Thermodynamics for Biological Systems: Classical and Statistical Aspects

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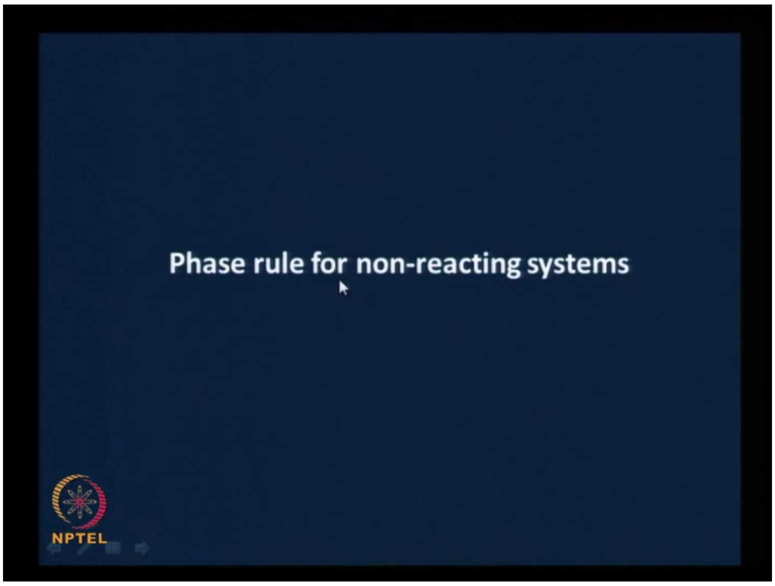
Lecture – 38
Phase Rule for Non-Reacting Systems

Welcome!

Now let us look at something that will be useful. You may have done this in earlier classes. But, it is good to know clearly what this really is, and the basis for this. That is why we are doing it here.



Phase rule for non-reacting systems

It is nothing but the phase rule for non-reacting systems. In this module, we are considering only non-reacting systems. Therefore, we will consider the phase rule for non-reacting systems here.

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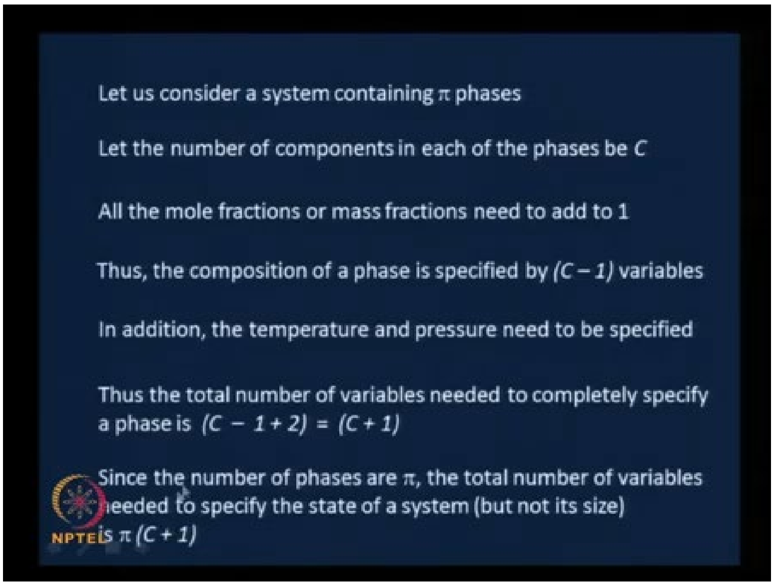

Let us consider a system containing π phases

Let the number of components in each of the phases be C

All the mole fractions or mass fractions need to add to 1

Thus, the composition of a phase is specified by $(C - 1)$ variables

In addition, the temperature and pressure need to be specified

Thus the total number of variables needed to completely specify a phase is $(C - 1 + 2) = (C + 1)$

Since the number of phases are π, the total number of variables needed to specify the state of a system (but not its size) is $\pi (C + 1)$

Let us consider a system containing π number of phases. You know, gas, liquid, vapour and solid and so on. Let us say in general, it contains π phases. We also saw that it is not limited to just these phases. They could be 2 distinct liquid phases, they could be many distinct liquid phases, and they could be many distinct solid phases. … Little difficult to imagine … different vapour phases but, certainly they could be different liquid phases and different solid phases. Therefore, let us say in general, that the system contains π phases, and let the components in each phase be C. And we are going to implicitly assume that each component is present in each of the phases. Or each component is present in all the phases.

If the number of components in each phase is C, we know that the mole fractions or the mass fractions need to add up to 1. For example, if the mole fraction is x_i, $x_1 + x_2 + x_3 +$ and so on till $+ x_n$ must equal 1. So, this automatically gives us a relationship to be satisfied between the concentrations of the C components in each phase. Therefore, the composition of the phase is specified by $(C – 1)$ variables.

Suppose there are 5 components. We need to know the concentrations of 4 components. The last component, we can always get by adding the mole fractions of these 5 and equating it to 1. Therefore, if we have 4, we can always find the fifth one. Therefore, the composition of a phase is specified by $(C – 1)$ variables. In addition, the temperature and pressure need to be specified because, they are conditions of equilibrium; equality of temperature and equality of pressure across phases are conditions that need to be satisfied for equilibrium.

Therefore, the total number of variables that are needed to completely specify a phase $(C - 1 + 2) = (C + 1)$. That is (C – 1) variables of compositions, we saw, plus 2 variables, temperature and pressure. You add all these together, you get $(C + 1)$.

We said that each of these components is present at all the phases, and the total number of phases is π. Therefore, the total number of variables needed to specify the state of the system, but, not its size, of course, is π phases times $(C + 1)$ variables that are required to specify in each phase. Therefore, $\pi (C + 1)$

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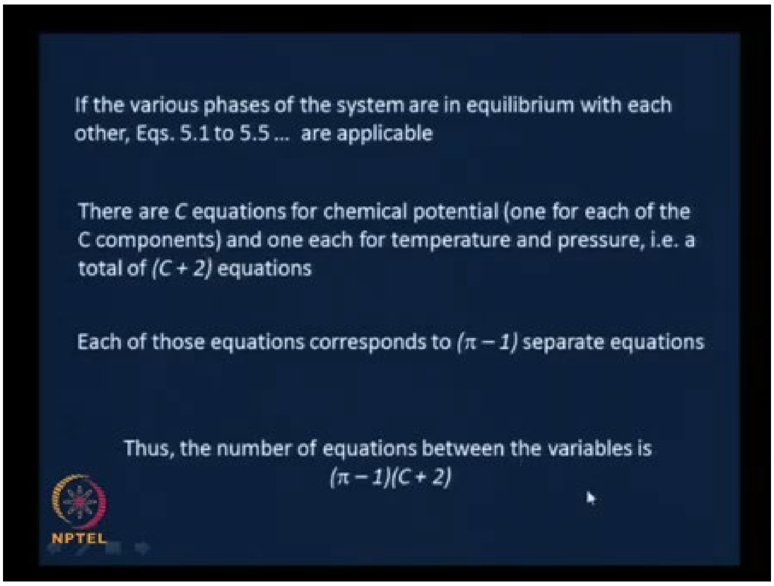

If the various phases of the system are in equilibrium with each other, Eqs. 5.1 to 5.5 ... are applicable

There are C equations for chemical potential (one for each of the C components) and one each for temperature and pressure, i.e. a total of $(C + 2)$ equations

Each of those equations corresponds to $(\pi - 1)$ separate equations

Thus, the number of equations between the variables is $(\pi - 1)(C + 2)$

If the various phases of the system are at equilibrium with each other, then the conditions of equilibrium can be applied. Equations 5.1 to 5.5, which is

$$T_\alpha = T_\beta = T_\gamma = \cdots$$

$$P_\alpha = P_\beta = P_\gamma = \cdots$$

$$\mu_{1,\alpha} = \mu_{1,\beta} = \mu_{1,\gamma} = \cdots$$

$$\mu_{2,\alpha} = \mu_{2,\beta} = \mu_{2,\gamma} = \cdots$$

$\mu_{3,\alpha} = \mu_{3,\beta} = \mu_{3,\gamma} = \cdots$

…

There are C equations for chemical potential, one for each of the C components that are present – that we saw. … So, you have C such equations, if you have C components.

Therefore, we have C equations for chemical potential, one for each of the C components, and one each for the temperature and pressure, Therefore, we have a total of (C + 2) equations. And, each of those equations corresponds to (π – 1) separate equations. Because, T alpha equals T beta is one equation, T alpha equals T gamma equals another equation, and so on and so forth. Therefore, each of those equations corresponds to (π – 1) separate equations. And therefore, the number of equations between the variables is (π – 1) separate equations times (C + 2) equations.

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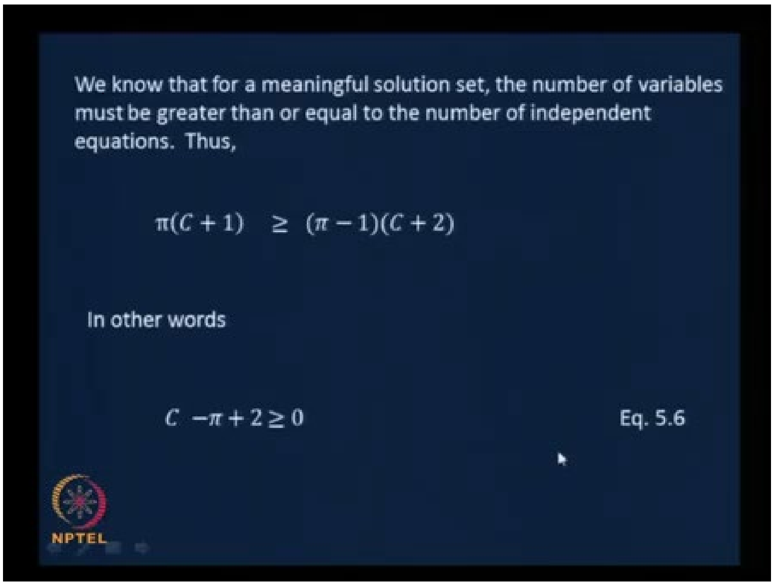

We know that for a meaningful solution set, the number of variables must be greater than or equal to the number of independent equations. Thus,

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

In other words

$$C - \pi + 2 \geq 0 \qquad \text{Eq. 5.6}$$

Why did we do all this? It is because of this: we know that for a meaningful solution set – knowing some set of variables, we are trying to solve for the other set of variables that are unknown – for a meaningful solution set, the number of variables must be greater than or equal to the number of independent equations. Otherwise, we do not get a unique solution. Thus, number of variables, must be greater than the number of equations, for a general case.

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

Now we have completely generalized this. We said π phases and C components, and we got the number of variables as π (C + 1). We got the number of independent equations between them as $(\pi - 1)(C + 2)$. And, we are using the mathematical criterion that the number of variables must be greater than or equal to the number of independent equations between them, if we need to solve them uniquely.

Therefore, $\pi(C + 1) \geq (\pi - 1)(C + 2)$. In other words, if you transpose this,

$$(C - \pi + 2) \geq 0$$

You can do the transposition and check. We will call this equation 5.6.

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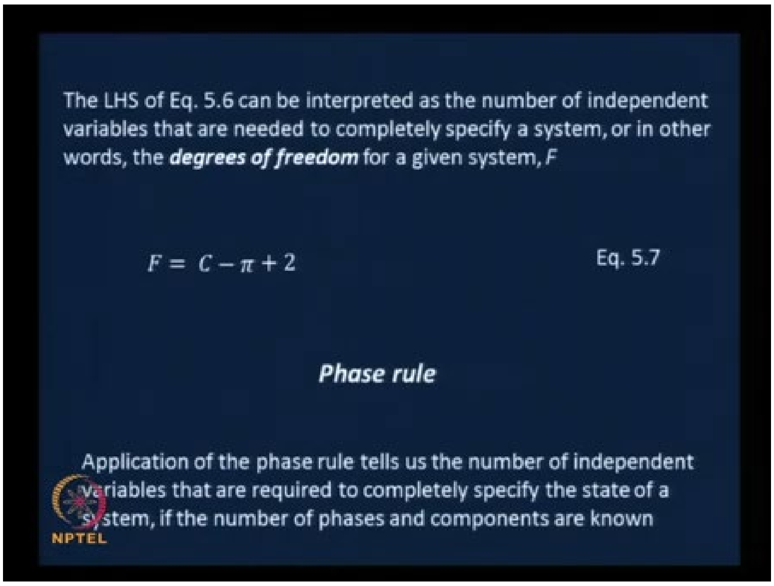

The LHS of Eq. 5.6 can be interpreted as the number of independent variables that are needed to completely specify a system, or in other words, the ***degrees of freedom*** for a given system, *F*

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

Phase rule

Application of the phase rule tells us the number of independent variables that are required to completely specify the state of a system, if the number of phases and components are known

The left hand side of 5.6, which is $(C - \pi + 2)$ can be interpreted as the number of independent variables that are needed to completely specify the system, or in other words, the number of degrees of freedom for a given system. And let us indicate the number of degrees of freedom by F.

Therefore,

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

This is the number of variables that are needed to completely specify the system. Let us call this equation 5.7. And, some of you would have already realized that this is indeed called the phase rule. Application of the phase rule tells us the number of independent variables that are required to completely specify the state of a system, if the number of phases and components are known. And of course, we have assumed the equilibrium conditions. We have written the phase rule for pi phases in equilibrium with each other.

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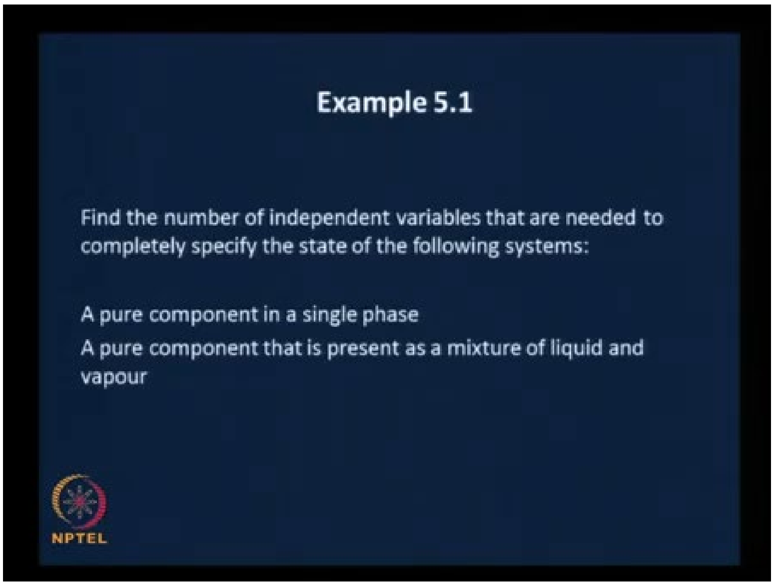

Example 5.1

Find the number of independent variables that are needed to completely specify the state of the following systems:

A pure component in a single phase

A pure component that is present as a mixture of liquid and vapour

To get more comfortable, let us do this example. Find the number of independent variables that are needed to completely specify the state of the following systems:

- a pure component in a single phase – that is the first system,
- a pure component that is present as a mixture of liquid and vapour

Please take about 10 minutes. We have done a few things till now in this particular class. Please take a few minutes, go back and see what we have done, and see what you need to solve this particular example. Take about 10 minutes for that. I will come back and tell you the solution. Go ahead please.

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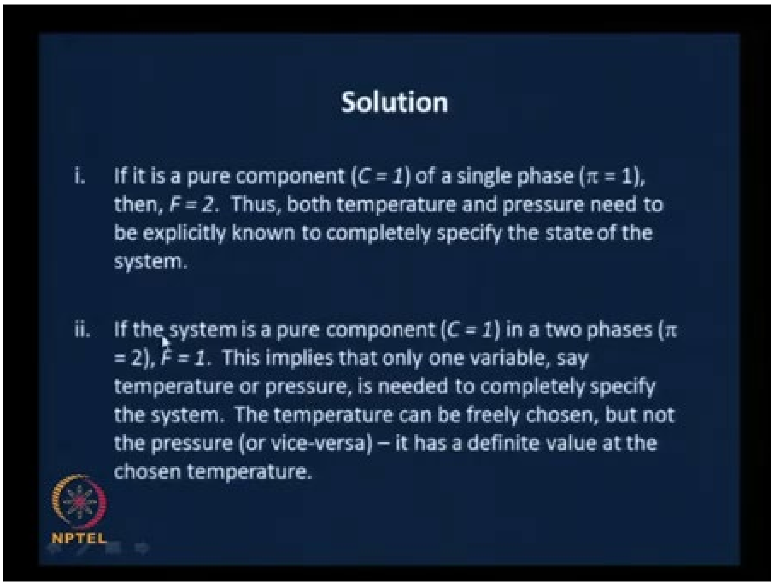

Solution

i. If it is a pure component ($C = 1$) of a single phase ($\pi = 1$), then, $F = 2$. Thus, both temperature and pressure need to be explicitly known to completely specify the state of the system.

ii. If the system is a pure component ($C = 1$) in a two phases ($\pi = 2$), $F = 1$. This implies that only one variable, say temperature or pressure, is needed to completely specify the system. The temperature can be freely chosen, but not the pressure (or vice-versa) – it has a definite value at the chosen temperature.

This was a straight forward application of the phase rule. Therefore, most of you would have gotten the solution already.

The solution is as follows, we said the first system is a pure component, which means C is 1 single phase which means π is 1 and therefore, for $F = (C - \pi + 2)$ …this and this cancel … we get F equals 2. Therefore, both temperature and pressure need to be explicitly known. You know, F essentially implies the number of independent variables that are needed to fix the state of a particular system. Typically, temperature and pressure can be taken to be those variables of choice. The temperature and pressure need to be explicitly known to completely specify the state of the system.

The second example was, if the system is a pure component – C equals 1, in 2 phases – π equals 2, then F equals C minus pi plus 2 and that turns to be 1. In this case we just need 1 variable say temperature or pressure; that is only thing that is needed to completely specify the state of the system. What this also means, or another way of looking at this, is that the temperature can be freely chosen but, not the pressure, or the pressure can be freely chosen, but the temperature cannot be freely chosen. It has a definite value for a particular other variable. For example, if the temperature can be freely chosen, the pressure will have a definite value for the chosen temperature. If the pressure can be freely chosen, then the temperature will have a definite value for that chosen pressure.

See you in the next class.