Hydrogen Energy: Production, Storage, Transportation and Safety

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Lecture - 47

Fundamentals of Metal hydrides for Solid State Hydrogen Storage Part – 1

In the previous class we have studied metal hydrides which is a special class of solid state hydrogen storage materials and we will study few more fundamental aspects of metal hydrides this is an important class of solid state hydrogen storage materials because of several advantages. Like they can offer a safe method of hydrogen storage with a very high volumetric energy density and at the same time reversibility can be ensured.

Now, in this particular class of material which is metal hydrides, they have wide variety of applications and their hydrogen storage characteristics can be tuned or tailored. For example, these metal hydrides can be used for thermal energy storage or hydrogen compression or hydrogen purification and a wide variety of stationary application. For example, if it is to be used for hydrogen compression then there are metal hydrides available which operates at a higher hydrogen pressure.

At the same time when it is to be used for thermal energy storage applications in that case there are metal hydrides which operate at a higher operating temperature and for stationary applications if the requirement is of optimum conditions of temperature and pressures, then there are metal hydrides which operate in these range like close to ambient conditions ambient temperature or close to ambient pressure. At the same time their properties can be tailored or tuned that also we will see.

Towards the end of this section on metal hydride, we will also learn how to design systems which store these metal hydrides. So, the hydrogen storage systems design we will also see and we will see that these are different from the systems that we have studied earlier for compressed state like the tanks the vessels which used to store compressed hydrogen which used to store at very high pressures and these are also different from those which were designed for liquid state storage like the super insulated vessels which could store at 20 K

So, the design in terms of these metal hydride based materials is very different. So, that also we will learn. Now when we see these metal hydrides usually the metals they combine with hydrogen directly to form metal hydride.

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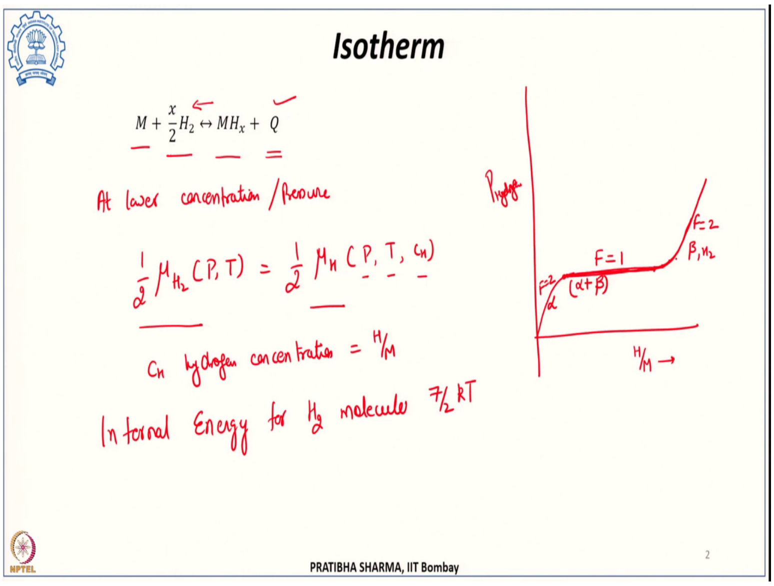

Isotherm

$$M + \frac{x}{2}H_2 \leftrightarrow MH_x + Q$$

At lower concentration / Pressure

$$\frac{1}{2}\mu_{H_2}(P,T) = \frac{1}{2}\mu_H(P,T,C_H)$$

C_H hydrogen concentration = H/M

Internal Energy for H_2 molecule 7/2 RT

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So, if we see this reaction the hydride forming metal it reacts with hydrogen to form metal hydride in the forward direction. So, in the forward direction this Q, is the heat of formation or the enthalpy of formation.

So, in the forward direction when metal reacts with hydrogen to form metal hydride Q amount of heat is being released. So, the forward reaction is an exothermic reaction that is the hydrogen uptake process while the reverse reaction when we want release of hydrogen from metal hydride then in the reverse reaction metal hydride decomposes to give metal and hydrogen and that much amount of Q needs to be supplied. So; that means, it is an endothermic reaction.

For this reaction the thermodynamic aspects of the reaction can be considered by drawing the pressure composition isotherm where the pressure of hydrogen if it is plotted with hydrogen concentration it could be H/M in that case we can see that there are different regions in the curve and these regions are initially there is a low pressure region or at lower concentration of hydrogen or lower pressure what happens is hydrogen enters into the host lattice, metal lattice and that gets randomly arranged into the host lattice.

And the concentration that slowly varies in this case. So, that is a solid solution phase which is known as alpha phase which is being formed. Now in this alpha phase if we consider the thermodynamic equilibrium condition then the chemical equilibrium chemical potential can be written as where μ_{H2} this is the chemical potential for hydrogen molecule μ_H is the chemical potential for hydrogen atom into the host metal, P is the pressure operating pressure, T is the temperature and C_H is the concentration of hydrogen.

So, this is the hydrogen concentration and this is expressed as H/M where H/M is the number of hydrogen atoms divided by the number of metal atoms. So, this is how the concentration changes now when it is the low concentration region and in equilibria when this gas and this phase mu H they are in equilibrium the internal energy if we consider for hydrogen molecule then that is 7/2 kT.

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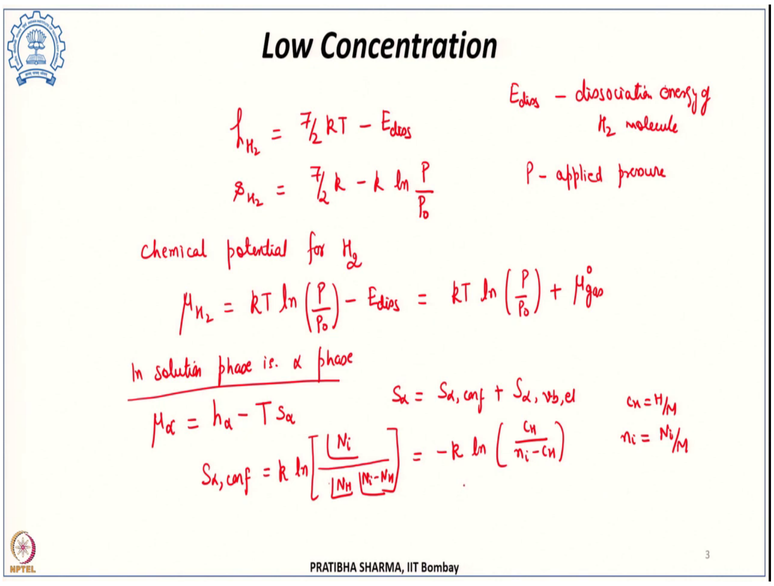

Low Concentration

$h_{H_2} = \frac{7}{2}kT - E_{diss}$

$s_{H_2} = \frac{7}{2}k - k\ln\frac{P}{P_0}$

E_{diss} – dissociation energy of H_2 molecule

P – applied pressure

Chemical potential for H_2

$\mu_{H_2} = kT\ln\left(\frac{P}{P_0}\right) - E_{diss} = kT\ln\left(\frac{P}{P_0}\right) + \mu^0_{gas}$

In solution phase i.e. α phase

$\mu_\alpha = h_\alpha - Ts_\alpha$

$S_\alpha = S_{\alpha,conf} + S_{\alpha,vib,el}$

$S_{\alpha,conf} = k\ln\left[\frac{\underline{\lfloor N_i}}{\underline{\lfloor N_H}\,\underline{\lfloor N_i - N_H}}\right] = -k\ln\left(\frac{c_H}{n_i - c_H}\right)$

$c_H = H/M$

$n_i = N_i/M$

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Now, the correspondingly the enthalpy and entropy if we note down then the enthalpy is 7/2 kT - the dissociation energy.

So, the $E_{dissociation}$ is the dissociation energy of hydrogen molecule into the hydrogen atom. Similarly, we can write the entropy for hydrogen gas and that can be written as 7/2k - k × ln(P/P_0). So, where P is the applied pressure. Now if we again write down the chemical potential for hydrogen gas for H_2 molecule then this is given as kTln(P/P_0) - the dissociation energy or we can also write it as kTln(P/P_0) + the standard hydrogen gas chemical potential.

Now, this is under low concentration of hydrogen or low pressure. Now in under these condition as the pressure rises the concentration of hydrogen into the metal matrix keep on rising this continues until a point where the hydrogen metal or the alpha phase starts to convert into beta phase.

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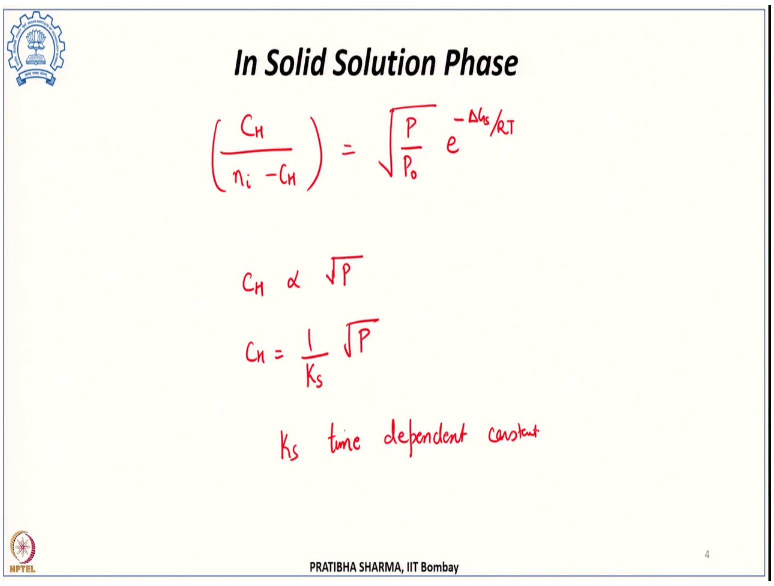

In Solid Solution Phase

$$\left(\frac{C_H}{n_i - C_H}\right) = \sqrt{\frac{P}{P_0}}\, e^{-\Delta G_s/RT}$$

$$C_H \propto \sqrt{P}$$

$$C_H = \frac{1}{K_s}\sqrt{P}$$

K_s time dependent constant

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So, if we go back to the previous figure at a point this alpha phase starts to convert into beta phase or the hydride phase starts to form.

In this region which is the flat region now both the phases coexist alpha and beta. We have also seen in the last class that in this flat plateau region since there are three phases a total of three phases alpha beta and the hydrogen and there are two components involved as such the number of degrees of freedom is one in this flat plateau region. So, that is at a higher concentration when the hydride phase starts to form.

Now, when this F = 1; that means, number of degrees of freedom is 1; that means, the concentration keeps on increasing at a constant pressure. So, the concentration is increasing in this plateau with a constant pressure. Now thereafter when this beta phase there is a saturation and now there is only beta phase which is existing and the alpha phase disappears. So, thereafter again the number of degrees of freedom are two in this region as in the alpha region.

What happens after this is, again there are two phases the beta phase and the hydrogen phase there are two phases and there are two components. So, the number of degrees of freedom is two in this third region and this corresponds to dissolution of hydrogen into the hydride phase or this is a solid solution phase of hydrogen into the hydride phase. So, that occurs in the third region. Now let us see in the solid solution phase which is the alpha phase, the chemical potential in the alpha phase is given by the enthalpy in the alpha phase minus T times the entropy in the alpha phase.

Now, this entropy in the alpha phase this is sum of two terms the first term is the configurational entropy and the second term is corresponding to the vibrational or electronic contributions. Now this configurational entropy this arises because there are interstitial sites onto which there are possible allocations of hydrogen atom. Let us say if there are Ni number of interstitial sites and if there are N_H number of atoms to be arranged in it in that case we can write this configurational entropy as kln(Ni factorial over NH factorial over Ni minus NH factorial).

Now, when since we are considering the low concentration case applying this condition of low concentration we can write this expression as we can apply the sterling approximation and we can write this as minus of $k \times \ln(C_H/n_i - C_H)$ where C_H is the hydrogen concentration, n_i is the number of interstitial sites per metal atom. So, C_H is nothing, but H/M and n_i is number of interstitial sites available per metal atom.

Now, again if we substitute that into the expression then we can get it as this expression as $C_H/(Ni – CH)$ and that is equal to under root of $(P/P_0)^{e-\Delta G/RT}$, where ΔG is Gibbs free energy over RT. Now this particular expression this shows that if we consider the low concentration region in that case the concentration is proportional to under root of P and that is what is the Sievert’s law.

The Sievert’s law states that the amount of the hydrogen being dissolved into the metal phase is proportional to the square root of the applied pressure. So, this is the expression of Sieverts law that is C_H the concentration of hydrogen is equal to $1/K_s$ under root of P where K_s is a time dependent constant and Sieverts law therefore, it relates the pressure.

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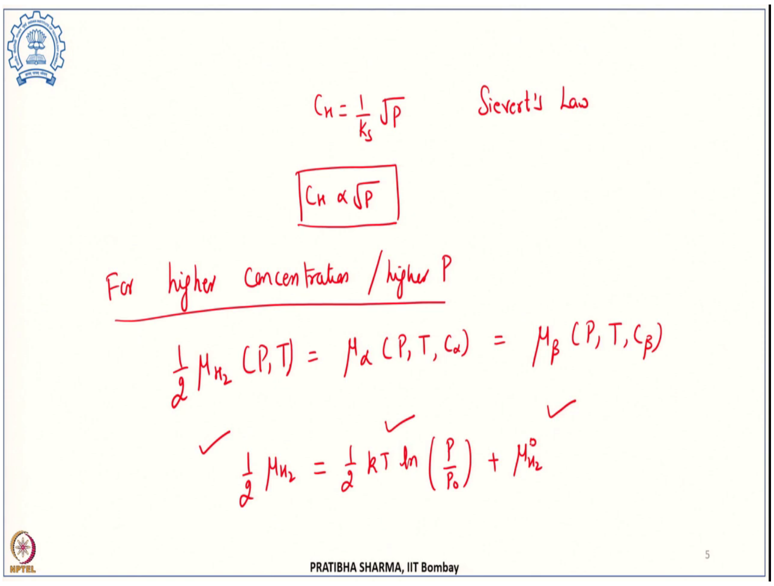

$C_H = \frac{1}{K_s}\sqrt{P}$ Sievert's Law

$$\boxed{C_H \propto \sqrt{P}}$$

For higher concentration / higher P

$$\frac{1}{2}\mu_{H_2}(P,T) = \mu_\alpha(P,T,C_\alpha) = \mu_\beta(P,T,C_\beta)$$

$$\checkmark\ \frac{1}{2}\mu_{H_2} = \overset{\checkmark}{\frac{1}{2}kT\ln\left(\frac{P}{P_0}\right)} + \overset{\checkmark}{\mu^0_{H_2}}$$

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So, 1/Ks root of P that is what is known as Sieverts law. So, under low concentration this is the relationship that is being followed of the concentration with the pressure. Now if we consider for higher pressure for higher concentration or for higher pressure; that means, when the hydride metal hydride formation takes place or beta phase formation takes place in that case there are three phases hydrogen, alpha and beta phase.

So, the chemical thermodynamic or the thermodynamic equilibrium suggest that the chemical potential of the hydrogen in the gaseous form is equal to the chemical potential of the alpha phase which is a function of pressure, temperature, the composition in the alpha phase and that is also equal to the chemical potential of the beta phase. So, the chemical potential of hydrogen, alpha and beta phase all the three coincides.

Now, this chemical potential of hydrogen in the gaseous phase that is equals to ½ (k T ln(P/P_0) that we have seen and plus the standard chemical potential of the hydrogen.

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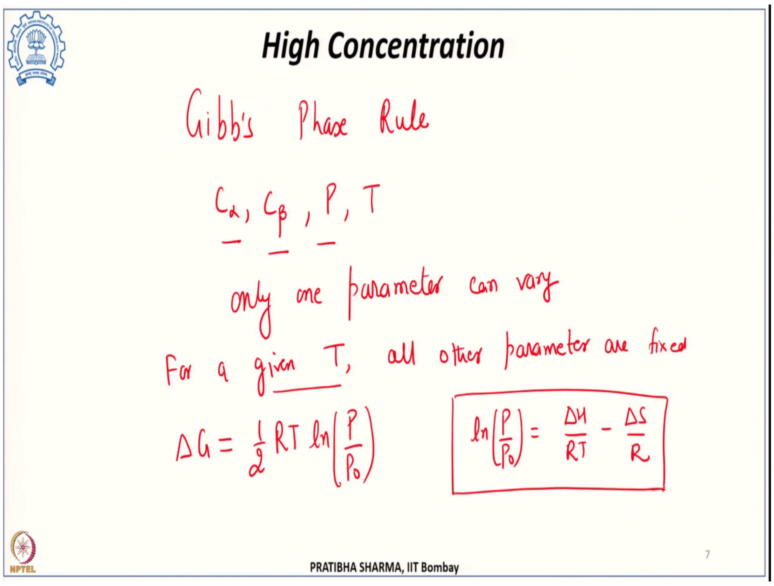

High Concentration

Gibb's Phase Rule

$\underline{C_\alpha}, \underline{C_\beta}, \underline{P}, T$

only one parameter can vary

For a $\underline{\text{given } T}$, all other parameter are fixed

$$\Delta G = \frac{1}{2} RT \ln\left(\frac{P}{P_0}\right)$$

$$\boxed{\ln\left(\frac{P}{P_0}\right) = \frac{\Delta H}{RT} - \frac{\Delta S}{R}}$$

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Now, using the Gibbs Phase rule if we apply the Gibbs Phase rule in this particular region then we know that from the Gibbs phase rule there is only one degree of freedom. So, out of the four variables the concentration in the alpha phase concentration in the beta phase, pressure and temperature only one parameter can vary only one of the parameter is allowed to vary.

So, what we do is in this case the variable here is taken as for a given temperature all the other parameters are fixed, other parameters are C of alpha, C of beta and the pressure in the two phase alpha plus beta phase or the flat plateau region on the all these parameters are fixed for a particular temperature. Now if we now write the chemical potential or Gibbs free energy for this high concentration region we can write it as $\Delta G = 1/2RT\ln(P/P_0)$.

Or this can also be written as $\ln(P/P_0) = \Delta H/RT - \Delta S/R$. Now this expression is known as Van't Hoff equation. So, $\ln(P/P_0) = \Delta H/RT - \Delta S/R$.

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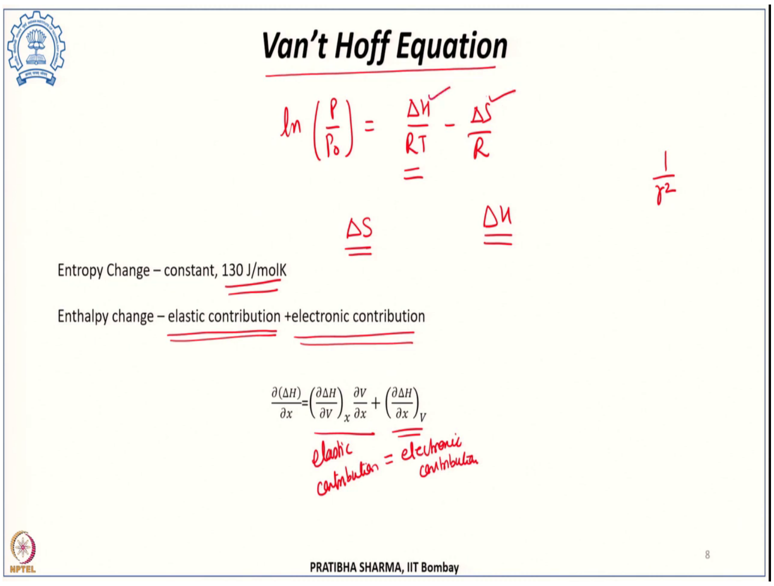

Van’t Hoff Equation

$$\ln\left(\frac{P}{P_0}\right) = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

$\frac{1}{r^2}$

ΔS ΔH

Entropy Change – constant, 130 J/molK

Enthalpy change – elastic contribution +electronic contribution

$$\frac{\partial(\Delta H)}{\partial x} = \left(\frac{\partial \Delta H}{\partial V}\right)_x \frac{\partial V}{\partial x} + \left(\frac{\partial \Delta H}{\partial x}\right)_V$$

elastic contribution = electronic contribution

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Now, this expression is known as the well-known Van’t Hoff of equation. Now here we see ΔS. Now this ΔS is the entropy change. Now this entropy change corresponds to the change in the entropy of hydrogen molecule which was earlier in the gaseous phase and now has got into or dissolved into the metal hydride phase or it enters into the hydride phase.

So, there is a loss of entropy of that hydrogen molecule and this remains constant. So, that for all the metal hydride system this remains constant its value is 130 joule per mole kelvin and this does not depend upon the nature of the metal. However, if we see the other term which is corresponding to ΔH. Now this ΔH or the enthalpy change has two contribution. Now what happens is, when it enters into host metal matrix there is a sort of repulsive forces that acts into the lattice because there is because of the incorporation of hydrogen there is a distortion of the lattice and that is experienced as a force which is exerted as a repulsive force.

Now, since this is a repulsive force that is acting as such what happens is the potential energy of the hydrogen in fact, decreases, but the energy of the lattice it increases and also there is a local distortion that will take place within the lattice. Now this local displacement field it falls as a $1/r^2$ value and its symmetry depends upon both the crystal symmetry as well as the symmetry of the atomic that hydrogen site.

Now, what happens is when a second hydrogen atom enters into that pre expanded lattice now what happened was like when hydrogen atom entered there was a distortion in the lattice there was a repulsive force that got applied and thus that resulted into expansion of the lattice.

Now in that pre expanded lattice if a second hydrogen enters into it the change in the second hydrogen potential energy will be less compared to if the first hydrogen would have been absent.

Now, as such what happens is the crystal energy it decreases. This decrease in the crystal energy is when two hydrogen atoms they come closer and this is further limited by there will be a repulsive interaction that will occur between the hydrogen atom till then it decreases. Because of that the heat of solution will decrease in proportion to the hydrogen concentration. So, that is the elastic contribution that arises in the enthalpy change. So, there is an elastic contribution the first term and then there is another contribution which is the electronic contribution.

Now, this electronic contribution this arises because of the all volume independent terms or effects. Now this comes into the material because the hydrogen atom which enters into the lattice comes with an extra electron. Now the several studies they have shown that this electronic contribution that has a very systematic variation with the group number and the correspondingly this is the second term which is the electronic contribution.

Also the first principal studies that have shown that these elastic contributions and the electronic contribution they are almost equal in magnitude. Now this ΔH since ΔS here is almost constant. So, ΔH is a very important factor in the Van't Hoff equation and that tells about several aspects like the stability of the metal hydride and we will see that plays a very important role in the design of metal hydride systems.

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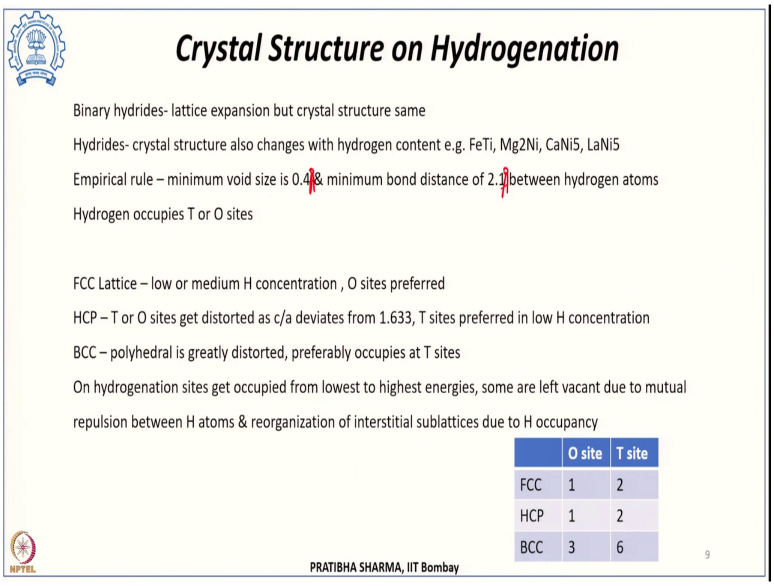

Crystal Structure on Hydrogenation

Binary hydrides- lattice expansion but crystal structure same

Hydrides- crystal structure also changes with hydrogen content e.g. FeTi, Mg2Ni, CaNi5, LaNi5

Empirical rule – minimum void size is 0.4Å & minimum bond distance of 2.1Å between hydrogen atoms

Hydrogen occupies T or O sites

FCC Lattice – low or medium H concentration , O sites preferred

HCP – T or O sites get distorted as c/a deviates from 1.633, T sites preferred in low H concentration

BCC – polyhedral is greatly distorted, preferably occupies at T sites

On hydrogenation sites get occupied from lowest to highest energies, some are left vacant due to mutual repulsion between H atoms & reorganization of interstitial sublattices due to H occupancy

	O site	T site
FCC	1	2
HCP	1	2
BCC	3	6

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Now, if we see the impact of this hydrogenation onto the crystal structure, now as I mentioned that when hydrogen enters into the host metal it causes a distortion or expansion of the lattice.

Now, it has been observed like in case of binary hydrides, this expansion is observed, but it was observed that the crystal structure remains same. So, some of the metal hydrides the crystal structure does not change only the expansion is observed; however, in some of the other hydrides even the crystal structure changes as the hydrogen content changes.

Examples are like FeTi or Mg2Ni or CaNi5 or LaNi5. Now there lies in empirical rule which says that this minimum void size should be 0.4 angstrom and the minimum bond distance between the two hydrogen atoms it should be 2.1 angstrom. Now the positions where this hydrogen when it enters into the metal lattice it will occupy the interstitial positions the positions that it will occupy will be either the tetrahedral sites or the octahedral sites.

Now, looking at the three main crystal lattice like the FCC lattice. So, if it is a low to medium hydrogen concentration the hydrogen atom will prefer to occupy the octahedral sites. If however, it is an HCP lattice then these tetrahedral or octahedral sites these are accompanied by a sort of polyhedra and that gets distorted these are enclosed in a polyhedra and that regular polyhedra gets distorted.

Now, this distortion occurs as the lattice parameters ratio c/a it deviates from 1.633 and under the low concentration of hydrogen, hydrogen will occupy these tetrahedral sites preferably in the HCP crystal lattice. Similarly, in the BCC crystal lattice there will be this polyhedra that will get highly distorted because of the incorporation of hydrogen atom and in them hydrogen will preferably occupy the tetrahedral sites.

Now, if we see the different crystal structures like the FCC has one octahedral site and two tetrahedral site, HCP has 1 octahedral and 2 tetrahedral site, BCC has 3 octahedral and 6 tetrahedral sites. Now the hydrogenation that will take place it will be on the sites in such a way that the lower energy sites will get occupied first and then the higher energy sites. So, the order goes as from the lowest to the highest energy.

However, it has been also observed that some of the sites are still left vacant. This is because of the either the mutual repulsion that occurs between the hydrogen-hydrogen atoms or because there is a reorganization of the interstitial sublattices that occurs because of the already hydrogen being occupied in these sites. So, this is how the crystal structure is being considered on hydrogenation; however, the electronic structure also changes on hydrogenation what happens on hydrogenation is the symmetry of the electronic states that gets modified. And the bandwidth also reduces due to the lattice expansion.

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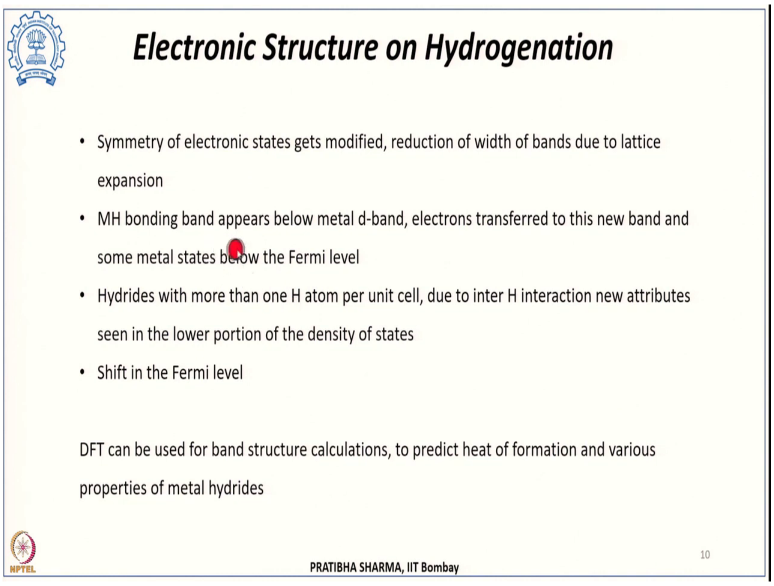

Electronic Structure on Hydrogenation

- Symmetry of electronic states gets modified, reduction of width of bands due to lattice expansion
- MH bonding band appears below metal d-band, electrons transferred to this new band and some metal states below the Fermi level
- Hydrides with more than one H atom per unit cell, due to inter H interaction new attributes seen in the lower portion of the density of states
- Shift in the Fermi level

DFT can be used for band structure calculations, to predict heat of formation and various properties of metal hydrides

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The metal hydride bonding that appears below and that bonding another band appears below the metal d-band and these electrons are transferred to the new metal that band which is being formed and some of the metal states are also formed below the Fermi level. Now the hydrides which have more than one hydrogen atom per unit cell, due to the inter hydrogen interaction there are certain new attributes that could be seen in the lower portion of the density of states.

At the same time a shift in the Fermi level is also observed. There can be several calculation DFT calculations that can be done to do the band structure calculations to find out what will be the heat of formation, what will be the different properties like mechanical properties or other properties of metal hydride.

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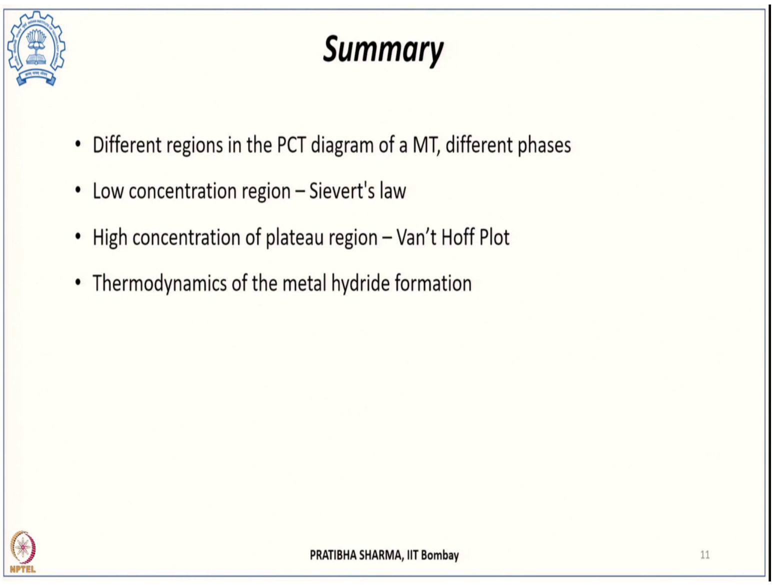

Summary

- Different regions in the PCT diagram of a MT, different phases
- Low concentration region – Sievert's law
- High concentration of plateau region – Van't Hoff Plot
- Thermodynamics of the metal hydride formation

So, to summarize this portion, we have seen that there are different regions existing in the pressure composition temperature isotherm the alpha phase alpha plus beta phase or beta phase and there are like at under low concentration region, it follows the Sievert law while at high concentration of the plateau region it follows the Van’t Hoff equation.

The thermodynamics of the metal hydride we have seen, we have also seen how the there is with sites in the crystal structure are occupied on hydrogenation, what is the change in the electronic structure and in the next class we will try to see certain other properties associated with metal hydride, how the pressure composition isotherms they vary in the real case. So, ideally it used to be a flat plateau what happens in the real case that all we will see in the next class.

Thank you.