Material Science
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Lecture No 2
Internal Energy Enthalpy

In the last class we told you that in this course we are going to study the structure property relationship in materials which are used by the engineers in the practice of their profession and then before we started talking about the structures of materials we said that is a look into the certain aspect of equilibrium and kinetics in materials which we shall be using time and again.

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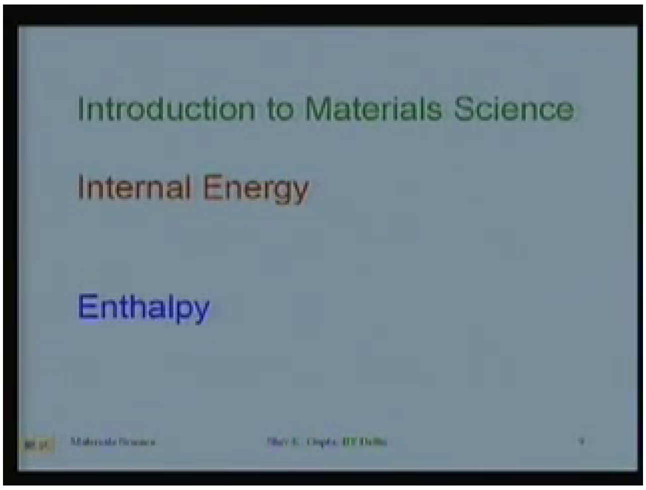

Introduction to Materials Science

Internal Energy

Enthalpy

While discussing that we talked about the intensive properties of materials like pressure and temperature then extensive properties that is what we are talking about internal energy, enthalpy and towards the end I was telling that if this energy is to be considered for the stability of a material, it does not match with our common experience like about the melting point it is the water which is stable not ice and the enthalpy or the internal energy of water is more than that of ice, so that stability criterion is what we have to look at so should start from there.

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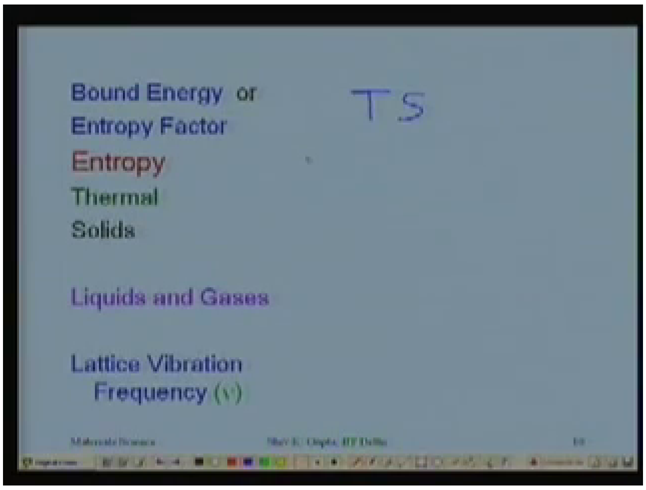
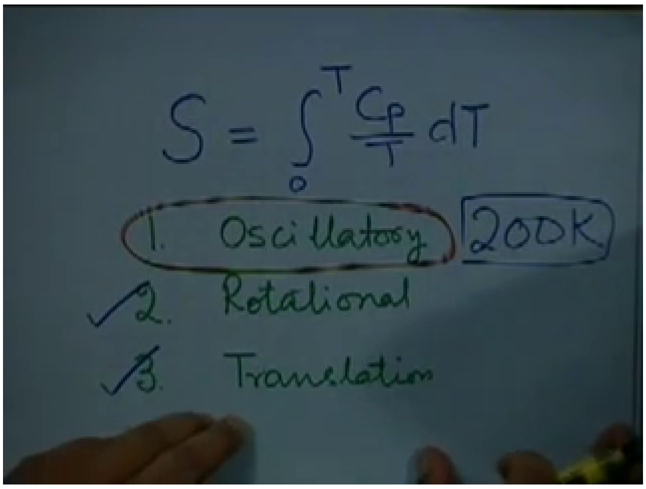


Bound Energy or
Entropy Factor
Entropy
Thermal
Solids

Liquids and Gases

Lattice Vibration
Frequency (ν)

TS



$$S = \int_0^T \frac{C_p}{T} dT$$

1. Oscillatory $\boxed{200K}$
✓2. Rotational
✓3. Translation

The material has certain internal configuration and to that configuration certain energy is involved which is called the bound energy that energy is bound to the system and that configuration of the material, it is not available for material to do any kind of work. This bound energy is also called the entropy factor and we write as T is the temperature in absolute and S is the entropy. Entropy we have studied in school what is called thermal entropy and it is defined as… Define the entropy as integral of 0 to T Cp by T dT. If you compare this with the other properties we define internal energy and enthalpy there is no constant term here means entropy at 0 Kelvin is 0.

This is by and large true for what we called thermal entropy materials whether they are solids or liquid or gas is the 3 states of matter but when it comes to solids which could be of 2 kinds crystalline and non-crystalline, in the non-crystalline we shall be materials we have seen the structure is similar to that of liquids but in case of crystalline structures which we are going to study in this course we shall see the atoms have regular arrangement periodically repeating pattern is there means there are certain set configurations possible in the crystalline solid that also give rise to the entropy before I come to talk about that difference between solids and the other 2 states as a matter liquid and gases.

There are 3 kinds of motion any atom can have one is the oscillatory motion 2nd one is rotational and 3rd is translation. In the case of solids starting from 0 Kelvin and up this is the only motion available at 0 Kelvin of course there is no motion available, oscillatory motion is the only motion available atoms in the solid-state only when they are about to reach a melting point that some rotational motion also begins otherwise there is not the characteristics of solids while liquids and gases can be characterised by rotational motion and the translation motion.

In other words these 2 motions are not there in my solids so therefore atoms in the crystalline solids are oscillating about their mean position what I call a fixed position of the atom in the solid or the crystal and they are oscillating with varying amplitude and varying direction, however starting from 0 Kelvin even the frequency begins to increase because at 0 Kelvin everything is 0 consider frequency 0 it begins to rise by the time it reaches about 200 Kelvin that this frequency stabilises and we call this frequency the lattice vibration frequency.

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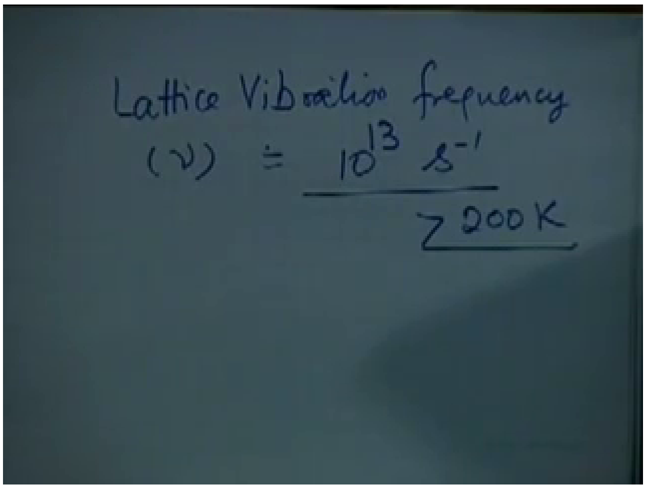

Lattice Vibration frequency

$(\nu) \doteq 10^{13}\ s^{-1}$

$> 200\ K$

And this lattice vibration frequency is 10 to the power 13 per second at temperature which exceeds about 200 Kelvin and remains constant at that. Most materials we are using are temperature (())(8:44) Kelvin so we shall use this as the lattice vibration frequency for all our studies in this course. This is about 10 to the power 13 per second, okay.

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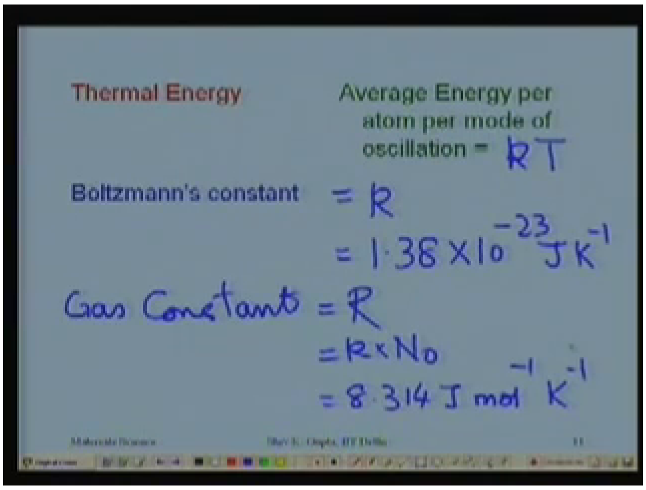

Thermal Energy

Average Energy per atom per mode of oscillation = kT

Boltzmann's constant $= k$

$= 1.38 \times 10^{-23}\ J K^{-1}$

Gas Constant $= R$

$= k \times N_0$

$= 8.314\ J\ mol^{-1}\ K^{-1}$

Alright this oscillatory energy which is available to the atoms and the crystalline solids or non-crystalline solids also atoms are oscillating about their positions but there is no regular arrangement in case of non-crystalline solids. This is referred to as the thermal energy and defined as average energy per atom per mode of oscillation may define as k into temperature in absolute where k is the Boltzmann's constant. Well it is slightly different from what you studied in gases studied about 3 by 2 kT , okay and Boltzmann's constant k is 1.38 10 to the power minus 23 joule per Kelvin.

This Boltzmann's constant once multiplied by another constant what is called Avogadro's numbers which is quantity of one mole becomes the universal gas constant which is equal to k into N 0 and that is equal to 8.314 joule now since we have multiplied by this Avogadro's numbers N 0 express it per mole per Kelvin. Why I am saying this is because this interchangeable use of k and R would be coming in this course and you have to be aware about it.

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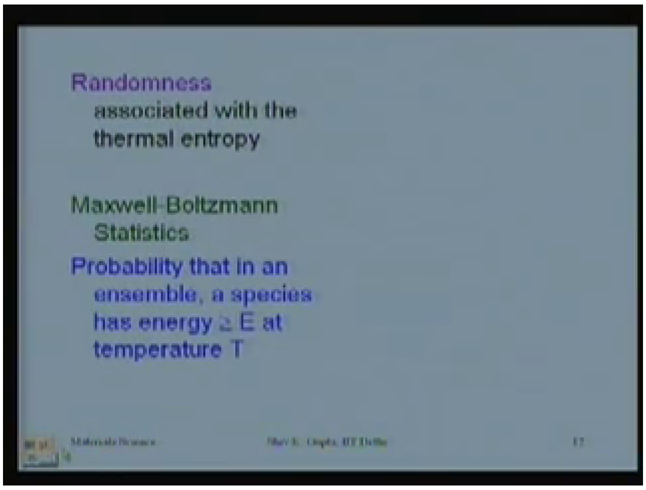

Randomness
associated with the
thermal entropy

Maxwell-Boltzmann
Statistics

Probability that in an
ensemble, a species
has energy ≥ E at
temperature T

Alright, now since we talked about thermal energy you have also studied may be that entropy measures randomness in materials. What randomness does it measure talks about thermal entropy. I have just said atoms are oscillating about their mean position, their amplitude of oscillation is varying the direction of oscillation is varying. Now in the process what happens is the 2 neighbours at times may collide, during the collision one can transfer the energy to the other and thereby one can gain the energy other can lose the energy. In another words this amplitudes could be wearing from 0 to very high and directions can also get change during collision.

So randomness therefore is in the direction as well as in the amplitude, an amplitude is a measure of the energy therefore atoms do not have the same energy which are oscillating about their mean position the one which has a higher amplitude has a higher energy, the one which has a lower amplitude has a lower energy, so energy is varying from a very small value to a large value and when I talk about the crystals, even a crystal of the size 1 centimetre by 1 centimetre by 1 centimetre may have of the order of 10 to the power 23 atoms and it, so I am talking about a very large ensemble of atoms where every atom is having random amplitude and random direction of oscillation, so this randomness associated is in the direction…

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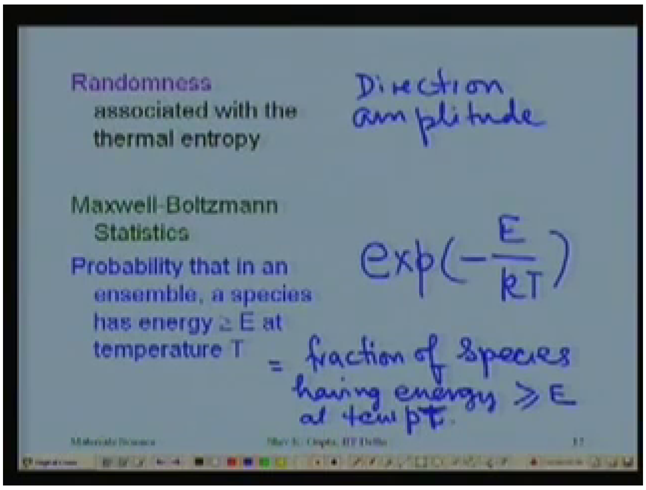

Randomness associated with the thermal entropy

Direction
amplitude

Maxwell-Boltzmann Statistics

Probability that in an ensemble, a species has energy ≥ E at temperature T

$\exp\left(-\frac{E}{kT}\right)$

= fraction of species having energy ≥ E at temp T.

So randomness associated with thermal entropy is in the direction of oscillation and amplitude of oscillation since it is an ensemble of very large number of atoms you can talk of statistics, you can talk of an average energy, we can talk of energy greater than a particular value and things like that. We have also seen the Maxwell Boltzmann statistics in case of gases earlier this statistics we use besides we will be using another statistics which we will talk about later quite similar to this but what the Maxwell Boltzmann statistics says in an ensemble where the energy are varying from a small value of a large value and these keeps varying at the same time when they are colliding change of energy is taking place the probability that in an ensemble species has an energy greater than or equal to a given value E at a given temperature T is given by effect number exponential of minus E by kT.

This probability when I adapt for all the atoms and then divided by the total number of atoms available shall give me the fraction of atom which are the energy greater than equal to the E value E, so this is also equal to fraction of species at temperature T. Now having looked at this thermal entropy and the randomness this measures we shall look at the another kind of entropy which does not exist in liquids and gases, it exist only in crystalline solids not even in non-crystalline solid because we are talking about certain arrangements which are called the configurations of atoms in the given space which is the crystal.

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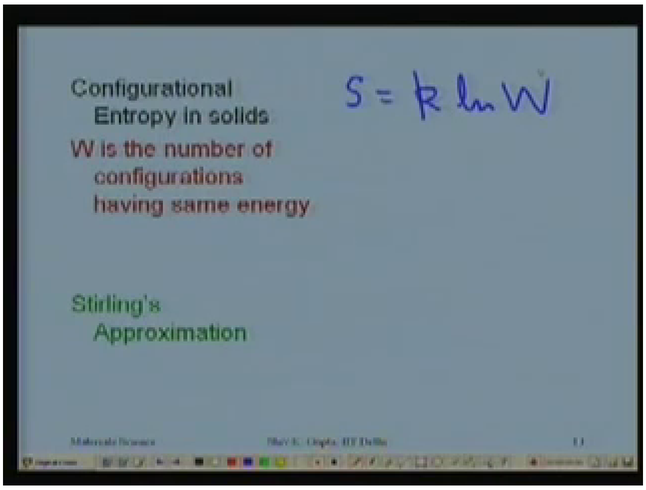
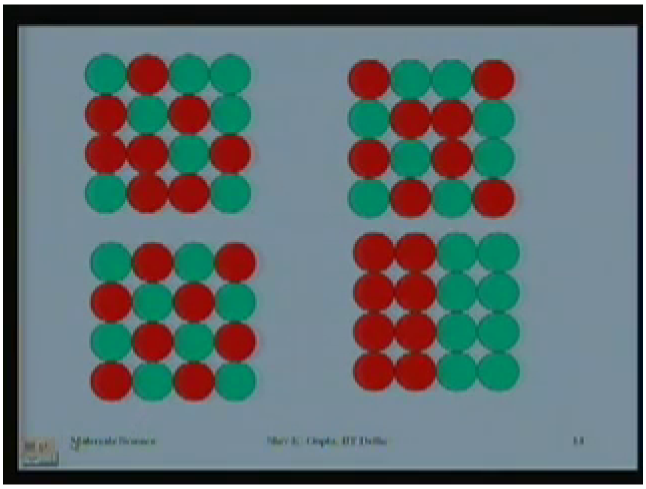


Configurational Entropy in solids

W is the number of configurations having same energy

Stirling's Approximation

$S = k \ln W$



And let us say I have W as the number of configuration of the same energy that is possible for me to define configurational entropy in solids as Boltzmann's constant time natural logarithm of W where W is the number of configurations having the same energy. Now just to look at this… I take here model containing nearly 16 atoms, 8 atoms of the green kind other 8 atoms of the red kind. I have tried to arrange them in for possible ways here, out of these you can see these the arrangements where here greenest is neighbour to…

In here we see that the this red is surrounded by green here, green there, green there that means you can say let us say it is A atom this is the B atom, AB bond this is also an AB bond, this is also an AB bond, this is also an AB bond but in here we find this is a AA bond and here we find again this is an AA bond again AB bond like here we have BB bond and so on and so forth. Same is true about the 2nd arrangement here there are AA bonds, BB bonds and AB bonds but the other 2 arrangements which I am showing here see there are only AB bonds there is no AA bond there is no BB bond. Look at here I have only AA bonds and BB bonds this is just an interface here but on this side this is all AA bonds, on the right side if they are all BB bonds there are no AB bonds here while there are no AA bonds and BB bonds here. This and these 2 arrangements probably do not have the same energy as compared to the other 2 where there is their locations where A and B are randomly decided.

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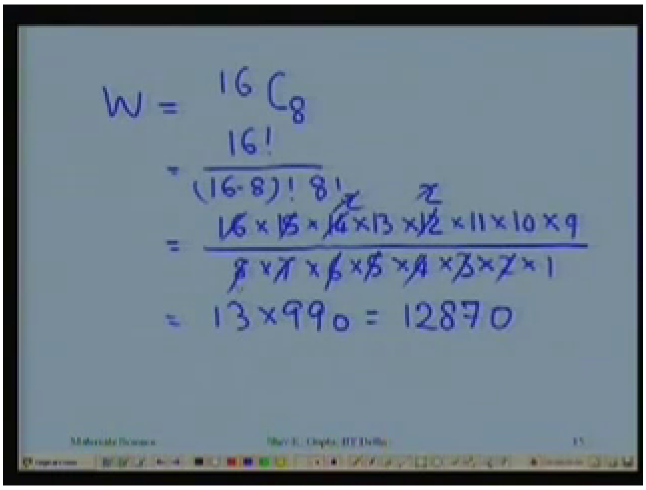

$$W = {}^{16}C_8 = \frac{16!}{(16-8)!\,8!} = \frac{\cancel{16}\times\cancel{15}\times\overset{2}{\cancel{14}}\times13\times\overset{2}{\cancel{12}}\times11\times10\times9}{\cancel{8}\times\cancel{7}\times\cancel{6}\times\cancel{5}\times\cancel{4}\times\cancel{3}\times\cancel{2}\times1} = 13\times990 = 12870$$

But if I look at how many arrangements do I have then it is possible for me to work out the W as 16 C 8 which can be written as 16 factorial divided by 16 minus 8 factorial multiplied by 8 factorial can simplify this we will see that 16 into 14 into 13, 12, 11, 10, 9 divided 8, 7, 6, 5… it is very easy to simplify this 8 into 2 cancel 16 and let us say 6 cancel with 12, 7 cancel with 14 then I have 5 into 3 cancel with 15 and I am left with 4 this 2 and 2 will cancel with this 4, I am left with 13, 11, 10 and 9 that makes it 11 into 999 that is 13 into 990 and that should not be difficult to work out it should be there are 12,870 arrangements possible out of which only 2 are the kinds where I have only AB bonds or I have AA bonds and BB bonds those are called the ordered arrangements.

There are only 2 ordered arrangements while rest of them are all random arrangements, so I neglect 2 here it will not affect me when I work out with the natural logarithm of this number but once I have talked about 23 atoms and I try to work out this number W it becomes a very large number and then subtraction of 2 is just no problem and we can do that approximation, right? So while talking about the W strictly it is number of configurations of the same energy but I have shown you that some are more having more energy some are having less energy and that the arrangements which have different energy are only 2 like in this case of with 2 atoms if we have more atoms I could have more kind of configurations of that kind.

Student: Why the 2 which we are leaving are have different energies than others?

Professor: Yes, it is a very good question AA bond does not have the same energy as the AB bond, BB bond does not have the same energy as the AA bond, so all 3 bonds have different energies where I have an ensemble only AB bonds of one energy where I have AA bonds is one energy where I have only BB bonds another, so this energy is going to be different of the ensemble, right? Right.

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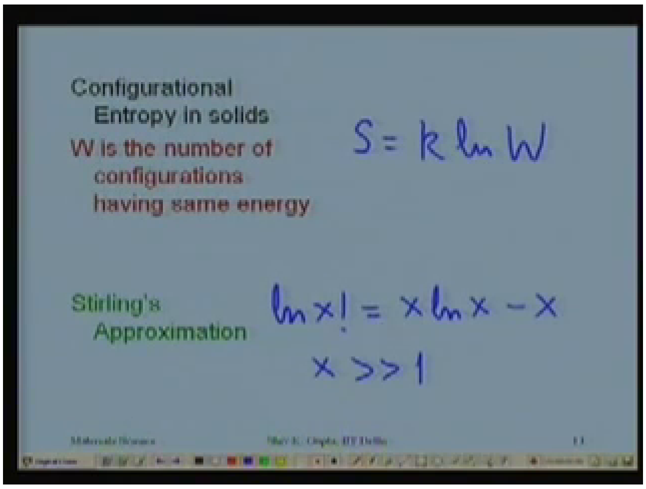

Configurational Entropy in solids

W is the number of configurations having same energy

$S = k \ln W$

Stirling's Approximation

$\ln x! = x \ln x - x$

$x >> 1$

Coming back to this will be wrote this entropy as W going to be very large number of times and factorial 10 to the power 23, so normally we use Sterling's approximation to simplify that it says logarithm of x factorial is x log x minus x, so (())(26:23) x is greater than greater than 1, so that Sterling's approximation we make use of simplify this number. So now we have seen the entropy of 2 kinds one the thermal entropy talked about thermal entropy and the configurational entropy.

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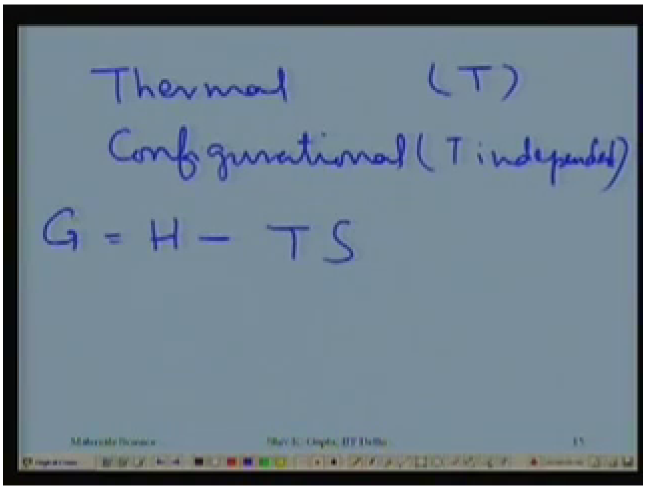

Thermal (T)

Configurational (T independent)

$G = H - TS$

So my solid is going to have thermal entropy as well as the configurational (())(27:35). Thermal entropy is temperature dependent, configurational entropy is independent (())(27:42) the configurations of atoms it does nothing to the temperature, so this is temperature dependent and this is temperature independent. Now this sum of the 2 entropy is the entropy of my crystalline solids then the bound energy is therefore which is T into S is to be is bound to the configuration of the system and therefore from my enthalpy of the internal energy if I subtract this it becomes my free energy.

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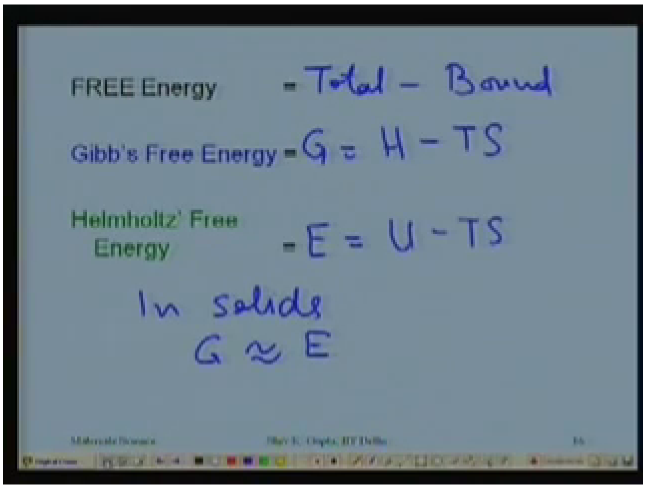

FREE Energy = Total – Bound

Gibb's Free Energy = $G = H - TS$

Helmholtz' Free Energy = $E = U - TS$

In solids

$G \approx E$

Free energy is the total energy and the bound energy is the entropy factor, so we define it 2 ways one is the Gibb's free energy which I just said is G is enthalpy minus the bound energy and Helmholtz free energy we define as E is equal to U minus TS. In case of solid I already said that PV term is negligible so difference between the internal energy and enthalpy is negligible, so for us Gibb's free energy and Helmholtz free energy also almost same and therefore we use them interchangeably as and when required, okay. So for us in solids… alright the

Student: In Maxwell Boltzmann we defined the fraction as (())(30:22) minus E by RD.

Prof: E by kT I said.

Student: So that E is what?

Prof: E is energy, energy of the species you talking about it is oscillating, so what is that energy with which it is oscillating that is the energy we are referring to, okay.

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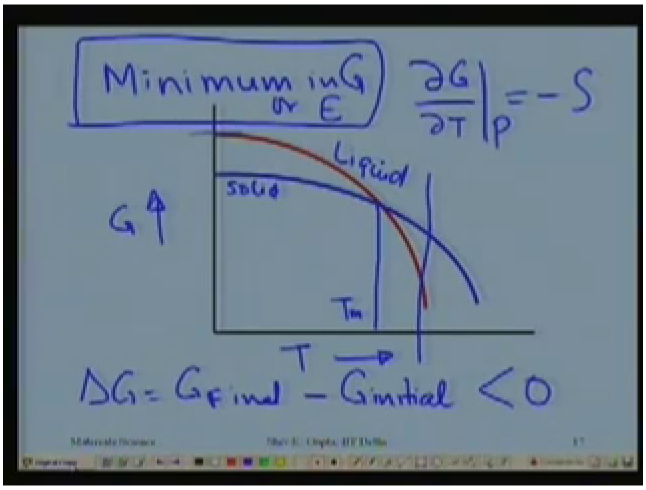

Now here I have free energy, in the case of enthalpy we saw that enthalpy of the solid starting from 0 Kelvin rises as the temperature rises at the melting point the material absorbs the latent heat of fusion beyond that again the liquid again the enthalpy increases but in case of free energy, free energy continues to decrease with increasing temperature is a problem which we are going to work out which says that the slope of this curve is nothing but minus of entropy.

An entropy at 0 Kelvin is 0 so therefore we see the slope of this curve is 0 and this keeps on rising as the temperature rises but the sign is negative, so slope of this curve keeps on increasing with temperature, the rise in temperature that is for one state of the matter similarly for the 2nd state of matter I have the 2nd curve, so let us say this is for the solid and that is for the liquid and now you can see that if the free energy of the solid here is the melting point, below the melting point is lower and above the melting point is a free energy of the liquid which is lower and therefore that is a stable state of the material so I can use for stability criterion, the free energy of the material, okay.

Comparing with what we talked about the rectangular block where we discussed the potential energy now we are talking about the free energy, right and therefore we can say that material would be in its stable stage if its free energy is at its minimum. If it is a global minimum it is the most stable state of the material and if it is simply a local minimum it is a metastable state of the material and metastable state as I said is very important for most materials what we use are there in their metastable state.

For example majority of the materials may be available as oxide in the most stable state at room temperature but the steel which we use, the steel bridges they stand therefore 100 years

150 years. Steele has stayed there for 150 years without oxidising the way has taken care of it, so for all practical purposes that is the stable state of the material that is why we are worried about the metastable state, so which state the free energy is the minimum, the local minimum (())(34:27) metastable state, global minimum is the most stable state. So the stability criterion is going to be a minimum in free energy, G is the Gibbs free energy, E is the Helmholtz free energy.

Now if I take a block of ice and keep it at room temperature which is above the melting point of the ice means it is somewhere here I have to do nothing it will keep on melting by itself. Such a process is called spontaneous process and if a process is spontaneous the change in free energy associated with must be negative. The change is always defined as G in the final state and G in the initial state but it is not always true but if the free energy change of a process is negative is less than 0 the process would be spontaneous on the other hand if the process is taking place spontaneously like the example I took keep a block of ice here it will keep melting by itself because the change in free energy has to be negative.

So that is about the stability and if I go back to the rectangular block you consider its potential energy because there was no change in its entropy whether I keep the block vertically up or horizontally down its entropy does not change, so I could talk about its potential energy which you can say is the change in the energy of the system that is the only change which is taken place otherwise I should always talk about the free energy of the system if I am looking at the stability.

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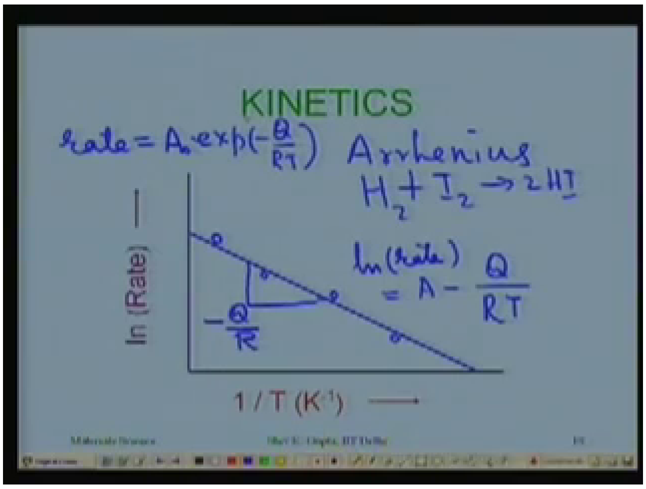

KINETICS

$rate = A_0 \exp(-\frac{Q}{RT})$ Arrhenius

$H_2 + I_2 \rightarrow 2HI$

$\ln(rate) = A - \frac{Q}{RT}$

Next coming to kinetic which also you have done in school particularly you have done the… This we have seen with the help of Arrhenius plot which in a kind of reaction like hydrogen combined with iodine to form hydrogen iodide. Starting the rate of the process Arrhenius found a plot like this which plotted against the reciprocal of the temperature in absolute form a straight line with a negative slope. This slope is given as the value usually minus Q by R this logarithmic relationship can be written as logarithm of rate is equal to some constant minus Q by RT or you can rewrite this to put it in terms of exponential form rate is equal to some constant let us call it A 0 times exponential of minus Q by RT. A and A 0 are related can see that, so this is what you are seen in the school the Arrhenius plot, we shall try to rationalise this.

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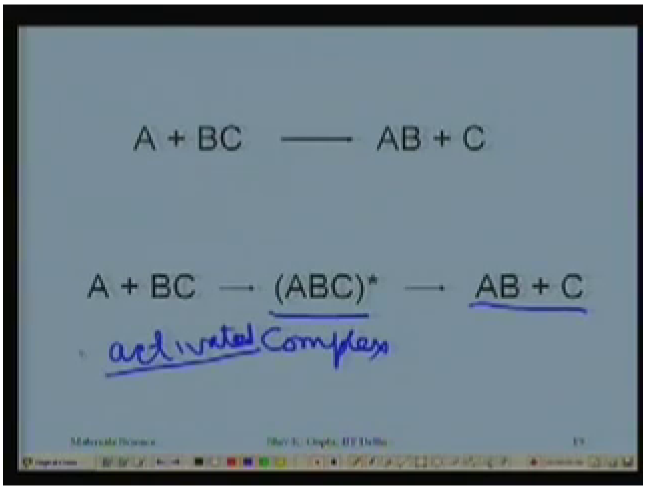

$$A + BC \longrightarrow AB + C$$

$$A + BC \rightarrow \underline{(ABC)^*} \rightarrow \underline{AB + C}$$

activated Complex

Let us consider a process where species A and BC combine or react to form the product AB and C. If you look at this product formation BC the bond B and C must break the bond between B and C must break and a bond between A and B should form that kind of a process is to take place. All BC must break their bonds and then all A should go to the B get attracted to B to form the bond looks little improbable thing to happen when you have species of the order 10 to power 23 but rather what seems to be possible is A and BC because these species have energy varying because they are all oscillating about their mean positions, their energies are varying as some of them have very high energy when you have high energy you can do many things and it is possible for it to form a very high energy complex ABC they are all together and this ABC complex also oscillates like any other at A or BC molecule or say AB molecule they keep oscillating and during oscillation it is possible that they split.

It can split back to become A and BC or it can split to become AB and C, so if splits become AB and C the reaction goes forward but it comes back its possibilities there probability is there probability is not 0 for it going back but this looks probable some species will have very high energy, a high energy complex can form. This is called an activated complex and this activation of this extra energy is provided with by the thermal energy we know that they are oscillating and this is varying from 0 value to a very high value.

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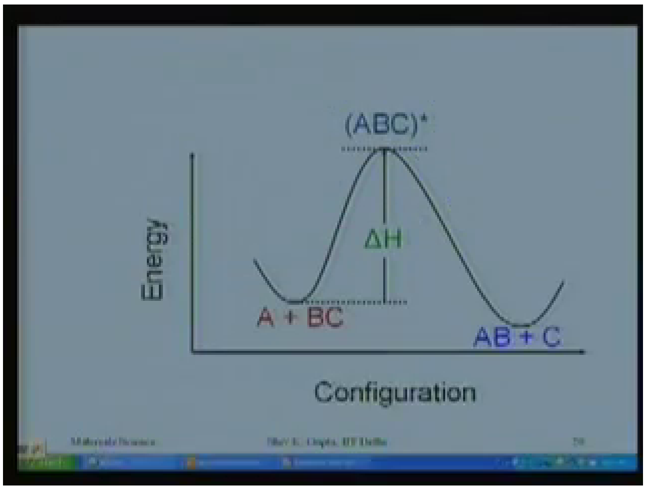

This energy I have shown here for the reactants this is the average energy here at this level, this is the average energy of the reactants, average energy does not mean that every species shall have that energy and some will have less than it some will have more than that and as I said kT is the average energy but energy can be very large very high too and this is the activated complex, all species of this A and BC which can have energy greater than this are in position to form this kind of a complex, energy should be greater than this let us call it Delta H star, it could be great… Once it is greater than this is possible it to form this complex but this complex as I said is form it is oscillating it can go back or it can go forward while going back goes to little higher energy when it goes here it is little lower energy, it is going forward because this is a lower free energy state its average energy is also lower there.

So more chances of it going there and less chances of going there, so net is it is going there since what if we consider then the only thing we have to make an assumption that this A and BC is all the time in thermal equilibrium. Once they are in thermal equilibrium my Maxwell Boltzmann statistics keep working keep telling me that there is a fraction which has energy greater than this and that complex is always there it is all the time available or it to split to go to the product side though it is a very small fraction we will see the but the small fraction it taking the reaction forward, right.

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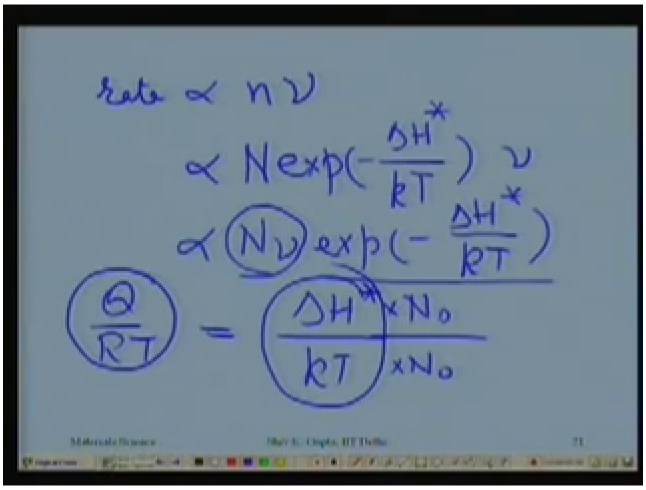

$$\text{rate} \propto n\nu$$
$$\propto N\exp\left(-\frac{\Delta H^*}{kT}\right)\nu$$
$$\propto (N\nu)\exp\left(-\frac{\Delta H^*}{kT}\right)$$
$$\frac{Q}{RT} = \frac{\Delta H^* \times N_0}{kT \times N_0}$$

So we can try to rationalise this with the help of this knowledge and say the rate is proportional to that is the species which have energy greater than Delta H star alright and once I have these species which are complex activated complex the oscillating and oscillating with the lattice vibration frequency, so the rate is the vibration frequency because in one oscillation can either go to the product side or it can go back, so it is only that rate at which it is going on.

The fraction which have energy greater than equal to Delta H star we know from the Maxwell Boltzmann statistics small n would be total number of species which I have times exponential of minus Delta H star by kT times new or we can write this as N times new exponential of… You can say that this with the proportionality constant will form the pre-exponential term what you saw that A in the Arrhenius relationship and this forms the exponential term the difference only is in their they have used Q by RT and here I have Delta H star by kT. Now if I multiply this numerator by N 0 the Avogadro's numbers and denominator also by N 0 the number remains the same at N 0 into k becomes R and Delta H star into N 0 becomes Q.

Why we normally do this is handling of numbers, Delta H star is in the range of one electron volt that means 1.6 10 to the power minus 19 joules but when I multiply this by Avogadro numbers it comes in the range of 6 kilojoules, it is in the range of kilojoules now and I call it kilojoules per mole, number becomes handy and it is not 10 to the power minus 19 which I have to work with and similarly in the denominator also is multiplied by this and k the Boltzmann constant becomes the gas constant, so this Q by RT what we use and the Delta H star by kT other same number they are not different, this will be coming in this course again and again that is what I said and you should aware of it. Well this was the use of Maxwell

Boltzmann statistics into rationalising Arrhenius relationship which we have studied and we shall see some more details (())(48:14) in solids than what we have done in…right?

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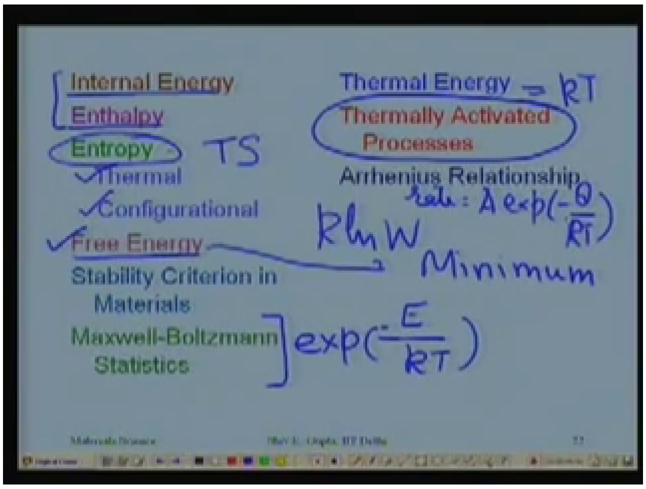

Internal Energy
Enthalpy
Entropy TS
Thermal
Configurational
Free Energy
Stability Criterion in Materials
Maxwell-Boltzmann Statistics $\exp(-\frac{E}{kT})$

Thermal Energy = kT
Thermally Activated Processes
Arrhenius Relationship
rate: $A\exp(-\frac{Q}{RT})$
$k\ln W$
Minimum

So what I have talked about so far is the extensive property like internal energy, extensive property like enthalpy for solids they are both same, not different. Then I talked about in solids the entropy, the 2 kinds one is thermal entropy another one is the configurational entropy, thermal entropy is what we have studied in school also and definition remains the same. Configurational entropy works only for the crystalline solids and not even for non-crystalline solids where there are no configurations. Again (())(49:24) entropy like thermal entropy they cannot be negative minimum value can be 0 because of the definition if you recall k log W.

The minimum value of W can be 1, alright it is a situation in an ordered (())(49:44) Then I can have only AB bonds absolutely audit solid no other bond, no AA no BB. A is surrounded by B, B is surrounded by… it is an (())(49:55) is only one arrangement for such a configuration, the configuration entropy is 0, okay. So that is about the entropy which also give rise to the bound energy in the system. This energy is bound to the system not available so that has to be subtracted from the energy available internal energy enthalpy, the total energy once it is subtracted I get the free energy and free energy is the one which we use as a criterion for stability and it should be a minimum and a minimum and free energy is the criterion for stability. Then we also talked about the Maxwell Boltzmann statistics which gives us the probability of any species having energy greater than or equal to E or for that matter a fraction of species having energy greater than or equal to E in a given ensemble where I have large number of this is exponential minus E by KT.

Then we have also talked about the thermal energy, average thermal energy in a crystalline solid as I said since the atom are oscillating about their mean position. For that matter even in the non-crystalline solid atoms do oscillate about their mean position and that is the average thermenergy is kT. You know I talked about certain processes for working of the kinetics the rate of a reaction where thermal energy is helping the process to go forward, in what way? It is the thermenergy is which is allowing a complex to form because during oscillations species are colliding changing their energy some energies are becoming higher and it is possible for an activation complex or activated complex to form and it is this which can split to form the product.

So such processes where thermal energy helps the processed go forward are called thermally activated processes, right? And then we saw the Arrhenius relationship where the rate is defined as some constant times exponential of minus Q by RT and it is for a thermally activated process because the way we have tried to explain this I need to form a thermally activated complex and therefore the thermal energy is helping the process and that is where is a rate for a thermally activated process, right. So with this we end this introduction on equilibrium and kinetics in the next class on we shall start with the crystal structures.