Thermodynamics for Biological Systems:
Classical and Statistical Aspects
Prof. G.K. Suraishkumar
Department of Biotechnology
Indian institute of Technology - Madras

Lecture – 48
Equilibrium Constants

Welcome!

Let us move forward. Now, let us look at equilibrium constants. I am sure you know what equilibrium constants are. You must have done this in your 11-th standard, 12-th standard chemistry, and probably in some other courses in the engineering discipline or in the biotechnology course before you took this course. So, you already know what equilibrium constants are, what I am going to give you here is a formalism from the fundamentals to get at equilibrium constants. So, you will know where it all rests on, and so it will be much easier for you to have an overall picture in terms of some fundamental thermodynamic quantities.

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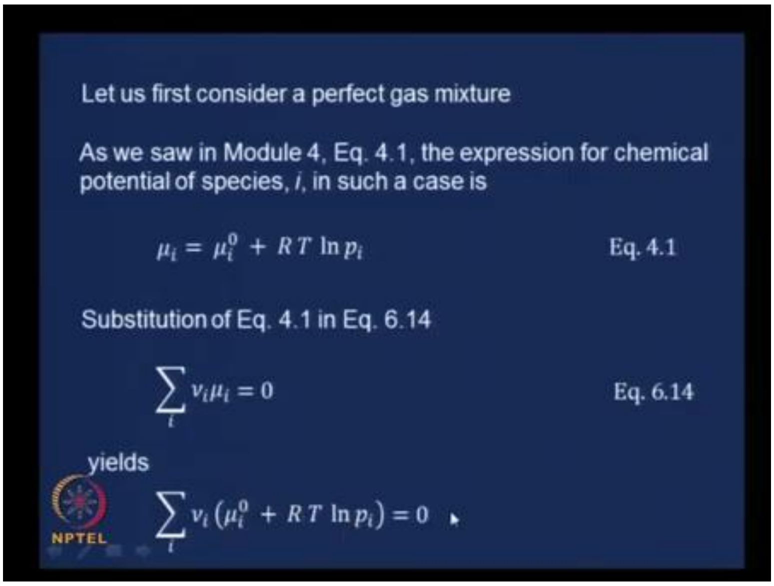

Let us first consider a perfect gas mixture

As we saw in Module 4, Eq. 4.1, the expression for chemical potential of species, *i*, in such a case is

$$\mu_i = \mu_i^0 + R\,T\,\ln p_i \qquad \text{Eq. 4.1}$$

Substitution of Eq. 4.1 in Eq. 6.14

$$\sum_i \nu_i \mu_i = 0 \qquad \text{Eq. 6.14}$$

yields

$$\sum_i \nu_i \left(\mu_i^0 + R\,T\,\ln p_i\right) = 0$$

To do that, let us first consider a perfect gas mixture. As we saw in module 4, especially equation 4.1, the expression for chemical potential of species i, in the case of a perfect gas mixture was

$$\mu_i = \mu_i^0 + R\,T\,\ln p_i$$

If you substitute equation 4.1 in equation 6.14 – equation 6.14 is the condition for reaction equilibrium

$$\sum_i \nu_i \mu_i = 0$$

to yield

$$\sum_i \nu_i \left(\mu_i^0 + R\,T\, \ln p_i\right) = 0$$

This is this condition here.

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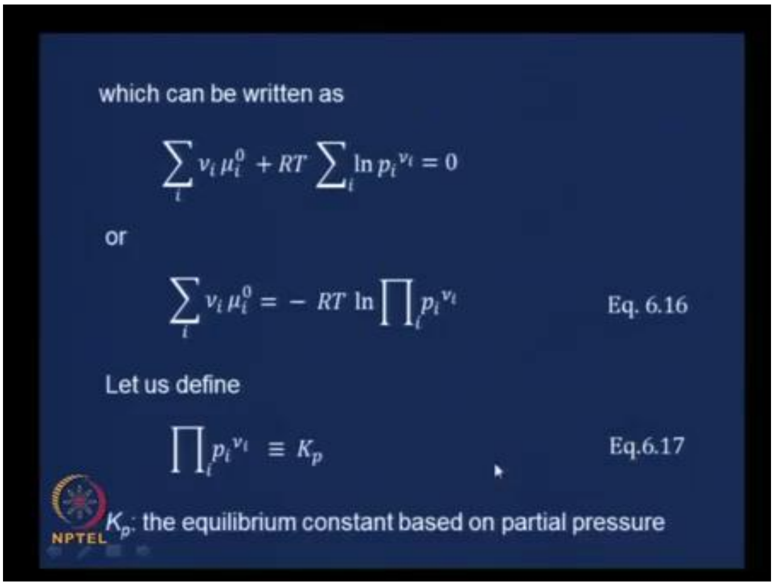

which can be written as

$$\sum_i \nu_i \mu_i^0 + RT \sum_i \ln {p_i}^{\nu_i} = 0$$

or

$$\sum_i \nu_i \mu_i^0 = - RT \ln \prod_i {p_i}^{\nu_i} \qquad \text{Eq. 6.16}$$

Let us define

$$\prod_i {p_i}^{\nu_i} \equiv K_p \qquad \text{Eq.6.17}$$

K_p: the equilibrium constant based on partial pressure

This can, of course, be written as we just multiplying the terms and combining them appropriately using the definitions of log and the definitions of log of a to the power b and so on. We are going to do that now. So, if you do that

$$\sum_i \nu_i\, \mu_i^0 + RT \sum_i \ln {p_i}^{\nu_i} = 0$$

You can work this out by looking at the properties of the log function. And this is summed over all i; this equals 0. Or you can write this as

$$\sum_i \nu_i\, \mu_i^0 = - RT \; ln \prod_i {p_i}^{\nu_i}$$

Product of … is represented by this big pi here Let us call this equation 6.16. Let us define this particular quantity,

$$\prod_i {p_i}^{\nu_i} \equiv K_p$$

You would recall Kp, the equilibrium constant with respect to partial pressure. That, essentially comes from this. So, product over i p i power nu i is defined as K p; equation 6.17.

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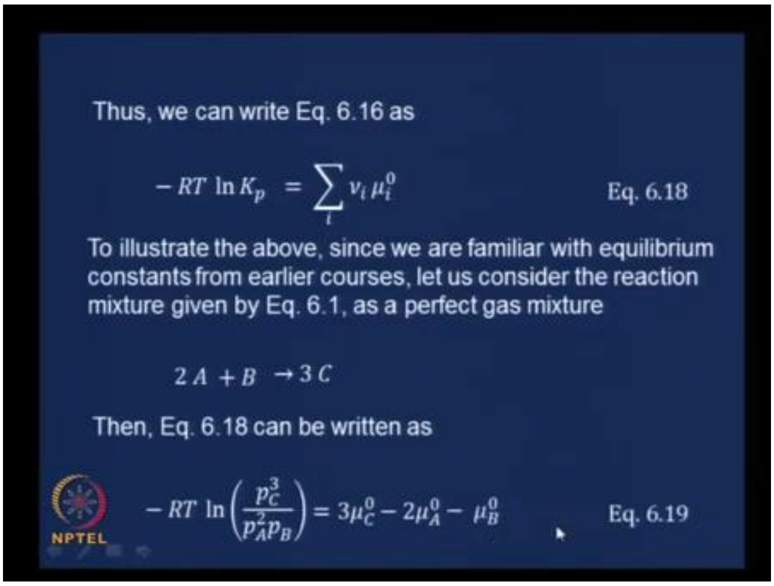

Thus, we can write Eq. 6.16 as

$$-RT \ln K_p = \sum_i \nu_i \mu_i^0 \qquad \text{Eq. 6.18}$$

To illustrate the above, since we are familiar with equilibrium constants from earlier courses, let us consider the reaction mixture given by Eq. 6.1, as a perfect gas mixture

$$2A + B \rightarrow 3C$$

Then, Eq. 6.18 can be written as

$$-RT \ln\left(\frac{p_C^3}{p_A^2 p_B}\right) = 3\mu_C^0 - 2\mu_A^0 - \mu_B^0 \qquad \text{Eq. 6.19}$$

And therefore, we can write 6.16 as

$$-RT \ln K_p = \sum_i \nu_i \mu_i^0$$

Therefore, we have a means of getting Kp in terms of the mu i naught values, the standard chemical potentials of i species multiplied by the appropriate stoichiometric constants and summed over all i would lead to minus RT ln Kp. Let us call this equation 6.18. To illustrate the above … to get it into familiar territory … since we are familiar with equilibrium constants from earlier courses, let us consider the reaction mixture given by equation 6.1, which 2A plus B giving you 3C. Let us consider that for a minute to be a perfect gas mixture.

In such a case, this is the equation … equation 6.18 for this particular reaction can be written as minus RT ln Kp. What was ln Kp? … Ln of the product of pi power nu i. You know that nu i is positive for the products and negative for the reactants. Therefore, if you multiply that all together

$$-RT\ \ln\left(\frac{p_C^3}{p_A^2 p_B}\right) = 3\mu_C^0 - 2\mu_A^0 - \mu_B^0$$

We will call this equation 6.19. Therefore, this must be very familiar to you in terms of the equilibrium constant. How do find that if given the partial pressures is like this, and you can relate it to the standard chemical potentials for that particular reaction.

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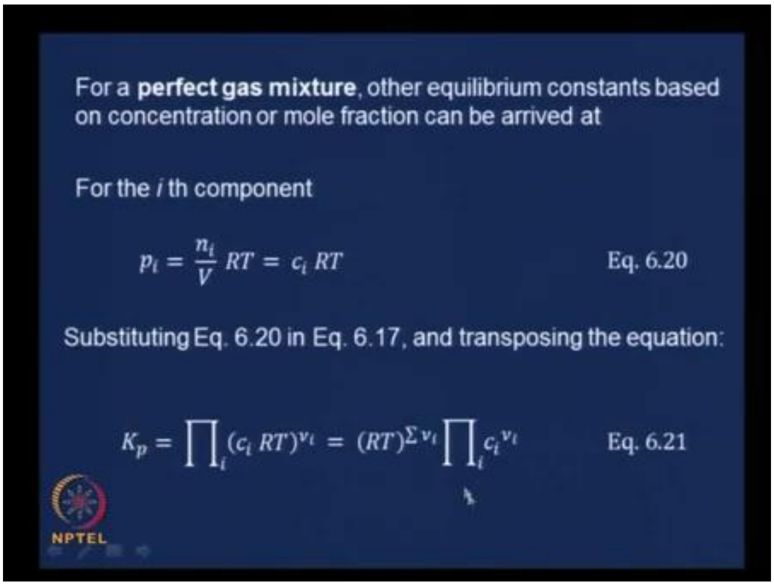

For a **perfect gas mixture**, other equilibrium constants based on concentration or mole fraction can be arrived at

For the *i* th component

$$p_i = \frac{n_i}{V} RT = c_i\, RT \qquad \text{Eq. 6.20}$$

Substituting Eq. 6.20 in Eq. 6.17, and transposing the equation:

$$K_p = \prod_i (c_i\, RT)^{\nu_i} = (RT)^{\Sigma \nu_i} \prod_i c_i^{\nu_i} \qquad \text{Eq. 6.21}$$

Let us stay with the perfect gas mixture for a little while longer. As you can recall, there are many other equilibrium constants. The earlier one was based on partial pressure. You could have an equilibrium constant based on concentration, based on mole fraction, and so on. They can be arrived at as follows. For the i-th component the partial pressure can be written as,

$$p_i = \frac{n_i}{V} RT = c_i\, RT$$

This is from the ideal gas equation. Perfect gas mixture … so, mixture of ideal gases and so on. So, ni by V RT is partial pressure. … ni by V … is nothing but the definition of the concentration, the molar concentration. Therefore, ci RT. Let us call this equation 6.20 in this context.

If we substitute equation 6.20 in equation 6.17 … we will get …

Can you do this bit of algebra right now? Just substitute 6.20 in 6.17 and get this expression. Take about 5 minutes to do that which can further be written as this is just the algebra part … the log and raising it to powers, and so on. You need to get comfortable with this. So, I will give you about 5 minutes to do this. Go ahead please.

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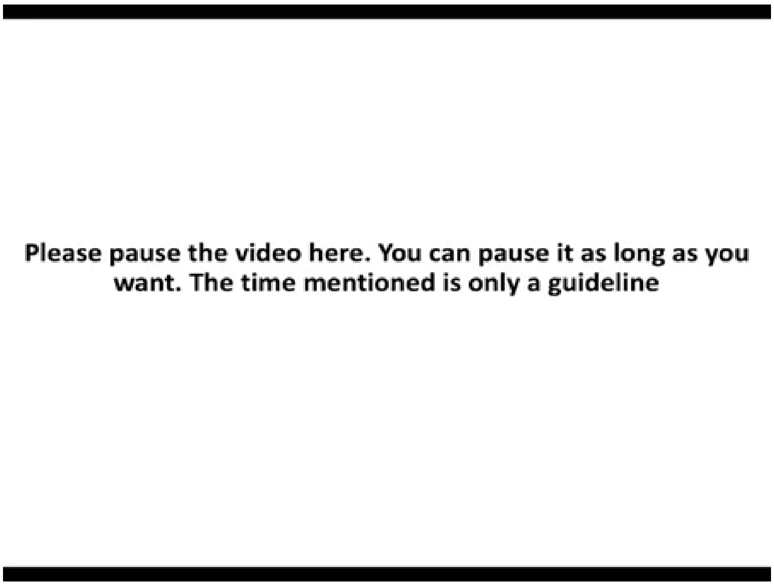

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You should have arrived at

$$K_p = \prod_i (c_i\, RT)^{\nu_i} = (RT)^{\sum \nu_i} \prod_i {c_i}^{\nu_i}$$

Let us call this equation 6.21. This is the definition of Kp.

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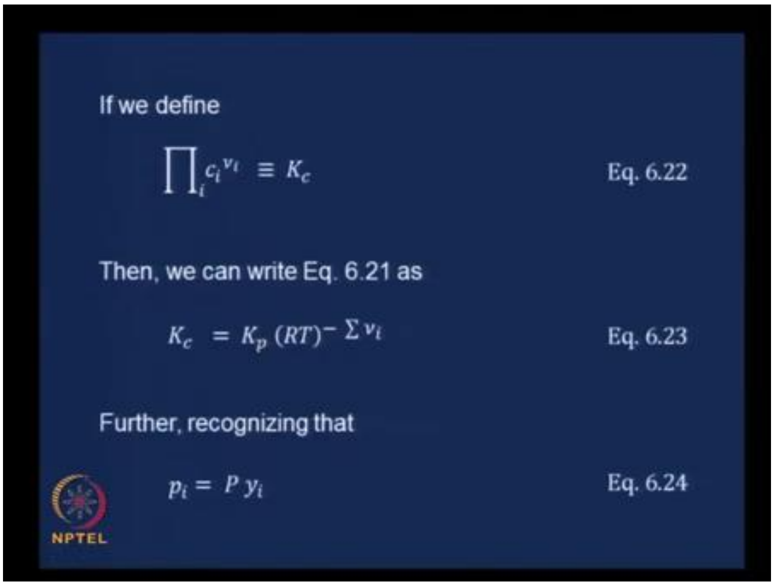

If we define

$$\prod_i c_i^{\nu_i} \equiv K_c \quad \text{Eq. 6.22}$$

Then, we can write Eq. 6.21 as

$$K_c = K_p (RT)^{-\sum \nu_i} \quad \text{Eq. 6.23}$$

Further, recognizing that

$$p_i = P y_i \quad \text{Eq. 6.24}$$

We call this as K c,

$$\prod_i c_i^{\nu_i} \equiv K_c$$

Then, it is easy to see that Kc is nothing but

$$K_c = K_p (RT)^{-\sum \nu_i}$$

Let us call this equation 6.23. Just not this, there is probably one more. Let us recognise that

$$p_i = P y_i$$

equation 6.24. Let me leave you with this for another 10 minutes to derive Ky. You know the equilibrium constant based on the mole fractions yi. Can you go ahead and do it on the same lines as we did it for this. I will present the results after 10 minutes, go ahead.

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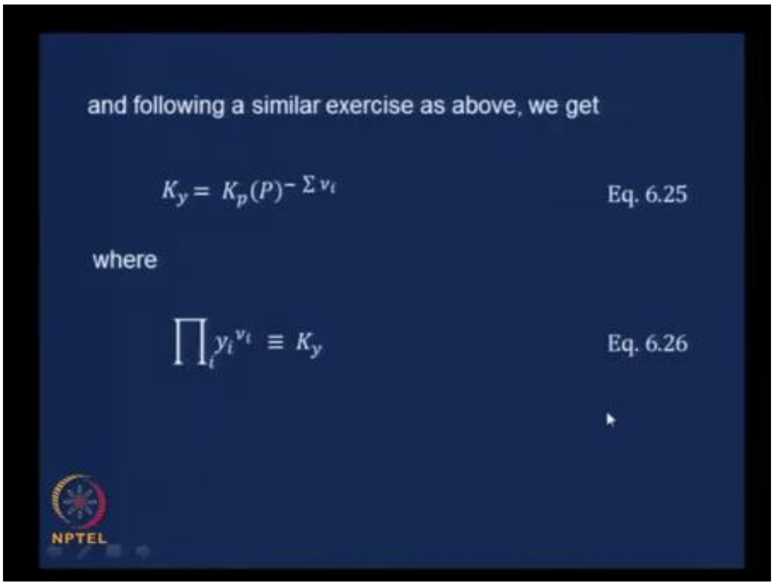

and following a similar exercise as above, we get

$$K_y = K_p (P)^{-\sum \nu_i} \quad \text{Eq. 6.25}$$

where

$$\prod_i {y_i}^{\nu_i} \equiv K_y \quad \text{Eq. 6.26}$$

Taking pi equals the total pressure times the mole fraction yi, if we follow a similar exercise as above … writ Ky in terms of K c and so on, you should get

$$K_y = K_p (P)^{-\sum \nu_i}$$

Hopefully, you got this in your own exercise.

$$\prod_i {y_i}^{\nu_i} \equiv K_y$$

Let us call that equation 6.26.

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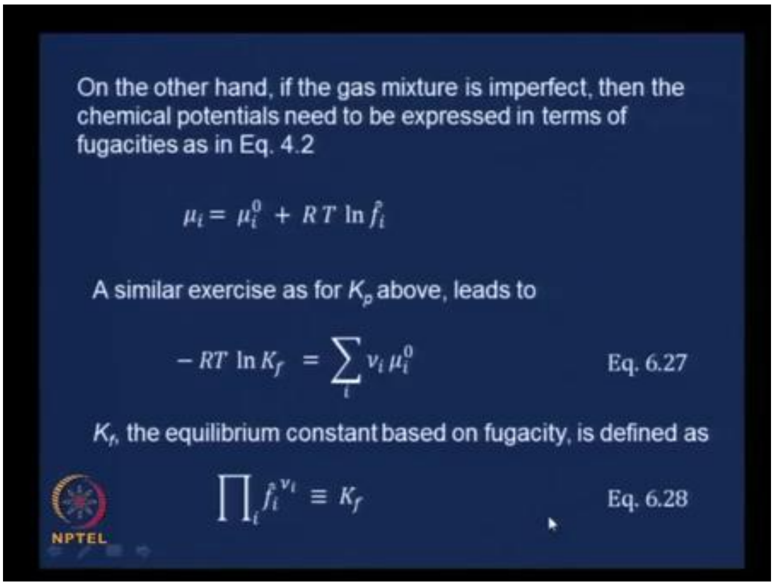

On the other hand, if the gas mixture is imperfect, then the chemical potentials need to be expressed in terms of fugacities as in Eq. 4.2

$$\mu_i = \mu_i^0 + R\,T \ln \hat{f}_i$$

A similar exercise as for K_p above, leads to

$$-RT \ln K_f = \sum_i \nu_i \mu_i^0 \qquad \text{Eq. 6.27}$$

K_f, the equilibrium constant based on fugacity, is defined as

$$\prod_i \hat{f}_i^{\nu_i} \equiv K_f \qquad \text{Eq. 6.28}$$

Now, all those equations that we derived so far, the equilibrium constants, were applicable for perfect gas mixtures. If the gas mixture is imperfect which is usually the case, then, the only change that we need to make, since we are working in terms of chemical potentials is that, the chemical potential needs to be expressed in terms of fugacities instead of partial pressures. This … was given in equation 4.2. Chemical potential in terms of fugacities,

$$\mu_i = \mu_i^0 + R\,T\ ln\,\hat{f}_i$$

Replace fugacities wherever there were partial pressures earlier. If we do a similar exercise … I leave this for you to do as a homework.

So, if you do a similar exercise as for Kp

$$-RT\ \ln K_f = \sum_i \nu_i\,\mu_i^0$$

Kf, the equilibrium constant based on fugacity is defined as,

$$\prod_i \hat{f}_i^{\nu_i} \equiv K_f$$

Let us call that equation 6.28. … We are almost out of time. When we meet in the next class, we will take things further.

See you then.