Thermo-mechanical and Thermo Chemical processes

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Thermodynamic of Gaseous Nitriding - I

Greetings to everyone. So, in this lecture, today we will talk about the thermodynamics of gaseous nitriding in particular, but for that we will also look at the general gaseous phase thermodynamics and the gas solid equilibrium thermodynamics. So, thermodynamics of gaseous reactions, we have discussed briefly in the last class , now we will take a particular reaction which is of more importance for us in the context of nitriding and see actually how we can apply the equilibrium on to this reactions.

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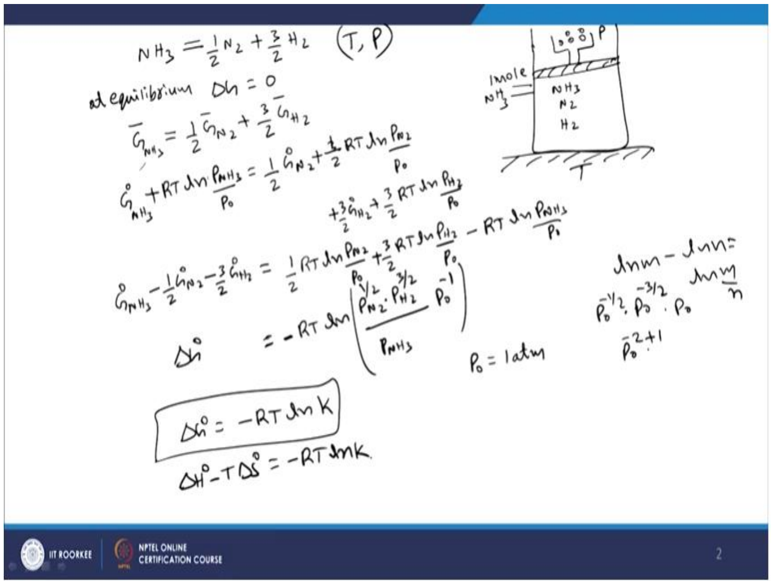

$NH_3 = \frac{1}{2}N_2 + \frac{3}{2}H_2$ (T, P)

at equilibrium $\Delta G = 0$

$$\bar{G}_{NH_3} = \frac{1}{2}\bar{G}_{N_2} + \frac{3}{2}\bar{G}_{H_2}$$

$$G^o_{NH_3} + RT\ln\frac{P_{NH_3}}{P_0} = \frac{1}{2}G^o_{N_2} + \frac{1}{2}RT\ln\frac{P_{N_2}}{P_0} + \frac{3}{2}G^o_{H_2} + \frac{3}{2}RT\ln\frac{P_{H_2}}{P_0}$$

$$G^o_{NH_3} - \frac{1}{2}G^o_{N_2} - \frac{3}{2}G^o_{H_2} = \frac{1}{2}RT\ln\frac{P_{N_2}}{P_0} + \frac{3}{2}RT\ln\frac{P_{H_2}}{P_0} - RT\ln\frac{P_{NH_3}}{P_0}$$

$$\Delta G^o = -RT\ln\left(\frac{P_{N_2}^{1/2}\cdot P_{H_2}^{3/2}}{P_{NH_3}}\,P_0^{-1}\right)$$

$P_0 = 1\,atm$

$\ln m - \ln n = \ln\frac{m}{n}$

$P_0^{-1/2}\cdot P_0^{-3/2}\cdot P_0$

P_0^{-2+1}

$$\boxed{\Delta G^o = -RT\ln K}$$

$$\Delta H^o - T\Delta S^o = -RT\ln K$$

So, for the dissociation of ammonia gas, it goes into nitrogen and hydrogen (refer to above figure). So, this reaction is very important because of considering the huge importance of synthesizing ammonia that means, reverse reaction is very difficult. So, it requires a lot of effort, whereas, the forward reaction that means, dissociation of ammonia happens quite naturally that already implies that it is a very unstable compound ammonia.

So, now for this reaction if we want to understand what is the equilibrium. So, what are we interested in this? For example, we have a reaction chamber in which we have introduced one mole of ammonia and we have maintained it at a constant pressure like this (refer to above figure) kind of a piston and a cylinder combination by controlling these weights.

We know that we have maintained the constant pressure and we have kept it at a constant temperature by placing it into a furnace, which is maintained at that temperature. Now, we know that such a reaction runs, once the ammonia is placed inside and then finally, we end up with in this system, ammonia molecules, N_2 molecules and H_2 molecules. Now, what will be the composition of this gas mixture for the given temperature and pressure.

That is what we would like to know. That is what we can achieve from the equilibrium thermodynamics. So, how we can do that in this particular reaction is, for at equilibrium $\Delta G = 0$ of this reaction. Now, how we can look at that, the Gibbs energy is actually a state function which depends on the temperature, pressure and the composition of the system.

Now, here we are looking at this reaction at constant temperature, constant pressure. So, that means we are only looking at what would be the composition at equilibrium the system wants to have. So, that is our objective. So, now, when we have a mixture of things in a system that will have as a mixture as a certain value of Gibbs energy and in that mixture, all these individual components carry some amount of Gibbs energy that is called the partial molar Gibbs energy of this species.

So, that is nothing but the chemical potential. So, it is called either partial molar Gibbs free energy of a component or chemical potential of a component is one and the same. So, we use this partial molar Gibbs energy with a bar on the top of the species. So, for example, for this reaction for the $\Delta G = 0$, then partial molar Gibbs energy of ammonia that is represented by this bar $\bar{G}_{NH_3}$.

If this is not there, that means it is a Gibbs energy of that system

$$\bar{G}_{NH_3} = \frac{1}{2}\bar{G}_{N_2} + \frac{3}{2}\bar{G}_{H_2}$$

Now, if we write down what would be the value of actually the partial molar Gibbs energy of a component that is always given with reference to a reference state. So, this has been I have explained this in the last lecture, how we choose a reference state.

So, now for that reference state value of this chemical potential is given by with the symbol not on top G^0. And then $G^0_{NH_3}$now, this is about the reference state. Now, actually with reference to that in the actual mixture what we are considering, its Gibbs energy is given by the RTln partial pressure of NH_3

$$\bar{G}_{NH_3} = G^0_{NH_3} + RTlnP_{NH_3}$$

As you can see that by telling about the partial pressure of NH_3 in a gas mixture, that means we are connecting actual composition of the mixture with the chemical potential.

That means $G^0_{NH_3}$remains the same, but depending on the magnitude of these three constitutes in the system, P_{NH_3} can change. So, that is how the chemical potential would depend $\frac{P_{NH_3}}{P_0}$. Now, this P_0 is actually coming from the way we define the pressure dependence of this quantity at any given temperature. So, that means, P_{NH_3} value is defined that $G^0_{NH_3}$ for P_0 of pressure.

So, similarly we can write for the $\bar{G}_{N_2}$ and $\bar{G}_{H_2}$,

$$\frac{1}{2}G^0_{N_2} + \frac{1}{2}RTln\frac{P_{N_2}}{P_0} + \frac{3}{2}G^0_{H_2} + \frac{3}{2}RTln\frac{P_{H_2}}{P_0}$$

So now we are writing the chemical potential of the ammonia here $G^0_{NH_3} + RTln\frac{P_{NH_3}}{P_0}$,
and this belongs to the chemical potential of the nitrogen $\frac{1}{2}G^0_{N_2} + \frac{1}{2}RTln\frac{P_{N_2}}{P_0}$
and $\frac{3}{2}G^0_{H_2} + \frac{3}{2}RTln\frac{P_{H_2}}{P_0}$ is actually representing the chemical potential of hydrogen.

Now, if we rearrange these terms,. So, all these reference state values of the Gibbs energy or the chemical potential we are moving it on one side,

$$G^0_{NH_3} - \frac{1}{2}G^0_{N_2} - \frac{3}{2}G^0_{H_2} = \frac{1}{2}RTln\frac{P_{N_2}}{P_0} + \frac{3}{2}RTln\frac{P_{H_2}}{P_0} - RTln\frac{P_{NH_3}}{P_0}$$

And if you rearrange these terms, means using the mathematical relation $lnm - lnn = ln\frac{m}{n}$. Right hand side becomes

$$RTln\frac{P_{N_2}^{\frac{1}{2}}P_{H_2}^{\frac{3}{2}}P_0^{-1}}{P_{NH_3}}$$

This is what we can represent now all these quantities together. Now, we need to define what is the reference pressure. Suppose, this reference pressure was chosen for all the gaseous species for ammonia we have chosen, for N_2 as well as H_2 for all these cases if we choose the reference pressure as 1 atmospheric pressure. And then

$$G^0_{NH_3} - \frac{1}{2}G^0_{N_2} - \frac{3}{2}G^0_{H_2}$$

quantity actually is the standard Gibbs energy of this reverse reaction of this.

So, if we write the standard Gibbs energy of this $NH_3 = \frac{1}{2}N_2 + \frac{3}{2}H_2$ forward reaction that would have been the standard Gibbs energies of these, products minus the reactants if it is the other way around that means it is $-\Delta G_0$ of this reaction. So, that is how we can write that ΔG^0 and then this minus symbol to the other side

$$\Delta G^0 = -RTln\frac{P_{N_2}^{\frac{1}{2}} P_{H_2}^{\frac{3}{2}} P_0^{-1}}{P_{NH_3}}$$

So, if you look at this quantity here $\frac{P_{N_2}^{\frac{1}{2}} P_{H_2}^{\frac{3}{2}} P_0^{-1}}{P_{NH_3}}$, that is actually the equilibrium constant.

So, by that we write that $\Delta G^0 = -RTlnK$

So, this is the kind of relation, which you can use all the time whenever we have a equilibrium of the reactions. So, now, how we can get these values for example, so, the ΔG^0 it is coming from the standard Gibbs energies of the species in the reference state. That means, if you have a known the values of Gibbs energies of ammonia gas and N_2 gas and H_2 gas as they are in a pure state, then we will be able to compute ΔG^0.

But we need to know these values as a function of temperature for a given pleasure. So, $\Delta G^0$is represented as $\Delta H^0 - T\Delta S^0 = -RTlnK$.

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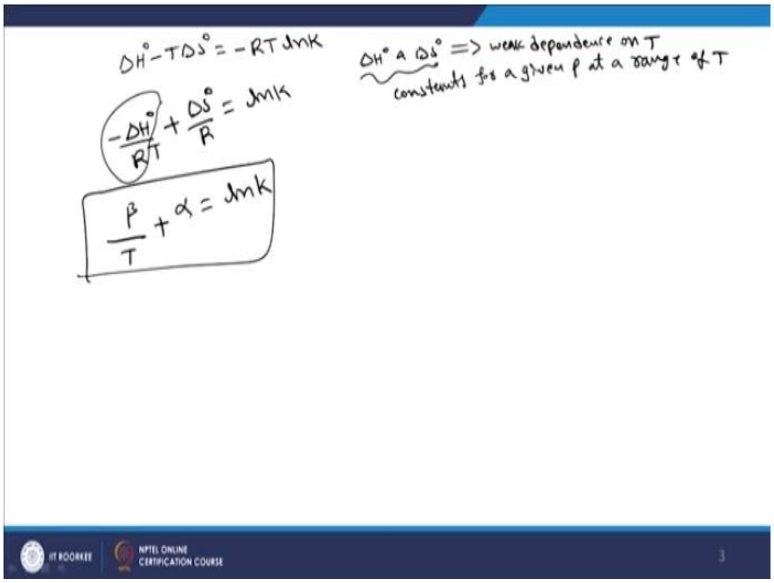

$$\Delta H^\circ - T\Delta S^\circ = -RT\ln K$$

$$\frac{-\Delta H^\circ}{\cancel{R}T} + \frac{\Delta S^\circ}{R} = \ln K$$

$$\boxed{\frac{\beta}{T} + \alpha = \ln K}$$

ΔH° a ΔS° => weak dependence on T

constants for a given p at a range of T

So, now, if we take that to the now, what we are writing is that $\Delta H^0 - T\Delta S^0 = -RTlnK$. Now, for any given temperature, so, we need to know the ΔH^0 and ΔS^0 this can be obtained, if we know the specific heats of the gases involved, then one can calculate the enthalpy and entropies, then one can actually get the ΔH^0 and ΔS^0.

But for most reactions, ΔH^0 and ΔS^0 having a very weak dependence on temperature. That means we can treat them as constants for a given pressure at a range of temperature. So that means by treating them as constant ΔH^0 and ΔS^0 that means they do not change with temperature. So, then actually we can say that these quantities can be written as $\frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} = lnK$

So what we can see is that $\frac{-\Delta H^0}{R}$ quantity is a constant, if we say that as a β, so that is $\frac{\beta}{T}$ if I give $\frac{\Delta S^0}{R}$ quantity as α as a constant then $\frac{\beta}{T}$ + α = lnK. So, now, we need the values of this β and α to know the equilibrium constant of a particular reaction. So, from where we these values are already measured and are tabulated for most important reactions, as one can see.

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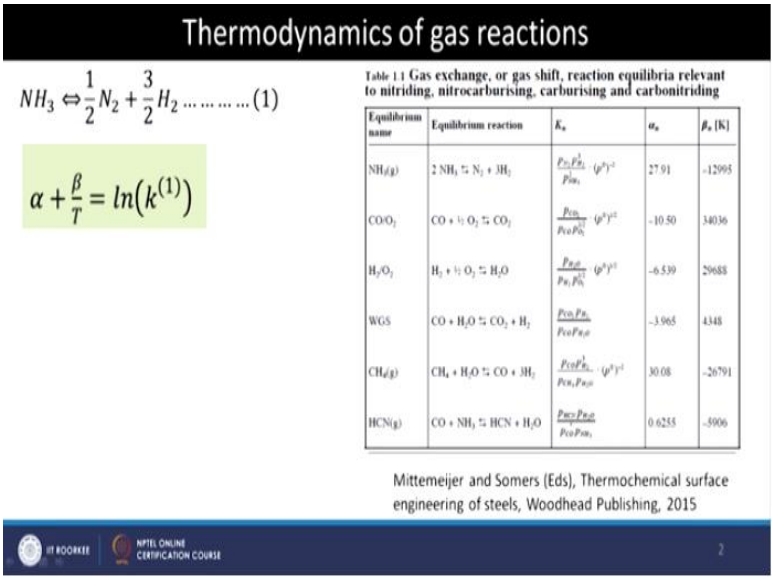

Thermodynamics of gas reactions

$$NH_3 \Leftrightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2 \dots\dots\dots (1)$$

$$\alpha + \frac{\beta}{T} = ln\left(k^{(1)}\right)$$

Table 1.1 **Gas exchange, or gas shift, reaction equilibria relevant to nitriding, nitrocarburising, carburising and carbonitriding**

Equilibrium name	Equilibrium reaction	K_n	α_n	β_n [K]
$NH_3(g)$	$2\ NH_3 \leftrightarrows N_2 + 3H_2$	$\frac{p_{N_2} p_{H_2}^3}{p_{NH_3}^2} \cdot (p^0)^{-2}$	27.91	-12995
CO/O_2	$CO + \frac{1}{2}O_2 \leftrightarrows CO_2$	$\frac{p_{CO_2}}{p_{CO} p_{O_2}^{1/2}} \cdot (p^0)^{1/2}$	-10.50	34036
H_2/O_2	$H_2 + \frac{1}{2}O_2 \leftrightarrows H_2O$	$\frac{p_{H_2O}}{p_{H_2} p_{O_2}^{1/2}} \cdot (p^0)^{1/2}$	-6.539	29688
WGS	$CO + H_2O \leftrightarrows CO_2 + H_2$	$\frac{p_{CO_2} p_{H_2}}{p_{CO} p_{H_2O}}$	-3.965	4348
$CH_4(g)$	$CH_4 + H_2O \leftrightarrows CO + 3H_2$	$\frac{p_{CO} p_{H_2}^3}{p_{CH_4} p_{H_2O}} \cdot (p^0)^{-2}$	30.08	-26791
$HCN(g)$	$CO + NH_3 \leftrightarrows HCN + H_2O$	$\frac{p_{HCN} p_{H_2O}}{p_{CO} p_{NH_3}}$	0.6255	-5906

Mittemeijer and Somers (Eds), Thermochemical surface engineering of steels, Woodhead Publishing, 2015

Here in this (refer to above slide) table looking for the details, one can refer to the source. So, it is a edited book with Mittemeijer and Somers as the editors and it has got all the fundamental information as well as the applied knowledge which is essential for practitioners, very well summarized in the source. So, what you see in this table which I have taken it directly from the source, so for the different reactions involving gases, this is the dissociation of ammonia, this is oxidation of carbon monoxide, in all these cases the equilibrium constant, the corresponding values of α and β are already available from literature. So, one can use those values to calculate the value of for example, the equilibrium constant. So, now actually, if we want to change the situation of this equilibrium, for example one can actually first of all see that how we can shift the equilibrium to the left or right depending on your requirement of whether you want to enhance a particular reaction species in the chamber or decrease the particular amount of species in the reaction chamber that one can do that.

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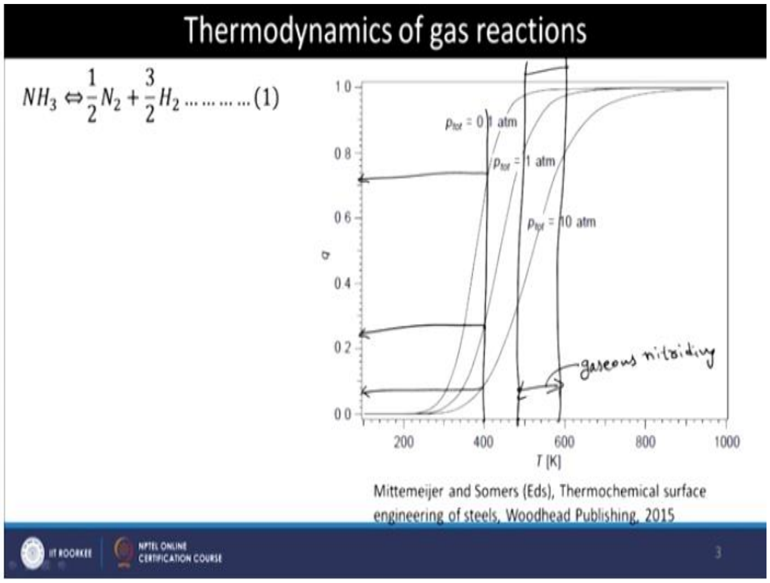

Thermodynamics of gas reactions

$$NH_3 \Leftrightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2 \ldots\ldots\ldots\ldots(1)$$

Mittemeijer and Somers (Eds), Thermochemical surface engineering of steels, Woodhead Publishing, 2015

For example, here it is shown (refer to above figure) for this reaction of ammonia dissociation. Here is this y-axis Q that means actually the fraction of decomposed ammonia that means what is the amount of decomposed ammonia which is present. It means you started with one mole of ammonia and now actually what are the number of moles of ammonia which has decomposed into N_2 and H_2.

So, this is plotted here (refer to above figure). This is zero means, entire ammonia is remained as ammonia, no N_2 and H_2 has formed and then actually as a function of temperature it starts to dissociate. So, as you can see that, these values are given for three values of pressure. You have one atmospheric pressure and less than that and more than that. So, now if you see that for any given temperature for example, 400K, if you see that the fraction of the ammonia which is available as dissociated is given by these (refer to above figure) values.

As one can see that by increasing the pressure one can reduce the amount of ammonia that has been dissociated. That is how one can change the equilibrium of this reaction at a given temperature by playing with the pressure of the system. So, that is how one can control this. So, what one can see that, at a normal temperature of interest which is usually applied in the field of nitriding that is usually in this range 450 to about 580. This is the band of temperature where we want to do the nitriding treatment. This is the temperature where usually one carries the gaseous nitriding. So, if you look at in this window, as you see that from these values if you say that we are operating at one atmospheric pressure more than 80% of ammonia as already dissociated, that means, if you are using ammonia in the reaction chamber for nitriding the thermodynamics predicts that at a given temperature you will have largely a decomposed ammonia that means, you will have a large amount of N_2 and H_2 in the reaction chamber.

So, now, this kind of knowledge about ability to tune the equilibrium, to actually change the reaction directions is very much useful although most practical processes operate in a non-equilibrium state but this works out as a very good tool to change the direction of your reactions. So, now looking at this kind of reaction equilibrium where all the species involved are gases. But as we see that in the purpose of this course is about where we want to introduce some components of the gas phase, which are usually interstitial element like nitrogen or carbon into our solid samples. That means, we need to know the solid and the gas mixture equilibrium. So now if we consider the nitriding.

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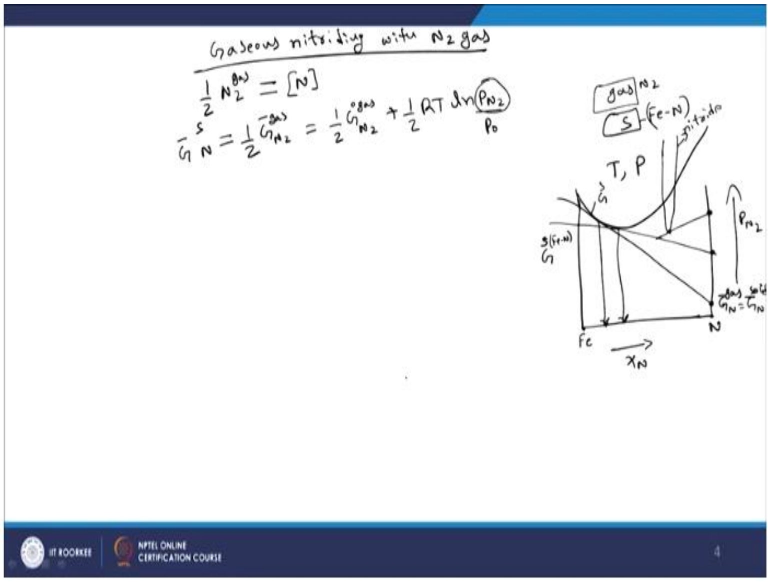

Gaseous nitriding with N2 gas

$$\frac{1}{2} N_2^{gas} = [N]$$

$$\bar{G}_N^{s} = \frac{1}{2}\bar{G}_{N_2}^{gas} = \frac{1}{2} G_{N_2}^{\circ gas} + \frac{1}{2} RT \ln \frac{\boxed{P_{N_2}}}{P_0}$$

So, if you want to use a gaseous nitriding with N_2 gas. First let us see, because if you look at into the nature the most easily available source of nitrogen is N_2 gas, so can we use that in order to introduce nitrogen into the samples like workpieces. So now actually how we can understand this reaction equilibrium. For example if we write this reaction equilibrium of N_2 gas in equilibrium with the solid having dissolved amount of nitrogen.

$$\frac{1}{2} N_2^{gas} = [N].$$

So, this reaction implies that one mole of the N has been dissolved into the solid. So, this square bracket implies that this nitrogen is now in the atomic form, but it is in the solid lattice okay. So, now in this reaction, if we want to write down what is the chemical potential of nitrogen, which is in the dissolved state in the solid. That is given as chemical potential of nitrogen in the solid is given as

$$\bar{G}_N^S = \frac{1}{2}\bar{G}_{N_2}^{gas}$$

So, I would switch back to this with the terminology which we have used in the previous slide that is with a this $\bar{G}_N^S$ that is the chemical potential of nitrogen in the solid is given $\frac{1}{2}\bar{G}_{N_2}^{gas}$ gas chemical potential. So, this if we elaborate this with reference respect to the reference state this will be

$$\bar{G}_N^S = \frac{1}{2}\bar{G}_{N_2}^{gas} = \frac{1}{2}G_{N_2}^{0\,gas} + \frac{1}{2}RTln\frac{P_{N_2}}{P_0}$$

again, assuming ideal behavior for the molecule of nitrogen gas.

Now, what one can see is that in order to have different values of $\bar{G}_N^S$ chemical potential, as you see that once you fix the reference state the value of $\frac{1}{2}G_{N_2}^{0\,gas}$ is constant. The only way you can change the value of chemical potential of nitrogen in the solid by changing the pressure of nitrogen, because there is no meaning for the partial pressure here $ln\frac{P_{N_2}}{P_0}$, because it is only the N_2 gas, so by changing the pressure of N_2. For example, if we have one atmospheric pressure of N_2 and you have chosen the reference state for the N_2 gas as P_0 as one atmosphere, then $\frac{P_{N_2}}{P_0}$ is ratio is 1. So $\frac{P_{N_2}}{P_0}$ term drops off. So that means chemical potentially simply $\frac{1}{2}G_{N_2}^{0\,gas}$. Now actually why we are looking at the chemical potential of the nitrogen in the solid.

So I will now briefly explain how we impose the chemical equilibrium between the different phases. For example, we have a solid, now I consider here for simplicity it is iron with some amount of nitrogen in it, is in equilibrium with a gas, which is simply the N_2. Now you want to understand this equilibrium. Now, this equilibrium can happen between this gas and solid at some particular value of the amount of N, which is dissolvable in the solid.

For example, when we looked at into the gas phase reactions, we have also seen that when it is in equilibrium, the composition of the gas mixture is constant. Now, the equilibrium also fixes what would be the composition of the solid at the equilibrium. Now, how we get that, we can get it for example, at a given temperature, pressure so that means at a constant temperature and pressure.

If we look at the Gibbs energy. This (refer to above figure) is the Gibbs energy of solid which we are plotting that is of iron nitrogen solid because that means I need to plot this for different amounts of nitrogen where I use the x-axis as the amount of nitrogen being added into that. So, this (refer to above figure) point represents the pure iron somewhere here we will have the pure nitrogen. This is varying from pure iron to pure nitrogen, what we are plotting is the fraction of nitrogen which is increasing in this direction.

Let us say this is the Gibbs energy of the solid which has been plotted as a function of nitrogen. Now, the Gibbs energy of the N_2 gas, that will be because the N_2 gas in this case is a pure N_2. So, this has no composition dependence, but for a given temperature and pressure it has a unique value, for example that can be anywhere on this axis. So, now N_2 is a very stable molecule.

So, because of that, it will have its Gibbs energy quite small they are largely negative, for example this is the Gibbs energy or the chemical potential of the nitrogen in the gas. Now for the corresponding value for the solid how we can get, that would be the amount of nitrogen this solid can have at this temperature and pressure. To get that value we construct a common tangent.

This (refer to above figure) point gives you what is the equilibrium amount of nitrogen that can dissolve into the solid iron for the given gas at a given temperature and pressure in this case it is N_2 gas. So, now this value if you want to increase at equilibrium, the possibility is to change the value of chemical potential of nitrogen in the outer atmosphere. So, this also belongs to now, G_N^S, $\bar{G}_N^{gas}$ or $\bar{G}_N^S$.

For example, as we can see here, by increasing the pressure of N_2 we can change the chemical potential of nitrogen that means we choose to this value. Then if we make a common tangent now, this is the equilibrium solubility of nitrogen which is higher than before. So, this is the actually where we are increasing the pressure in this direction for the N_2 gas.

That is how in principle you can try to change the amount of nitrogen which is dissolvable in the solid. But when we look at the phase diagrams, it is not that always only the solution phases develop, sometimes we develop some compounds. For example, iron and nitrogen has some compound and that has its own Gibbs energy, this (refer to above figure) is actually representing that Gibbs energy of let us say some iron nitride.

Now, actually, if you keep on increasing this, at some point, you will also stabilize such nitrides in the solid phase. It says that when you impose such a pressure of N_2 in the outer atmosphere, your solid will be now simply the iron nitride. So, this is how actually we can try to have different iron nitrogen phases being synthesizable using the change in the nitrogen pressure.

So, now you will see when you use actually the one atmospheric pressure nitrogen in the actual situations.

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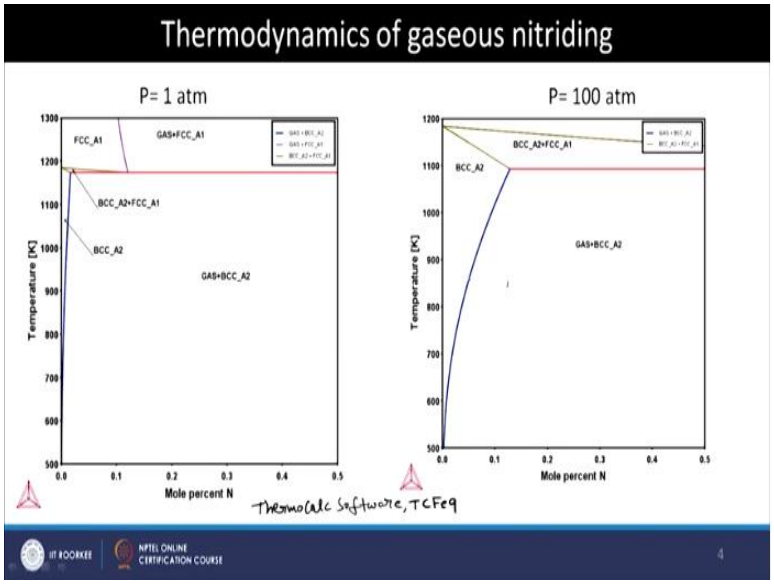

Thermodynamics of gaseous nitriding

ThermoCalc Software, TCFe9

What is shown here (refer to above figure) is the phase diagram of iron and nitrogen, you have a temperature as a function of nitrogen content and it provides what are all the equilibrium phases of the system and what are their compositions at a given temperature and pressure combination. The diagram was calculated at a pressure of one atmosphere. These diagrams have been obtained by calculations using the thermos-calc software.

So, this software has all the thermodynamic concepts already encoded so that it works on the thermodynamic methodology and it use using the data base TcFe9. So, this is actually when we impose a pressure of one atmospheric nitrogen on the solid iron, at different temperatures, what are all the phase combinations can come. What you see here is, this (refer to above figure) is the BCC iron phase and has a solubility within this nitrogen can dissolve.

Now, this is the maximum solubility in this phase that is about 0.04 or so, that is in the mole percent. Now, as we discussed in the previous slide, if we increase the pressure of nitrogen in the outer atmosphere, let us say in this case, we go to 100 atmospheres then you see the drastically enhanced solubility of nitrogen in the BCC iron. So, you can compare these values here now it is coming close to 0.1.

Now, other than that, what you see is that the moment you surpass the solubility, then you see that you will form simply the BCC iron is in equilibrium with N_2 gas that means, if you place a pure iron piece into a furnace atmosphere maintained at a constant temperature with this 1 atmosphere or 100 atmospheres of N_2 pressure, you will get some amount of nitrogen dissolved in the BCC iron and then you will have a that is all will be in equilibrium with N_2 gas.

You will not see any of the iron nitrogen phases started to appear here. Whereas, if you look at actual phase diagrams, which you Google it that is what you get for the iron nitrogen.

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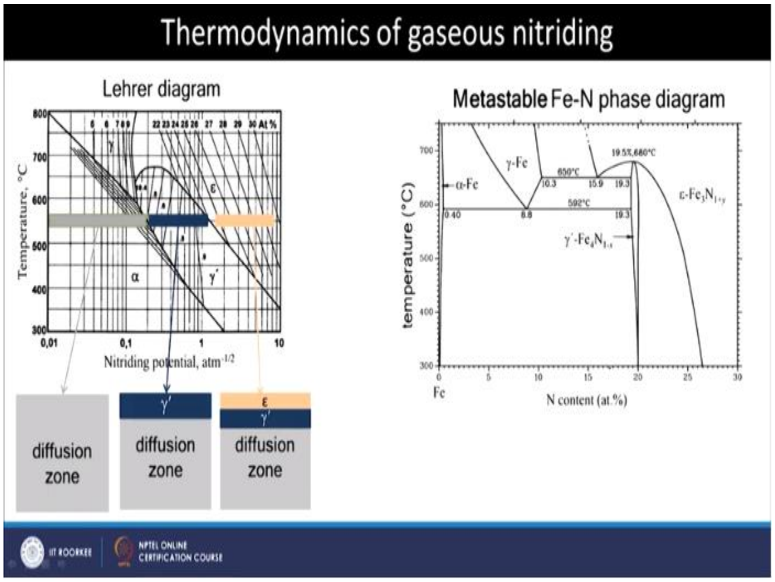

Thermodynamics of gaseous nitriding

That shows okay do not focus on this (refer to above figure) part of this slide, you just concentrate on this phase diagram, this is also iron nitrogen phase diagram. And here you see that there is a significantly higher solubility of nitrogen in the BCC iron as you see here in the BCC iron field and then you also have the iron nitrates being shown. So, now, as you see that in the previous phase diagrams, where we used N_2 gas we have seen that they are stable phase diagrams.

And now, these phase diagrams are metastable because all these iron nitrides would like to decompose to N_2 gas and solid iron. So, now still we are able to synthesize iron nitrides. So, that is only possible by using ammonia gas. So, now in the next lecture we will look into the details of how that is actually serving as a better nitriding agent than N_2 gas in realizing practically the nitriding of the steel thank you.

Keywords = Gaseous nitriding, Gibbs energy, temperature, pressure.