Thermodynamics for Biological Systems: Classical and Statistical Aspects

Prof. G.K. Suraishkumar
Department of Biotechnology
Indian institute of Technology - Madras

Lecture – 47
Phase Rule for Reacting Biosystems

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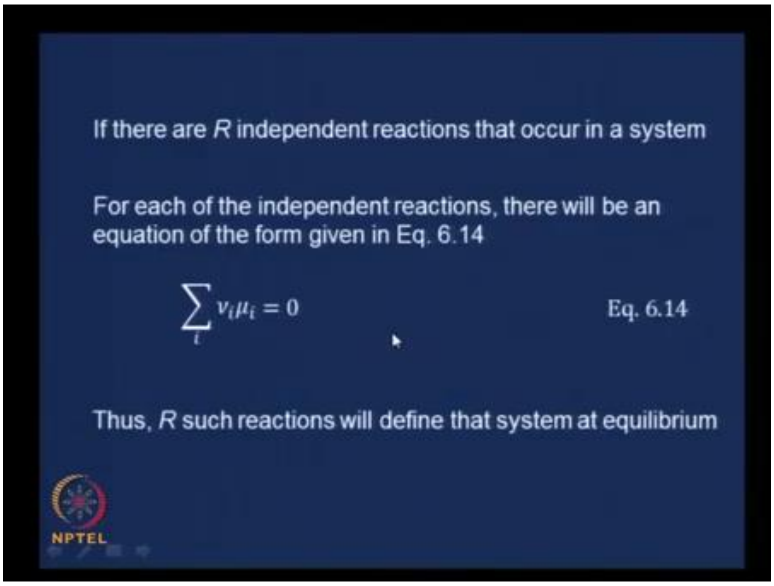

If there are *R* independent reactions that occur in a system

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.

$\sum_i \nu_i \mu_i = 0$

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.

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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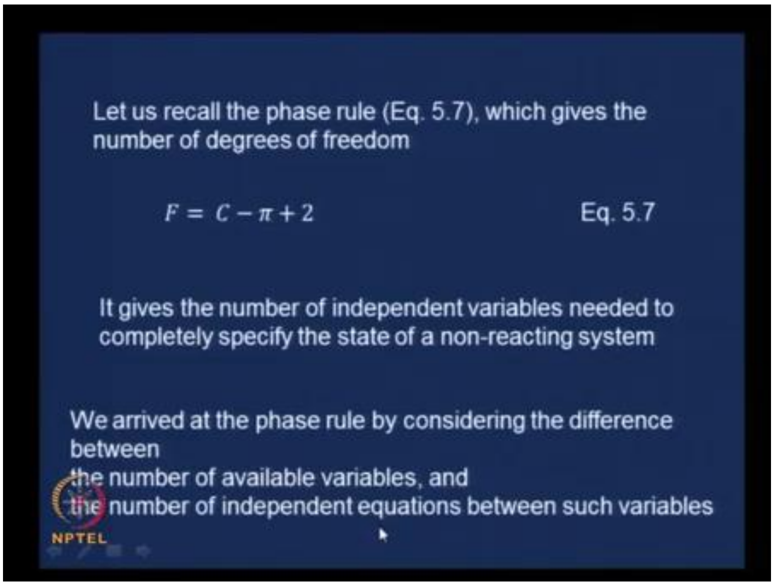

Let us recall the phase rule (Eq. 5.7), which gives the number of degrees of freedom

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

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 $F = C - \pi + 2$; 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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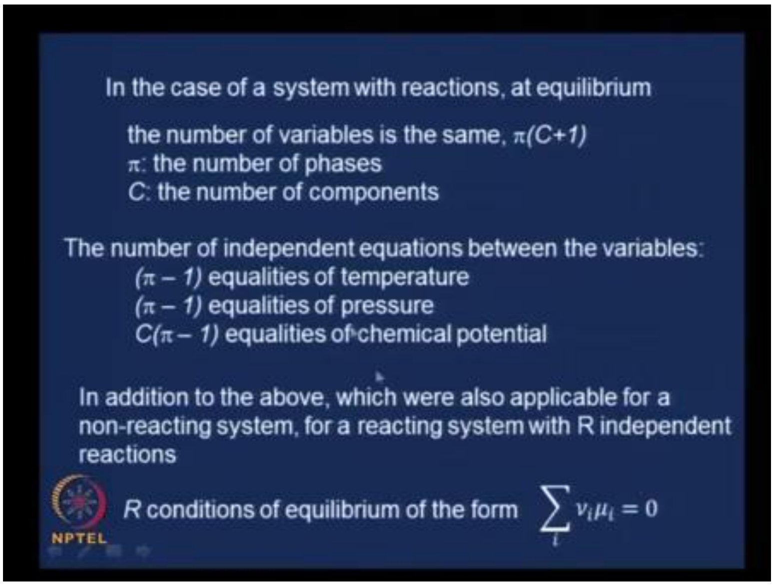

In the case of a system with reactions, at equilibrium

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, $\pi(C+1)$. There are no additional variables that are there. As mentioned earlier, π is the number of phases, and C is the number of components. The number of independent equations between the variables is $(\pi - 1)$ 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 $(\pi - 1)$ equalities of pressure that corresponds to equation 5.2, and $(\pi - 1)$ 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 $C(\pi - 1)$.

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,

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

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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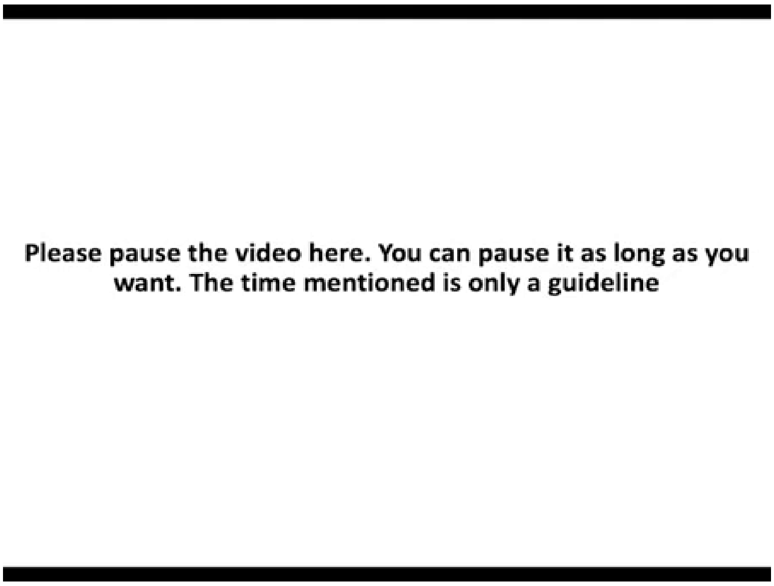

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So, we all know the background; the number of variables in the reacting system at equilibrium, the number of independent equations between the variables – all this is same as the case of the system without reactions. The only additional thing being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

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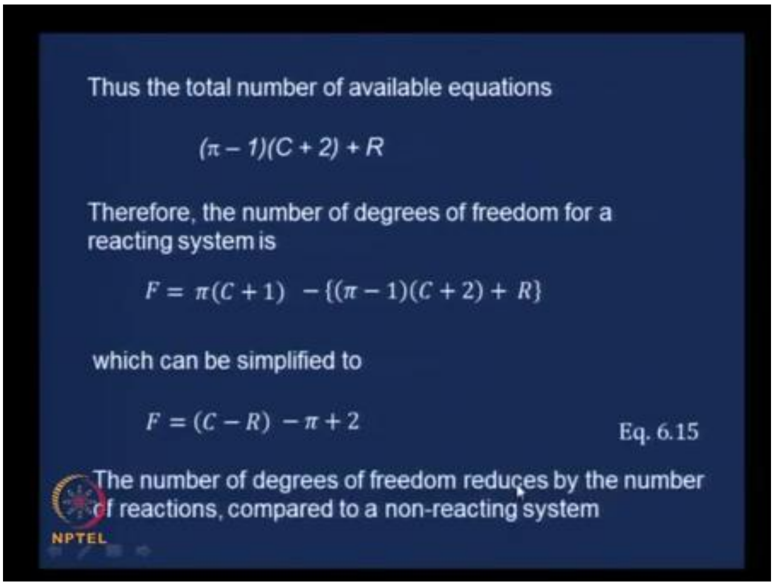

Thus the total number of available equations

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

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 $(\pi - 1)(C + 2) + R$, 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, gives the 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

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

So, as you can realize whatever was C earlier can be replaced by $(C - R)$. So, $F = (C - R) - \pi + 2$; 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.

See you in the next class.