Introduction to Molecular Thermodynamics
Prof. Srabani Taraphder
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture – 32
Chemical Reaction Equilibrium

Welcome, so, in today’s lecture, we are going to discuss chemical reaction equilibrium. So, basically, we are looking at the statistical thermodynamics or the molecular thermodynamics of an ideal gas mixture, where the components can undergo chemical reaction with each other now, in this particular reactive mixture of ideal gases.

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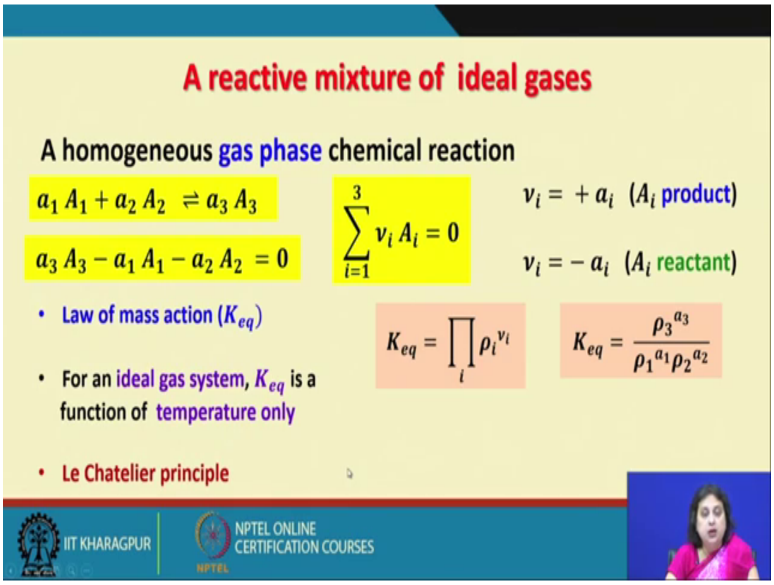

A reactive mixture of ideal gases

A homogeneous gas phase chemical reaction

$a_1 A_1 + a_2 A_2 \rightleftharpoons a_3 A_3$

$a_3 A_3 - a_1 A_1 - a_2 A_2 = 0$

$$\sum_{i=1}^{3} \nu_i A_i = 0$$

$\nu_i = +a_i$ (A_i product)

$\nu_i = -a_i$ (A_i reactant)

- Law of mass action (K_{eq})
- For an ideal gas system, K_{eq} is a function of temperature only
- Le Chatelier principle

$$K_{eq} = \prod_i \rho_i^{\nu_i}$$

$$K_{eq} = \frac{\rho_3^{a_3}}{\rho_1^{a_1} \rho_2^{a_2}}$$

We are going to focus our attention on a homogeneous gas phase chemical reaction that is typically something like this. So, you obviously, know that famous reaction between hydrogen and nitrogen giving rise to ammonia.

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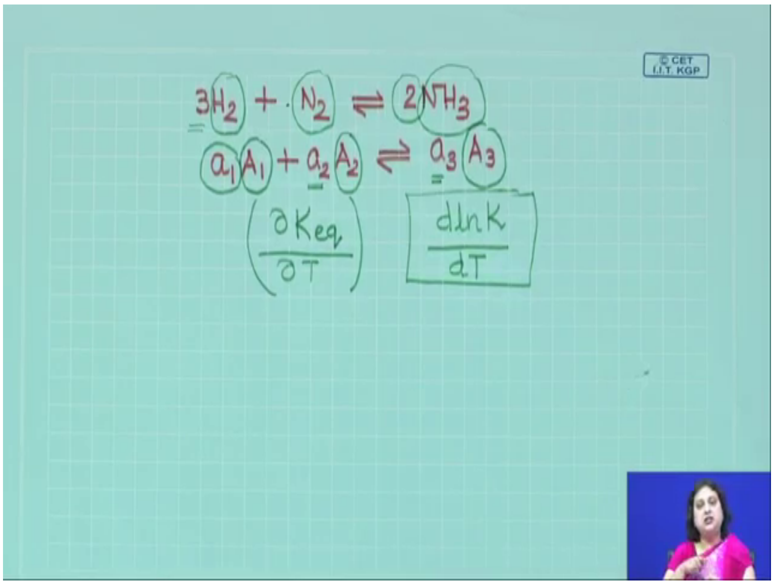

$$3H_2 + N_2 \rightleftharpoons 2NH_3$$

$$a_1A_1 + a_2A_2 \rightleftharpoons a_3A_3$$

$$\left(\frac{\partial K_{eq}}{\partial T}\right) \quad \boxed{\frac{d\ln K}{dT}}$$

So, if I take 3 moles of hydrogen reacted with one mole of nitrogen, I get 2 moles of ammonia. So, in this way, I am writing A 1, capital A 1, plus A 2, capital A 2, given rise to A 3 some A 3 ok. So, what is my A 1, the reactant A 1? If I compare it with this example, my reactant A 1 is this hydrogen molecule. So, what is this stoichiometric coefficient small a 1? In this example that is equal to 3. Similarly, I can identify A 2 with my reactant nitrogen, and the corresponding stoichiometric coefficient that I see in this equation is A 2 equal to 1.

Similarly, you see that A 3 can be denoted in terms of the ammonia; which is the product of the reaction and the stoichiometric coefficient that appears in this balanced chemical equation that gives me A 3 equal to 2. It whatever, I am going to discuss here, for the sake of simplicity, I am going to stick to this particular type of chemical reaction, although, any number of reactants given raise to any number of products can be handled, but once again for the sake of simplicity. Am going to keep myself focused on 2 reactants and one product, for which the stiochiometrically balanced chemical equation, is known, and in that a I if it is either a reactant or a product the stoichiometric coefficient in the balanced chemical equation is small ai. With this background in mind, I also would to write down rather artificially this equation.

So, it is as if I replace the reversibility sign here by an equality sign, and taken these 2 terms on the right-hand side and this is the equation that we get. So, this basically tells me that any general chemical reaction can be written in the form of an algebraic equation; which says that ais are the participants or any participant in the reaction the ith participant in the reaction and the nu i is the stiochiometric coefficient of the ith participant in the balanced chemical reaction; which is this, and therefore, as you understand nu I is equal to plus ai if this ith component is product. And it is equal to minus ai if this ith participant or ith component of the reactive mixture is a reactant. We will keep this in mind.

And then try and see with this description we are going to have in mind, the well-known result in gas phase reaction and especially chemical reaction equilibrium that is the law of mass action. So, what is the law of mass action? If you have a chemical reaction which has attained equilibrium, it has been shown using a large body of experimental data that you can always define a constant in terms of the concentration mass density or number density of each of the components present in the reaction mixture raised to the power of the corresponding stoichiometric coefficient in the balanced chemical equation.

And therefore, for this particular chemical reaction, we see that this is going to be rho 3 which is the product raised to the power of A 3, because for the reactant my nu 3 is equal to plus A 3, but for the reactants for the this is for the product for the for the reactants nu one is going to be minus A 1. And therefore, it comes to the denominator when I take away the sign. So, basically the law of mass action says that this reaction when it starts there is initially A 1 and A 2. And if you allow the reaction to proceed, it would start producing A 3 and eventually a situation would be reached when I would say that equilibrium has been reached the reaction does not seem to proceed either in the forward or the backward direction, and a constant ratio of these numbers are being maintained, which is known as the equilibrium constant.

So, we are going to see we are going to look at the reactive mixture of an ideal gas and try to understand why at all something like an equilibrium constant should exist in a simple case as shown here. The next thing that I would like to mention over here, in an ideal gas system if you have a homogeneous gas phase reaction, and individually this gas mixture of A 1 A 2 and A 3 is behaving like an ideal gas mixture at equilibrium, it depends on temperature and temperature only. Which means this constant value at a given temp this equilibrium constant; is a constant value at a given temperature. Now if for the same reaction you change the temperature. Then you will find that the system will establish equilibrium such that this k equilibrium value is another constant depending on what your new temperature is. So, once we ask this question; why is it. so that k equilibrium, if it exists is a function of temperature only.

For example, it does not depend on the pressure of the gas. And finally, there is something called the le chatelier principles that you must have encountered while studying the chemical equilibrium thermodynamics in chemical equilibrium.

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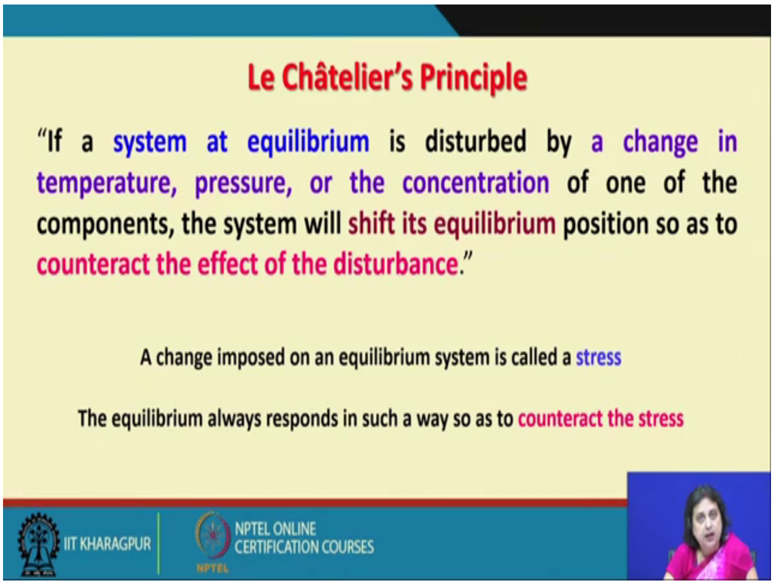

Le Châtelier's Principle

"If a system at equilibrium is disturbed by a change in temperature, pressure, or the concentration of one of the components, the system will shift its equilibrium position so as to counteract the effect of the disturbance."

A change imposed on an equilibrium system is called a stress

The equilibrium always responds in such a way so as to counteract the stress

So, what is the le chatelier principle? It says that if a system at equilibrium is disturbed by a change in factor like temperature pressure or concentration of one of the components, then the system will shift it is equilibrium position. So, as to counteract the effects of the disturbance so, basically when the system is in chemical is in equilibrium, then you impose certain change in the system so that this equilibrium is disturbed. So, basically what you have created is a stress.

And a system responds to the stress, such that it still goes back to an equilibrium, but it goes back to an equilibrium in such a way, that it counteract the stress of nullifies the effect of this external (Refer Time: 08:09). So, in this particular lecture, what we will be interested in is if I change the equilibrium temperature. Then what will be the effect on k equilibrium, I said k equilibrium is a function of temperature. Therefore, I can very easily find out what happens to the k equilibrium delta T. Actually, what we will be looking at is at del lnk del T this particular factor, as you will see from the next discussion. So, with this goal in mind, I have to establish that something like a law of mass action, can be justified the equilibrium constant for a homogeneous gas phase reaction is independent of pressure, but it depends on temperature, and finally, I would like to understand the behaviour of k as a function of T, such that I can justify the observation that led to formulation of the la chatelier principal.

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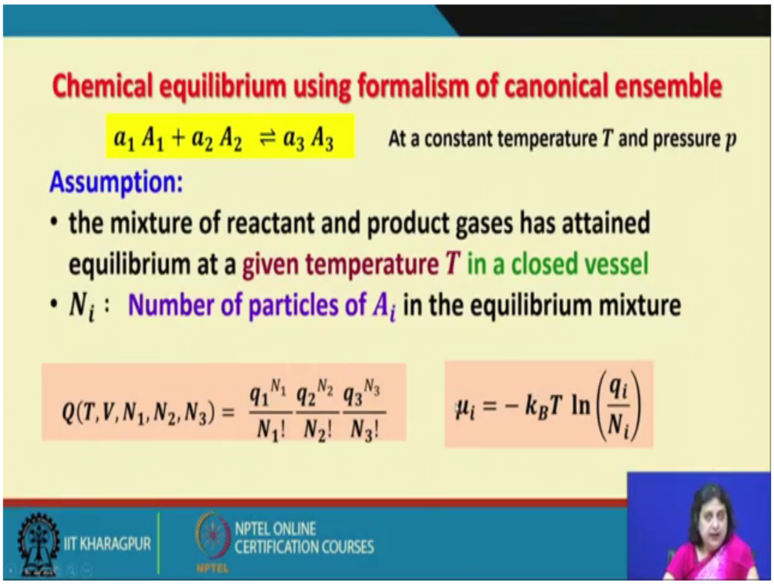

Chemical equilibrium using formalism of canonical ensemble

$a_1 A_1 + a_2 A_2 \rightleftharpoons a_3 A_3$ At a constant temperature T and pressure p

Assumption:

- the mixture of reactant and product gases has attained equilibrium at a given temperature T in a closed vessel
- N_i : Number of particles of A_i in the equilibrium mixture

$$Q(T,V,N_1,N_2,N_3) = \frac{q_1^{N_1}}{N_1!}\,\frac{q_2^{N_2}}{N_2!}\,\frac{q_3^{N_3}}{N_3!}$$

$$\mu_i = -k_BT\ \ln\left(\frac{q_i}{N_i}\right)$$

Now once again I am going to use the formalism of canonical ensemble for this simple chemical reaction. And am going to study this under a condition of constant temperature constant pressure, that is the usual condition. But in this case, I am going to assume certain things so that I am able to use the formalism of canonical ensemble. So, the first assumption is that at the mixture of the reactant and the product gases, has already attained the chemical equilibrium, at a given temperature in a closed vessel. So, even if the individual number of particles is change could change because of chemical reaction, what we observe is an apparent chemical equilibrium mixture which is at stand still ok.

Now what we will say that; obviously, then in this equilibrated mixture the number of particles of the component ai is given by Ni, and with time Ni remains constant that is our experimental observation. Now what is it that I have in my reaction mixture? At equilibrium I have some N 1 particles of the reactant A 1. I have some N 2 particles of reactant A 2, and in equilibrium with them, I have some N 3 particles of the product A 3. And therefore, very easily, I can write down that the canonical partition function for mixture like this; is written in terms of the individual single particle partition function of the component 1 component 2 and component 3. Now by definition we know that mu is equal to minus KBT.

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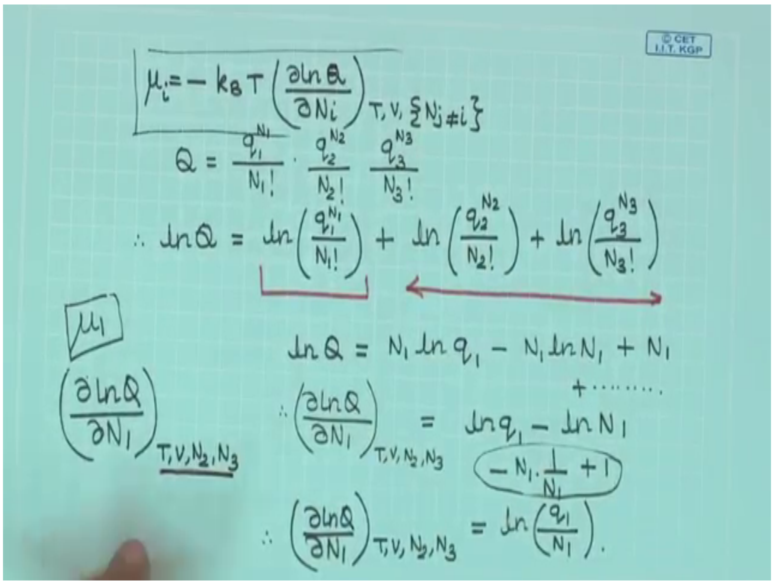

$$\boxed{\mu_i = -k_B T\left(\frac{\partial \ln Q}{\partial N_i}\right)_{T,V,\{N_j \neq i\}}}$$

$$Q = \frac{q_1^{N_1}}{N_1!}\cdot\frac{q_2^{N_2}}{N_2!}\,\frac{q_3^{N_3}}{N_3!}$$

$$\therefore \ln Q = \underbrace{\ln\left(\frac{q_1^{N_1}}{N_1!}\right)} + \ln\left(\frac{q_2^{N_2}}{N_2!}\right) + \ln\left(\frac{q_3^{N_3}}{N_3!}\right)$$

$$\boxed{\mu_1}$$

$$\left(\frac{\partial \ln Q}{\partial N_1}\right)_{\underline{T,V,N_2,N_3}}$$

$$\ln Q = N_1 \ln q_1 - N_1 \ln N_1 + N_1 + \cdots\cdots$$

$$\therefore \left(\frac{\partial \ln Q}{\partial N_1}\right)_{T,V,N_2,N_3} = \ln q_1 - \ln N_1 - N_1\cdot\frac{1}{N_1} + 1$$

$$\therefore \left(\frac{\partial \ln Q}{\partial N_1}\right)_{T,V,N_2,N_3} = \ln\left(\frac{q_1}{N_1}\right).$$

Del ln capital Q del Ni keeping T v, and all Nj is not equal to i, constant and this gives me mu i, or a chemical potential of the ith component in the equilibrium mixture. Now I have been able to show that for this particular system, my capital Q is nothing but q 1 to the power of N 1 divided by N 1 factorial, into q 2 to the power of N 2 divided by N 2 factorial into q 3 to the power of N 3 divided by N 3 factorial ok.

So, what is lnQ? Ln capital Q, that is; going to be nothing but ln of each of these terms right. N 1 divided by N 1 factorial plus ln of q 2 to the power of N 2 by N 2 factorial, and the also term that depends on N 3. So, q 3 to the power of N 3 divided by N 3 factorial, right. Now let me try to find out mu 1 ok. So, in that case, I have to find out this derivative del lnQ, del n 1 1 keeping temperature volume N 2 and N 3 constant. So, for this purpose, I have to focus on this quantity only.

Because, the rest will remain constant; under this given condition of taking the derivative so now, let me focus on what lnQ is for very large number on N 1. So, I can write this as N 1 ln q 1 minus N 1 ln N 1 plus N 1, using sterling approximation. And plus, terms which will remain constant under the constant condition of constant temperature volume constant N 2 and N 3. So, what is del lnQ del N 1 keeping T V and N 2 and N 3 constant. That gives me that I must be having lnq 1 minus ln N 1 minus N 1 into 1 by N 1 plus 1 ok. Now these 2 terms cancel with each other. So, what I am left with is del l del ln del q del N 1 under the condition of constant temperature volume N 2 and N 3. That is equal to ln q 1 by N 1, right. So, going back, since I know that mu 1 will be given by this relationship I can very easily write mu 1 would be equal to minus KBT del lnq del N 1 keeping temperature volume N 2 and N 3 constant.

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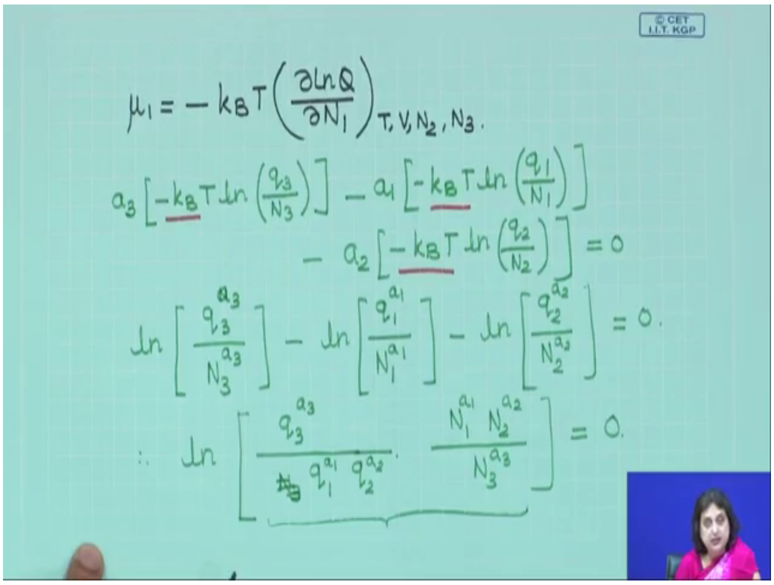

$$\mu_1 = -k_BT\left(\frac{\partial \ln Q}{\partial N_1}\right)_{T,V,N_2,N_3}.$$

$$a_3\left[-\underline{k_B}T\ln\left(\frac{q_3}{N_3}\right)\right] - a_1\left[-\underline{k_B}T\ln\left(\frac{q_1}{N_1}\right)\right] - a_2\left[-\underline{k_B}T\ln\left(\frac{q_2}{N_2}\right)\right] = 0$$

$$\ln\left[\frac{q_3^{a_3}}{N_3^{a_3}}\right] - \ln\left[\frac{q_1^{a_1}}{N_1^{a_1}}\right] - \ln\left[\frac{q_2^{a_2}}{N_2^{a_2}}\right] = 0.$$

$$\therefore \ln\underbrace{\left[\frac{q_3^{a_3}}{\cancel{N_3}\, q_1^{a_1}\, q_2^{a_2}} \cdot \frac{N_1^{a_1}\, N_2^{a_2}}{N_3^{a_3}}\right]} = 0.$$

So, in general I should be able to write that mu i the ith ith specie present in the reaction mixture is minus KBT ln qi by Ni. Now what is the consequence of these formulations?

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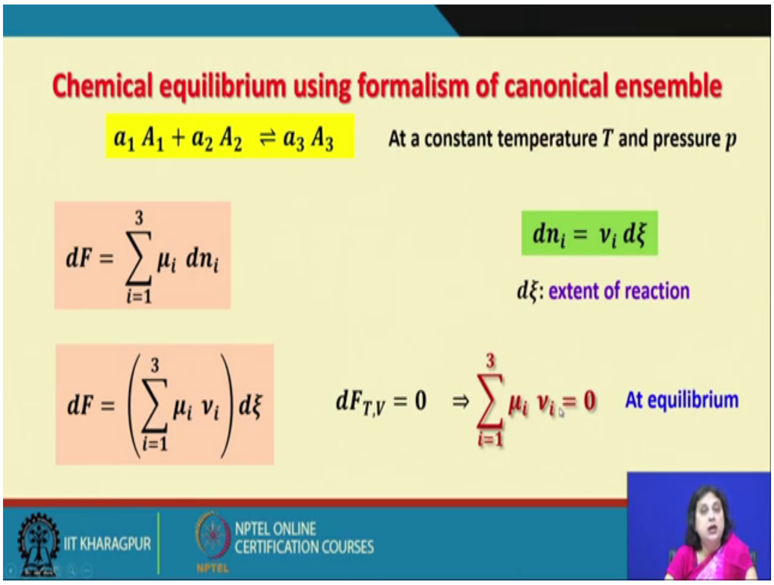

Chemical equilibrium using formalism of canonical ensemble

$a_1 A_1 + a_2 A_2 \rightleftharpoons a_3 A_3$ At a constant temperature T and pressure p

$$dF = \sum_{i=1}^{3} \mu_i \, dn_i$$

$$dn_i = \nu_i \, d\xi$$

$d\xi$: extent of reaction

$$dF = \left(\sum_{i=1}^{3} \mu_i \, \nu_i \right) d\xi$$

$$dF_{T,V} = 0 \Rightarrow \sum_{i=1}^{3} \mu_i \, \nu_i = 0$$

At equilibrium

If we go back and see that when the chemical reaction has achieved equilibrium, and I then do something to pert out this system slightly, then the system will still remain in equilibrium. Now this can be this (Refer Time: 15:31) can be induced in the system by making the system proceed in forward direction by a only very small amount say d psi amount. So, let us say the d psi is the extent of reaction. Now here this will result in change in the number of particles of each eh specie present in the medium as dni equal to mu I into d psi, and that is because of the existence of this stoichiometrically balanced chemical equation for the chemical reaction.

So, that basically tells me, that I can rewrite dF as this. Now by the design of my experiment d psi is not equal to 0. Therefore, if the system, still attains equilibrium in, that case I would say that even if I allow the system to move forward in one direction, in finite (Refer Time: 16:32) and if the system still retains equilibrium, I must be having this condition that under constant temperature and the constant volume condition dFTV must be equal to 0. But dFTV is given by this. As a result, I would say that the equilibrium condition for this chemical reaction mixture is that, I look at the stoichiometric coefficients in the balanced chemical equation, for each component in the reaction mixture, multiply it with the corresponding chemical potential, and then sum over all such components present in the reaction mixture, then at equilibrium for the equilibrium composition of the system this quantity this summation is going to be equal to 0.

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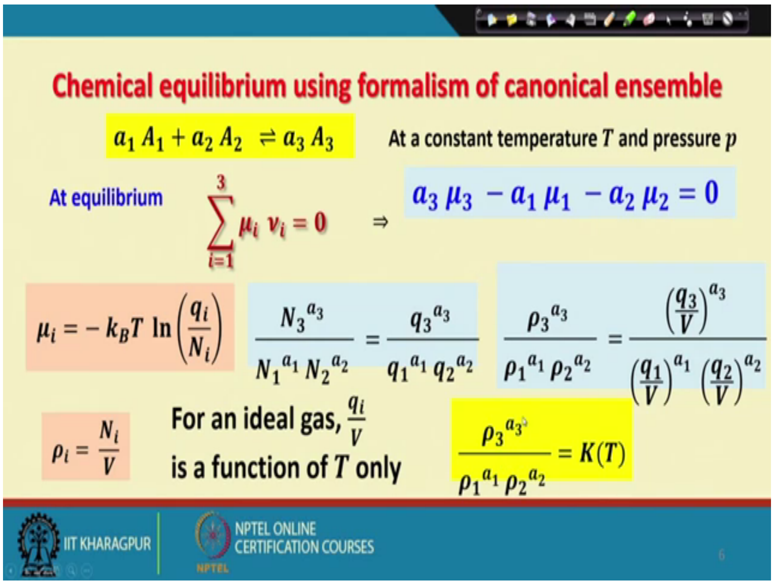

Chemical equilibrium using formalism of canonical ensemble

$a_1 A_1 + a_2 A_2 \rightleftharpoons a_3 A_3$ At a constant temperature T and pressure p

At equilibrium $\sum_{i=1}^{3} \mu_i \nu_i = 0 \Rightarrow a_3 \mu_3 - a_1 \mu_1 - a_2 \mu_2 = 0$

$$\mu_i = -k_B T \ln\left(\frac{q_i}{N_i}\right) \quad \frac{N_3^{a_3}}{N_1^{a_1} N_2^{a_2}} = \frac{q_3^{a_3}}{q_1^{a_1} q_2^{a_2}} \quad \frac{\rho_3^{a_3}}{\rho_1^{a_1} \rho_2^{a_2}} = \frac{\left(\frac{q_3}{V}\right)^{a_3}}{\left(\frac{q_1}{V}\right)^{a_1} \left(\frac{q_2}{V}\right)^{a_2}}$$

$\rho_i = \frac{N_i}{V}$ For an ideal gas, $\frac{q_i}{V}$ is a function of T only $\frac{\rho_3^{a_3}}{\rho_1^{a_1} \rho_2^{a_2}} = K(T)$

So now, we understand that at equilibrium can relationship like this is valid, then for this particular expression for this particular chemical reaction equilibrium, we can very easily write that a 3 mu 3 minus a 1 mu 1 minus a 2 mu 2 must be equal to 0. Now we have already shown that each of the individual mus are related to minus K T ln qi by Ni.

So now, let us write this particular expression that is given over here, in terms of the individual mus ok. So, what we have? What I must be having is a 3 then mu 3. So, what is mu 3? That is minus KBT ln q 3 by N 3. Then I have minus a 1 into the same expression that I have for mu 1 being putting here. So, this is given by this, then minus a 2 into minus KBT ln the contribution coming from q 2 and N 2. And therefore, at equilibrium, I must be having this quantity equal to 0.

Now I will simplify many of these things, as I see that, this k T terms can be easily dropped, because on this side I have 0. So, what I find is that I must be having ln q 3 to the power of n a 3 divided by N 3 to the power of a 3, then minus ln q 1 to the power a 1 divided by N 1 to the power of a 1 minus ln q 2 to the power of a 2 divided by N 2 to the power of a 2 that must be equal to 0 ok. Now I collect all these logarithmic terms. So, what I get is, I must be having ln q 3 to the power of a 3 divided by N 3 to the power of ok. Maybe I will I will write down the q terms together. So, divided by q 1 to the power of a 1 into q 2 to the power of a 2 into N 1 to the power of a 1 into N 2 to the power of a 2 divided by N 3 to the power of a 3. This entire thing must be equal to 0. Logarithm of this quantity is equal to 0. So, basically, I must be able to say, that whatever appears within this bracket must be equal to 1.

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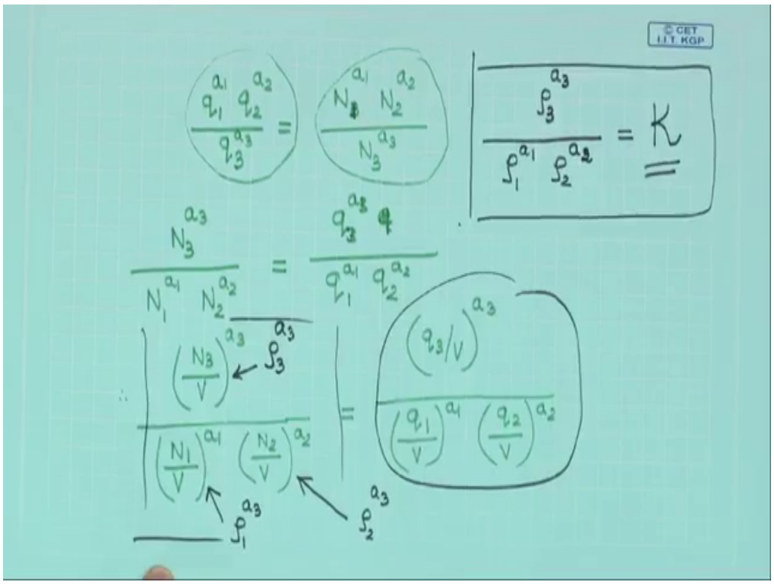

$$\frac{q_1^{a_1} q_2^{a_2}}{q_3^{a_3}} = \frac{N_1^{a_1} N_2^{a_2}}{N_3^{a_3}}$$

$$\boxed{\frac{\rho_3^{a_3}}{\rho_1^{a_1} \rho_2^{a_2}} = K}$$

$$\frac{N_3^{a_3}}{N_1^{a_1} N_2^{a_2}} = \frac{q_3^{a_3}}{q_1^{a_1} q_2^{a_2}}$$

$$\therefore \frac{\left(\frac{N_3}{V}\right)^{a_3}}{\left(\frac{N_1}{V}\right)^{a_1} \left(\frac{N_2}{V}\right)^{a_2}} = \frac{\left(q_3/V\right)^{a_3}}{\left(\frac{q_1}{V}\right)^{a_1} \left(\frac{q_2}{V}\right)^{a_2}}$$

$\rho_3^{a_3}$

$\rho_1^{a_3}$

$\rho_2^{a_3}$

As a result, now, we can write directly that q 1 to the power of a 1 by into q 2 to the power of a 2 divided by q 3 to the power of a 3 that is equal to N 3 to the power of; N 1 to the power of a 1 N 2 to the power of a 2 divided by N 3 to the power of a 3 ok. As we see that this ratio is already related to the number of particles present in the equilibrated reaction mixture under the given condition of constant temperature and volume. So, what I am going to do is, I am going to look at what happens to this term N 3 to the power of a 3 divided by N 1 to the power of a 1 and N 2 to the power of a 2. So, this is given by at equilibrium, this relationship ok.

So, that is going to be given by N q 3 to the power of a 3 divided by q 1 to the power of a 1 into q 2 to the power of a 2, clear? Now I divide each side each of these quantities by V. So, what I have here is N 3 by V to the power of A 3. Similarly, instead of N 1 I replace it with this quantity. Instead of N 2, I replace it with N 2 by V; where V is the total volume of the system. So, what do I have on the right-hand side? I have q 3 by V to the power or A 3 divided by q 1 by V to the power of A 1 into q 2 by V to the power of a 2.

So now as you see that, we have been able to formulate the left-hand side in terms of the number density of the components present in the chemical equilibrium mixture. So, this quantity is nothing but rho 3 to the power of a 3. And this quantity is nothing but rho 1 to the power of a 3, and this is rho 2 to the power of A 3. So now, I find that if I look very closely at the ratio that I have formed, what I have is in the numerator, I have the number density of the product or the concentration of the product raised to the power of stoichiometric coefficient present in it is balanced chemical equation, divided by concentration of the reactants each raised respectively to the power by the stoichiometric coefficient appearing in the balanced chemical equation. So, let me call this ratio as something like k. Now at equilibrium, this k is given by this. So now, let us have a look at what happens to this ratio defined as k.

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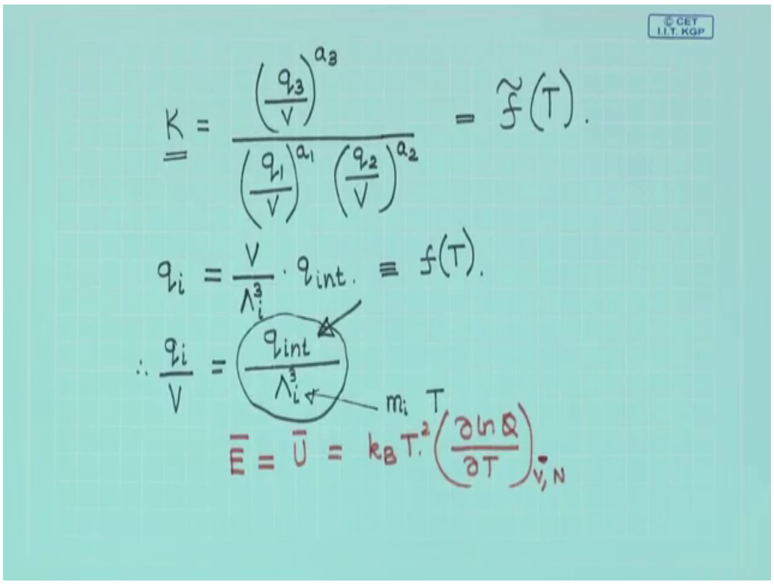

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$$\underline{\underline{K}} = \frac{\left(\frac{q_3}{V}\right)^{a_3}}{\left(\frac{q_1}{V}\right)^{a_1}\left(\frac{q_2}{V}\right)^{a_2}} = \tilde{f}(T).$$

$$q_i = \frac{V}{\Lambda_i^3} \cdot q_{int.} \equiv f(T).$$

$$\therefore \frac{q_i}{V} = \boxed{\frac{q_{int}}{\Lambda_i^3}} \quad m_i \quad T$$

$$\bar{E} = \bar{U} = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{V,N}$$

So now, I find that in this particular case capital k is given by q 3 by V to the power of a 3 divided by the same quantity written corresponding to the reactants. Now each of the reactants and the products, they are ideal gases. Therefore, I can write down that qi is going to be something like V divided by say lambda i a cube multiplied by q internal, right? So, what is qi by V? Qi by V this quantity is nothing but q internal divided by lambda i cubed. Now look at the nature of what I have on the right-hand side. This part depends on the chemical nature of the component i. And this depends not only on the mass mi of the ith component in the reaction mixture, but it also depends on temperature. Add therefore, I would say that this qi in this reaction mixture is a function of temperature for a given combination of reactants and products. Therefore, if I go back I see that k this ratio at a given temperature is some competitive function of temperature and temperature only. There is no dependence on pressure or any other external parameter. So, that is exactly what we have shown here, and then we conclude that yes, at a given temperature qi by V for every component i in the chemical reaction mixture is a function of temperature only. As a result, I would say that at a given temperature this ratio of concentration each ways to the power of the stoichiometric coefficient in the balanced chemical equation is a constant. And this constant is a function of temperature and temperature only.

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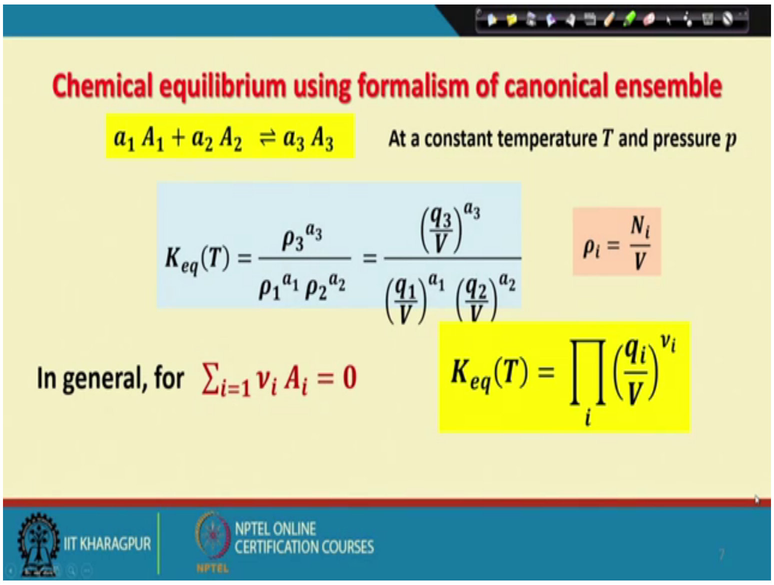

Chemical equilibrium using formalism of canonical ensemble

$a_1 A_1 + a_2 A_2 \rightleftharpoons a_3 A_3$ At a constant temperature T and pressure p

$$K_{eq}(T) = \frac{\rho_3^{a_3}}{\rho_1^{a_1}\,\rho_2^{a_2}} = \frac{\left(\frac{q_3}{V}\right)^{a_3}}{\left(\frac{q_1}{V}\right)^{a_1}\left(\frac{q_2}{V}\right)^{a_2}}$$

$$\rho_i = \frac{N_i}{V}$$

In general, for $\sum_{i=1} \nu_i A_i = 0$

$$K_{eq}(T) = \prod_i \left(\frac{q_i}{V}\right)^{\nu_i}$$

So, the last portion that we need to discuss over here is that. So, in general for given chemical reaction that is represented like this, I can write down the k equilibrium as a function of temperature, and in terms of the individual components of the equilibrium mixture this is given by a product of several terms. And the here i runs over all the reactants and the products present in the equilibrated mixture reaction mixture, and small qi is the single particle partition function for the ith component. And nu i is the associated stoichiometric coefficient as given by this balanced chemical equation. Now with this background in mind, you can now ask the question what happens if I change the temperature of the system k equilibrium is a function of the temperature. So, how will this quantity change as I change the temperature?

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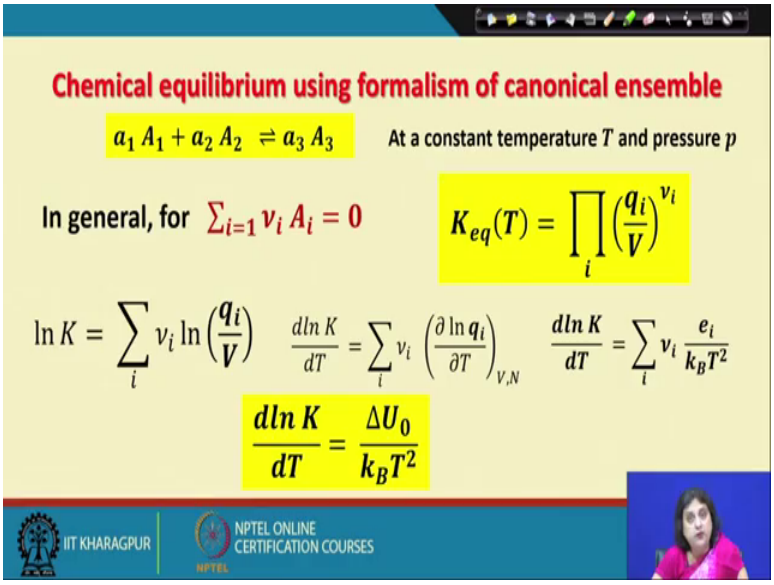

Chemical equilibrium using formalism of canonical ensemble

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At a constant temperature T and pressure p

In general, for $\sum_{i=1} \nu_i A_i = 0$

$$K_{eq}(T) = \prod_i \left(\frac{q_i}{V}\right)^{\nu_i}$$

$$\ln K = \sum_i \nu_i \ln\left(\frac{q_i}{V}\right) \quad \frac{d\ln K}{dT} = \sum_i \nu_i \left(\frac{\partial \ln q_i}{\partial T}\right)_{V,N} \quad \frac{d\ln K}{dT} = \sum_i \nu_i \frac{e_i}{k_B T^2}$$

$$\frac{d\ln K}{dT} = \frac{\Delta U_0}{k_B T^2}$$

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So, for this purpose what we do is, we just try and s take the logarithm of this k. So, logarithm of k is given by this expression; which is fairly simple, and then I try to find out what is dlnK dT, how does the logarithm of this equilibrium constant vary as a function of temperature? Now as you see, that this will be given by the mu i which is fixed for a given chemical reaction that remains unchanged. So now, what I have is, I have this temperature derivative of ln small qi and under conditions of V constant V and constant number of particles. Now as you would remember from the from the formalism, that the average energy e or inter or the internal energy is in general given in terms of the lnq derivative with respect to temperature as del lnq del T keeping constant volume and number of particles.

Now here what we have is something very, very similar. As you see that this is something which corresponds to some energy powered molecule of type i, because small qi is a single particle partition function. And therefore, I can very easily write this expression as dlnk dT is equal to mu i into ei by KBT square. Now what is this quantity?.

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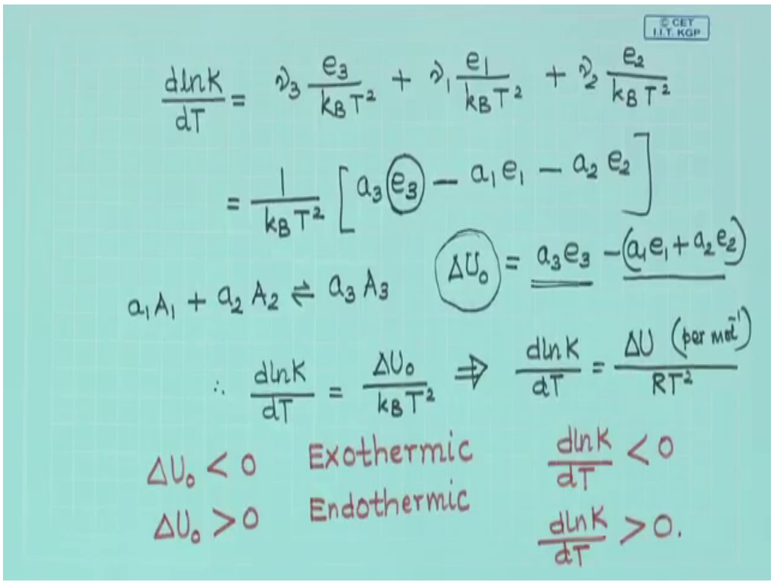

$$\frac{d\ln K}{dT} = \nu_3 \frac{e_3}{k_B T^2} + \nu_1 \frac{e_1}{k_B T^2} + \nu_2 \frac{e_2}{k_B T^2}$$

$$= \frac{1}{k_B T^2}\left[a_3 \boxed{e_3} - a_1 e_1 - a_2 e_2\right]$$

$$a_1 A_1 + a_2 A_2 \rightleftharpoons a_3 A_3 \qquad \boxed{\Delta U_0} = \underline{a_3 e_3} - \underline{(a_1 e_1 + a_2 e_2)}$$

$$\therefore \frac{d\ln K}{dT} = \frac{\Delta U_0}{k_B T^2} \Rightarrow \frac{d\ln K}{dT} = \frac{\Delta U \ (\text{per mol}^{-1})}{RT^2}$$

$$\Delta U_0 < 0 \quad \text{Exothermic} \quad \frac{d\ln K}{dT} < 0$$

$$\Delta U_0 > 0 \quad \text{Endothermic} \quad \frac{d\ln K}{dT} > 0.$$

So, for the given chemical reaction, if I write down explicitly what dlnK dT is turning out to be, I have here first for i equal to 3, that is mu 3, then e 3 by KBT square, then plus mu 1 e 1 by KBT square plus, mu 2 into e 2 by KBT square. Now I simplify this. I take 1 by KBT square outside, and for this equation I put in the respective values of the stoichiometric coefficient. So, this is a 3 e 3 minus a 1 e 1 minus a 2 e 2. So, what is it that I have here? What I have is this is the internal energy powered molecule of the reactant; this is multiplied by the stoichiometric coefficient appearing in the balanced chemical reaction minus, the same terms appearing for the reactants.

And therefore, I can say that for this reaction where a 1 moles of capital A 1 reacted with small a 2 moles of capital A 2 giving rise to small a 3 moles of capital A 3, then what is the change in reaction energy? Let me call it delta U not, then I find that this must be a 3 e 3 minus a 1 e 1 plus a 1 e 2 a 2 e 2. So, this is the total internal energy per molecule present before after the reaction, and this is the total internal energy present before the reaction.

So, this is nothing but the change in internal energy because of the reaction. And therefore, I can very easily write that dlnK dT that is equal to delta U naught by KBT square, right? If I have, if I do this entire exercise for per mole of the species, then dlnK dT will be related to delta U per mole divided by capital RT square. So now, we have got this very important result that dlnK dT is equal to delta U naught by K T square, which can eventually be written in terms of the per mole quantities. As I understand that I can have 2 different types of chemical reactions.

Type one where delta U naught, that is the energy content change as a system goes from the reactant to the product state is less than 0. Or basically I am talking about exothermic reactions, right? Or it may so happen delta U naught is greater than 0. In that case, I am talking about endothermic reactions ok. So, what I understand is that if I have an exothermic reaction then dlnk dT is less than 0. Therefore, the equilibrium constant will decrease if I increase the temperature. This means that, when the reactions; proceeds with release of heat increase in temperature actually pushes the equilibrium towards the reactant side.

Similarly, for delta U not greater than 0, I have dlnk dT greater than 0 and therefore, in this case, we will have with increase in temperature an increased value of k which will shift the equilibrium to more towards the products side. And that is exactly; what is the content of the le chatelier principle? So, what we have achieved over here is that we have achieved molecular definition of the equilibrium constant k. And we find that depending on the chemical nature of what a 1 a 2 or a 3 is, in this example we could have actually found out the qi by vs and therefore, connect the molecular properties to the overall equilibrium constant.

So, this is an application that we are going to take up in the assignment portion for this lecture; where we will be able to see that how the underlying molecular structure actually controls the equilibrium constant, or the overall yield of a given chemical reaction. So, that makes a molecular interpretation for getting higher yield or lower yield in a chemical reaction much more quantitative.

Thank you.