Chemical and Biological Thermodynamics: Principles to Applications
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Lecture - 26
Perfect gas Equilibria

Let us now continue our discussion on the equilibrium and equilibrium constants. And as usual we will first start with the perfect gases and then later on we will extend our discussion to deviation from perfect behaviour and eventually we will discuss for the liquids solutions also. So, let us discuss the equilibrium in perfect gases.

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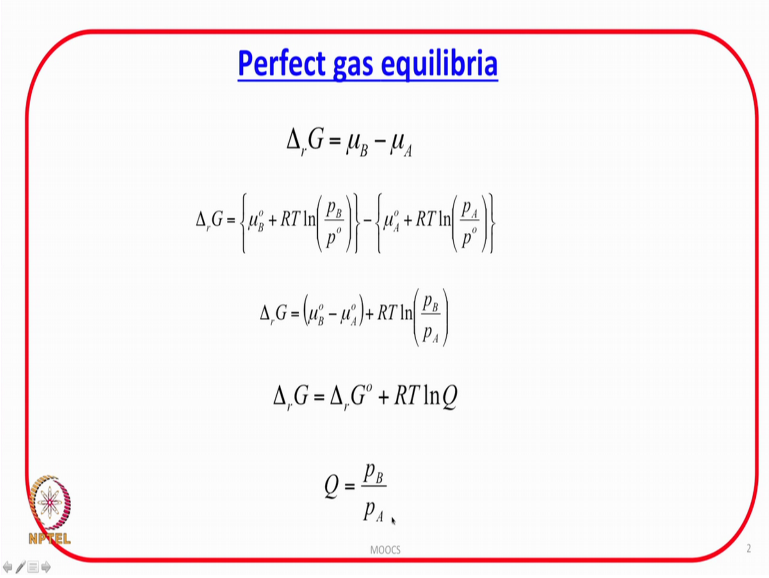

Perfect gas equilibria

$$\Delta_r G = \mu_B - \mu_A$$

$$\Delta_r G = \left\{\mu_B^o + RT\ln\left(\frac{p_B}{p^o}\right)\right\} - \left\{\mu_A^o + RT\ln\left(\frac{p_A}{p^o}\right)\right\}$$

$$\Delta_r G = \left(\mu_B^o - \mu_A^o\right) + RT\ln\left(\frac{p_B}{p_A}\right)$$

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

$$Q = \frac{p_B}{p_A}$$

The discussion in the previous lecture lead to derivation of this equation that the reaction gives function this is the slope of the variation of G with respect to phi is equal to difference in chemical potentials.

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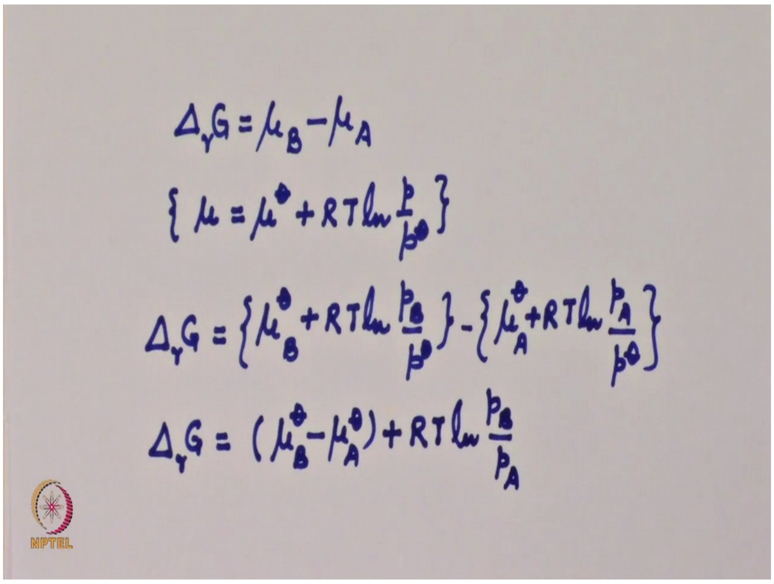

$$\Delta_r G = \mu_B - \mu_A$$

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

$$\Delta_r G = \left\{ \mu_B^{\ominus} + RT \ln \frac{p_B}{p^{\ominus}} \right\} - \left\{ \mu_A^{\ominus} + RT \ln \frac{p_A}{p^{\ominus}} \right\}$$

$$\Delta_r G = (\mu_B^{\ominus} - \mu_A^{\ominus}) + RT \ln \frac{p_B}{p_A}$$

So, if I write delta r G which I am repeatedly saying it is the slope this is equal to difference in chemical potential mu B minus mu A and we know that for a perfect gas mu is equal to mu naught plus RT log p by p naught this is the definition of chemical potential for a perfect gas. So, therefore, delta r G will be equal to let us write for mu B it will be mu B naught plus RT log p B by p naught this is for my B now for mu A it will be mu A naught plus RT log p A by p naught.

Further delta r G will be equal to I can write my B naught minus mu A naught and let us combine the logarithmic terms it will be RT log p B by p A let us go to the slide. Once you substitute for the chemical potentials for B and chemical potentials for A the resulting disc a equation as we discussed is delta r G is equal to mu B naught minus mu A naught plus RT log p B divided by p A p naught and p naught we will get cancelled, but in any case p naught is equal to 1 bar.

But we will discuss later on that expressing in terms of p naught is very important because it will help us in understanding whether the equilibrium constant has units or it does not have unit. Now this equation let us express into another form this is delta r G and this difference in standard state chemical potential is equal to standard state reaction give function Gibbs free Gibbs energy this also we have discussed in the previous lecture and instead of p B by p A let me write Q, what is Q in general? This I will discuss in the next lecture in terms of reaction quotient Q is actually call reaction quotient, but the details of reaction quotient I will discuss in the next lecture. But let us for the time being write Q as the ratio of the partial pressure of B and partial pressure of A. This equation delta r G is equal to delta rg naught plus RT log Q is a very important relation because it connects the slope this is actually a slope or the value of delta r G with Q, Q is the ratio of partial pressure of B and partial pressure of A; that means, it dip Q the value of Q depends on how much B is there and how much A is there in the reaction mixture and this Q will decide delta r G.

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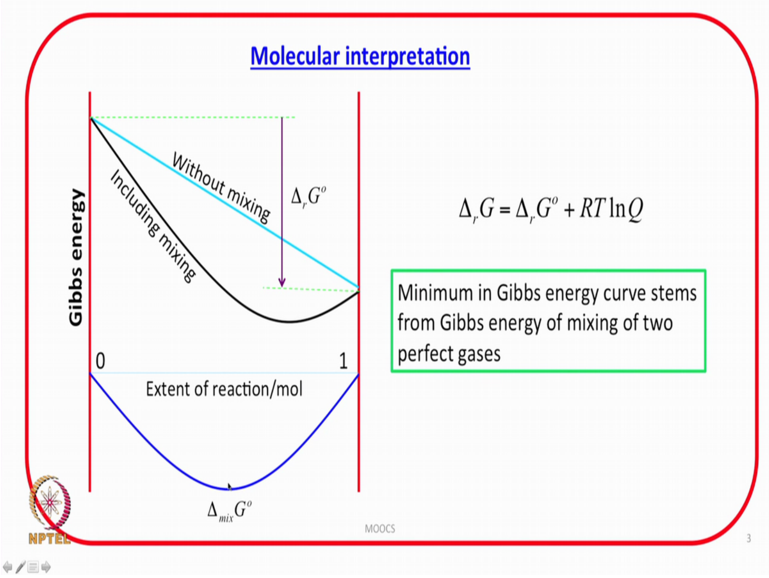

Molecular interpretation

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

Minimum in Gibbs energy curve stems from Gibbs energy of mixing of two perfect gases

And let us discuss the molecular interpretation of this equation that we have just derive the delta r G is equal to delta r G naught plus RT log Q.

How this Q affects the slope affects the value of delta r G, delta r G naught is constant because this is the difference in the chemical potential of the product and reactant. Let us take a look at this case. Here consider the plot of total Gibbs energy against the extent of reaction, total Gibbs energy means total Gibbs energy of everything reactant and product verses extent of reaction. Now let us consider the reaction of a or the transformation of a to B this is the reaction A going towards B that is the process, A will form B and let us assume that the B formed first of all let us consider there is no mixing with a without mixing, you have A and you have B and you do not allow them to mix.

In that case when the extent of reaction is one; that means, one mole of reactant has been converted to one mole of product then gives energy changes from this value to this value without mixing; that means, the path followed will be this light blue if you do not allow the product formed to mingle with the reactants then the path followed will be this. And the difference between the 2 is going to be delta r G naught because how do we define delta r G? Delta r G is equal to variation in Gibbs free energy with respect to extent of reaction at constant pressure and temperature.

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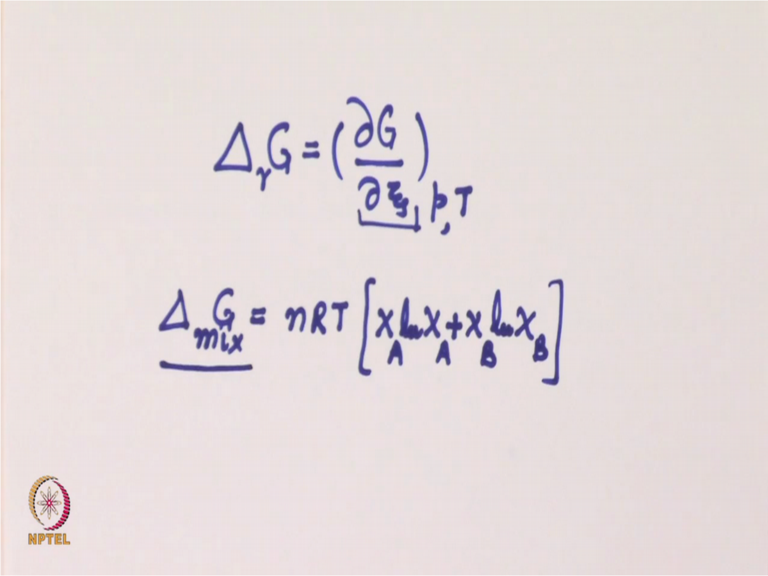

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T}$$

$$\underline{\Delta_{mix} G} = nRT\left[x_A \ln x_A + x_B \ln x_B\right]$$

So, when the change design finite changes one; that means, you are changing from pure a to pure B and I will write delta G naught in this case and the slow this actually is the slope for the entire for entire this blue line this slope will be equal to delta r G naught because what you have the vertical distance is change in Gibbs energy and horizontal distance is one therefore, slope is equal to delta r G naught and this difference this difference which represents the slope when 0 is when the extent of reaction changes from 0 to 1.

But if you allow the product form for example, when A is converted to B and B is allowed to mix with A then if you remember we have discussed the free energy of mixing to be equal to n RT, X A log X A plus X B log X B this contribution will start coming in if you allow A and B to mix and depending upon their mole fractions in the solution the variation look at the slide the variation of mixing Gibbs energy when mole fraction changes from 0 to organ the extent of reaction changes from 0 to 1 will vary like this, this is a u shaped curve.

Now, if you take the overall effect of this light blue line and the dark blue line including mixing the Gibbs free energy or Gibbs energy will vary like this and the minima of this curve corresponds to the position of equilibrium as discussed in the previous lecture. I repeat if the product form is not allowed to mix with the reactant then the blue line this path will be followed and this difference between the 2 is delta r G naught.

However, if you allow the product from to mingle with the reactants the free energy of mixing term will also contribute when you add the effect of without mixing and the mixing then including mixing the overall Gibbs energy change with extent of reaction is going to be according to this black line and this is the effect of the term Q because this RT log Q this the second term arises because of the mixing effects all right.

So, the minimum in Gibbs energy curve stems from Gibbs energy of mixing of 2 perfect gases, this minima is arising from the mixing effects.

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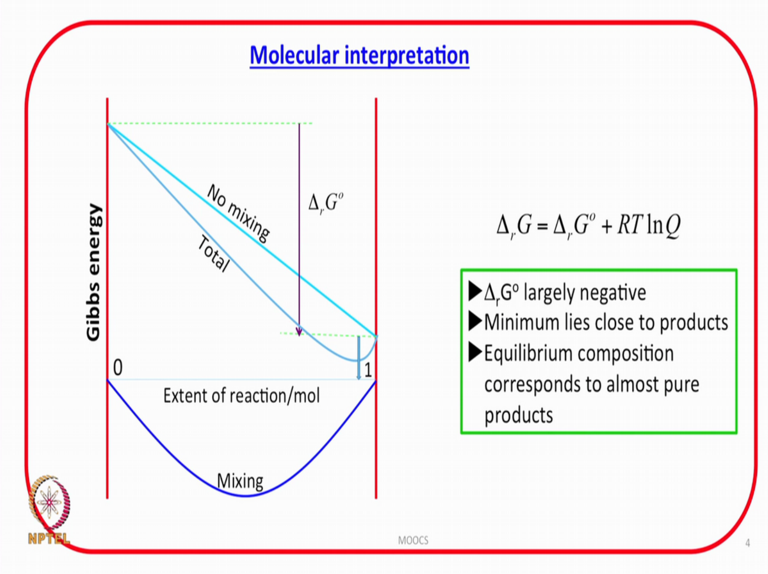

Molecular interpretation

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

- $\Delta_r G^o$ largely negative
- Minimum lies close to products
- Equilibrium composition corresponds to almost pure products

Let us continue with the molecular interpretation depending upon whether the equilibrium is live close to product or equilibrium is lying close to reactants. Now let us take a look at this figure. In this figure without mixing you see here the slope is more negative; that means, the value of delta r G 0 is largely negative, it is large and negative, large and negative means the minima in the free energy verses extent of reaction curve should appear close to psi equal to 1.

So, if this light blue line which is without mixing and dark blue line which is the variation of Gibbs energy versus extent of reaction with mixing the 2 are combined the resulting curvature or resulting curve is going to be the one shown under total and here if you see the minima is lying very close to the product.

So, if delta G naught is largely negative the minimum in the curve lies close to product; that means, the position of equilibrium is close to product and the reaction is essentially complete. So, this is what is commented over here the delta r G naught is largely negative minimum lies close to products and equilibrium composition corresponds to almost pure product that is what it means that the minima here is lying very close to the product that is why the equilibrium composition corresponds to almost pure products.

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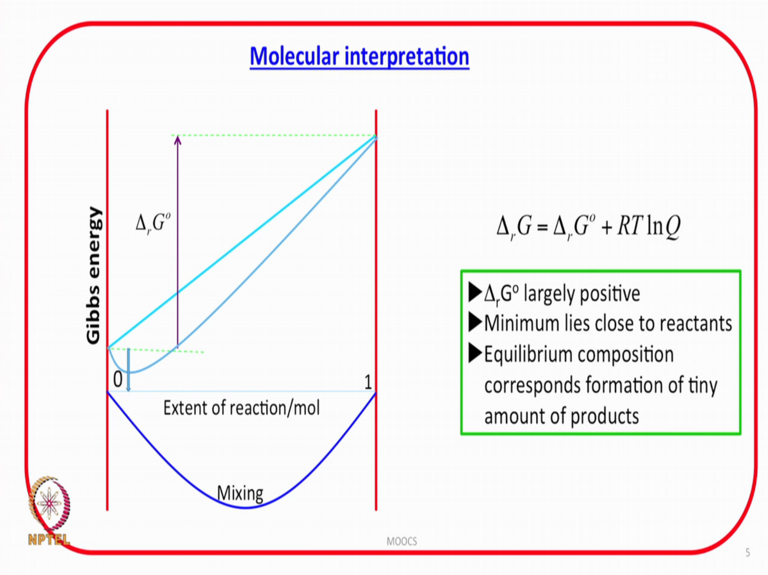

Molecular interpretation

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

- ▶$\Delta_r G^o$ largely positive
- ▶Minimum lies close to reactants
- ▶Equilibrium composition corresponds formation of tiny amount of products

Now, let us discuss another case molecular interpretation for the case where delta r G 0 is largely positive, the slope is positive here you see here and delta r G naught is largely positive; that means, reaction is not spontaneous and if you mix these 2 effects the light blue and dark blue the dark blue is because of the mixing effects, free energy dependence when you mix the resulting total curve is this one which is in which the minima is lying very close to the reactants; that means, the reaction does not proceed well.

And this is what is commented that if delta r G 0 is largely positive you see a largely positive the minimum lies close to the reactants and equilibrium composition corresponds to formation of a very small amount of product tiny product because this minima is lying very close to the reactants itself; that means, product formed is very very small.

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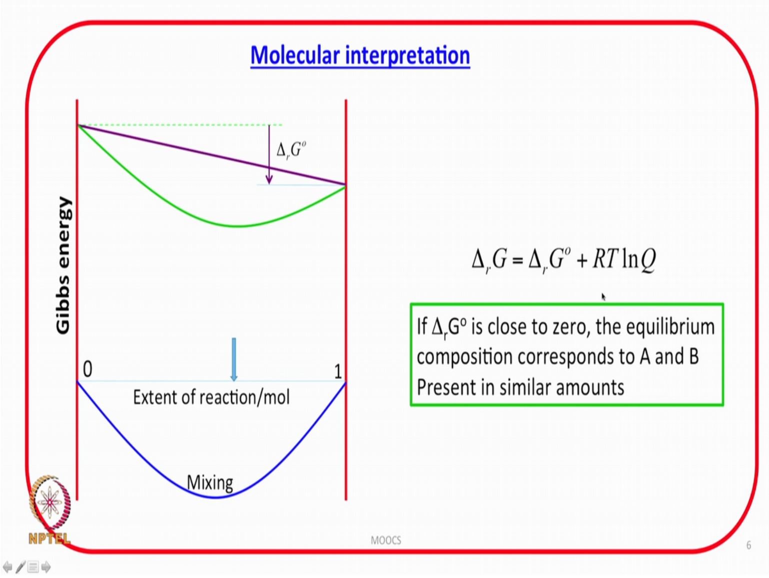

Molecular interpretation

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

If $\Delta_r G^o$ is close to zero, the equilibrium composition corresponds to A and B Present in similar amounts

The third case can be in which the slope is small; that means, the value of delta r G 0 is very small and then when you mix these to this plus this effect and this minima for position of equilibrium starts moving in between that and intermediate value and this minima will exactly correspond to midpoint in case Q is equal to 1.

That means, if this minima is at the midpoint here, actually here if you see this minima at this it is at this point where appreciable amount of product is formed and there is an appreciable amount of reactant also there and if the product formed is equal to the amount of reactant in the equilibrium mixture than Q will be equal to 1; that means, if the way partial pressure of B and A are same then log Q will be 0 because Q is equal to 1 and in that case delta r G will be equal to delta r G naught and that is what is commented if delta r G naught is close to 0 the equilibrium composition corresponds to A and B present in similar amounts.

So, I hope it is clear that the effect of mixing is actually represented in the second term in the RT log Q term, R is constant, T is a given temperature. In fact, it is the Q term which includes the effect of mixing ok.

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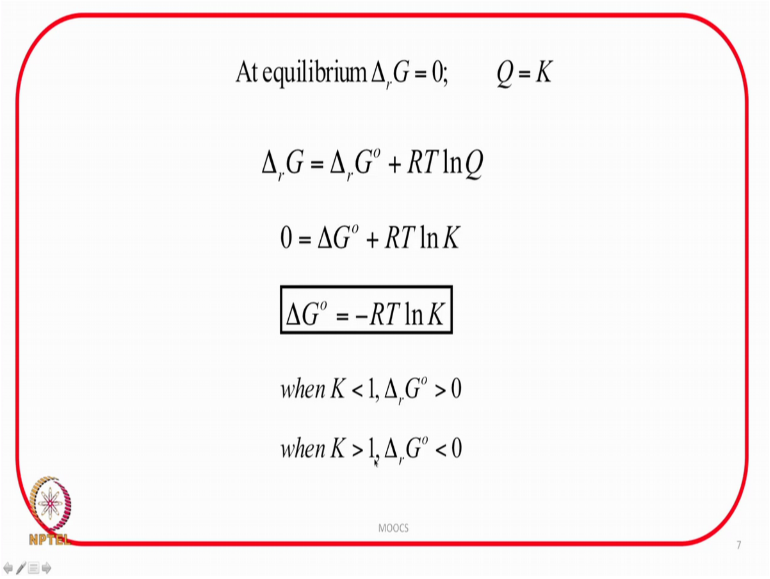

At equilibrium $\Delta_r G = 0$; $Q = K$

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

$$0 = \Delta G^o + RT\ln K$$

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

when $K < 1, \Delta_r G^o > 0$

when $K > 1, \Delta_r G^o < 0$

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Let us continue our discussion at equilibrium delta r G is equal to 0; that means, the slope is equal to 0 and we can replace Q by K. So, in this equation where this is slope at equilibrium we know that the slope is equal to 0 and if I put in place of Q the equilibrium constant then what we have, I have I substitute 0 for delta r G and I substitute K for Q and when I rearrange this I get delta G naught is equal to minus RT log K. This result is very important result because it connects the equilibrium constant with the standard state reaction Gibbs energy.

We have arrived at this equation by using perfect gas equilibria and you will see that we get exactly the same relation when we discuss when we consider not just the perfect cases or ideal cases even in general this relation will be true in general delta G naught is equal to minus RT log K; obviously, depending upon the value of K delta G naught will be positive or it will be negative. When it will be positive or negative? Suppose K is less than one if K is less than one then log of that less than one number will be negative and overall delta G naught will be positive that is what is commented over here if K is less than 1 delta r 0 is positive and if K is greater than 1 obviously, delta r 0 that is the standard state reaction Gibbs free energy is negative, and K is greater than 1, how much greater than 1 that will depend upon the amount and extent of the product formed.

So, what we have discussed is that from this general connection of the reaction Gibbs energy which is actually slope of reaction slope of slope of Gibbs energy with extent of reaction at equilibrium when it is equal to 0 Q becomes K. So, it rearranges to delta G naught is minus RT log K and then depending upon the value of K delta G naught will be positive or negative.

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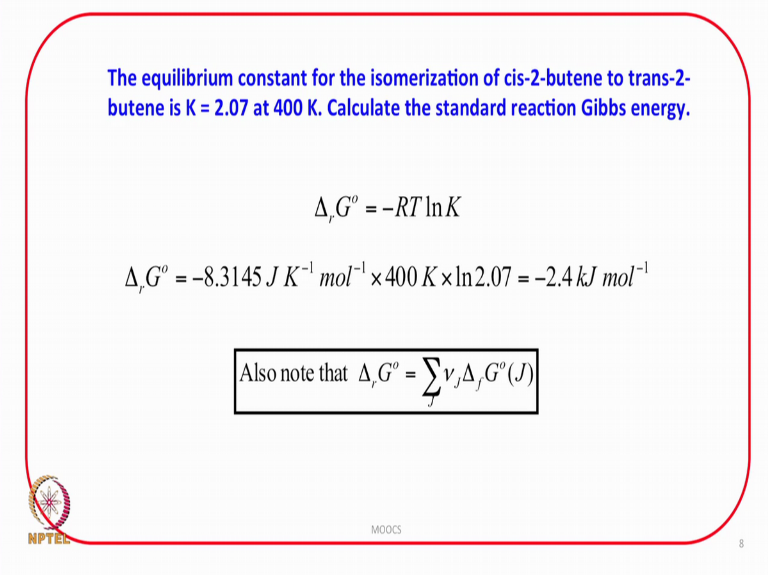

The equilibrium constant for the isomerization of cis-2-butene to trans-2-butene is K = 2.07 at 400 K. Calculate the standard reaction Gibbs energy.

$$\Delta_r G^o = -RT \ln K$$

$$\Delta_r G^o = -8.3145\, J\, K^{-1}\, mol^{-1} \times 400\, K \times \ln 2.07 = -2.4\, kJ\, mol^{-1}$$

$$\boxed{\text{Also note that } \Delta_r G^o = \sum_J \nu_J \Delta_f G^o(J)}$$

Let us take up an example and discuss it a little further. Let us consider this question which is the equilibrium constant for the isomerization of cis 2 butane to trans 2 butane is K is equal to 2.07 at 400 Kelvin.

Calculate the standard reaction Gibbs energy we are given the value of K which is just 2.07 K is very very small and we have been asked to calculate the value of the standard reaction Gibbs energy. We will immediately think of a relation, which connects equilibrium constant with the standard reaction Gibbs energy and this expression we actually just derive the delta G naught is equal to minus RT log K.

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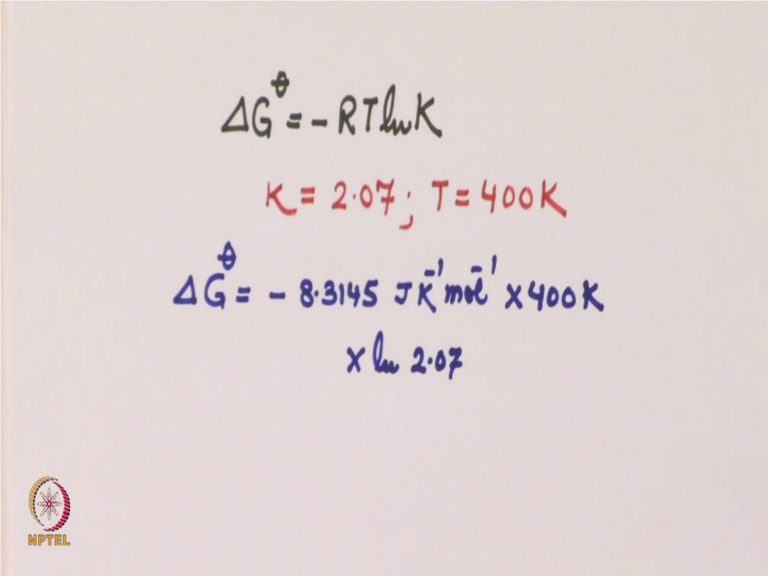

$$\Delta G^{\ominus} = -RT\ln K$$

$K = 2.07$; $T = 400K$

$$\Delta G^{\ominus} = -8.3145\ JK^{-1}mol^{-1} \times 400K \times \ln 2.07$$

Please remember that in this equation there is no n over here, sometimes we make a mistake of introducing n. When we talk about one more of a reaction then we do not need n over here all right.

The value of K is given to us as 2.07 and the value of temperature is given to us as 400 Kelvin. Therefore delta G naught is equal to minus r 8.3145 Joules per Kelvin per mol into 400 Kelvin into log of 2.07. And now you see the units eventually it is going to give you a value in joules per mole. Let us take a look at the slide the standard reaction Gibbs energy in terms of equilibrium constant the equation that we just derive and as I just showed that the standard reaction Gibbs energy when you substitute the values will turn out be minus 2.4 kilo Joules per mol. This example demonstrates how to calculate the value of standard reaction Gibbs free energy change for a reaction from the knowledge of the value of equilibrium constant.

Also please note that we have earlier discussed that it is possible to get standard reaction Gibbs energy of a reaction from the knowledge of the Gibbs energy of formation of the product and Gibbs energy of formation of the reactant. Delta G naught can come from the knowledge of equilibrium constant, delta G naught can also come from the knowledge of free energy of formation of the products and reactants and this must be kept in mind. So, whether the product will be formed or product will not be formed one can predict from the value of delta G naught if somehow we can get it or alternatively if we know or you know in another words if we know the value of K we can calculate delta G naught.

So, eventually if our goal is to get the higher value of K or a higher value of product then we want a largely negative value of delta G naught and in fact, in literature if the free energies of formation in the standard state for the reactants and products are known one can actually calculate the value of delta G naught and predict the value of K.

So, what we have discussed in this part of the lecture is to connect the standard reaction Gibbs energy which is the slope of the plot of Gibbs energy of the mixture versus the extent of reaction how it is connected to the spontaneity of the process and how we can get the equilibrium constant from a discussion of the standard reaction Gibbs energy. The value of equilibrium constant will decide the sign and magnitude of delta G naught.

And as later on we will discuss that the equilibrium constant is a very important for property not only in academic discussion, but industrial area also because eventually we would like to have a process or industry would like to have a process in which the large amount of product is formed, large amount of product is formed means the value of equilibrium constant should be high. We will discuss more about the equilibrium constant and the optimization of processes in the next lecture.

Thank you very much.