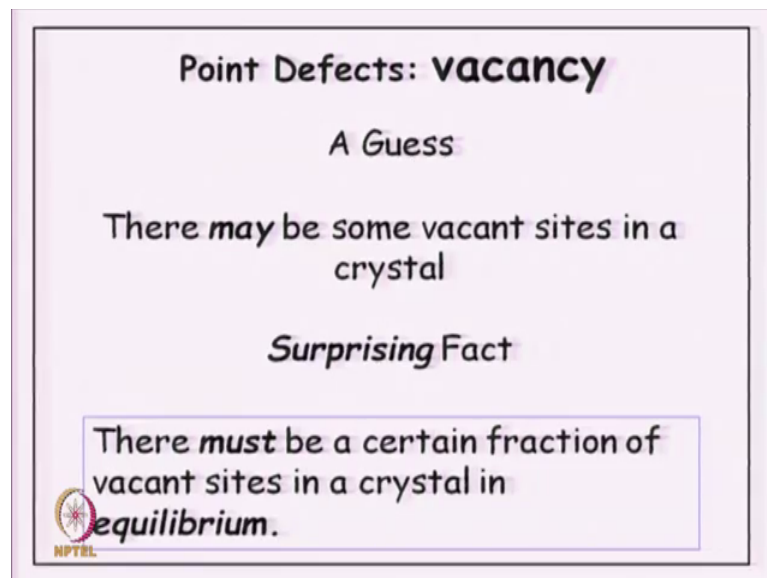


**Introduction to Materials Science and Engineering**  
**Prof. Rajesh Prasad**  
**Department of Applied Mechanics**  
**Indian Institute of Technology, Delhi**

**Lecture – 44**  
**Vacancies**

In this video we are going to discuss point defects.

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**Point Defects: *vacancy***

*A Guess*

There *may* be some vacant sites in a crystal

*Surprising Fact*

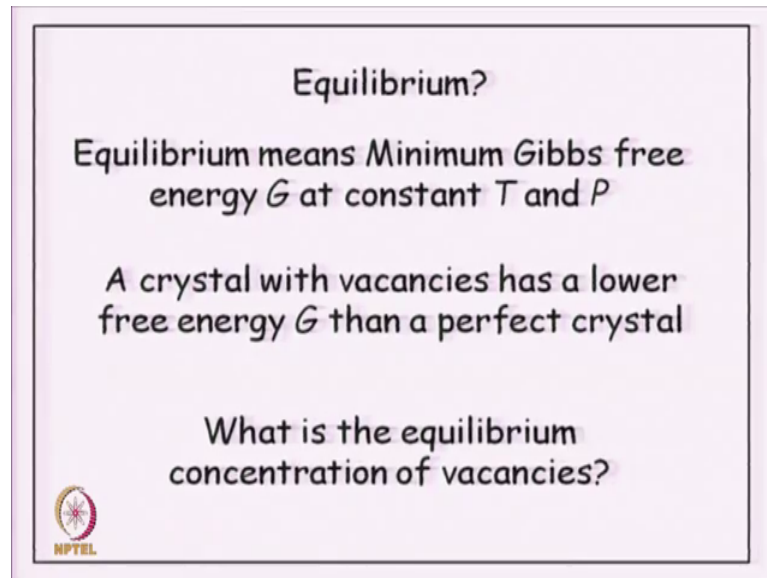
There *must* be a certain fraction of vacant sites in a crystal in *equilibrium*.

NPTL

So, one of the most important point defects is simply a vacancy and a vacancy is a vacant site in a crystal. So, we make a guess let us say that there may be some vacant sites in a crystal because nothing is really going to be perfect in our life and so some defects can be there, so there may be some vacant sites. But the real surprising fact is that there must be certain fraction of vacant sites in a crystal that there is no way we can make a crystal with no sites vacant that is possible only at absolute 0 and absolute 0 as you know from thermodynamics itself is unattainable.

So, we will see this in detail in this video why it is so that certain crystal sites have to be vacant. There should be certain concentration of vacancies in equilibrium in a crystal.

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Equilibrium?

Equilibrium means Minimum Gibbs free energy  $G$  at constant  $T$  and  $P$

A crystal with vacancies has a lower free energy  $G$  than a perfect crystal

What is the equilibrium concentration of vacancies?



So, we talked about equilibrium and by equilibrium here we mean a thermodynamic equilibrium at constant temperature and pressure, which means that we should have a minimum Gibbs free energy.

So, a crystal with vacancy should lower the free energy in comparison to the perfect crystal of course, this lowering cannot continue forever otherwise all the sites will be, all sites can never be vacant there will be no crystal. So, there will be certain equilibrium concentration which will minimize the free energy of the crystal. So, what is that equilibrium concentration of vacancy? So, we will try to formulate this or try to answer this Question.

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**Gibbs Free Energy  $G$  ?**

$$G = H - TS$$

$T$  Absolute temperature

$H$  ?

1. Enthalpy  $H = E + PV$   $E$  internal energy  
 $P$  pressure  
 $V$  volume
2. Entropy  $S$




So, since we want to have an equilibrium crystal, crystal in equilibrium. So, we should try to minimize the Gibbs free energy. So, what is Gibbs free energy? So, we know by the definition Gibbs free energy is  $H$  minus  $T S$ , where  $T$  is the absolute temperature and  $H$  is the enthalpy. An enthalpy  $H$  itself is defined as  $E$  plus  $PV$ , where  $E$  is the internal energy,  $P$  is pressure and  $V$  is volume, then  $S$  in the free energy expression as you know is entropy.

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**Boltzmann Formula for Entropy  $S$**

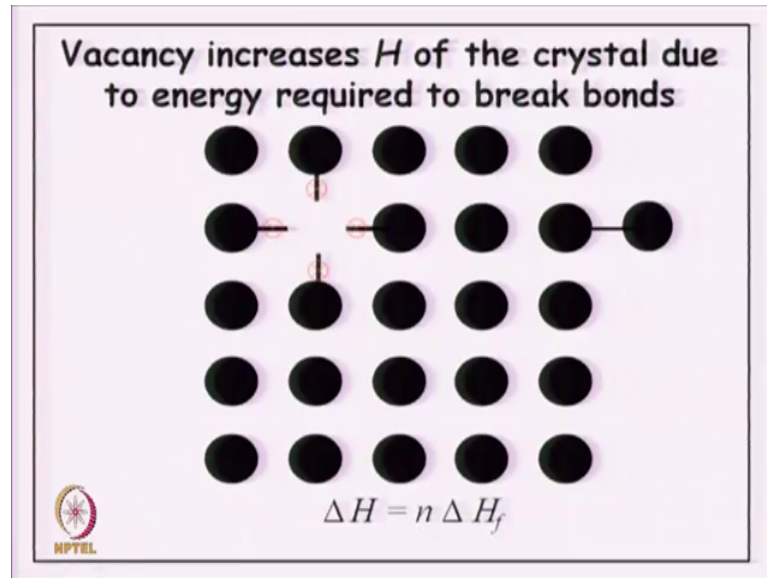
$$S = k \ln W$$

$k$  Boltzmann constant  
 $W$  Number of microstates corresponding to a given macrostate



For the current case the entropy  $S$  is best given by the Boltzmann formula  $S$  is equal to  $k \log W$  this is a statistical relationship given by Boltzmann where  $k$  is the Boltzmann called constant and  $W$  is the number of microstates corresponding to a given macro state.

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Let us see what we mean by this. The meaning of  $W$  is the number of microstates corresponding to a given macro state. So, vacancy increases enthalpy  $H$  of the crystal due to breaking of bonds. So, energy is required to break the bond. So, in particular I am now currently focusing bonds formed by the central atom and in this two dimensional example this central atom is forming 4 bonds.

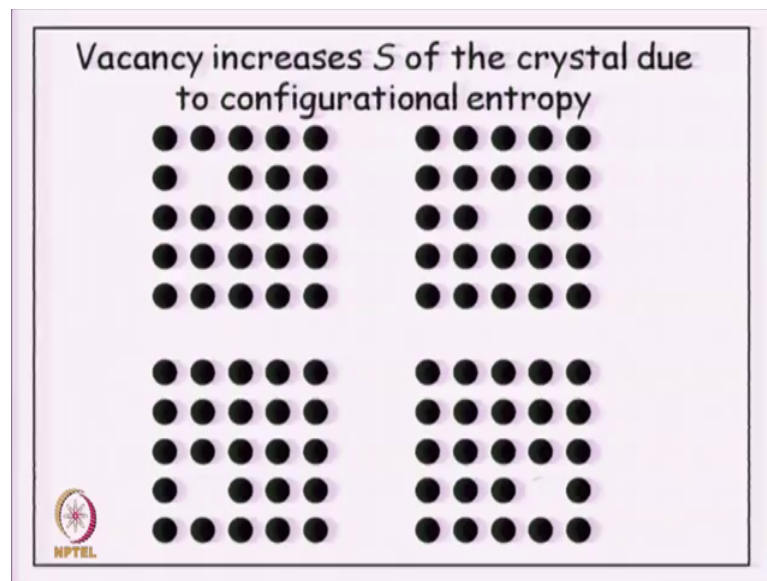
Now, if I want to create a vacancy there I will have to break these bonds. So, let me break these bonds and by breaking this bond now I can remove the atom, but you can see if I simply remove the atom the number of atoms is decreasing, this is not going to happen the number of atoms should be conserved. So, really to create the vacancy I have to remove the atom from its normal place and then place it somewhere else.

Now, in this system that somewhere else that somewhere else we will see can be many locations in a real crystal like it can be the dislocation core, we have already seen in the case of climb dislocation climb that if atoms go and join the dislocation core then their location from which they move will be created vacancy. So, these atoms can join dislocation core or they can join grain boundary or if none of these are present like in the crystal shown here they can come to the surface. So, I place them on the surface.

. So, on the surface it will again form a bond. So, although 4 bonds were broken to remove this atom from here one bond has been regenerated to put it on the surface. So, effectively for this atom 3 bonds are broken. So, certain effective number of bonds have to be broken to create a vacancy in a crystal and each bond breaking will require certain amount of energy and the certain amount of enthalpy to be provided to the crystal to make this replacement of atom from its normal location to let us say a less favorable location in this case the surface.

So, if we now think that each such creation of vacancy is requiring an enthalpy  $\Delta H_f$ ,  $f$  the subscript,  $f$  is for formation. So, enthalpy of formation of a single vacancy is  $\Delta H_f$  and if I am creating  $n$  vacancy then the total enthalpy increased due to the creation of  $n$  vacancies little  $n$  vacancies will be  $n$  times  $\Delta H_f$ . Of course, we are assuming that  $n$  is very small. So, only quite a few sites are vacant and also they are far apart such that the number of bonds broken is constant for each vacancy.

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Now, let us try to see the meaning of  $W$ , the number of microstates corresponding to a given microstate. So, I am showing you here a let us see 5 by 5, 25 atom crystal, but one side is vacant. So, we really have 24 atoms with one vacancy, but this vacancy can be located here as in this first figure or somewhere else as in the second figure or third figure or fourth figure. So, these are 4 example of where a single vacancy could have been located in this crystal.

Now, if you think in terms of real atoms and atomic positions that is if you are thinking really automatically then all these configurations are different. But if you think in terms of macroscopic behavior the thermodynamic behavior of the material then you do not expect them to be different macroscopic property, you do not expect to be different because of their different locations of vacancies in these crystal. For example, they should have the same temperature or they should have the same pressure and the same macroscopic volume. So, none of these a macroscopic parameter will change if the vacancy shifts from one location to another location in these systems.

So, microscopically if we think of exact atom positions then these are 4 different microstates, but macroscopically thermodynamically they will behave as a single macro states. So, I will say that these are 4 different microstates corresponding to the same macro state.

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**Configurational entropy due to vacancy**

Number of atoms:  $N$

Number of vacancies:  $n$


Total number of sites:  $N+n$

The number of microstates:

$$W = {}^{N+n}C_n = \frac{(N+n)!}{n!N!}$$

Increase in entropy  $S$  due to vacancies:

$$\Delta S = k \ln W = k \ln \frac{(N+n)!}{n!N!}$$

$$= k[\ln(N+n)! - \ln n! - \ln N!]$$


So, now we can think of configurational entropy due to vacancy as in if there are  $n$  number of atoms and we create  $n$  vacancies in the crystal little  $n$  vacancies in the crystal capital  $N$  number of atoms and little  $n$  number of vacancies then the total number of sites which we are playing with is  $N$  plus  $n$  because vacant site also we are counting as site. So, there are atomic sites, the filled sites, capital  $N$  and they are vacant sites the little  $n$ .

So, the number of microstates in this case will be in how many ways from  $N$  plus capital  $N$  plus small  $n$  sites we can find little  $n$  sites to put my vacancies. So, this as you know

from a mathematics is  $N$  plus  $n$  divided by  $n$  or factorial of  $N$  plus  $n$  divided by  $n$  factorial. So, this becomes the number of microstates in the presence of vacancies.

Now, according to the Boltzmann expression the entropy  $S$  due to this introduction of these  $n$  vacancies in the crystal will be given by the formula  $\Delta S = k \log W$ . So, this will be the increase in entropy of the crystal due to the introduction of vacancies. So, I replace the value of  $W$  as we have just calculated here into this and then expand the logarithm to get this final expression.

So, far so good, but these numbers the factorials the argument of the factorial made argument of the log  $N$  plus  $n$  factorial this is a very very large number we are talking of a atomic system. So, even a mole Avogadro number of atoms will be  $10$  to the power  $23$  atoms. So, this will be a very large number. So, there is a process to simplify finding logarithm of factorial a large factorials and that will come to be very very useful for us. So, if we will look at that approximation that mathematical approximation given by sterling known as a Stirlings approximation and that is log of factorial  $N$  for large  $N$  its simply  $N \log N - N$ .


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**Stirlings Approximation**

$$\ln N! \approx N \ln N - N$$

$N$	$\ln N!$	$N \ln N - N$
1	0	-1
10	15.10	13.03
100	363.74	360.51

100! = 9332621544394415268169923885626670049071596826438162146859296389521759999322991560894146397615651828625369792082722375825118521091686400000000000000000000000



So, here you can see that here we have to find first the factorial of a large number and then top take the log. Here that finding factorial has been removed we have to simply take log of  $N$  multiplied by  $N$  minus  $N$  mathematically this simplifies the process very

much. for example, if you now let us see how good is this approximation. So, let us begin with the first column I am making of  $N$  and then second column is the exact value  $\log N$  factorial and the third column is the approximate value  $N \log N$  minus  $N$ .

Let me begin with a very small number just 1. So, for 1 log factorial  $n$  is 0 and  $N \log N$  minus  $N$  is minus  $N$ . So, this is quite different and when you can see that difference. But anyway the approximation is for large  $N$ , so at the moment we have not reached that large limit an approximation is not good. But even if we go to 10 we start finding that it is becoming a good approximation.

Now, log factorial  $N$  exact value was about 15 whereas, the approximation is giving a value of 13. So, we are making an error of 2 in 15 which is still 12.33 percent error. But if you go to 100 now the exact value comes to 363 and the approximation is only 360. So, now, the error is only 3 in 360 it is less than a percent.


So, even for 100 the approximation is within 1 percent to the actual value and as we go to larger and larger value you will find that actually the difference saturates to about 3. So, a difference of 3 will be coming in a much much larger value Avogadro number of atoms for example, if you go to this will be a very large number and the error will hardly be perceivable.

So, Stirlings approximation is a very good approximation for large  $N$  and you will appreciate the mathematical simplicity if you really try to calculate this number log factorial  $N$  for that first you have to calculate factorial  $N$  and factorial  $N$  itself is an extremely huge number. here by mathematica I have calculated and showing you hundred factorial up to the last digit and you can see it is a really really huge number.

So, first calculating the factorial will become very a huge task and then you have to take logarithm of this large number whereas, in this case we will take only log of 100 and multiplied by 100 and subtract 100. So, you will get 360. So, by much less work you are getting a very good approximation. So, let us now use this Stirlings approximation into our work.



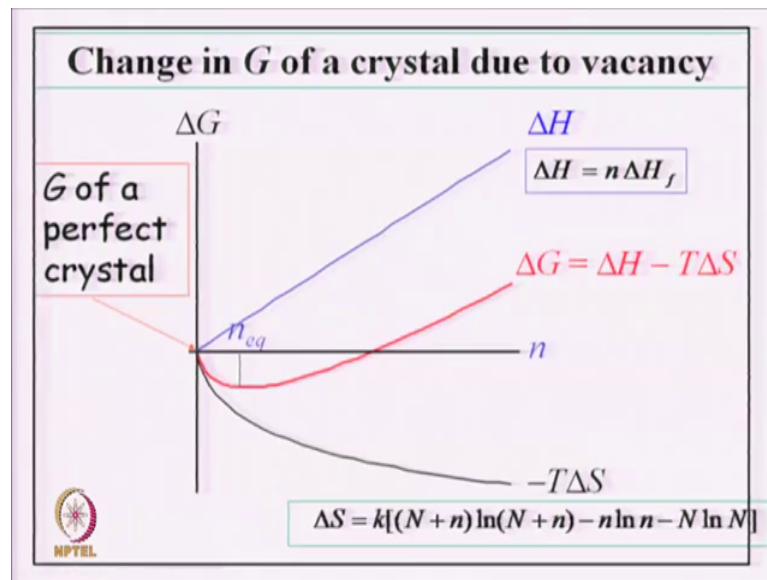
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$$\Delta S = k \ln W = k[\ln(N+n)! - \ln n! - \ln N!]$$
$$\ln N! \approx N \ln N - N$$
$$\Delta S = k[(N+n) \ln(N+n) - n \ln n - N \ln N]$$
$$\Delta H = n \Delta H_f$$


We have already seen that we have come to this expression for increase in entropy due to introduction of little  $n$  vacancies in a crystal composed of capital  $N$  atoms.

Now, we have this Stirlings approximation and we applied a Stirlings approximation to this expression to simplify it to this form. Now, there are no factorials I have simply capital  $N$  plus a small  $n$  log capital  $N$  plus small  $n$  minus small  $n$  log  $n$  minus capital  $N$  log capital  $N$ . So, we have a simplified expression for the entropy increase due to the introduction of a small  $n$  number of vacancies in capital  $N$  atom number of atoms. And we also have an expression for enthalpy, so now, we have the two components which we require for our free energy the enthalpy increase and the entropy increase. So, if we put these two together with the temperature we will get the change in free energy of the crystal.

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So, let us do that graphically. So, on the x axis I have the number of vacancies and on the y axis the change in free energy, but we will do it in a steps. Now, if  $n$  is 0 if there are no vacancies. So, that is our perfect crystal. So, the perfect crystal is sitting at the origin here.

Now, our increase in enthalpy was simply  $n$  times  $\Delta H_f$ . So, and since  $n$  is our x axis it is simply a straight line with  $\Delta H_f$  as its slope. So, we have a straight line for enthalpy. But if you plot the entropy change which was this logarithmic expression which we derived and minus  $T$  times  $\Delta S$  because that is what goes in making  $\Delta G$  then you have a curve like this because of this minus sign this curve is a negative curve and you have this.

The sum of these two  $\Delta H$  and minus  $T\Delta S$  will be  $\Delta G$ . So, you can add these two. You can see that initially this  $\Delta S$  curve has a very high slope and then gradually the slope decreases whereas, the  $\Delta H$  curve has a constant slope. So, initially minus  $T\Delta S$  term will be dominant and the  $\Delta G$  curve will come down. but gradually as its slope decreases and this keeps growing at a constant rate. So,  $\Delta H$  will start becoming dominant and the curve will come up. So, if you plot this curve you get something like this. The red curve now is the sum of this blue curve and the black curve,  $\Delta G$  is sum of  $\Delta H$  minus  $T\Delta S$ . So, I have this free energy curve.

Once you have this free energy curve you now realize that this is showing a minimum at certain number of vacancies so that means, this number of vacancy where you have this minimum in the curve is the equilibrium number of vacancy which this crystal will accept which this crystal will be happy with. So, that particular vacancy number I now label as  $n_{eq}$ , so  $n_{eq}$  is the number of vacancies at which the free energy of the crystal at this temperature is minimum.

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**Equilibrium concentration of vacancy**

$$\Delta S = k[(N+n)\ln(N+n) - n\ln n - N\ln N]$$


$$\Delta H = n\Delta H_f$$

$$\Delta G = n\Delta H_f - T k[(N+n)\ln(N+n) - n\ln n - N\ln N]$$

$$\left. \frac{\partial \Delta G}{\partial n} \right|_{n=n_{eq}} = 0$$

$$\frac{n_{eq}}{N} = \exp\left(-\frac{\Delta H_f}{kT}\right)$$

With  $n_{eq} \ll N$



So, then equilibrium concentration of vacancy is easy to find all you have to do is start with your expression of delta S and delta H and construct your delta G which we have already done graphically and then differentiate this expression because at equilibrium this delta G is minimum. So, del of delta G by del n will be equal to 0 the slope of the curve at the minimum point will be 0.

So, if we simply differentiate this expression I leave this algebra for you please do that. So, simply differentiate this expression and apply this condition then you will find what is the equilibrium number of vacancies. Here I am showing it as a ratio to the total number of atoms. So, equilibrium number of vacancies divided by total number of atoms is equal to exponential of minus delta H f by kT. In getting this final expression in your algebra you will have to apply this approximation that the equilibrium concentration of vacancy is much much smaller than the number of atoms.


So, this is the final expression which you are looking for and this is what answers our original question that what is the equilibrium concentration of vacancy. This ratio, this ratio is what we are calling the equilibrium concentration of vacancy and that is an exponential function exponential minus delta H f by kT recall the delta H f was enthalpy of formation of one vacancy, k is Boltzmann constant and T is temperature.

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$$\frac{n_{eq}}{N} = \exp\left(-\frac{\Delta H_f}{kT}\right)$$

Al:  $\Delta H_f = 0.70 \text{ eV/vacancy}$   
 Ni:  $\Delta H_f = 1.74 \text{ eV/vacancy}$

$n/N$	0 K	300 K	900 K
Al	0	$1.45 \times 10^{-12}$	$1.12 \times 10^{-4}$
Ni	0	$5.59 \times 10^{-30}$	$1.78 \times 10^{-10}$



Let us look at some values. So, aluminum has an enthalpy of formation of 0.70 electron volt per vacancy and delta H f is 1.74 electron volt per vacancy for nickel. So, nickel has enthalpy of formation of vacancy about 2 times more than that of aluminum, more than 2 time. So, you can see aluminum is has a weaker bonding has a lower melting point. So, has a lower enthalpy of formation because bonds are weak and lower melting point means bonds are weaker, and remember enthalpy of formation was nothing, but enthalpy for breaking the bonds to create the vacancy.

So, since the bond energies are less in aluminum the corresponding enthalpy for formation of vacancy is also a smaller, similarly in nickel, nickel is a high melting point material. So, the bonds are very strong and to break those stronger bonds you will have to provide more energy. So, enthalpy of formation of vacancy is higher in nickel.

Now, if you use this expression to calculate for 0 Kelvin of course, if T is 0 the argument is infinity an exponential of minus infinity will always be 0, so whether its aluminum or nickel there is 0 concentration of vacancy at absolute 0. But at all other temperature there


will be certain fraction of sites which will be vacant and these are the fractions shown here, but you can see that at most reasonable temperature at the room temperature for example, aluminum has only one in about 10 to the power 12 sites vacant and similarly this will have about 5 in 10 to the power 30 sites vacant.

So, this vacancy concentration is really really very small at low temperature. But because of the exponential relationship and it depends upon the material and there are several orders of magnitude difference in the vacancy concentration of nickel and aluminum. Aluminum is much much larger number of vacancies at room temperature than nickel has. But as you start heating and at 900 a Kelvin you have in aluminum about 1 site in 10 to the power 4 vacant. So, in 10,000 sites there is one vacancy now the vacancy concentration this is very high vacancy concentration aluminum at 900 Kelvin is very close to its melting point.

So, close to the melting point vacancy concentration becomes quite high whereas, nickel is still far away from it is a melting point. So, although the vacancy concentration has gone several orders of magnitude higher at 900 k, but it is still much lower than it is melting the temperature is still much lower than its melting point. So, it can go is still higher values like 10 to the power of minus 4 as this also a starts reaching its melting point. In fact, one theory of melting is that the vacancy concentration becomes so high that the crystal is no more able to support itself and just collapses. So, you get melting.

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$\frac{n_{eq}}{N} = \exp\left(-\frac{\Delta H_f}{kT}\right)$	$\frac{n_{eq}}{N} = \exp\left(-\frac{\Delta H_f}{RT}\right)$
$\Delta H_f$ : Enthalpy of formation of a single vacancy	$\Delta H_f$ : Enthalpy of formation of a mole of vacancies
$k$ : Boltzmann constant	$R$ : Gas constant

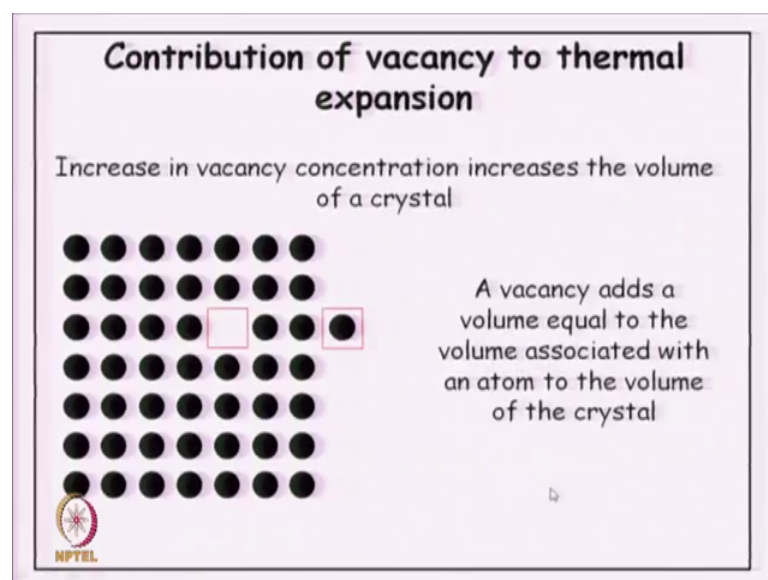


This like just tries to clarify one confusion that sometimes the expression is written with  $k$  and sometimes the expression is written with  $R$ . The difference is both are correct expression, but the interpretation for  $\Delta H_f$  changes. If I write it with  $k$  as I was doing it till now then it is enthalpy of formation of a single vacancy that is why I recall that I wrote for aluminum and nickel when I was writing the value I was writing electron volts per vacancy. So, it is for one vacancy then you use Boltzmann constant. But of course, if you multiply both numerator and denominator here by an Avogadro number then  $\Delta H_f$  will change to enthalpy of formation of a mole of vacancy whereas, Avogadro number times Boltzmann constant will become gas constant  $R$ .

So, there is really both are the same expression a given differently one with  $\Delta H_f$  by  $kT$  another with  $\Delta H_f$  by  $RT$ , but we have to be careful about the unit or the interpretation of  $\Delta H_f$  if it is  $k$  its enthalpy of formation of a single vacancy and if it is  $R$  in the denominator then  $\Delta H_f$  is enthalpy of formation of a mole of vacancies.

With this we end our discussion on vacancy, but let us discuss a few more kinds of defect or other.

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Let us first discuss one interesting effect of vacancy to thermal expansion of the crystal. This is a, this is very very interesting and this is one way by which this  $\Delta H_f$  can be experimentally determined. So, let us do that. So, increasing vacancy concentration increases the volume of a crystal. So, vacancy actually contributes to the expansion, how

does that happen let us see. You remember the diagram which we made where we said that if we create a vacancy the atom has to be put on the surface.

So, if I put it on the surface there then I have added one site on the surface. So, I have added an extra volume to the crystal initially the volume was limited by this square boundary in this two dimensional example, but now here the boundary has expanded to include this atom. So, the overall volume of the crystal has increased. So, vacancy adds a volume equal to the volume associated with an atom to the volume of the crystal. You can think of this system now you can see there are 3 4 5 6 7 and then 3 3 6 and 7 this is a 7 by 7 is square which I have made, so its 49, they were supposed to be 48, then there is 49 atoms here, but there is 1 vacant site.

So, now total number of sites is 50 and the vacant site is also occupying the same volume as the occupied side. So, although there are only 49 atoms 7 into 7 49 atoms I have a volume corresponding to 50 atoms because there is one vacant side. So, every vacancy adds volume equal to the volume associated with an atom to the volume of the crystal.

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**Contribution of vacancy to thermal expansion**


Thus vacancy makes a small contribution to the thermal expansion of a crystal

Thermal expansion =

lattice parameter expansion

+

Increase in volume due to vacancy

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Thus vacancy makes a small contribution to thermal expansion of a crystal. Thus the total thermal expansion we can write as two components, one is because of the lattice parameter expansion. So, of course, when you are heating the crystal the bond length also is changing atom to atom distance is changing.

So, there is an increase, there is increase in the bond length. So, that is the lattice parameter expansion and the other one is increase in volume as we just discussed due to vacancy.


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**Contribution of vacancy to thermal expansion**

$V = Nv$        $V = \text{volume of crystal}$   
 $\Delta V = N \Delta v + V \Delta N$        $v = \text{volume associated with one atom}$   
 $N = \text{no. of sites (atoms+vacancy)}$

$$\frac{\Delta V}{V} = \frac{\Delta v}{v} + \frac{\Delta N}{N}$$

Total expansion
Lattice parameter increase
Vacancy contribution



So, if we write the total volume of the crystal as total number of sites times the volume per site. So,  $V$  is the total volume of the crystal, little  $v$  is volume associated with one atom and  $N$  is the total number of sites. So, its atom plus vacancy we are assuming that vacancy is also occupying the same volume as atom. So, the total volume of the crystal will be  $N$  times  $v$  if we simply differentiate this expression then  $\Delta V$  will be capital  $N$  times  $\Delta v$  plus capital  $V$  times  $\Delta N$ . So, we get this expression by simply differentiating.

And if I divide this by the original expression  $V$  is equal to  $N v$  we can write in terms of fraction. So, total fractional increase in volume is this fraction the first fraction plus the second fraction. If you look at the first fraction the left hand side is of course, the total expansion, but on the right hand side the first fraction will correspond to the lattice parameter increase because this little  $v$  is the volume associated with one atom.

So, and how the volume per atom will increase? The volume per atom will increase only if the lattice parameter increases you recall, that every unit cell had certain fixed number of atoms. So, we if we have body centered cubic crystal then in the body centered cubic crystal there will be two atoms per lattice point, sorry two atoms per unit cell. So, if the



lattice parameter increases then the two atoms per unit volume will decrease the number of atoms per unit volume will decrease or the volume per atom will increase.

So, this is the increase in volume per atom due to lattice parameter increase. Now, the second term the  $\frac{\Delta n}{N}$  is because of the increase in the number of sites. How the number of sites can increase? The number of atoms is fixed number of atoms are conserved. So, the total number of sites will change only if there are more vacancies getting added to the system. So, this  $\Delta N$  is nothing, but the number of vacancies. So, the second term is coming from vacancy contribution.

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**Experimental determination of  $n/N$**


$$\frac{\Delta V}{V} = \frac{\Delta v}{v} + \frac{\Delta N}{N}$$

$$\frac{3\Delta L}{L} = \frac{3\Delta a}{a} + \frac{n}{N}$$

$$\frac{n}{N} = 3 \left( \frac{\Delta L}{L} - \frac{\Delta a}{a} \right)$$

Linear  
thermal  
expansion  
coefficient

Lattice  
parameter as a  
function of  
temperature by  
XRD

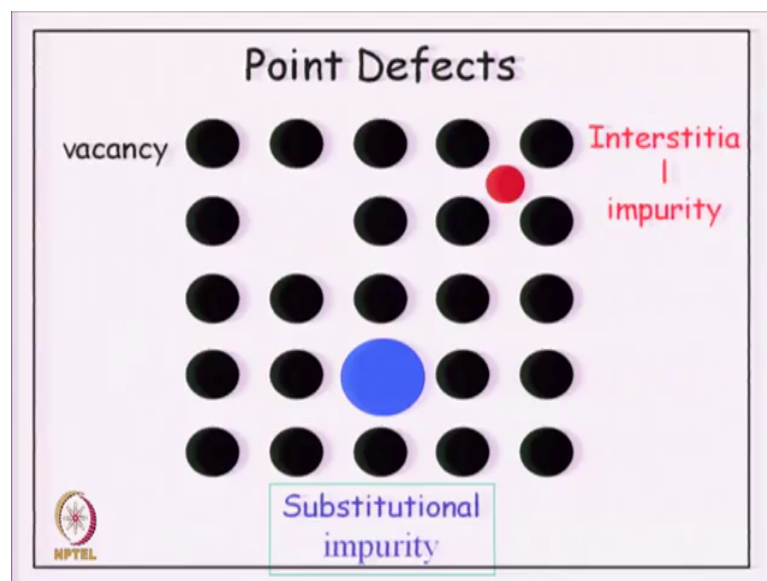


So, if we write like this  $\frac{\Delta V}{V}$  in our expression the fractional increase and then I am changing it to from volume increase to length increase and you know from your a basic physics that the fractional change in volume is 3 times the fractional changing length in case of thermal expansion. So, the first one the way on the LHS I change it to 3 times  $\frac{\Delta L}{L}$  fractional changing length.  $\frac{\Delta V}{V}$  is due to the volume change of the crystal, due to lattice parameter increase. So, this is 3 times  $\frac{\Delta a}{a}$ , where  $a$  is the lattice parameter. And here we have already said that this  $\Delta n$  the change in the number of sites has to be due to the addition of vacancies and since we have added between  $n$  vacancies. So, for  $\frac{\Delta n}{N}$  I am writing this small  $n$  for number of vacancies.

You can now write you rearranged this into this form where now this  $n$  by  $N$  which was my vacancy concentration I have written on the left hand side and the other terms on the right. If you do careful experiments both the terms on the right hand side can be measured. So,  $\Delta L$  by  $L$  is the linear thermal expansion coefficient. Well, it is not a linear thermal expansion coefficient it is due to the linear thermal expansion and you can find that by thermal expansion experiments. And this  $\Delta a$  by  $a$  is the lattice parameter change and if you do X-ray diffraction as a function of temperature you can measure what is the change in the lattice parameter as a function of temperature. So, you can find  $\Delta a$  by  $a$ .

So, you will then get the fraction of vacant sites in your crystal. So, if this fraction of vacant site is measured as a function of temperature you can then use your equilibrium concentration for formula to find  $\Delta H_f$ . So, this is one way of getting  $\Delta H_f$ .

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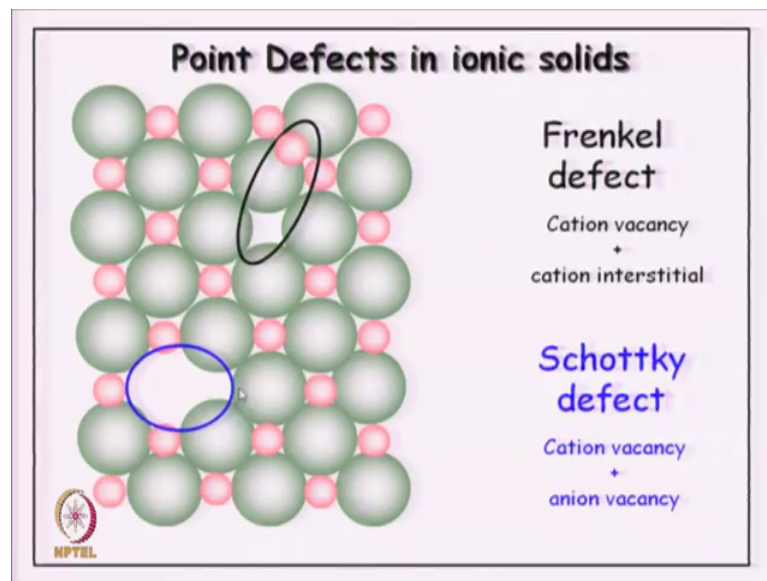
So, we have talked about point defects, but the only point defect which we have mentioned till now is the vacant site. So, there is a vacancy which is missing of an atom.

But then there are other kinds of point defects. So, for example, they may be an interstitial impurity by (Refer Time: 35:00) sorry this is L coming from here. So, interstitial impurity and this is the an atom which is sitting on a some sort of void or in testes of the crystal. So, this red atom is an interstitial impurity. But this blue atom is sitting at a location where black atom should have been sitting, so this is a substitutional

impurity you have met it in interstitial and substitutional solid solution when we discussed that topic.

So, now we are, we are looking these atoms which are located either in the inter stress or located at the atomic site, but is a different atom as point defects. So, they are interstitial and substitutional point defects.

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In ionic crystal we have one two more varieties of defects which can be there. So, here I am showing a schematic of an ionic crystal. So, you can think of the larger one as anion and this smaller red one as cation.

So, various kinds of point defects are possible in such ionic solid. So, for example, there is one which is called Frenkel defect this defect is created if a cation is moved from its normal location to some other interstitial site in the crystal. So, we have, you actually have a pair of vacancy pair of defects together there is a cation vacancy as well as a cation interstitial.

A simple cation vacancy or a simple anion vacancy is not possible because that will lead to charge imbalance in the crystal and thus the energy of the crystal such crystal will be much higher because of the charge imbalance. So, they are not may seen, but Frenkel defect in which a cation is simply misplaced from its site to some other interstitial site creating the cation interstitial and a cation vacancy this is known as Frenkel defect.

The other kind of defect is a Schottky defect. In this you create a pair of vacant site, again simple anion vacancy or simple cation vacancy is not possible, but it is possible that the entire, the whole pair a cation anion pair is missing from the regular side. So, this kind of defect is called Schottky defect. So, this completes the discussion on point defects we will go to discussing line defects in future videos.