Thermodynamics (Classical) for Biological Systems

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Module No. # 06

Reaction Equilibria

Lecture No. # 35

Phase rule for Reacting Biosystems, Equilibrium constants

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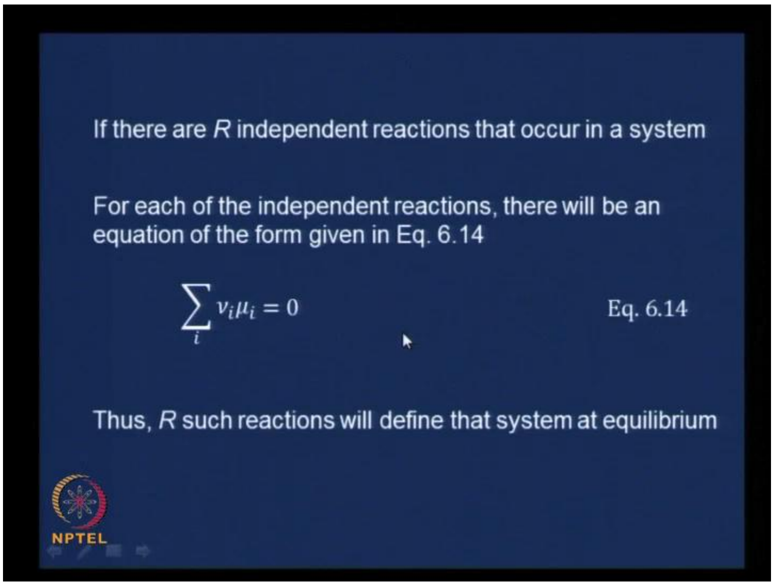

If there are *R* independent reactions that occur in a system

For each of the independent reactions, there will be an equation of the form given in Eq. 6.14

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

Thus, *R* such reactions will define that system at equilibrium

Welcome! to this class.

In the last class, in this module on reaction equilibrium, we saw one of the fundamental relationships for reaction equilibrium, and that happens to be for an independent reaction the sum over i nu i, this is a stoichiometric co-efficient, mu i is a chemical potential of that species i, the product of that, and sum over all i that equals 0. We also said that if there are R independent reactions that occur in our system, then we have one such equation for each of the R independent reactions. Therefore, R such reactions will define that system at equilibrium. This is one of the very significant results, equation 6.14. It is very nice and compact, and it is good to remember this. This will automatically become a part of the memory; the recall is very easy for this equation.

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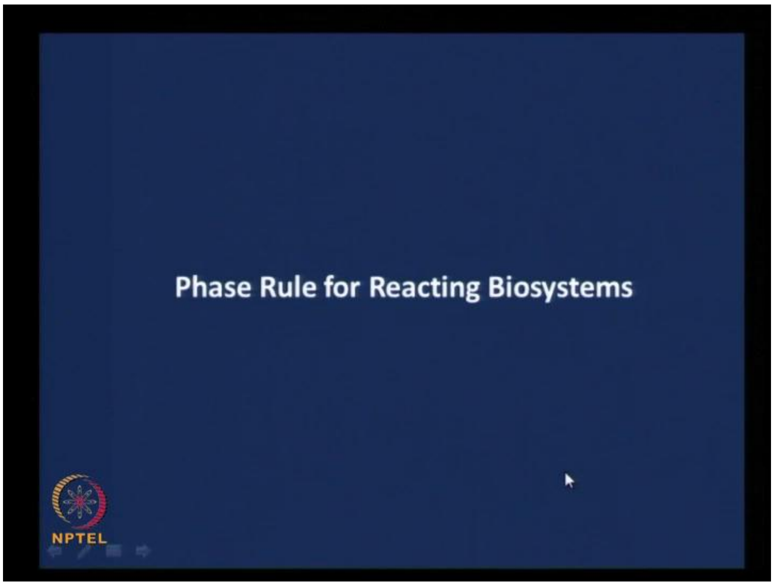

Phase Rule for Reacting Biosystems

What we are going to do next is to look at phase rule for reacting biosystems. The way we are going to do that is through some sort of an interactive method. We have already derived the phase rule for non-reacting systems in the previous module. What I am going to do is, give you some thoughts again on the background to that, and I will give you all the data; and then let you come up with the phase rule for reacting biosystems. I will give you time for that in this class.

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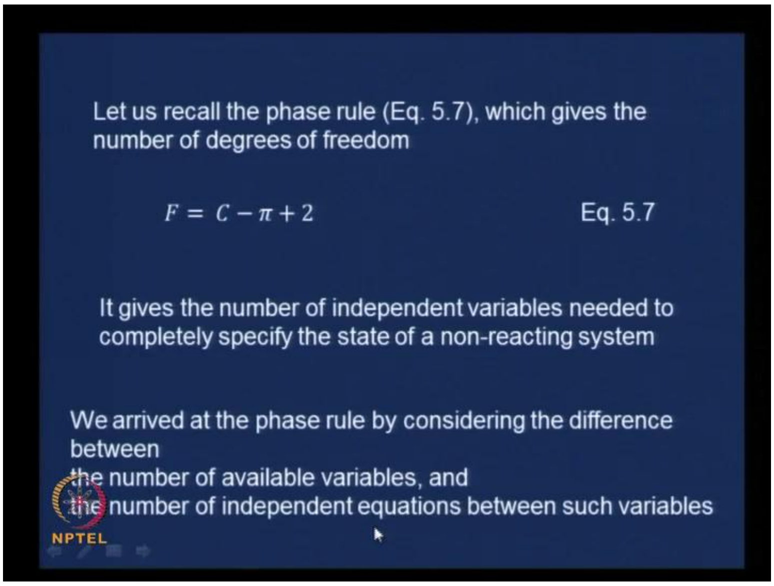

Let us recall the phase rule (Eq. 5.7), which gives the number of degrees of freedom

$$F = C - \pi + 2 \qquad \text{Eq. 5.7}$$

It gives the number of independent variables needed to completely specify the state of a non-reacting system

We arrived at the phase rule by considering the difference between
the number of available variables, and
the number of independent equations between such variables

If you think about, or if we recall the phase rule, equation 5.7, and that gave the number of degrees of freedom. In other words, the number of degrees of freedom is the number of independent variables that are required to complete the description of the system. We saw that the phase rule for the non-reacting system was F the number of degrees of freedom is C minus pi plus 2; C, the number of components in each phase of the system, pi the number of phases. This was our equation 5.7 in the previous module. Let us recall, that we arrived at the phase rule by considering the difference between the number of available variables, and the number of independent equations between such variables.

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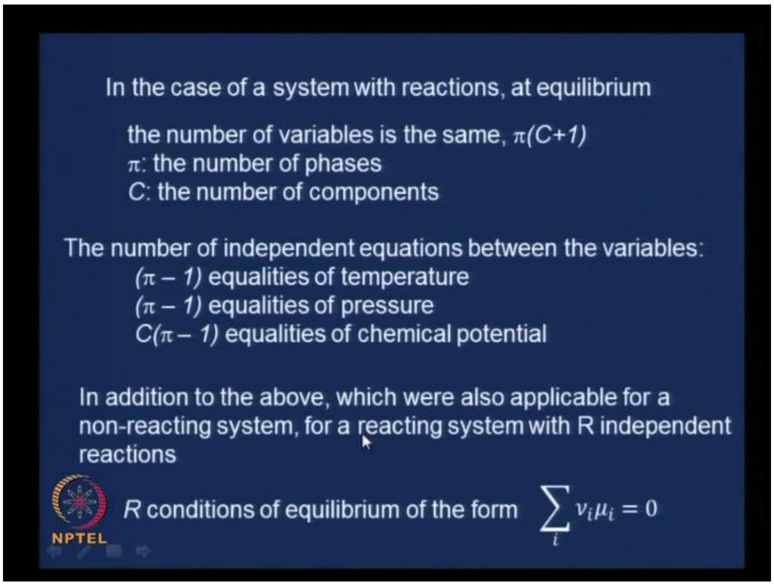

In the case of a system with reactions, at equilibrium

the number of variables is the same, $\pi(C+1)$
π: the number of phases
C: the number of components

The number of independent equations between the variables:
$(\pi - 1)$ equalities of temperature
$(\pi - 1)$ equalities of pressure
$C(\pi - 1)$ equalities of chemical potential

In addition to the above, which were also applicable for a non-reacting system, for a reacting system with R independent reactions

R conditions of equilibrium of the form $\sum_i \nu_i \mu_i = 0$

In the case of a system with reactions at equilibrium, the number of variables is the same, pi into C plus 1. There are no additional variables that are there. As mentioned earlier, pi is the number of phases, and C is the number of components. The number of independent equations between the variables is pi minus 1 equalities of temperature … recall that T alpha equals T beta and so on. So, if there are pi phases, you could consider that one composite equation as pi minus 1 equations, or equalities of temperature. In a similar fashion there are pi minus 1 equalities of pressure that corresponds to equation 5.2, and pi minus 1 equalities or equations of chemical potential for each component. We can write one for each component and therefore, the total number of such equalities of the chemical potential is C into pi minus 1.

So, all this remains the same even for a system with reactions at equilibrium. The only additional thing is that for a reacting system with R independent reactions, we have R conditions of equilibrium of the form, sum over i nu i mu i equals 0. I am going to leave you with this background. This is more than enough background to derive the phase rule for reacting biosystems. Please, go ahead and do it. You can take about 15 minutes since you doing it for the first time. It will give you a lot more confidence in the material itself. Go ahead and do it, and I will present the solution or the phase rule for reacting biosystems after about 15 minutes. Go ahead please.

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So, we all know the background; the number of variables in the reacting system at equilibrium, the number of independent equations between the variables – all this is same as the case of the system without reactions. The only additional thing being these R conditions of equilibrium of the form sum over nu i mu i equals 0.

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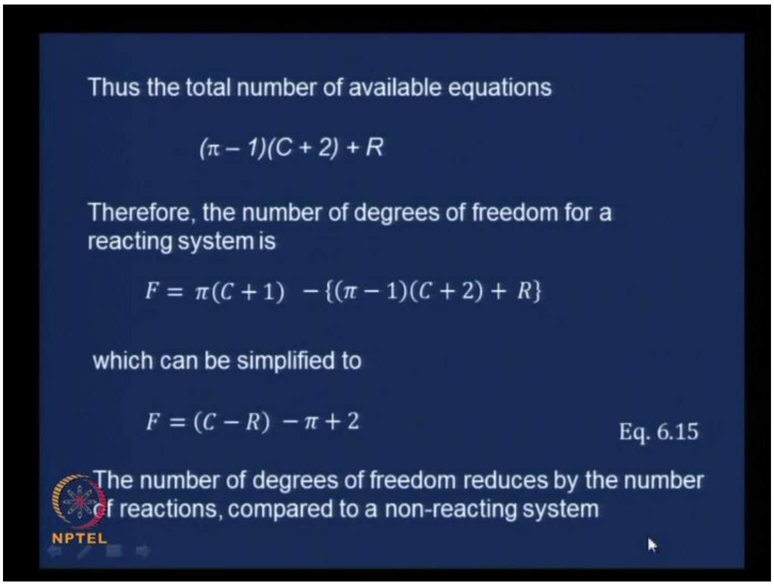

Thus the total number of available equations

$$(\pi - 1)(C + 2) + R$$

Therefore, the number of degrees of freedom for a reacting system is

$$F = \pi(C+1) \ - \{(\pi - 1)(C+2) + R\}$$

which can be simplified to

$$F = (C - R) \ - \pi + 2 \qquad \text{Eq. 6.15}$$

The number of degrees of freedom reduces by the number of reactions, compared to a non-reacting system

So, how did we go about deriving the phase rule earlier? We looked at the total number of available equations which is pi minus 1 into C plus 2, as for the case without reactions plus this R. The number of variables minus the number of available equations, available independent equations between those variables, actually, givens a degrees of freedom that we saw. Therefore, F the number of degrees of freedom is pi into C plus 1, the number of variables, minus the number of equations between them, independent equations between them. If we rearrange this, essentially some algebra, we would get C minus R minus pi plus 2.

So, as you can realize whatever was C earlier can be replaced by C minus R. So, C minus R minus pi plus 2 – hopefully you got this in your own efforts – gives the number of degrees of freedom in a system with R reactions. Let us call this equation 6.15. … As can be seen, the number of degrees of freedom reduces by the number of reactions, compared to a non-reacting system.

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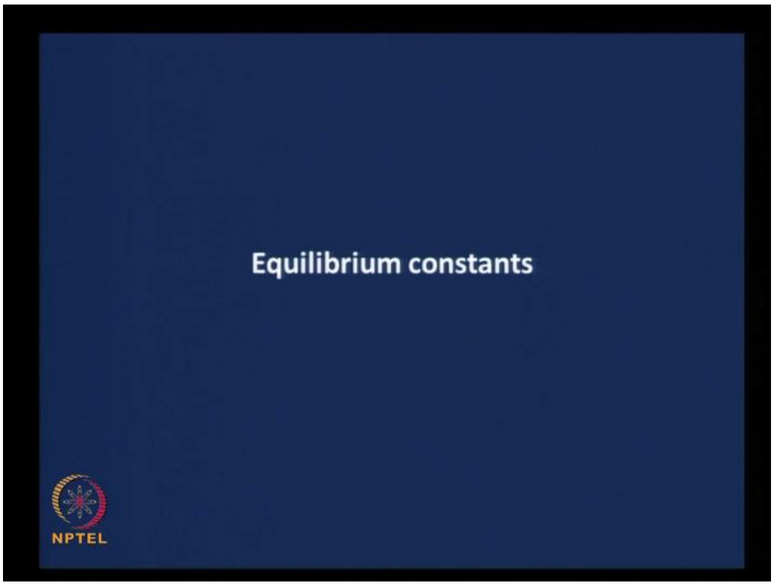

Equilibrium constants

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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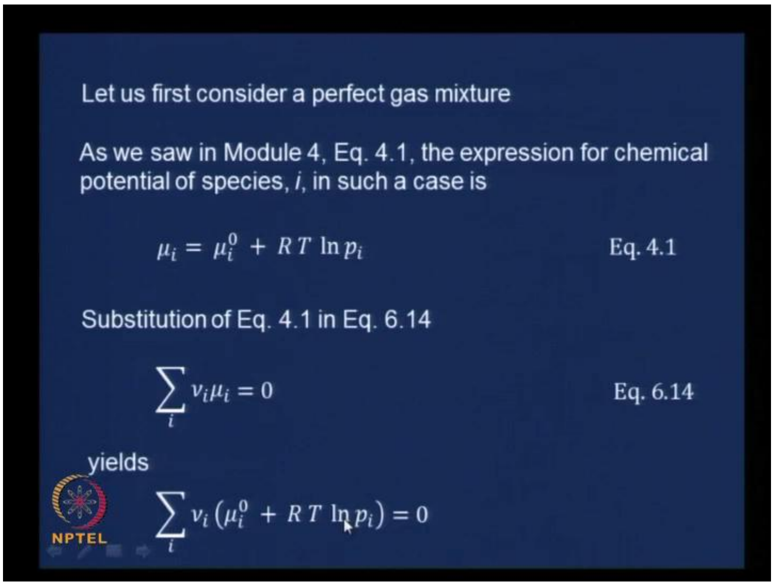

Let us first consider a perfect gas mixture

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

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

Substitution of Eq. 4.1 in Eq. 6.14

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

yields

$$\sum_i \nu_i \left(\mu_i^0 + RT \ln p_i\right) = 0$$

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 equals mu i naught plus RT ln p i, which is the partial pressure of component i in the mixture. If you substitute equation 4.1 in equation 6.14 – equation 6.14 is the condition for reaction equilibrium sum over nu i mu i equals 0. Now, we are going to substitute mu i with mu i naught plus R T ln p i. If we do that then we could write sum over nu i into mu i naught plus R T ln p i equals 0. This is this condition here.

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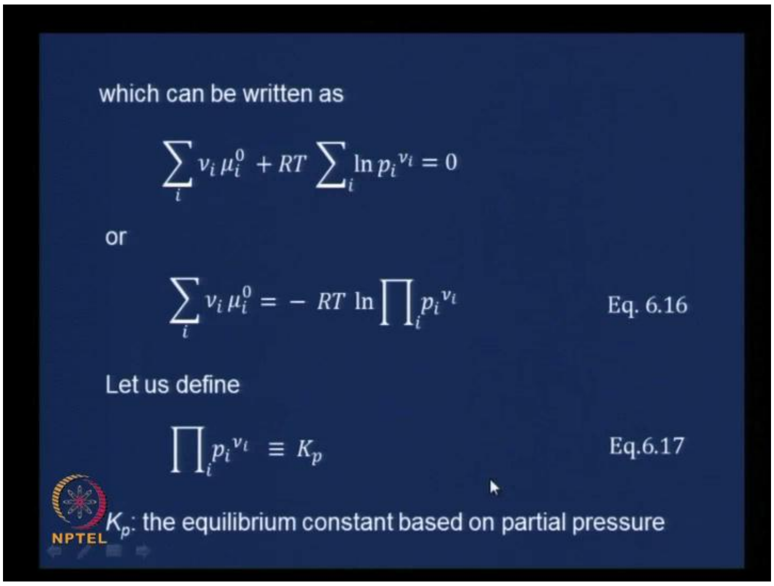

which can be written as

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

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

Which 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 over i nu i mu i naught plus RT, is a constant here, T is a constant here … sum over i ln of p i power nu i, if you recall, this would have been nu i ln p i which is, ln of p i power nu i. 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 nu i mu i naught sum over i equals minus RT – this is some of log, which is nothing but log of the product; that we all know.

Product of … as represented by this big pi here … product of p i power nu i. Let us call this equation 6.16. Let us define this particular quantity, product over i p i power nu i the stoichiometric co-efficient, the partial pressure time raised to the power of this stoichiometric co-efficient, for each of the species involved, as K p. You would recall K p, 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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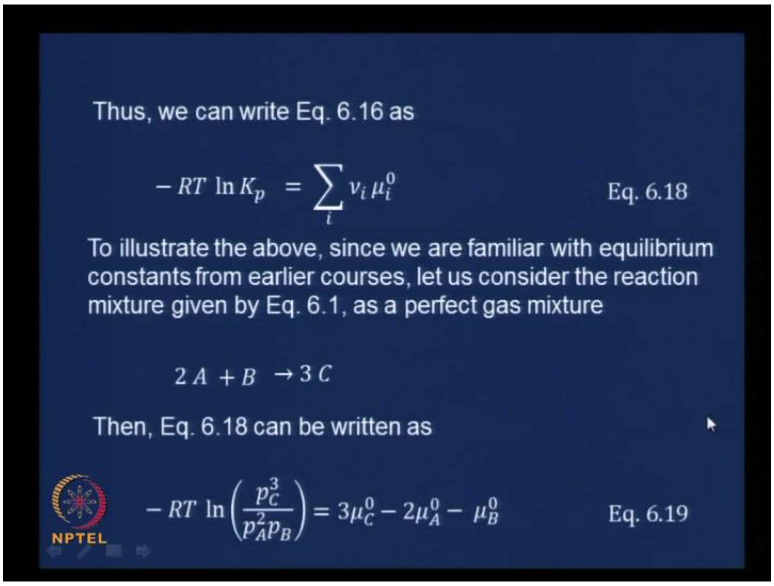

Thus, we can write Eq. 6.16 as

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

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

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

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And therefore, we can write 6.16 as minus RT ln K p equals sum over i nu i mu i naught. Therefore, we have a means of getting K p 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 K p. 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 K p. What was ln K p? … Ln of the product of p i power nu i. You know that nu i is positive for the products and negative for the reactants. And therefore, if you multiply that all together it be p C cubed into p A to the power of minus 2 into p B to the power of minus 1, which can be written as p C cubed divided by p A squared p B … and of course, the ln comes from here. This equals 3 mu C naught minus 2 mu A naught. Sum over i nu i mu i naught 3mu C naught minus 2mu i naught minus mu B naught. 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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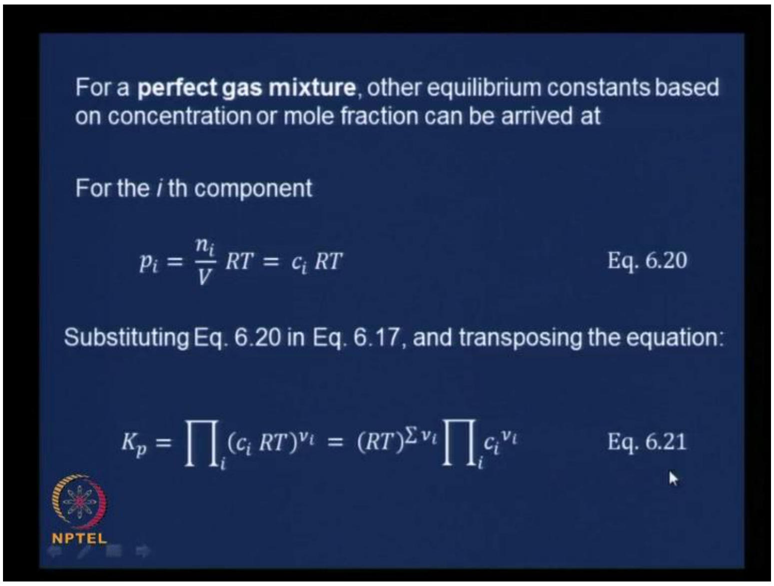

For a **perfect gas mixture**, other equilibrium constants based on concentration or mole fraction can be arrived at

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, n i by V RT. This is from the ideal gas equation. Perfect gas mixture

… so, mixture of ideal gases and so on. So, n i by V RT is partial pressure. … n i by V … is nothing but the definition of the concentration, the molar concentration. Therefore, c i RT. Let us call this equation 6.20 in this context.

If we substitute equation 6.20 in equation 6.17 … that will become very clear right now … and transposing, we will get K p equals pi into c i RT, the whole power nu i. 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 you know 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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You should have arrived at K p equals product over i c i RT the whole power nu i which can of course, be written as RT to the power of sum over nu i times the product of c i power nu i. Let us call this equation 6.21. This is the definition of K p.

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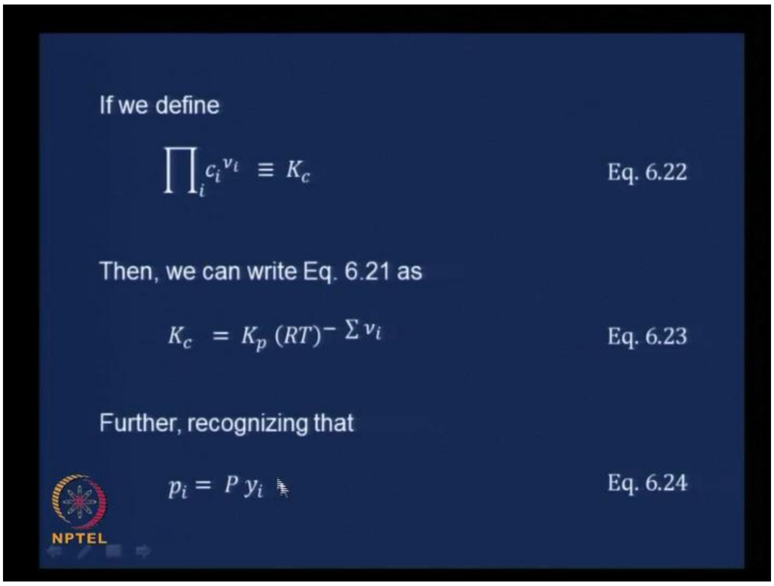

If we define

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

Then, we can write Eq. 6.21 as

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

Further, recognizing that

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

If we call this as K c, product over i c i power nu i as K c. Then, it is easy to see that K c is nothing but K p into RT raised to the power of minus sum over all these stoichiometric constants, nu i. Let us call this equation 6.23. Just not this, there is probably one more. Let us recognise that p i is nothing but P into y i - equation 6.24. Let me leave you with this for another 10 minutes to derive K y. You know the equilibrium constant based on the mole fractions y i. 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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Taking p i equals the total pressure times the mole fraction y i.

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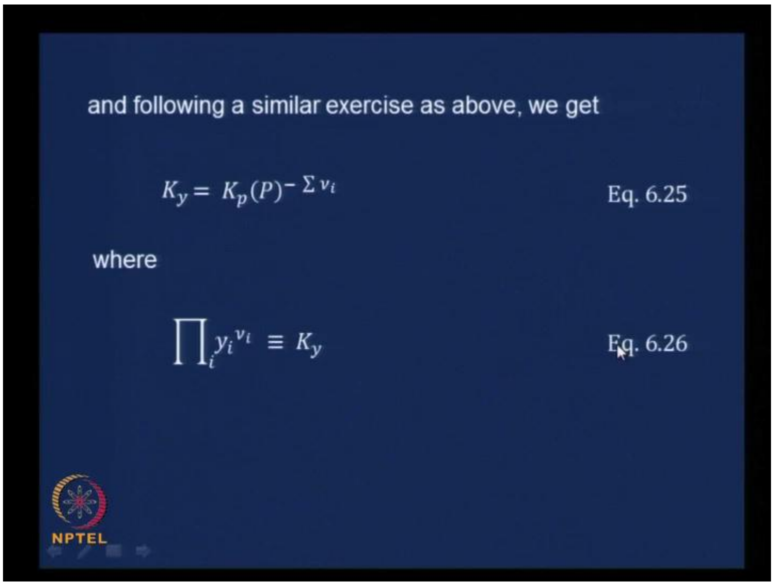

and following a similar exercise as above, we get

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

where

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

If we follow a similar exercise as above … write … K y in terms of K c and so on, you should get K y is nothing but K p into P raised to the power of minus sum over all nu i. Hopefully, you got this in your own exercise. Where our … K y is defined as product over i y i the mole fraction raise to the power of nu i, the stoichiometric co-efficient. Let us call that equation 6.26.

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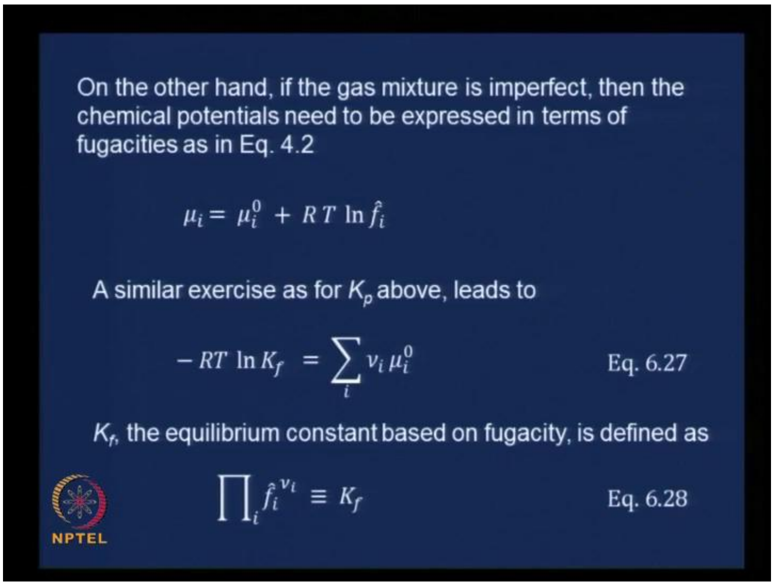

On the other hand, if the gas mixture is imperfect, then the chemical potentials need to be expressed in terms of fugacities as in Eq. 4.2

$$\mu_i = \mu_i^0 + RT \ln \hat{f}_i$$

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 equals mu i naught plus RT ln f i hat. 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 K p we should get minus RT ln K f. K f is the equilibrium constant based on fugacities, as equal to sum over i nu i mu i naught where K f, the equilibrium constant based on fugacity is defined as, product over i f i hat raised to the power of nu i; that is our 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.