Non-Metallic Materials
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Module - 02
Defects, and reaction kinetics of non - metallic materials, carbonaceous materials
Lecture - 08
Laws of thermodynamics, reaction kinetics

Welcome to the lecture of Non-Metallic Materials. We are in module 2, Defects and reaction kinetics of non-metallic material and today, I will be covering the thermodynamic aspect of non non-metallic materials.

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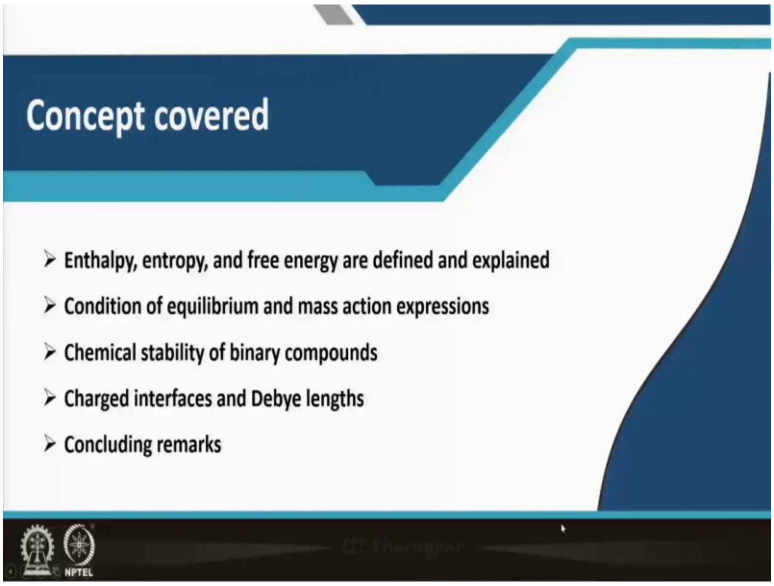

Concept covered

- Enthalpy, entropy, and free energy are defined and explained
- Condition of equilibrium and mass action expressions
- Chemical stability of binary compounds
- Charged interfaces and Debye lengths
- Concluding remarks

Now, the concept that I will cover probably this is known to you; you have heard this terminology; enthalpy, entropy, free energy. But it is redefined and it is explained in view to its correlation with the non-metallic materials. Next, I will cover the condition of equilibrium and mass action, mass action expressions, how to write it.

A part of it, you have seen the defect, whenever I taught the defect part of another lecture, in this particular module, you have seen it that how to write this mass action expression; but it will be more clarified. In fact, the all concept whatever I taught in defect, you will find it useful if you know this particular lecture. Then, we will take up the chemical stability of the binary compound.

When the compound is stable, then I will introduce the concept of the charge interface which is so important for ceramic material when you are talking about the flocculation or de-flocculation, the slip casting; these are important methodology for preparation of ceramic material which I will be covering later part of the course; and some important conclusion highlighting the salient features of the thermodynamical concept which is important for non-metallic materials that I will introduce.

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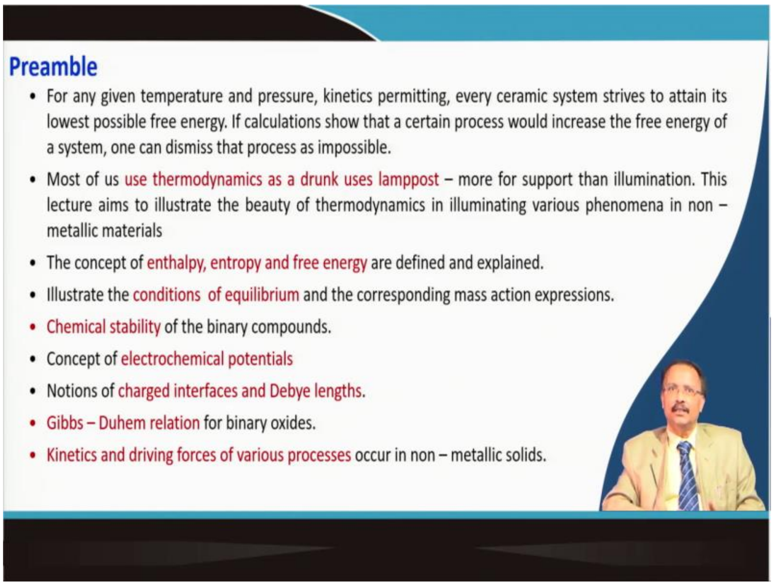

Preamble

- For any given temperature and pressure, kinetics permitting, every ceramic system strives to attain its lowest possible free energy. If calculations show that a certain process would increase the free energy of a system, one can dismiss that process as impossible.
- Most of us use thermodynamics as a drunk uses lamppost – more for support than illumination. This lecture aims to illustrate the beauty of thermodynamics in illuminating various phenomena in non – metallic materials
- The concept of enthalpy, entropy and free energy are defined and explained.
- Illustrate the conditions of equilibrium and the corresponding mass action expressions.
- Chemical stability of the binary compounds.
- Concept of electrochemical potentials
- Notions of charged interfaces and Debye lengths.
- Gibbs – Duhem relation for binary oxides.
- Kinetics and driving forces of various processes occur in non – metallic solids.

So, as I said that for any given temperature and pressure, the kinetic permitting every ceramic system to attain its lowest possible free energy. So, in a blunt way, if we calculate and if we find that the free energy of a system increases; then, we will discard that this is utterly impossible. This reaction will not take place.

But when it reduces, then we will find that it is thermodynamically reasonable. So, usually thermodynamic we read and this is a nice explanation that is given in the book by Barsoum, that it is we use thermodynamics just the drunk people, they use a lamp post. It is more than a support than to get illumination.

So, it is just to support something, we use thermodynamics. But this lecture, I am trying to illuminate the application of thermodynamics in understanding various material science related problem. So, in that respect, it is important to relook the enthalpy, entropy, free energy calculation, the definition and the condition of the equilibrium that should be highlighted and mass action, reaction, expressions you should be comfortable in writing.

Then, you should know about the chemical stability and as I mentioned that the charge surface, Debye length, Zeta potential, this concept should be clarified and for binary oxide, we will define the Gibbs - Duhem relation that what is the relativity, I mean you must have heard in your second year course or in third year in undergraduate curriculum, it is taught. And finally, the kinetics and driving forces of various selective process in non-metallic solids, that I will explain that how thermodynamics plays a major role.

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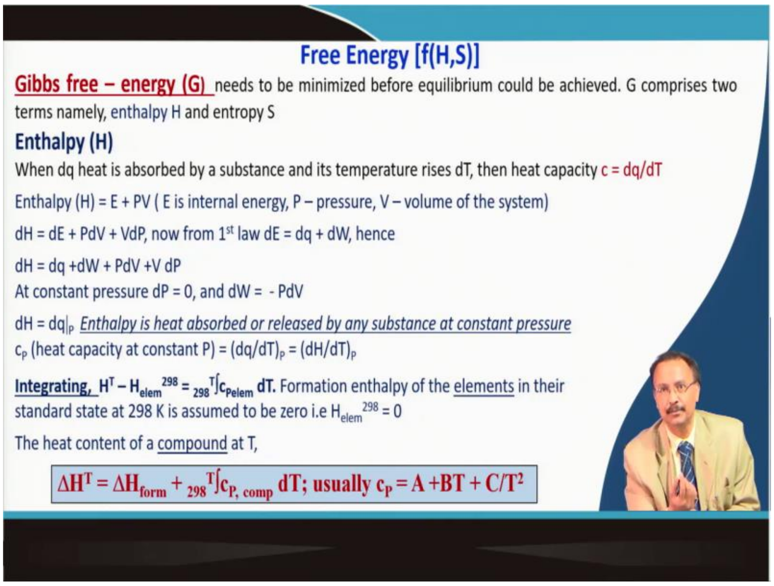

Free Energy [f(H,S)]

Gibbs free – energy (G) needs to be minimized before equilibrium could be achieved. G comprises two terms namely, enthalpy H and entropy S

Enthalpy (H)

When dq heat is absorbed by a substance and its temperature rises dT, then heat capacity c = dq/dT

Enthalpy (H) = E + PV (E is internal energy, P – pressure, V – volume of the system)

dH = dE + PdV + VdP, now from 1st law dE = dq + dW, hence

dH = dq +dW + PdV +V dP

At constant pressure dP = 0, and dW = - PdV

$dH = dq|_P$ *Enthalpy is heat absorbed or released by any substance at constant pressure*

c_P (heat capacity at constant P) = $(dq/dT)_P = (dH/dT)_P$

Integrating, $H^T - H_{elem}^{298} = {}_{298}\int^{T} c_{Pelem}\, dT$. Formation enthalpy of the elements in their standard state at 298 K is assumed to be zero i.e $H_{elem}^{298} = 0$

The heat content of a compound at T,

$$\boxed{\Delta H^T = \Delta H_{form} + {}_{298}\int^{T} c_{P,\,comp}\, dT;\ \text{usually } c_P = A + BT + C/T^2}$$

Now, the first starting point is Gibbs free-energy. This needs to be minimized before equilibrium is reached. So, this G that comprises two term; one is enthalpy which is denoted by H and another one is entropy. Now, if you just select this enthalpy, when a heat dq is absorbed by a substance and its temperature is raised by dT from its initial temperature, then the heat capacity you know that is dq by dT and enthalpy, it is having two component; one is internal energy E and pressure and volume of the system.

So, if you just differentiate it, then dH = dE + PdV + VdP right? Now, from the First law, you know that change in internal energy is change the heat content dq and the work done dW. So, you put it back, you get the expression dH = dq + dW + PdV + V dP. Now, if you consider the pressure remains constant, it is the reaction is happening at constant pressure. So, P is equal to constant. So, your dP = 0 and we know that the work done is nothing but - PdV.

So, just replace this in the equation, you get at constant pressure, enthalpy change is equal to your heat absorbed or released by any substance at constant pressure. So, I have defined this and we end up this relation and finally, if you take the derivative of this enthalpy at constant pressure, that is equal to dq/dT at constant pressure and which is nothing but heat capacity right?

So, if you integrate this relation, then for a elemental solid, you get enthalpy at a temperature T and the element enthalpy which actually it is 0 at a temperature which is room temperature, close to room temperature. Now, if it is a compound, then this is nothing but formation enthalpy. So, it goes to the other site and you can calculate the enthalpy at a particular temperature; change in enthalpy at a particular temperature.

A formation enthalpy and integration from room temperature up to that particular temperature, T C P of that compound the specific heat at constant pressure and dT. Usually, c_p this is having a relation something like A + BT + C/T^2. This is A, B, C, they are constant and accordingly, this enthalpy you can calculate back. So, I will try to set up certain problem so that these ideas are clarified.

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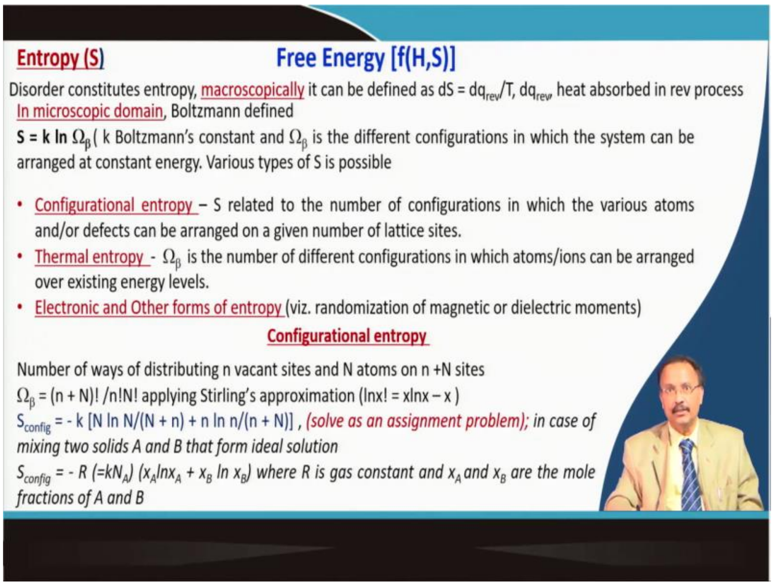

Entropy (S) **Free Energy [f(H,S)]**

Disorder constitutes entropy, macroscopically it can be defined as $dS = dq_{rev}/T$, dq_{rev}, heat absorbed in rev process

In microscopic domain, Boltzmann defined

$S = k \ln \Omega_\beta$ (k Boltzmann's constant and Ω_β is the different configurations in which the system can be arranged at constant energy. Various types of S is possible

- Configurational entropy – S related to the number of configurations in which the various atoms and/or defects can be arranged on a given number of lattice sites.
- Thermal entropy - Ω_β is the number of different configurations in which atoms/ions can be arranged over existing energy levels.
- Electronic and Other forms of entropy (viz. randomization of magnetic or dielectric moments)

Configurational entropy

Number of ways of distributing n vacant sites and N atoms on n +N sites

$\Omega_\beta = (n + N)! / n!N!$ applying Stirling's approximation ($\ln x! = x\ln x - x$)

$S_{config} = - k [N \ln N/(N + n) + n \ln n/(n + N)]$, *(solve as an assignment problem); in case of mixing two solids A and B that form ideal solution*

$S_{config} = - R (=kN_A) (x_A \ln x_A + x_B \ln x_B)$ *where R is gas constant and x_A and x_B are the mole fractions of A and B*

Now, you come to the topic which is entropy. Now, you have seen that when I talked about defect, we talked about configurational entropy, we talked about thermal entropy. So, there are various types of entropy and we found the relation of putting a one cation and defect, how you can arrange it in terms of configurational entropy or in terms of thermal entropy.

Now, exactly let us have a better view on the basic concept of those entropy. So, entropy basically this denotes the disorder; disorder of the system and macroscopically if you see, you can define this as dq in a reversible process by T. So, dq is the heat absorbed in a reversible process and in the microscopic domain, it was Boltzmann, who defined that this entropy is related to Boltzmann constant and the term which is Ω_β.

So, Ω_β is the different configuration in which the system can be arranged at constant energy. Various types of entropy is possible; the first one is configurational entropy, where this entropy is related to number of configuration in which various atoms or defects like point defects can be arranged in a given number of lattice.

Second one is the thermal entropy, so this is a number of different configuration in which atom and ions can be arranged over the energy levels right. So, that is thermal entropy or you can have electronic entropy. Electron also can go from valence band to conduction band, when sufficient energy you put in terms of kT and depending on what type of band gap it is having; for ceramic, the band gap is quite large; but as you know that when you introduce the defect inside, then there are defect levels also inside the band gap.

So, that electronic entropy is also there and there are other forms of entropy which is related to the ordering of either magnetization or the dielectric moment, in case of ferroelectric material. I will talk about it, this type of material in my forthcoming lectures. So, this is also other form of entropy. So, if you start with configurational entropy, number of ways you can distribute in vacant site and N atom. So, total there are n plus N; small n plus capital N, these many sites.

Then, this Ω_β, you can define as factorial of n plus capital N divided by small n factorial into capital N factorial. So, this is the way number of way you can actually distribute in vacant site in n number of N vacant site as well as n number of atom in total n plus N sites. So, one can put starling approximation in it which tells that $\ln x! = x \ln x - x$

So, you can just work it out to get the configurational entropy. Configurational entropies is still this formula k into ln of this. So, now if you take ln here, then you can just work it out as an assignment problem I will set. So, ln in n plus ln of the x part that is n plus N. So, you work it out, you will come up with this relation and which I have used, when I talked about defect in the earlier lecture.

Now, this is something similar when two A and B, two solids are mixed to form a solid solution kind of thing and see here, in this case you have something similar this type of relation, where k is replaced by the gas constant R which is nothing but Boltzmann constant into Avogadro number and then, you have the phase fraction of a ln of x A and phase fraction of B, in that in the solution solid solution in ln of x B.

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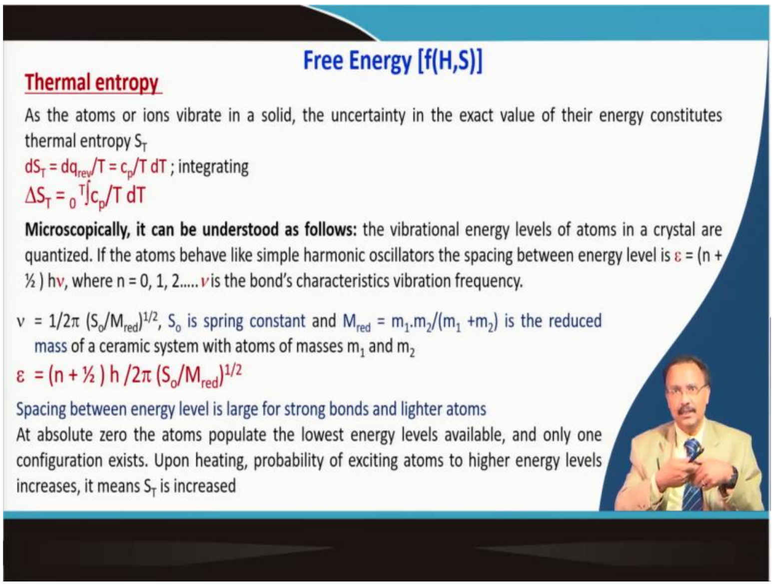

Free Energy [f(H,S)]

Thermal entropy

As the atoms or ions vibrate in a solid, the uncertainty in the exact value of their energy constitutes thermal entropy S_T

$dS_T = dq_{rev}/T = c_p/T\, dT$; integrating

$\Delta S_T = {}_0\int^T c_p/T\, dT$

Microscopically, it can be understood as follows: the vibrational energy levels of atoms in a crystal are quantized. If the atoms behave like simple harmonic oscillators the spacing between energy level is $\varepsilon = (n + ½)\, h\nu$, where n = 0, 1, 2….. ν is the bond's characteristics vibration frequency.

$\nu = 1/2\pi\, (S_o/M_{red})^{1/2}$, S_o is spring constant and $M_{red} = m_1.m_2/(m_1 + m_2)$ is the reduced mass of a ceramic system with atoms of masses m_1 and m_2

$\varepsilon = (n + ½)\, h/2\pi\, (S_o/M_{red})^{1/2}$

Spacing between energy level is large for strong bonds and lighter atoms

At absolute zero the atoms populate the lowest energy levels available, and only one configuration exists. Upon heating, probability of exciting atoms to higher energy levels increases, it means S_T is increased

So, this is something similar related as far as the configuration entropy is concerned. Then, let us talk about the thermal entropy and as these atoms vibrate in a solid, its uncertainty is there about its energy which constitute the thermal entropy. So, thermal entropy can be defined by dq reversible process by T which is C P by T dT. And then, you integrate it, you get this thermal entropy from 0 to T C P by T into dT.

So, if you microscopically try to understand it, the vibrational energy of the atoms in a crystal, they are basically quantized and the atom behave like a simple harmonic oscillator. The spacing between this energy level that is denoted by epsilon which is n plus half into h nu; h is the Planck's constant and nu is the frequency right.

So, it can have the value of 0, 1, 2 etcetera the value of n and the frequency is the bond characteristics, the vibration frequency. So, now, this vibrational frequency, this υ, this is nothing but 1 by 2π into spring constant divided by reduced mass of these two component. So, you have a solid which constitute m and m 1 and m 2. So, this reduced mass is m 1 into m 2 divided by m 1 plus m 2.

So, that reduce mass and the whole thing is under root over. So, you replace this relation here which is epsilon the spacing, spacing of the energy level this is n plus half into you replace the new term here hυ. So, h will remain there divided by 2 pi into this. So, that equation tells you that the spacing of the energy level is large for strong bond because the spring constant is high, the bond strength is high; so, then the spacing is high and lighter atoms.

So, your m_{red}, this one is for constitutes lighter atom. Then, of course, this spacing is also large because the denominator is reducing. At absolute zero all the atoms populate in the lower energy level, and only the one configuration exist; but when you heat it, the probability of exciting of atom to higher energy level increases; that means, your thermal entropy that also is increased.

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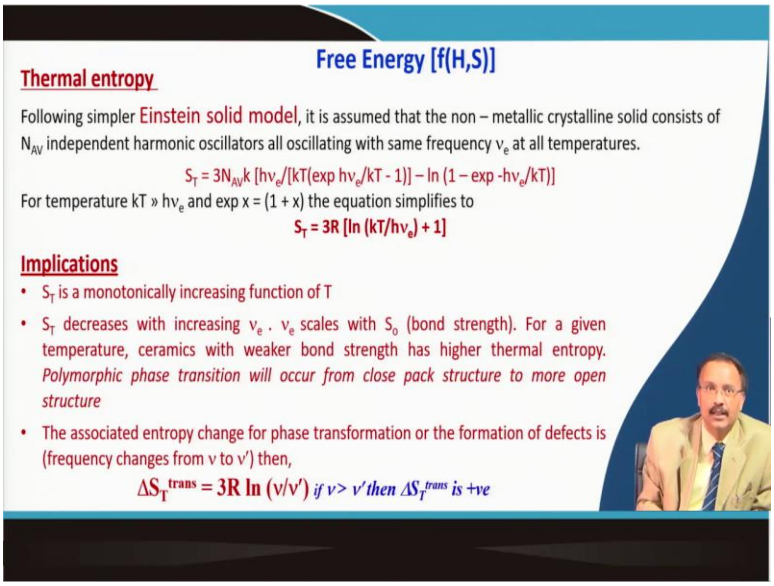

Free Energy [f(H,S)]

Thermal entropy

Following simpler Einstein solid model, it is assumed that the non – metallic crystalline solid consists of N_{AV} independent harmonic oscillators all oscillating with same frequency ν_e at all temperatures.

$$S_T = 3N_{AV}k\,[h\nu_e/[kT(\exp h\nu_e/kT - 1)] - \ln(1 - \exp -h\nu_e/kT)]$$

For temperature kT » $h\nu_e$ and exp x = (1 + x) the equation simplifies to

$$S_T = 3R\,[\ln(kT/h\nu_e) + 1]$$

Implications

- S_T is a monotonically increasing function of T
- S_T decreases with increasing ν_e . ν_e scales with S_0 (bond strength). For a given temperature, ceramics with weaker bond strength has higher thermal entropy. *Polymorphic phase transition will occur from close pack structure to more open structure*
- The associated entropy change for phase transformation or the formation of defects is (frequency changes from ν to ν′) then,

$$\Delta S_T^{trans} = 3R\ln(\nu/\nu') \text{ if } \nu > \nu' \text{ then } \Delta S_T^{trans} \text{ is +ve}$$

So, Einstein, he told that this non metallic many of the non-metallic crystalline solids, they have a independent harmonic oscillator and all oscillates in the same frequency. So, this frequency, I have taken at nu e at all temperatures and came up with this relation and this relation, I can simplify because the k T is usually much larger.

This is the energy term, this is also hυ is energy term, its much larger and we know that exponential of x is 1 by x from the series. Then, we come up with this relation that the thermal entropy is 3 into R which is R is the gas constant and it depends on the single type of frequency plus 1.

So, what is the implication for this? That this thermal entropy monotonically increases, when you increase the temperature and it decreases, when the frequency is increased. So, you know that the frequency will increase, when the bond strength is low. So, then it has more chance to vibrate. So, it scales with the bond strength.

So, for a given temperature, ceramic which is having weaker bond strength, has thermal higher thermal entropy and therefore, in polymorphic phase transformation, it occurs from a closed pack structure to more open structure. So, that is the reason. So, if the associated entropy changes for the phase transformation, then the frequency also start to change.

And then, this equation, one can write that the change in entropy is simplified like this 3 R into ln of two different frequency will be there; one before phase transformation, other phase transformation. So, when this frequency is more than the next one nu dash, then this thermal entropy is positive factor.

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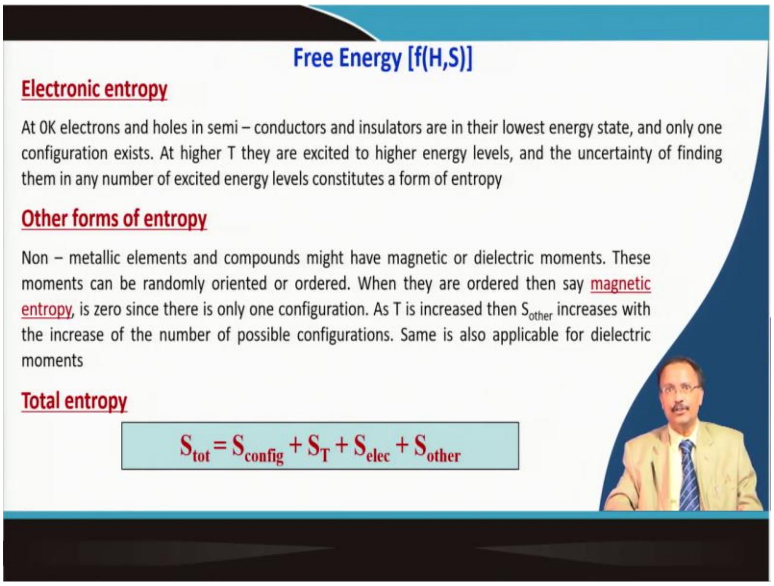

Free Energy [f(H,S)]

Electronic entropy

At 0K electrons and holes in semi – conductors and insulators are in their lowest energy state, and only one configuration exists. At higher T they are excited to higher energy levels, and the uncertainty of finding them in any number of excited energy levels constitutes a form of entropy

Other forms of entropy

Non – metallic elements and compounds might have magnetic or dielectric moments. These moments can be randomly oriented or ordered. When they are ordered then say magnetic entropy, is zero since there is only one configuration. As T is increased then S_{other} increases with the increase of the number of possible configurations. Same is also applicable for dielectric moments

Total entropy

$$S_{tot} = S_{config} + S_T + S_{elec} + S_{other}$$

Now, electronic entropy as I told at zero degree Kelvin, electrons and holes in semiconducting material and ceramic or oxide material can be considered as a wide band gap semiconductor. They are all at a lowest energy state and only one type of configuration exist.

But once you increase the temperature, they are excited to higher energy level and the uncertainty improves I mean increases to find a particular electron in the excited state. Other form of energy is the magnetic entropy or dielectric material, they are ordering and disordering of either the electron spin or the cation in case of ferroelectric material.

So, that the material of non-metallic material which is having magnetic or dielectric moment, they are the other form of energy is also equally other form of entropy is also equally important and the total entropy, then you can find as configurational plus thermal plus electronic and this other type of entropy. So, that all constitute this kind of configurational entropy.

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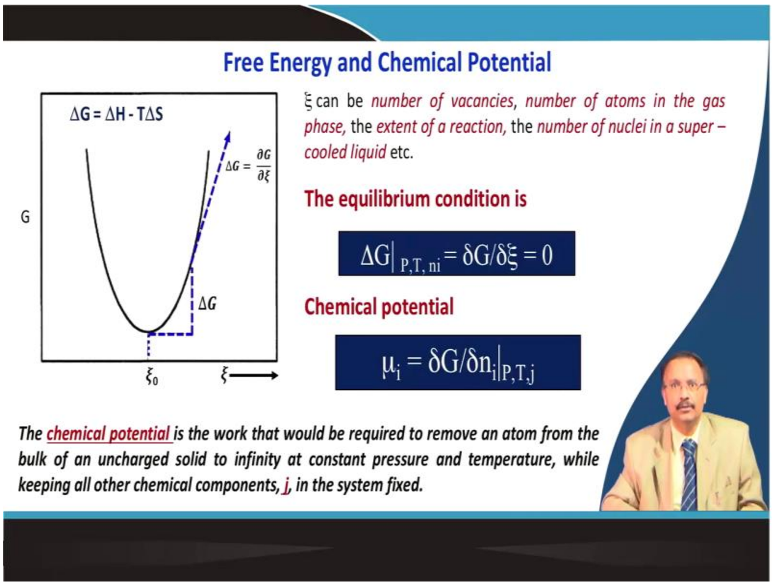

Free Energy and Chemical Potential

ξ can be *number of vacancies, number of atoms in the gas phase,* the *extent of a reaction,* the *number of nuclei in a super–cooled liquid* etc.

The equilibrium condition is

$$\Delta G|_{P,T,ni} = \delta G/\delta \xi = 0$$

Chemical potential

$$\mu_i = \delta G/\delta n_i|_{P,T,j}$$

The chemical potential is the work that would be required to remove an atom from the bulk of an uncharged solid to infinity at constant pressure and temperature, while keeping all other chemical components, j, in the system fixed.

Now, here you know that if I plot the free energy as a variable, now this variable can be number of vacancies, number of atoms in the gas phase or the extent of a particular reaction or the number of nuclei that is formed in a super cool liquid like in glass ceramics, when I will teach, then you will see that the formation of nuclei from a super cooled liquid it forms.

So, this ξ is that parameter and which is plotted with the free energy and in the equilibrium condition, you know that the slope of this ΔG which is partial differentiation of G with the ξ parameter. This is flat slope 0. So, the equilibrium condition when this ΔG which is this slope, δG/δξ, this one is 0. And this is of course, at a constant pressure and temperature and also, for number of species in that.

So, these are constant. So, when this is 0, then this one is the in the equilibrium state. So, I can define now the chemical potential which is $\delta G/\delta n_i$ at constant pressure temperature and the number of chemical components. So, this is can be defined as the chemical potential.

So, physically, it is the work that will be required to remove an atom from the bulk of an uncharged solid, electrically neutral solid to infinity at constant pressure and temperatures; P, T is constant and all other chemical components j in the system when it is fixed.

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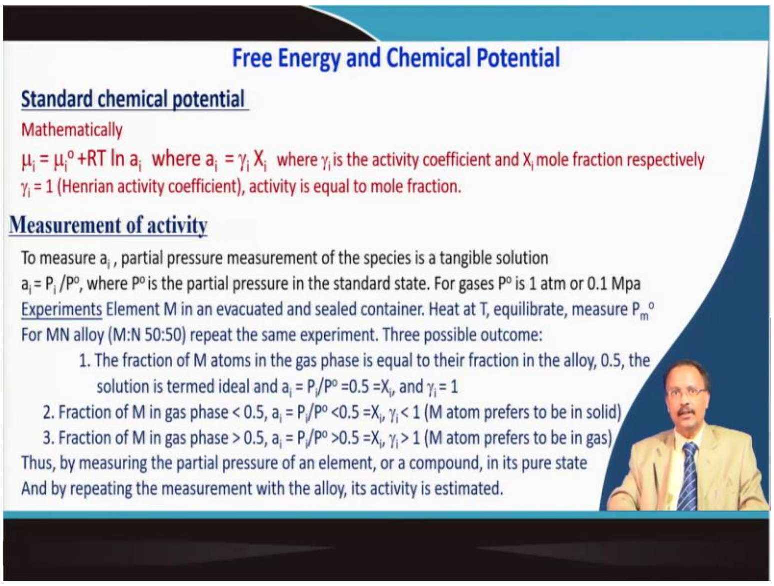

Free Energy and Chemical Potential

Standard chemical potential

Mathematically

$\mu_i = \mu_i^o + RT \ln a_i$ where $a_i = \gamma_i X_i$ where γ_i is the activity coefficient and X_i mole fraction respectively

$\gamma_i = 1$ (Henrian activity coefficient), activity is equal to mole fraction.

Measurement of activity

To measure a_i, partial pressure measurement of the species is a tangible solution

$a_i = P_i / P^o$, where P^o is the partial pressure in the standard state. For gases P^o is 1 atm or 0.1 Mpa

Experiments Element M in an evacuated and sealed container. Heat at T, equilibrate, measure P_m^o

For MN alloy (M:N 50:50) repeat the same experiment. Three possible outcome:

1. The fraction of M atoms in the gas phase is equal to their fraction in the alloy, 0.5, the solution is termed ideal and $a_i = P_i/P^o = 0.5 = X_i$, and $\gamma_i = 1$
2. Fraction of M in gas phase < 0.5, $a_i = P_i/P^o < 0.5 = X_i$, $\gamma_i < 1$ (M atom prefers to be in solid)
3. Fraction of M in gas phase > 0.5, $a_i = P_i/P^o > 0.5 = X_i$, $\gamma_i > 1$ (M atom prefers to be in gas)

Thus, by measuring the partial pressure of an element, or a compound, in its pure state

And by repeating the measurement with the alloy, its activity is estimated.

Now, if you mathematically see the chemical potential that is defined as chemical potential at a standard state plus RT gas constant and temperature and ln of activity, activity which is also defined as activity coefficient which is defined by γ_i and the mole fraction of the component that is present in the system. So, this γ_i, this is usually 1 and activity is equal to mole fraction.

So, if this value the Henrian activity, if it is 1; then, this activity sorry gamma 1 gamma i is 1, then activity is equal to the mole fraction. Now, we will have to measure the activity. What exactly, how you can measure it? So, usually to measure the activity, we measure the partial pressure of the species and this is one of the tangible solution; otherwise measurement of activity is problematic.

So, this activity can be defined as at a particular system condition if it is P i with respect to the partial pressure in standard state. So, that is actually the activity. For gas phase, you can consider that P 0 term is 1 atmosphere or about 0.1 mega Pascal. Now, the experiment that is done to estimate this partial pressure is that you take a chamber and evacuate it and put a single element M inside it, seal the container and heat it and just wait till it equilibrate and measure the partial pressure.

So, that partial pressure of the material M that is a standard one that is measured. Then, you form an alloy which is MN and say the composition of the alloy this is 50 - 50; so, if you take that alloy and repeat the same experiment. So, there are three possible outcome that you can have; 1st one, the mole fraction of M atom in the gas phase equal to the fraction in the alloy; so, which is 0.5.

So, if that is the case, then your activity as I defined P i by P 0 that is 0.5 which is equal to the mole fraction because gamma is 1; the Henrian activity coefficient is 1. So, this is one solution. 2nd one, M in the gas phase that will be less than 0.5; so, in that case, activity will be partial pressure divided by partial pressure in standard condition which is the mole fraction along with gamma i will be less than 1.

So, in that case, the M atom will prefer to be in the solid; it will not go into the vapor phase. With temperature, it is having a high boiling solid. And 3rd one is that in this metal will go out from this alloy to the vapor phase. So, the partial vapor pressure is high. So, P i by P 0 is more than 0.5. So, M atom prefers to be in the gas phase. So, if you measure the partial pressure of the element or a compound in pure state and repeat this measurement with an alloy, then you can measure the activity.

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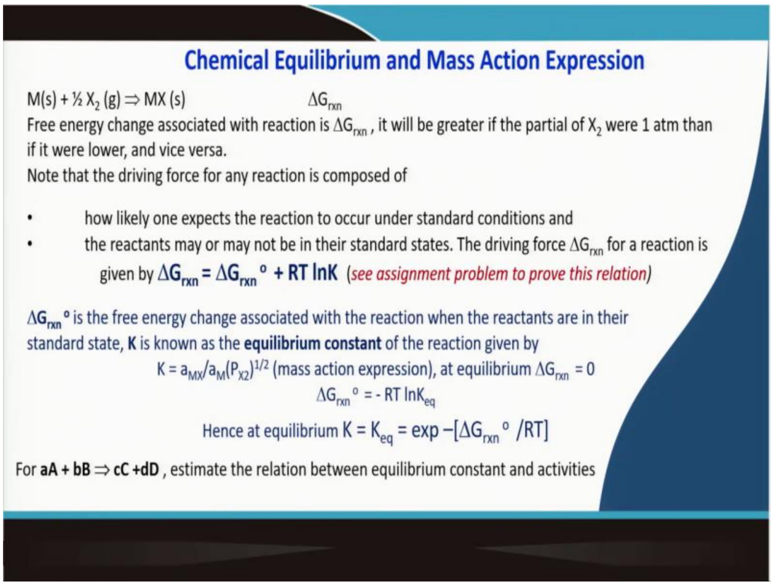

Chemical Equilibrium and Mass Action Expression

$M(s) + \frac{1}{2} X_2\,(g) \Rightarrow MX\,(s)$ ΔG_{rxn}

Free energy change associated with reaction is ΔG_{rxn} , it will be greater if the partial of X_2 were 1 atm than if it were lower, and vice versa.

Note that the driving force for any reaction is composed of

- how likely one expects the reaction to occur under standard conditions and
- the reactants may or may not be in their standard states. The driving force ΔG_{rxn} for a reaction is given by $\Delta G_{rxn} = \Delta G_{rxn}^{\circ} + RT \ln K$ (*see assignment problem to prove this relation*)

ΔG_{rxn}° is the free energy change associated with the reaction when the reactants are in their standard state, **K** is known as the **equilibrium constant** of the reaction given by

$K = a_{MX}/a_M(P_{X2})^{1/2}$ (mass action expression), at equilibrium $\Delta G_{rxn} = 0$

$\Delta G_{rxn}^{\circ} = - RT \ln K_{eq}$

Hence at equilibrium $K = K_{eq} = \exp -[\Delta G_{rxn}^{\circ} /RT]$

For **aA + bB ⇒ cC +dD** , estimate the relation between equilibrium constant and activities

Now, let us talk about the chemical equilibrium and how it is related to the mass action expression. So, you consider that this is the typical one typical reaction, where a solid which is M, it is reacting with a gaseous phase to form a compound like MX right. So, this is an equation. And you can define the free energy change which is associated with this is del G rxn. So, of course, it will be greater if the partial pressure of the gas phase were 1 atmosphere, then if it were lower. So, it will depend on that and also vice versa when one is less than 1 atmosphere.

So, the driving force for this reaction is composed of two kind of parameter. The first one how likely one expect the reaction to occur under standard condition that is zero state and the reactant may or may not be in the standard set. So, then in that case the driving force, the free energy change of the reaction is given by this relation. So, again, we will prove it as part of the assignment problem.

The del G rxn is the standard one plus RT ln of K. Now, this is the free energy change associated with the reaction, when all the reactants are in their standard state and K is known as the equilibrium constant. So, from the mass action expression, you can write that this is the activity of the product divided by activity of the reactants.

So, this is the relation. So, this is called mass action relation. Now, at equilibrium, this del G rxn is 0 that we already I have shown. Now, if this is 0, then actually del G rxn 0 that is nothing but minus RT lnK. Now, this K is K equilibrium. So, from this relation, you can actually calculate K equilibrium that is exponential of minus del G rxn 0 by RT.

So, I leave it to you, to for a general reaction of any ceramic system. Estimate this relation between the equilibrium constant and its activity. I will stop today and we will continue the topic in my next part of this lecture.

(Refer Slide Time: 28:06)

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Thank you so much for your attention.