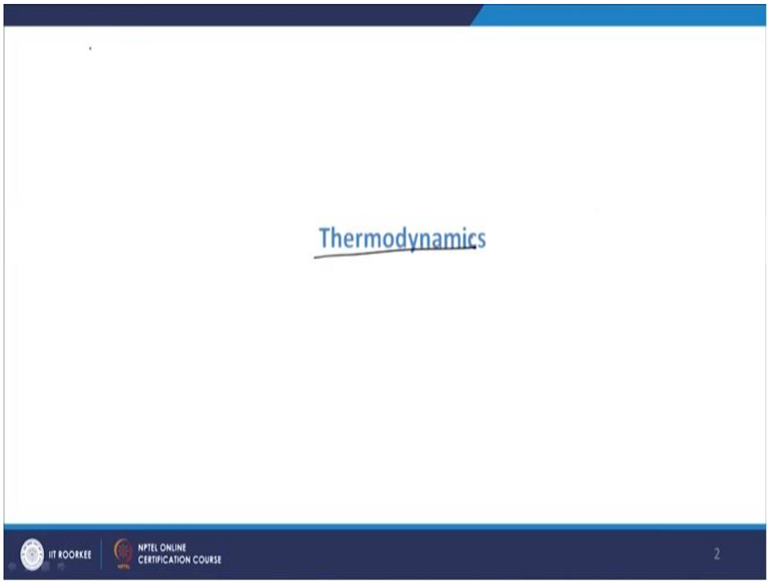
Thermo-mechanical and Thermo Chemical processes

Prof. Sai Ramadu Meka
Department of Metallurgical and Materials Engineering
Indian Institute of Technology – Roorkee

Module No # 07
Lecture No # 33
Thermodynamic Aspects of Thermo- Chemical Treatments: Preliminaries

Greetings to everyone so, today we will be covering a topic on thermodynamic aspects of thermo-chemical processes. So, in the last lectures we have discussed about what are the different ways we can actually introduce interstitial elements into the solid substrates to enhance the properties of the surfaces. So, in that context we have discussed about introducing nitrogen, carbon and boron and how these three processes are fundamentally different.

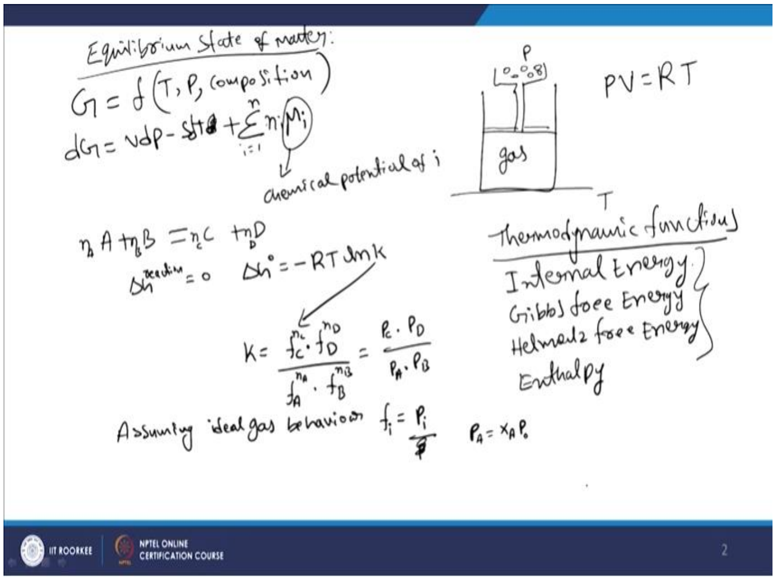
(Refer Slide Time: 01:06)



Thermodynamics

Now, difference in these processes comes from actually the underlying thermodynamics of these processes. So, today in this lecture will talk about some basic concepts of chemical equilibrium based on the thermodynamic principles and then we will move on to the individual processes. So, what does the thermodynamics tell us?

(Refer Slide Time: 01:29)



Equilibrium State of matter:

$G = f(T, P, \text{composition})$

$dG = VdP - SdT + \sum_{i=1}^{n} n_i \mu_i$

chemical potential of i

$PV = RT$

$n_A A + n_B B = n_C C + n_D D$

$\Delta h^{\text{reaction}} = 0 \quad \Delta h^\circ = -RT \ln K$

$K = \frac{f_C^{n_C} \cdot f_D^{n_D}}{f_A^{n_A} \cdot f_B^{n_B}} = \frac{P_C \cdot P_D}{P_A \cdot P_B}$

Assuming ideal gas behaviour $f_i = \frac{P_i}{\cancel{P}}$ $\quad P_A = x_A P_0$

Thermodynamic functions

Internal Energy

Gibbs free Energy

Helmolz free Energy

Enthalpy

It tells about actually the equilibrium state of existence or equilibrium state of matter, if we leave enough time several contents in a system at a given constant external influences. What are these external influences? Let us actually take a system of a container having some gas (refer to above figure) for example, and we can maintain this at some constant pressure by connecting this with piston kind of an arrangement or by placing some weights on top. We know that what is the pressure acting on the system and by placing it on a constant temperature reservoir we are maintaining constant temperature. Now, what would be the state of the gas in the system, if you leave it for enough time that means, once it is at equilibrium.

So, that is what actually we are interested in, based on the thermodynamic concepts. So, for example in this case, if it is an ideal gas, this P and T given combination will fix the volume of the gas according to this relation

$$PV = RT$$

So, here is the V is the molar volume. So now actually we do not have to talk about all the parameters, the moment we say the pressure and the temperature is fixed, its volume is fixed.

So, this is the kind of situation we will encounter also in the context of gas metal interactions. So, it is not possible to go back to the very basic level of thermodynamics. So, I just want to briefly explain some of the concepts which are helpful for us to follow the current thermodynamics. So there are different thermodynamic functions. In that, we have so called internal energy, we have a Gibbs free energy, we have a Helmholtz free energy and enthalpy (refer to above figure).

So, these are the four thermodynamic potentials, some of them have originated from the combination of the first and second laws of thermodynamics i.e. the internal energy and the Gibbs energy, and Helmholtz free energy and enthalpy are actually the derived function so called auxiliary functions which also have the nature of the state functions.

For the Gibbs energy which we will be always considering in our course, the state of the Gibbs energy of a system depends on temperature, pressure and composition. So, if we want to say that the Gibbs energy of a particular system is constant that implies that it has a constant temperature, pressure and its chemistry is fixed, that means number of moles of different constituents in the system. So, the change in this Gibbs energy is represented by

$$dG = VdP - SdT + \sum N_i \mu_i$$

($N_i \mu_i =$ summation of the products of all number of moles multiplied by the chemical potential of the corresponding species).
This μ_i is nothing but the chemical potential of i.

So, this is how we can say that the Gibbs energy change for a system can be represented.
So, you have a mixture of, let us say 2, 3 constituents in the system, now, each one is having its own chemical potential.

So, it s like a gravitational potential or electric potential. This is about how fast it can move across the gradients just because of the differences in the chemical potential. So now when it comes to this chemical potential, which we will be considering now more in detail, so for example, we are interested in the reactions. So, let us say that we have a reaction

$$A + B = C + D$$

if you have an equilibrium for such a reaction, and let us say that number of moles of A, number of moles of B, number of moles of C and number of moles of D are given as n_a, n_b, n_c, n_d respectively.

So, if this reaction is under equilibrium, that implies

$$\Delta G^{reaction} = 0$$

So, that means actually if we relate equilibrium with the equilibrium constant, then it will be

$$\Delta G^{0} = -RTlnK$$

So, this K is actually the equilibrium constant. So, how we can write this equilibrium constant? Let us assume that A,B,C,D all of them are gases and then when we write the equilibrium constant as

$$K = \frac{f_C^{n_C} - f_D^{n_D}}{f_A^{n_A} - f_B^{n_B}}$$

So, this is how we represent the equilibrium constant of reaction. So, the fugacity ($f_{c)}$ is nothing but an effective pressure, which a gas is able to exert.

So, if we assume an ideal gas behavior for individual gases as well as when they are present in the gas mixture, so then we can replace fugacity by the partial pressure. Let us say fugacity of *i* can be replaced by the partial pressure of *i* that can be simply the partial pressure. So, fugacity is represented by the partial pressure.

If I write in the form of ideal situation so these (refer to above figure) things can be replaced by

$$\frac{P_C \times P_D}{P_A \times P_B}.$$

Now, from the Dalton's Law of partial pressure, partial pressure is related to the total pressure with respect to the mole fractions.

Let us say partial pressure of A

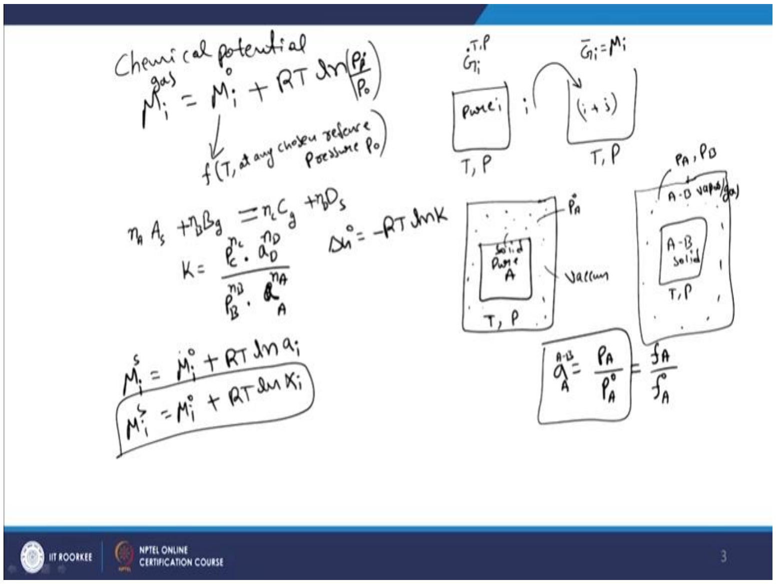
$$P_A = X_A * P_0.$$

So, with this we can relate actually the partial pressure with the total pressure via the mole fractions of A. So, if we know that from how many number of moles our reaction starts, let us say that we start with a certain number of moles of A and B then in principle we can find out what would be the equilibrium amounts of A, B and C, D in the reaction chamber after it reaches the equilibrium.

So, that means we can write the value of K, these all partial pressures can be represented with the mole fractions and then by knowing the total size of the system or at least the initial states of the system from what number of moles we are starting, we can actually in principles solve for the number of moles of individual species.

So, this exercise can be done by the using the ΔG^0 values. That means by knowing the ΔG^0 values you will be able to find out the equilibrium composition of individual species in the system. Now, ΔG^0 what does this ΔG^0 stands for? Let us go back to the chemical potential, how we can write the expression for a chemical potential.

(Refer Slide Time: 12:10)



Chemical potential

$$\mu_i^{gas} = \mu_i^0 + RT\ln\left(\frac{P_i}{P_0}\right)$$

f(T, at any chosen refere Pressure P_0)

$$n_A A_s + n_B B_g = n_C C_g + n_D D_s$$

$$K = \frac{P_C^{n_C} \cdot a_D^{n_D}}{P_B^{n_B} \cdot a_A^{n_A}}$$

$$\Delta\mu^0 = -RT\ln K$$

$$\mu_i^s = \mu_i^0 + RT\ln a_i$$

$$\boxed{\mu_i^s = \mu_i^0 + RT\ln X_i}$$

$$\boxed{a_A^{A-B} = \frac{P_A}{P_A^0}} = \frac{f_A}{f_A^0}$$

So, the chemical potential μ_i means that chemical potential of component is

$$\mu_i = \mu_i^0 + RTln\frac{P_i}{P_0}$$

Where P_i/P_o is partial pressure of i^th component.

So, now what is μ_i^0 stands for? So, concept of chemical potential comes into picture when we are talking about the mixture of either gases or mixing in solid state that means when we have a mixture.

So, it is like a partial molar volume. For example, when we mix 2, 3 things together, we can still say what is the partial molar volume as if this entire volume is occupied by that many numbers of moles, with what would be the pressure exerted by them we can able to calculate what would be the partial molar volume. So, for example let us say that there is pure *i* gas, which I can keep at a given temperature, pressure and that will have some value of Gibbs energy G_i. This *i* because it is in a pure state I use the term G^0. Now, if I mix this *i* okay into some mixture like i+ j and it is also kept at some temperature and pressure.

Now what would be the Gibbs energies associated with *i* in this mixture? What will be the G_i` that means it is a partial molar Gibbs energy of *i* in the mixture i+ j. That is where we also use the symbol often μ_i, this means actually the actual partial molar Gibbs energy or writing it in the form of a chemical potential is one and the same. So, now in order to say what is the chemical potential in the mixture, we need to have a reference state with respect to that how it is changing.

That is where we have some reference state, it is not necessarily the pure *i* which we consider. So, now this μ_i^0 is actually function of temperature, at any chosen reference pressure P_0. So, that means this reference state one can choose not necessarily always a pure *i* can be chosen as a reference state, it can be even a compound of i + j in which I can fix the reference state.

We will see how it helps in choosing a reference state for a convenience in mathematically deriving the expressions. This is about the chemical potential of *i*. And now, this (refer to above figure) is the reference state potential and then this is the reference state pressure P_0. If it is a pure *i* as in the reference state then this (refer to above figure) part will vanish because then the partial pressure will become total pressure,

$$P_0 = P$$

then this

$$RTln\frac{P_i}{P_0} = 0$$

then what we are talking is about the Gibbs energy of that particular species in their reference state.

So, now actually if once we know the reference state, how these reference states can be chosen that will be always important to clearly indicate. For example, if we want to see the reaction equilibrium which we discussed in the previous slide. So, this reaction in which we saw that we have all the gases, now I can have a reaction where some species are gases and some are in solid state that means I have a reaction having

$$A_{solid} + B_{gas} = C_{gas} + D_{solid}$$

Again, you can have number of moles of A number of moles of B number of moles of C and number of moles of D

$$n_A\ A_s + n_B\ B_g = n_C\ C_g + n_D\ D$$

So, now this S stands for the you know the solid and g stands for gaseous state. Now when we write the equilibrium constant for this

$$n_A\ A_s + n_B\ B_g = n_C\ C_g + n_D\ D_s$$

reaction. now for this side actually where we have a gas if you are assuming ideal nature. So, then we right actually the partial pressure of P_C^{nc}multiplied by when we have solid we use that term activity, $a_D^{n_D}$, I will come to what is the meaning of activity in this case, divided by similarly on other side $P_B^{n_B}$and $a_A^{n_A}$

$$K = \frac{P_C^{n_C} \times a_D^{n_D}}{P_B^{n_B} \times a_A^{n_A}}$$

This is how we can write the equilibrium constant. And then we can again relate it to the $\Delta G^0$of this reaction with this RTlnK

$$\Delta G^0 = -RTlnK$$

Now what is this activity? The activity is nothing but let us say that we have a pure A solid kept at some temperature and pressure (refer to above figure) then it develops certain equilibrium vapor phase, that means suppose this is under vacuum initially then some amount of A atoms will leave the solid, they evaporate and create actually a certain vapor pressure of A in the chamber and then this vapor phase will come in equilibrium with the solid phase.

That value is called as a P_A^0. That means the equilibrium vapor pressure of A for pure solid A. Now similarly like in a gas mixture if I have a AB solid again kept at some constant temperature and pressure and then I evacuated the chamber and leave it then slowly the A and B atom starts to evaporate and you produce here a AB vapor or gas.

So initially A and B atoms starts to evaporate after some time it stops. So we are in the once we reach an equilibrium, now here we can talk about partial pressure of A and a partial pressure of B. We can define the partial pressure of A and B in the atmosphere around the AB solid.

Now the activity, when we say that very often, we use somebody is very active or not active then we always say that with reference to something. So, when it comes to this situation, this is also about the same. Suppose if it is one A solid that has a certain pressure P_A in a mixture, this ratio of pressure of solid in mixture to pressure of pressure of pure solid is considered as a activity.

$$a_A = \frac{P_A}{P_A^0}$$

This is how we define the activity of A. Now, this value depends on what kind of mixture we taking. So, in a AB solid mixture, then when we define activity of A that is equivalent to the equilibrium partial pressure of A exerted by the AB solid divided by the vapor pressure of A $\frac{P_A}{P_A^0}$ at a given temperature.

So, that is how we define the activity. So, by definition it is activity is dimensional less. So, now, if your vapor phase whatever is developing, which we are considering to equilibrate with the condensed phase i.e. the solid that may not necessarily behave ideally so, if that vapor phase is behaving non ideally then you use more precisely fugacity of A divided by Fugacity of A in the reference state i.e. $\frac{f_A}{f_A^0}$.

So, one can actually design a situation such that in the reference state that is behaving ideally, but in other situation, it is behaving non-ideally where I will take the fugacity. So, by taking them one can actually get an interpretation for the activity. So, in that case, how do we write the activity in the solid state

$$\mu_i^{gas} = \mu_i^0 + RTln\frac{P_i}{P_0}$$

So, what we write here this is for the gas phase this expression what we wrote here is for a gaseous phase

$$\mu_i^{gas} = \mu_i^0 + RTln\frac{P_i}{P_0}.$$

For a solid chemical potential of component *i* in a solid is given by μ_i^0, again this is about the in a reference state, the chemical potential plus RTln here the term activity of *i* will be used

$$\mu_i^s = \mu_i^0 + RTlna_i$$

Here we are using actually fugacity in case of gas mixture, but in case of a solid mixture, we are using the activity of that particular component *i*. If we assume that it is ideal solution, that means, this vapor phase here simply follows ideal solid solution.

Then we can replace this $a_i$by the mole fraction

$$\mu_i^s = \mu_i^0 + RTlnX_i$$

So, now one may wonder when we take this reference state as in a pure state. then actually there is no meaning for partial molar Gibbs energy or the chemical potential. It is simply that Gibbs energy. We only talk about partial molar Gibbs energy when we are talking about a mixture.

Because this is always written in this fashion because you can choose also a mixture in which the element is present as a reference state. It is not necessarily that it is always a pure element we take that is why it is always written as a chemical potential of i in the reference state. It may turn out to be only simply G_0 that is that Gibbs energy if we take a reference state as a pure component, which we are considering.

So, with this little bit of, you know the thermodynamic introduction. I would now move on to actually talking about the actual process of nitriding, how we can deal with the thermodynamics of gaseous nitriding okay, thank you.

Keywords- Thermodynamic, Gibbs free energy.