Chemical and Biological Thermodynamics: Principles to Applications
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Lecture - 27
Equilibrium constant

Today we will discuss equilibrium constant and associated quantities in details. In one of the previous lectures we derived a relationship between standard reaction Gibbs energy and equilibrium constant, but that was based upon perfect gas equilibrium. Today we will derive a relationship between standard reaction Gibbs energy and equilibrium constant for all general reactions in which the reactants and products need not be perfect gases or need not be ideal solutions.

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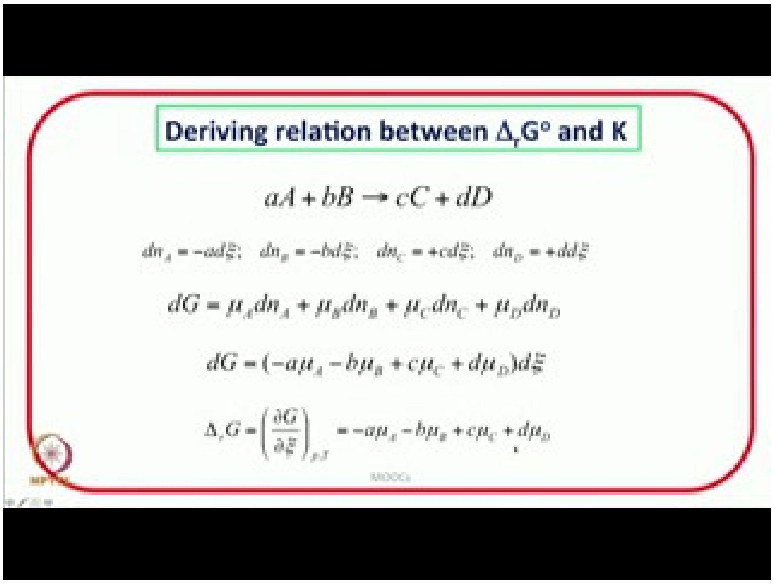

Deriving relation between $\Delta_r G°$ and K

$$aA + bB \rightarrow cC + dD$$

$$dn_A = -ad\xi; \quad dn_B = -bd\xi; \quad dn_C = +cd\xi; \quad dn_D = +dd\xi$$

$$dG = \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \mu_D dn_D$$

$$dG = (-a\mu_A - b\mu_B + c\mu_C + d\mu_D)d\xi$$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T} = -a\mu_A - b\mu_B + c\mu_C + d\mu_D$$

So, let us proceed towards the method to derive a relationship between standard reaction Gibbs energy and equilibrium constant. Let us start by taking an example of a general reaction of the type - a moles of A are reacting with b moles of B and this form c moles of C plus d moles of D.

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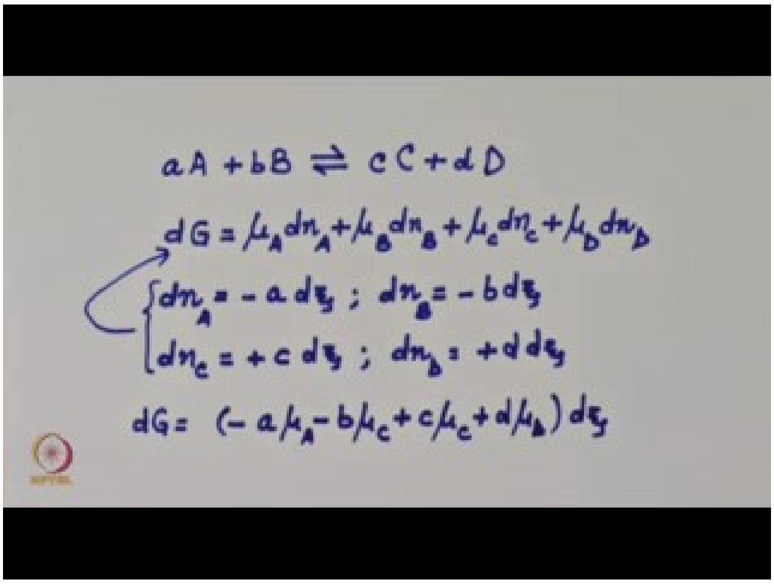

$$aA + bB \rightleftharpoons cC + dD$$

$$dG = \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \mu_D dn_D$$

$$\begin{cases} dn_A = -a\,d\xi \; ; \; dn_B = -b\,d\xi \\ dn_C = +c\,d\xi \; ; \; dn_D = +d\,d\xi \end{cases}$$

$$dG = (-a\mu_A - b\mu_C + c\mu_C + d\mu_D)\,d\xi$$

And as we discussed earlier that in order to derive a relationship between standard reaction Gibbs energy and equilibrium constant there are 2 3 steps - first step is let us write down when the reaction advances by a small amount the change in Gibbs energy will be equal to mu A dn A plus mu B dn B plus mu C dn C plus mu D dn D. This is the first step, you write down the change in reaction Gibbs energy in terms of chemical potential this is at constant pressure and temperature. And now since the reaction is advancing by a small amount and we have earlier introduced this advancement in terms of the extent of reaction which was represented by a simple psi.

So, we can immediately write dn A change in the number of moles of A, A is being consumed. So, this will be minus a times d psi, similarly dn B, b is being consumed this will b minus psychometric number B times the advancement of the reaction and dn C will be equal to here I will put a plus sign c times d psi and dn D is equal to plus d times d psi. What we have is now in terms of the extent of reaction we have expressions for dn A, dn B, dn C, dn D which can be substituted in this expression and let us see what do we get, we get dG is equal to once I substitute here I will get minus a times mu A minus b times mu C plus c times mu C plus d times mu D, if I take d psi out of it right.

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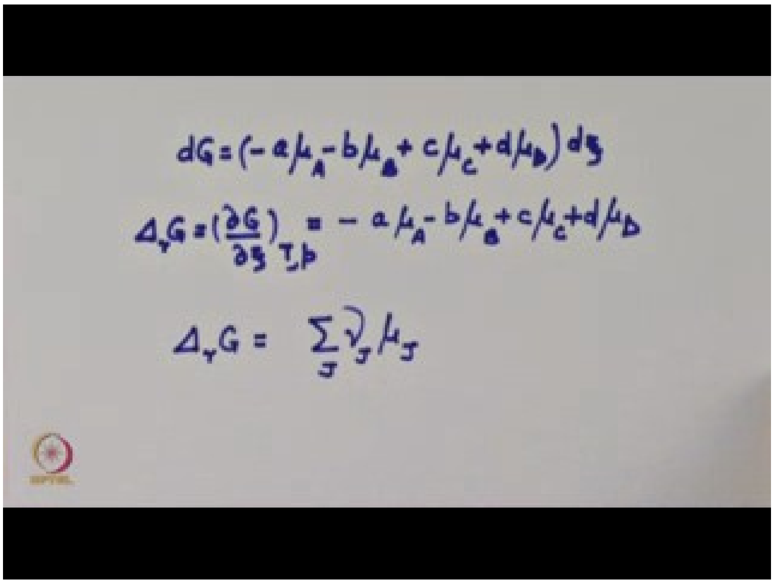

$$dG = (-a\mu_A - b\mu_B + c\mu_C + d\mu_D)\,d\xi$$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{T,p} = -a\mu_A - b\mu_B + c\mu_C + d\mu_D$$

$$\Delta_r G = \sum_J \nu_J \mu_J$$

So, let us continue what we have done is now we have come up with an equation that dG is equal to minus a times mu A minus b times mu B plus c times mu C plus d times mu D and we have d psi and remember that pressure and temperature are anyway kept constant. Now we know that earlier we define the reaction Gibbs energy to be slope of Gibbs energy with respect to extent of reaction at constant temperature and pressure from this expression this is minus a times mu A minus b times mu B plus c times mu C plus d times mu D.

So, we have been able to express the reaction Gibbs energy which is the slope of the Gibbs energy versus extent of reaction in terms of chemical potentials and these chemical potentials are weighted by their psychometric number. I can write this expression also as summations J mu J chemical potential of J, a general form of writing this expression is this because this mu J is a psychometric number which is positive for the product and negative for the reactant.

Now let us go to the slide and discuss this in a little detail what we did was we started with this reaction a general reaction a moles of A plus b moles of B forming c moles of C plus d moles of D and we defined the change in amount of A B C and D in terms of the extent of reaction psi is the extent of reaction. So, d psi is a small advancement hence and as I just discuss negative sign comes with the reactant because reactants are consumed and positive sign comes with the product because product is being formed and then what we did was we expressed dG in terms of chemical potential this is at constant pressure and temperature.

And we further went on to discuss or to derive an expression for the reaction Gibbs energy which is the slope of Gibbs energy verses extent of reaction in terms of chemical potentials.

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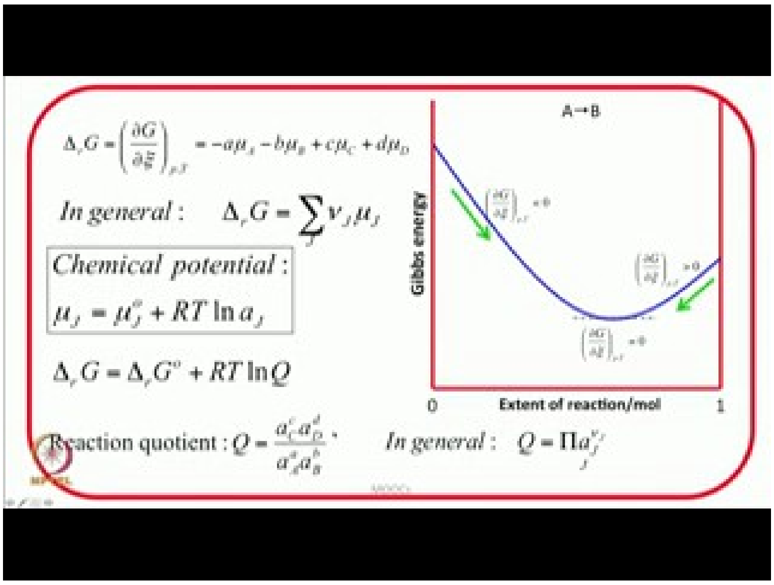

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T} = -a\mu_A - b\mu_B + c\mu_C + d\mu_D$$

In general : $\Delta_r G = \sum_J \nu_J \mu_J$

Chemical potential :
$\mu_J = \mu_J^o + RT \ln a_J$

$$\Delta_r G = \Delta_r G^o + RT \ln Q$$

Reaction quotient : $Q = \frac{a_C^c a_D^d}{a_A^a a_B^b}$, *In general :* $Q = \Pi_J a_J^{\nu_J}$

Now, when G is plotted against psi obviously, we expect a minima and the position of the minima represents the position of equilibrium. This minima depending upon the value of equilibrium constant we will discuss very soon will be either close to the products or close to the reactants, but in any case let us assume the present case on this side as we discussed earlier the reaction is spontaneous.

So, whether the slope is positive or negative it will depend upon the chemical potentials of A B C and D and if this overall value turns out to be negative at that composition the reaction will be spontaneous in the forward direction and if overall the slope turns out to be positive then at that composition of the reaction the reaction will be spontaneous in the reverse direction and wherever this value is 0; that means, wherever the slope is 0 that corresponds to position of equilibrium. And then we discussed that this reaction Gibbs function can be expressed this is an expanded form of this summation.

So, in general we can write reaction Gibbs function as summation J mu J mu J, where mu J is the psychometric number positive for the product and negative for the reactant. So, let me now again start with the same equation that we just drive that is delta r G is equal to minus a times mu A minus b times mu B plus c times mu C plus d times mu D.

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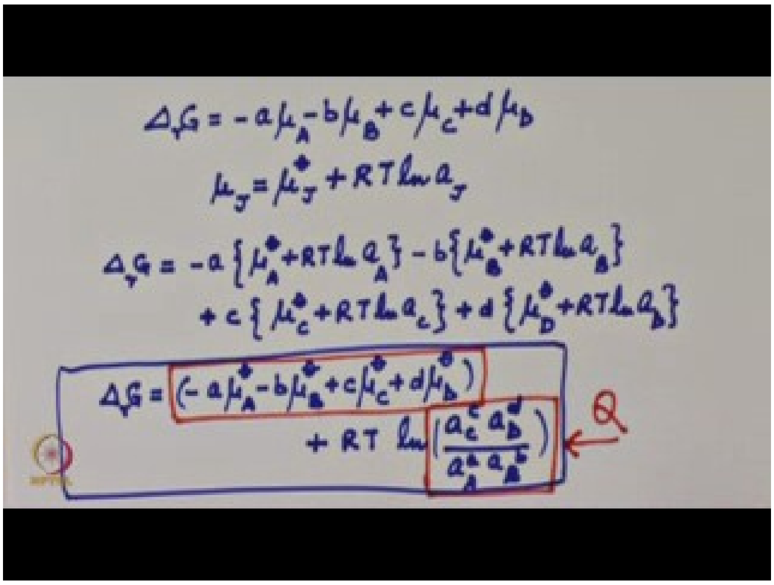

$$\Delta_r G = -a\mu_A - b\mu_B + c\mu_C + d\mu_D$$

$$\mu_J = \mu_J^{\ominus} + RT\ln a_J$$

$$\Delta_r G = -a\{\mu_A^{\ominus} + RT\ln a_A\} - b\{\mu_B^{\ominus} + RT\ln a_B\} + c\{\mu_C^{\ominus} + RT\ln a_C\} + d\{\mu_D^{\ominus} + RT\ln a_D\}$$

$$\boxed{\Delta_r G = \boxed{(-a\mu_A^{\ominus} - b\mu_B^{\ominus} + c\mu_C^{\ominus} + d\mu_D^{\ominus})} + RT\ln\boxed{\left(\frac{a_C^c a_D^d}{a_A^a a_B^b}\right)}} \leftarrow Q$$

And we have earlier discussed that mu of any species J can be written as the standard state chemical potential of that species plus RT log activity of that species this is a general expression or a general relationship between chemical potential and activity for all conditions in the sense that there is no assumption of ideality or non ideality we are just expressing chemical potential in terms of activity. So, this is applicable to all.

Now, what we will do is we will substitute this expression for chemical potential into the above equation we will come up with this equation delta r G is equal to minus a into mu A naught plus RT log activity of A this is for minus a times mu A then minus b inside I will have mu B naught plus RT log activity of B then I have plus c times mu C naught plus RT log activity of c plus d times mu D naught plus RT log activity of D.

Now, what I will do is I will combine all the terms which are therefore, chemical potentials and for activity. So, once you combine all those term the resulting expression is going to be minus a times mu A naught minus b times mu B naught plus c times mu C naught plus d times mu D naught this are the terms which are for the chemical potentials plus RT log now activity of a and activity of b are with the negative sign, therefore, these will come as denominators in the logarithmic term. So, in the numerator we have activity of C raise to the power c activity of D raise to the power d over activity of A raise to the power a activity of B raise to the power b.

Let us go to the slide. So, once in this equation we substitute mu is equal mu naught plus RT log activity of J we are coming up with an equation which is this one in this equation let us try to identify this part is the standard reaction Gibbs energy because this is equal to the difference in the standard state chemical potential of products minus that of the reactants waited by the psychometric number.

So, this is equal to the standard state reaction Gibbs energy and this ratio is the ratio of the product of activities of the products raise to the power equal to their psychometric number divided by the product of activities of reactants raise to power their respective psychometric number and this particular ratio I am going to call as Q which is reaction quotient.

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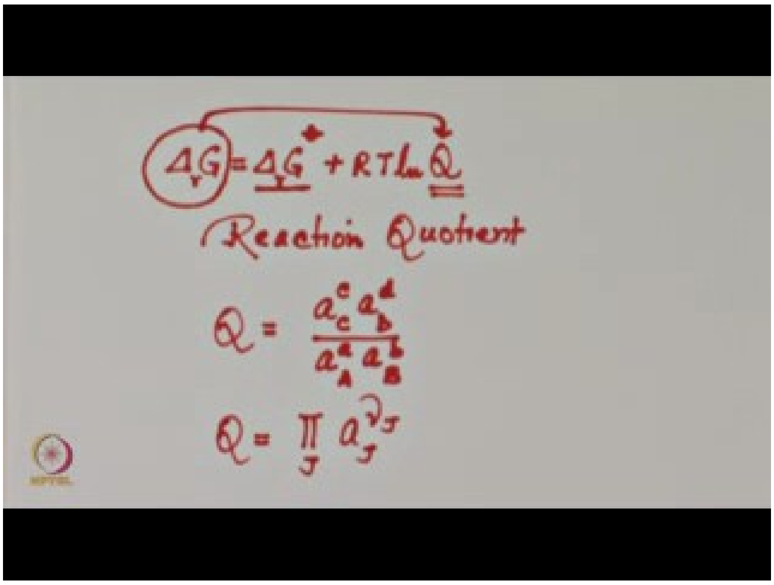

$$\boxed{\Delta_r G} = \underline{\Delta_r G^{\ominus}} + RT\ln \underline{\underline{Q}}$$

Reaction Quotient

$$Q = \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

$$Q = \prod_J a_J^{\nu_J}$$

So, this particular equation I am going to write as delta G is equal to delta G naught which is the difference in the standard state chemical potentials plus RT log Q, Q we will call as reaction quotient and Q what we obtain in this particular case which we are discussing is activity of C raise to the power c into activity of D raise to the power d over activity of A raise to the power a activity of B raise to the power b.

And now let us take a look at this equation delta G naught at a given temperature is constant; that means, if I put also r; that means, this slope will depend upon the value of Q. The spontaneity of the reaction will depend upon the reaction quotient and the reaction quotient represents the composition of the given reaction, since delta r G naught is constant at a given temperature the spontaneity of a process will depend upon the reaction quotient. Let us go to the slide now we have come up to this equation that delta r G is equal to delta r G naught plus RT log Q and we also defined Q for the given reaction to the activity of C raise to the power c into activity of D raise to the power d divided by activity of A raise to the power a into activity of B raise to the power b.

In general we are writing reaction quotient as product of activity of J raise to the power mu J that is if I write, in general Q will be equal to the product activity of J raise to the power mu J. Once again the psychometric number will be product will be positive for the product and negative for the reactant and once you expand this for the given reaction you will get this expression.

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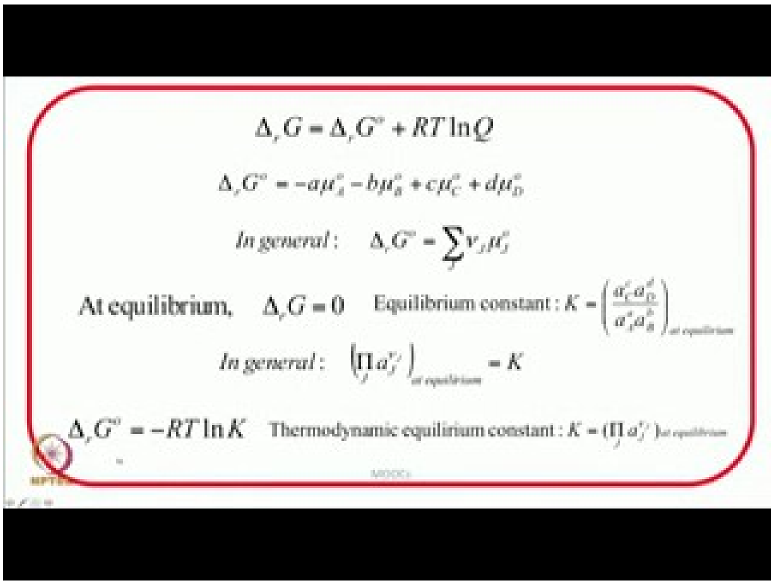

$$\Delta_r G = \Delta_r G^{\circ} + RT\ln Q$$

$$\Delta_r G^{\circ} = -a\mu_A^{\circ} - b\mu_B^{\circ} + c\mu_C^{\circ} + d\mu_D^{\circ}$$

In general : $\Delta_r G^{\circ} = \sum_J \nu_J \mu_J^{\circ}$

At equilibrium, $\Delta_r G = 0$ Equilibrium constant : $K = \left(\frac{a_C^c a_D^d}{a_A^a a_B^b}\right)_{at\ equilibrium}$

In general : $\left(\prod_J a_J^{\nu_J}\right)_{at\ equilibrium} = K$

$\Delta_r G^{\circ} = -RT\ln K$ Thermodynamic equilirium constant : $K = (\prod_J a_J^{\nu_J})_{at\ equilibrium}$

Let us keep this in mind and proceed what we have is delta r G is equal to delta r G naught plus RT log Q we have just derive this and we also discuss that this standard reaction Gibbs energy is equal to difference in the sum of the chemical potentials of products, and chemical potential of reactants with it by their psychometric number I can also express this in a general form and the expansion of this will result into this kind of expression.

In general after recognizing the standard reaction Gibbs function that it is constant at a given temperature we now invoke the equilibrium conditions. We know that at equilibrium delta r G is going to be 0 the slope is equal to 0 and equilibrium constant will be equal to the expression for Q at equilibrium. In other words Q at equilibrium is equal to K, so K will be then activity of C raise to the power c into activity of D raise to the power d divided by activity of A raise to the power a activity of B raise to the power b, but at equilibrium and once again as we expressed for Q we can also write for K that K in general is equal to pi J into activity at J at equilibrium.

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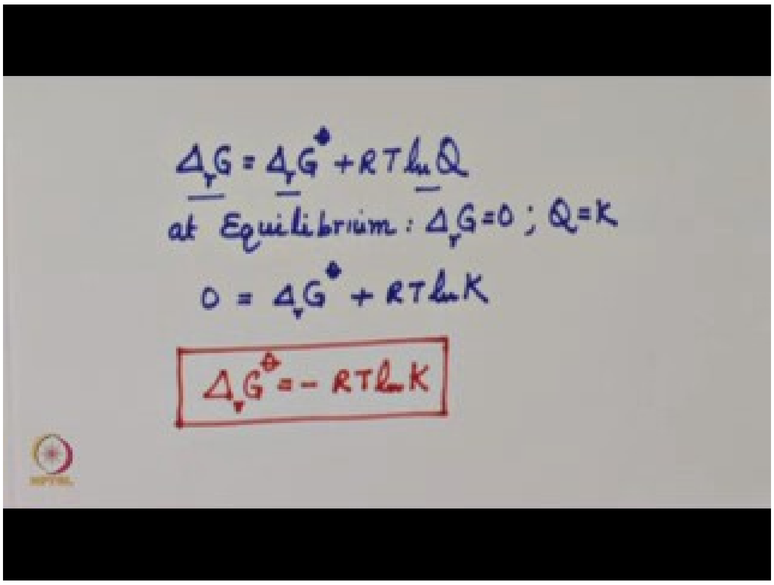

$$\underline{\Delta_r G} = \underline{\Delta_r G^{\ominus}} + RT\,\underline{\ln Q}$$

at Equilibrium : $\Delta_r G = 0$; $Q = K$

$$0 = \Delta_r G^{\ominus} + RT \ln K$$

$$\boxed{\Delta_r G^{\ominus} = -\,RT \ln K}$$

Now, after expressing delta G in terms of Q we have delta r G is equal to delta r G naught plus RT log Q and at equilibrium as we just discussed delta r G is equal to 0 and Q is equal to K. Once you substitute in this you get 0 is equal to delta G naught plus RT log K in other words if you rearrange this you get delta r G naught is equal to minus RT log K we have derived an equation for a general reaction delta r G naught is equal to minus RT log K and how we define equilibrium constant the equilibrium constant, K we got product J activity of J raise to the power psychometric number.

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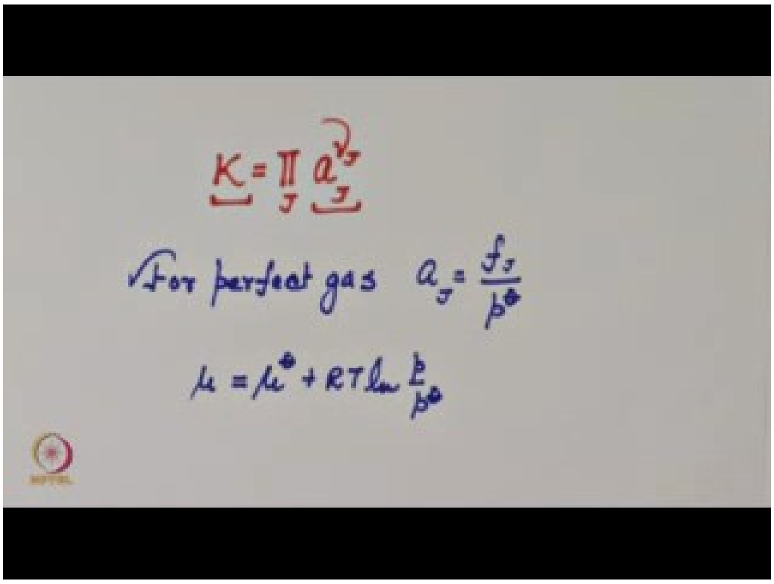

$$\underbrace{K}=\prod_J \underbrace{a_J^{\nu_J}}$$

✓For perfect gas $a_J = \frac{f_J}{p^\ominus}$

$$\mu = \mu^\ominus + RT\ln\frac{p}{p^\ominus}$$

Now, one thing to be recognized over here is that these activities are dimensionless quantities we have discussed earlier that activity is a dimensionless quantity. So, therefore, we do not expect any units for equilibrium constant this is a very important point which must be understood because in elementary textbooks and even in many research publications we find that the equilibrium constants are mentioned with units and as we derived here the thermodynamic equilibrium constant is actually expressed in terms of activities which are dimensionless quantities.

So, therefore, equilibrium constant thermodynamic equilibrium constant does not have any unit, if we are expressing any equilibrium constant or if we see any equilibrium constant mentioned with units then that is a practical equilibrium constant. And what is the difference between thermodynamic equilibrium constant and practical equilibrium constant that I will discuss a bit later. And let us go back to the slides now, we have now delta r G naught is minus RT log K, and we just discussed that K can be expressed in terms of the activities we also discussed that the activities do not have any dimensions therefore, equilibrium constant should be a dimensionless quantity.

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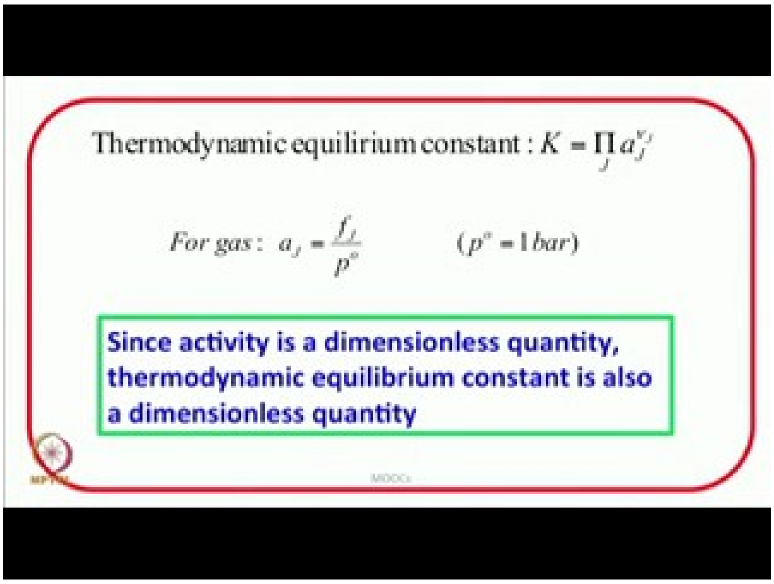

Thermodynamic equilirium constant : $K = \prod_j a_j^{\nu_j}$

For gas: $a_j = \frac{f_j}{p^\circ}$ $(p^\circ = 1\,bar)$

Since activity is a dimensionless quantity, thermodynamic equilibrium constant is also a dimensionless quantity

For a guess the activity should be written as fugacity divided by p naught where p naught is 1 bar this is done. So, that activity here does not have any unit and in fact, since activity does not have any unit it is a dimensionless quantity thermodynamic equilibrium constant is also a dimensionless quantity. For ideal gas we will write as I said activity is equal to fugacity, fugacity has units of pressure therefore, you put divide by 1 bar p naught is equal to 1 bar and in fact, if you apply the same discussion to perfect gases the chemical potential for a perfect gas will be equal to mu naught plus RT log p by p naught.

So, whatever is the psychometric number p by p naught is not going to have any unit and that is why even if a reaction is asymmetric means in which the number of moles of reactants and products in the gaseous forms are different even then the equilibrium constant will turn out to be a dimensionless quantity. Because each p is divided by p naught that makes it dimensionless and that is why when we derive a general expression for perfect gas we will write activities as fugacity divided by p naught and this we can actually demonstrate by taking one example.

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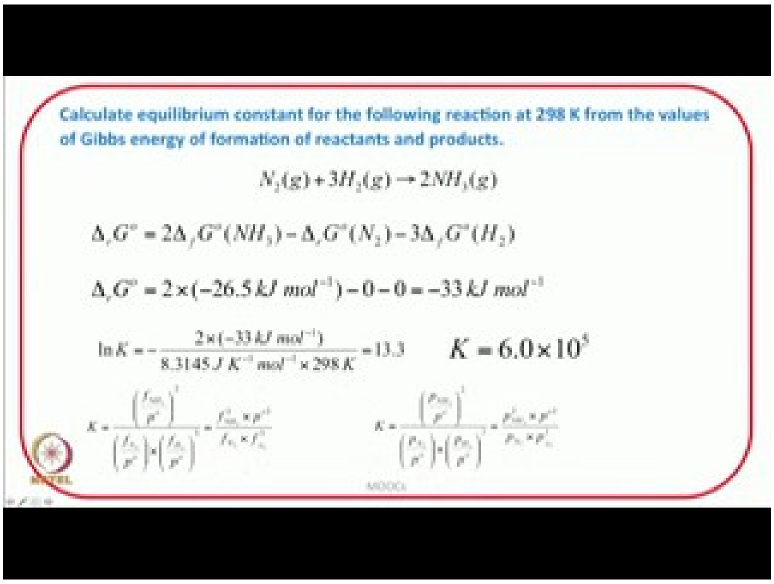

Calculate equilibrium constant for the following reaction at 298 K from the values of Gibbs energy of formation of reactants and products.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

$$\Delta_r G^\circ = 2\Delta_f G^\circ(NH_3) - \Delta_f G^\circ(N_2) - 3\Delta_f G^\circ(H_2)$$

$$\Delta_r G^\circ = 2\times(-26.5\,kJ\,mol^{-1}) - 0 - 0 = -33\,kJ\,mol^{-1}$$

$$\ln K = -\frac{2\times(-33\,kJ\,mol^{-1})}{8.3145\,J\,K^{-1}\,mol^{-1}\times 298\,K} = 13.3 \qquad K = 6.0\times10^5$$

$$K = \frac{\left(\frac{f_{NH_3}}{p^\circ}\right)^2}{\left(\frac{f_{N_2}}{p^\circ}\right)\times\left(\frac{f_{H_2}}{p^\circ}\right)^3} = \frac{f_{NH_3}^2\times p^{\circ 2}}{f_{N_2}\times f_{H_2}^3} \qquad K = \frac{\left(\frac{p_{NH_3}}{p^\circ}\right)^2}{\left(\frac{p_{N_2}}{p^\circ}\right)\times\left(\frac{p_{H_2}}{p^\circ}\right)^3} = \frac{p_{NH_3}^2\times p^{\circ 2}}{p_{N_2}\times p_{H_2}^3}$$

Let us take this example calculate equilibrium constant for the following reaction at 298 Kelvin from the values of Gibbs energy of formation of reactants and products the react the reaction is nitrogen plus 3 hydrogen forming 2NH 3. And as we discussed earlier we can get the reaction standard reaction Gibbs energy from the values of the standard Gibbs energies of formation for this reaction, standard Gibbs energy of the standard reaction Gibbs energy will be equal to twice the standard Gibbs free energy of formation of ammonia minus that of nitrogen minus 3 times that of hydrogen and we know for nitrogen and hydrogen which are elements the free energies of Gibbs energy is of formation of 0.

And therefore, we can get the value of delta r G naught from the value of Gibbs energy of formation of ammonia. So, delta G naught is minus 33 kilo Joules per and once you substitute into delta G naught is minus RT log K and get the value of K log K and hence the K turns out to be 6 into 10 raise to the power minus 10 raise to the power 5.

The formula that has been used here is delta G naught is minus RT log K. So, log K is minus delta G naught by RT and substitute the appropriate values. Carefully look at how K is expressed we need to express K as activity of ammonia raise to the power 2 divide by activity of nitrogen into activity of hydrogen raise to the power 3 and in place of activity I am writing f by p naught. Please note there since the term inside the bracket is a dimensionless quantity overall units of K overall or overall K is going to be also a dimensionless quantity.

So, this expression after you cancel p naught turns out to be fugacity of ammonia raise to the power 2 over fugacity of nitrogen into fugacity of hydrogen raise to power 3 this is as predicted by this equation and it will also have a term p naught raise to the power 2. So, that overall here 2 plus 2 - 4 and down there in the denominator 3 plus 1 - 4 total psychometric numbers are same and therefore, finally, there is going to be no unit. If the pressure is very very low then fugacities can be replaced by pressure we know that at very low pressure the gas is start behaving ideally.

So, therefore, fugacities can be replaced at very low pressure. So, this will be an approximate result not really quite exact result because at very low pressure your approximating fugacity by pressure. So, that is why when the pressure is very very low we can conveniently replace fugacity by pressure and get a very approximate result for the equilibrium constant.

So, what we have discussed in this lecture is how to derive a general relationship between the standard reaction Gibbs energy and equilibrium constant. We also discuss that thermodynamic equilibrium constant is a unitless quantity, is a dimensionless quantity because the equilibrium constant is actually a ratio of activities for the products and the reactance. And since activities are dimensionless quantities therefore, the equilibrium constant is also a dimensionless quantity.

We will discuss more about the thermodynamic equilibrium constant and practical equilibrium constant in the next lecture.

Thank you very much.