vacant. So, that is the miniscule that is that miniscule amount even at close to melting point. Beyond melting point of course, there is no point in talking about vacancy concentration because it will be liquid state and we have what we have derived is for solid state.

So, this is the maximum vacancy concentration that you would see as we mean that these values are true. So, this is a example one. Now, similar type of example can be given to you in a different form.

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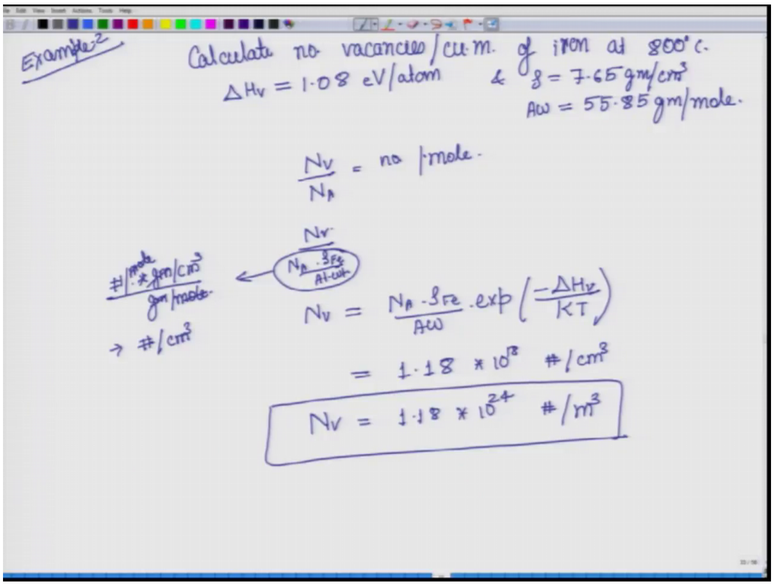

Example-2

Calculate no vacancies/cu.m. of iron at 800°c.

$\Delta H_v = 1.08$ eV/atom & $\rho = 7.65$ gm/cm^3

$A_W = 55.85$ gm/mole.

$\frac{N_V}{N_A}$ = no /mole.

$$\frac{N_V}{\frac{N_A \cdot \rho_{Fe}}{At\ wt}}$$

$$\frac{\#/mole \cdot * gm/cm^3}{gm/mole} \rightarrow \#/cm^3$$

$$N_V = \frac{N_A \cdot \rho_{Fe}}{A_W} \cdot \exp\left(\frac{-\Delta H_v}{KT}\right)$$

$$= 1.18 * 10^{18} \ \#/cm^3$$

$$\boxed{N_V = 1.18 * 10^{24} \ \#/m^3}$$

For example, you will be asked to calculate number of vacancies per cubic metre ok. So, it will be very similar to the question is similar, but it is given in a little different form per cubic metre of iron at some temperature let us say 800 degree Celsius, delta H v is equal to 1.08 electron volt per atom and it is given that rho so, these are some other quantities that you will need 7.65 gram per centimetre cube and what you will need is atomic weight which is equal to 55.85 gram per mole.

Now, if you remember the equation number of vacancies by N A then it is equal to number per mole. Now, if you multiply this N A which is Avogadro number into rho and divided by atomic weight then you have this unit of this would become and the density is for atomic weight the unit will be. So, this is number per mole and in gram per mole. So, what we have is mole gets cancelled gram gets cancelled and the unit becomes number per centimetre cube.

So, we can simply multiply with this factor rho Fe. So, this is what we will do N v is equal to N A into rho Fe and since we are not giving delta S by R we will assume that this is too small to be taken into account and we will simply calculate like this and what you will see is that you will get a quantity like this and what will be the unit like I said it will be number per centimetre cube.

So, this is like I said same question, but put it little differently. So, you have to apply yourself to see how to get the correct units and here we have per centimetre cube, but still it is not per cubic metre. So, we will multiply it with a factor of 6 10 to the power 6. So, it becomes 1.18 into 10 to the power 24 and that will become number per metre cube.

So, here what we are looking at is the with a different units we are looking at how many vacancies would be there in 1 cubic metre of iron or if we are talking about centimetre cube then one centimetre cube something as small as this what will be the number density. So, this is in 1 centimetre cube these many numbers. So, again it may look like a very large number, but you keep in mind that the number of sites are also very very large. So, this will be a very small fraction even at 800 degree Celsius it will be a very small fraction.

So, we will come back and we will solve another problem before we move on to one of our other topics related to point defect which is diffusing. So, we will continue this example solving in next in the next lecture.

Thank you.