Thermodyamics (Classical) for Biological Systems

Prof. G. K. Suraishkumar
Department of Biotechnology
Indian Institute of Technology Madras

Module No. # 05

Phase Equilibria

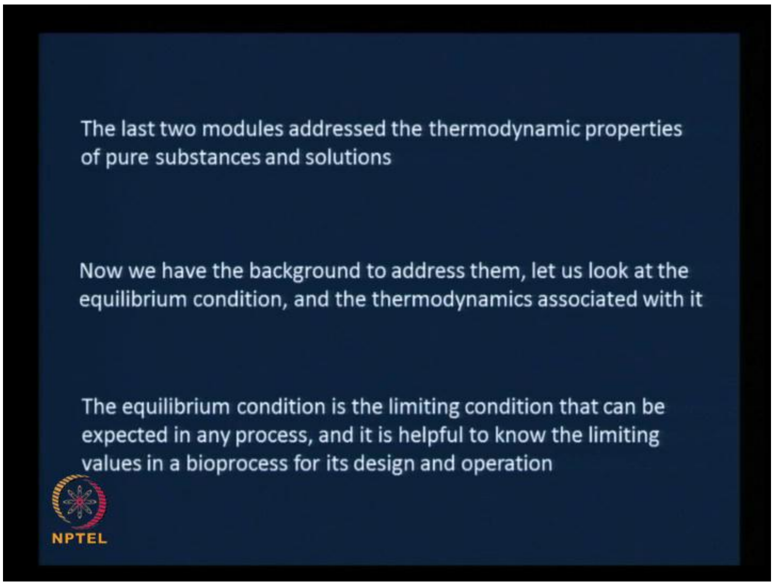
Lecture No. # 28

Criteria for Phase Equilibrium Phase Rule for Non-reacting Biosystems

Welcome!

In this lecture, let us begin module number 5. Module number 5 is on phase equilibria. We all know what phases are – the 3 phases that we are looking at in this particular course are the solid, liquid and the gas or the vapour phase. And we are going to look at the equilibria that concerns these phases in this particular module.

(Refer Slide Time: 00:44)



The last two modules addressed the thermodynamic properties of pure substances and solutions

Now we have the background to address them, let us look at the equilibrium condition, and the thermodynamics associated with it

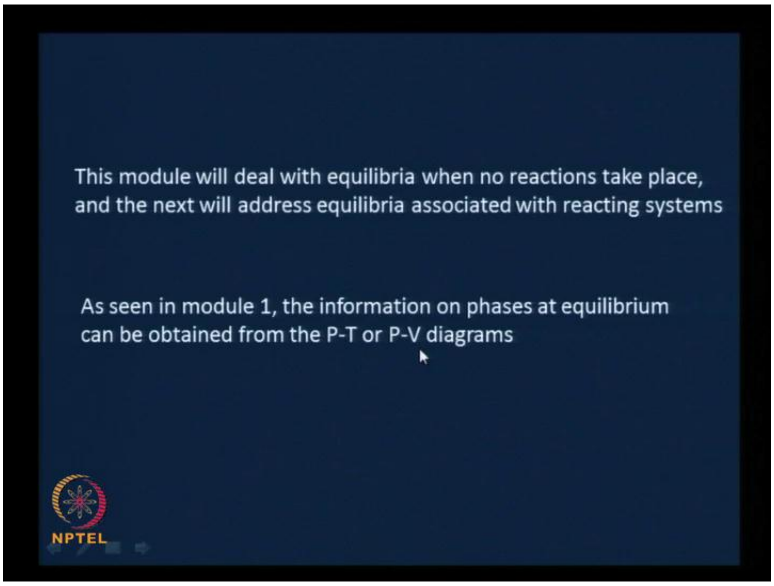
The equilibrium condition is the limiting condition that can be expected in any process, and it is helpful to know the limiting values in a bioprocess for its design and operation

The last two modules, you know, we had looked at pure components first and then the solutions. The last two modules addressed the thermodynamic properties of first, pure substances, that was module number 3. And then module number 4, looked at solutions or mixtures, which are essentially the things that arise when you put a lot of pure substances together, a minimum of 2 pure substances together. Now, we have the background to address them that is the pure substances as well as the mixture of pure substances.

And it is natural for us to look at the next aspect, which is the equilibrium condition, and of course, the thermodynamics associated with the equilibrium condition. A little while later, I will tell you what equilibrium actually is, what is the nature of equilibrium, and so on.

Very briefly, now, let me tell you that the equilibrium condition is the limiting condition that can be expected in any process. Any process is expected to ultimately reach equilibrium, and it is helpful to know the limiting values in a bioprocess for its design and operations. We just leave a process alone, it might attain equilibrium may be in a few milliseconds, microseconds, or may be over years. But, it is good to know the limiting values, so that we can design, keeping that in mind … knowing that is the maximum that we can achieve. And whatever we are going to actually achieve would be some fraction of what is maximally achievable.

(Refer Slide Time: 02:37)



This module will deal with equilibria when no reactions take place, and the next will address equilibria associated with reacting systems

As seen in module 1, the information on phases at equilibrium can be obtained from the P-T or P-V diagrams

This module will deal with equilibria when no reactions take place, and the next module, module number 6 will address equlibria associated with reacting systems. Therefore, in this particular module, we will not consider any reactions at all. Let us go back a little bit, to familiarize ourselves or recall whatever we did in module 2, because it becomes necessary here in the context of phase equilibria.

We saw in module 1 that the information on phases at equilibrium can be obtained from either the pressure verses temperature diagram or the pressure verses the specific volume diagram. If you recall those figures.

(Refer Slide Time: 03:31)

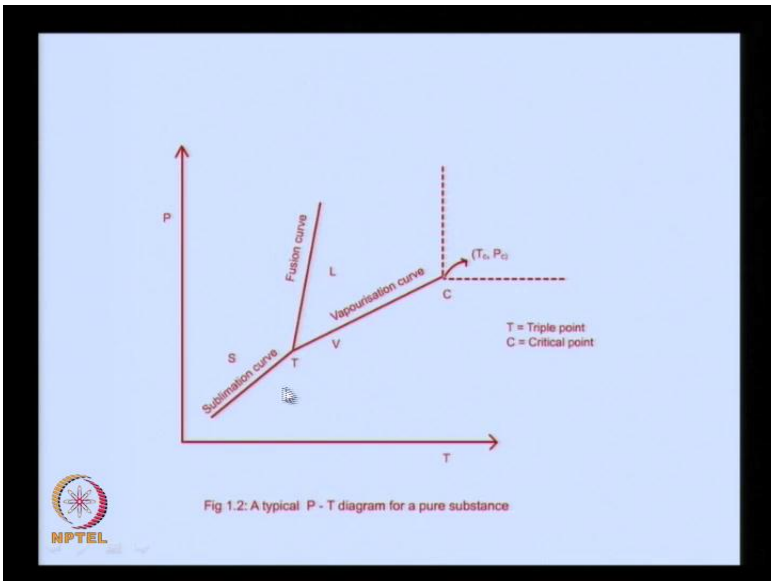


Fig 1.2: A typical P - T diagram for a pure substance

We will take a look at them again here. This is the P-T diagram. Of course, this is only for a pure substance, which mean only one type of substance. We need to interpret this as we saw earlier, as the space consisting of certain values of temperature and corresponding values of pressure. This is the sublimation curve, which is essentially a demarcating line between the region where the solid exists and the vapour exists.

On this line, you expect the conversion from the solid phase to the vapour phase or the gaseous phase. This is the fusion curve, … which is the demarcating line between the solid phase and the liquid phase of one substance, one pure substance. And therefore, along the fusion curve, we can expect the transition. Which means that if a substance is going from the solid to the liquid, that can happen only along these combinations of temperature and pressure – you know … x axis …y axis… so, (T, P) is each point here – that can happen only along the fusion curve.

Similarly, this is the vaporization curve, which is a transition or a limiting line between the liquid and the vapour phases. And therefore, if a liquid becomes a vapour, it has to happen under these conditions, or these combinations of temperature and pressure.

And we have also seen for completeness sake that this is the critical point, … beyond which the critical phase exists; which means above the critical pressure and above the critical temperature, we have the critical phase, which is very interesting in itself. But, we will not address that in this particular course. Therefore, … in this course we will essentially look at solid, liquid and vapour phases and the demarcating regions.

(Refer Slide Time: 05:54)

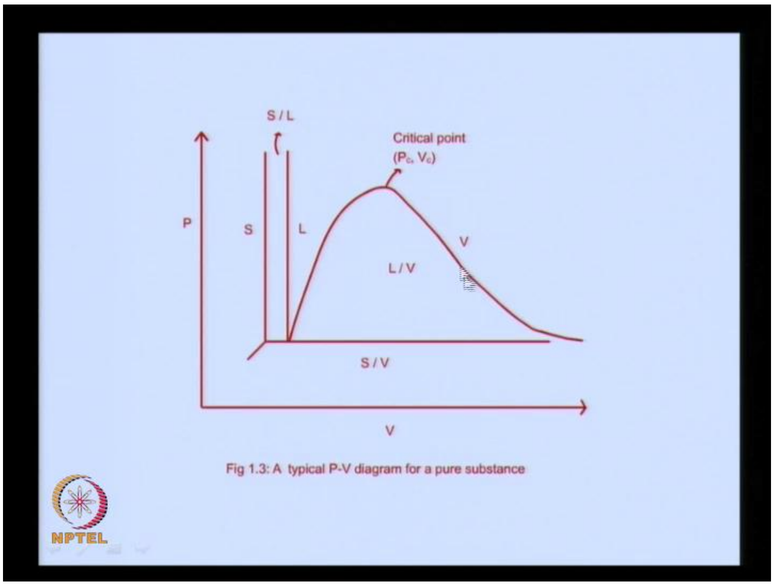
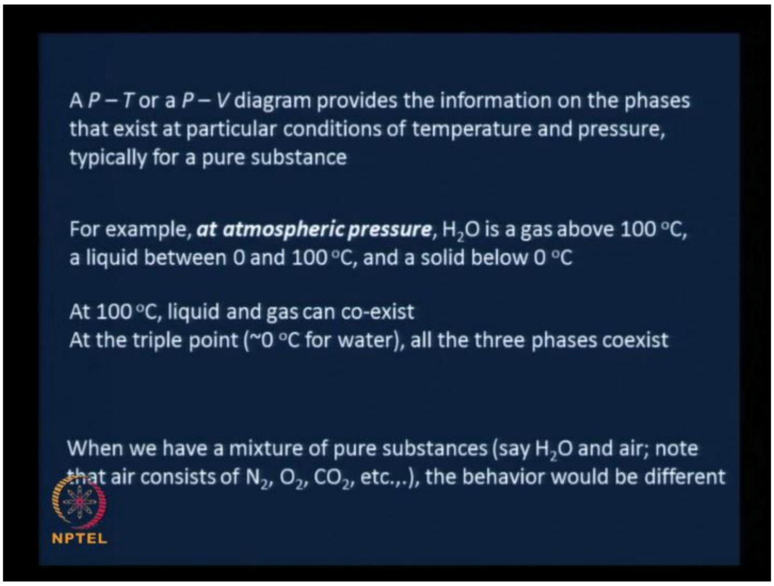


Fig 1.3: A typical P-V diagram for a pure substance

In contrast to this, if we look at pressure verses the specific volume diagram, for a pure substance, we saw that these combinations of specific volume and pressure … would result in a solid. These combinations of specific volume and pressure would result in a liquid, and these values of specific volume and pressure would result in a vapour. And there are regions – unlike the P-T diagram, where they were lines, combinations of temperature and pressure, where the transition took place – here, we have regions over which transitions from one phase to another phase take place.

For example, this region … is the region over which the transition from the solid to the liquid phase takes place. This is the region over which – the dome – is the region over which the transition from the liquid to the vapour phase takes place and so on.

(Refer Slide Time: 07:03)



A $P-T$ or a $P-V$ diagram provides the information on the phases that exist at particular conditions of temperature and pressure, typically for a pure substance

For example, ***at atmospheric pressure***, H_2O is a gas above 100 °C, a liquid between 0 and 100 °C, and a solid below 0 °C

At 100 °C, liquid and gas can co-exist
At the triple point (~0 °C for water), all the three phases coexist

When we have a mixture of pure substances (say H_2O and air; note that air consists of N_2, O_2, CO_2, etc.,.), the behavior would be different

We had already mentioned this: a P-T or a P V diagram provides the information on the phases that exist at particular conditions of temperature and pressure, typically for a pure substance.

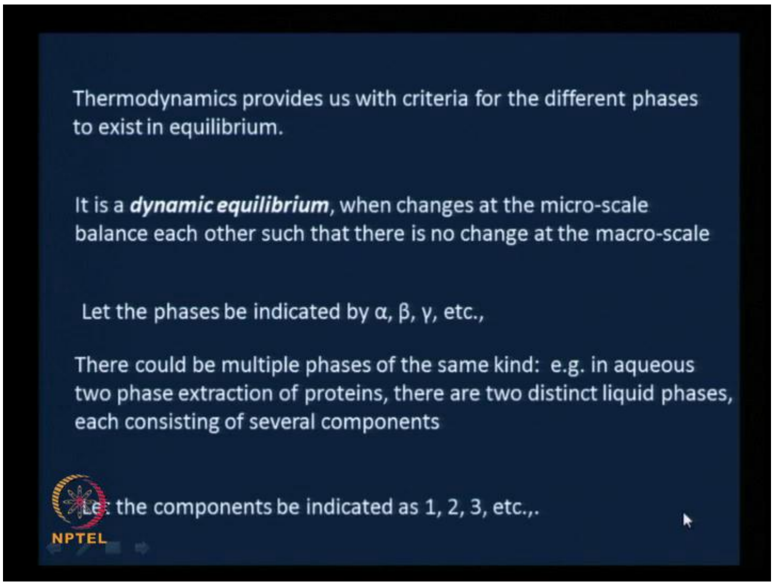
For example, at atmospheric pressure … you know, we said that only at a certain conditions of pressure, temperature and specific volume, do these transitions exist … at atmospheric pressure, 1 atmosphere pressure, H 2 O or water is a gas above 100 degree C, a liquid between 0 and 100 degree C, and a solid below 0 degree C.

At 100 degree C, you know, at that particular temperature, liquid and gas of H 2 O can co-exist. We are all talking about atmospheric pressure here. At the triple point, which is about 0 degree C for water, all the 3 phases such as solid liquid and vapour – they co-exist.

Now, we need to distinguish this pure substance from what we normally come across, which is the mixture of pure substances. I have given this example before, and just to dry home the point clearly, let me give it again. When we have a mixture of pure substances say water and air, this is something that we find around us all the time, you know there is air and there is some water vapour in it.

And if we note this, the air it itself consists of different species, nitrogen, oxygen, carbon dioxide and so on. Therefore, this mixture of water vapour and air contains all these plus water vapour. When we have such things the behavior of course, is going to be different. Therefore, we should not make the error of extending the phase diagram for a pure substance to that for mixtures. And it happens without us realizing; that is a reason why I am making the point here especially in the case of water and air. Please note this.

(Refer Slide Time: 09:18)



Thermodynamics provides us with criteria for the different phases to exist in equilibrium.

It is a ***dynamic equilibrium***, when changes at the micro-scale balance each other such that there is no change at the macro-scale

Let the phases be indicated by α, β, γ, etc.,

There could be multiple phases of the same kind: e.g. in aqueous two phase extraction of proteins, there are two distinct liquid phases, each consisting of several components

Let the components be indicated as 1, 2, 3, etc.,.

Thermodynamics provides us with the criteria for different phases to exist in equilibrium. It tells us a priori when they will be in equilibrium, and that is the power of thermodynamics.

It is at dynamic equilibrium, when changes at the micro scale balance each other so that there is no change at the macro scale. You know at the equilibrium conditions, things do take place, processes do take place. But, the rate of the process in one direction equals the rate of the process in the other direction at the micro scale. And therefore, both the rates cancel each other, and net at the macro scale, we do not find any major difference.

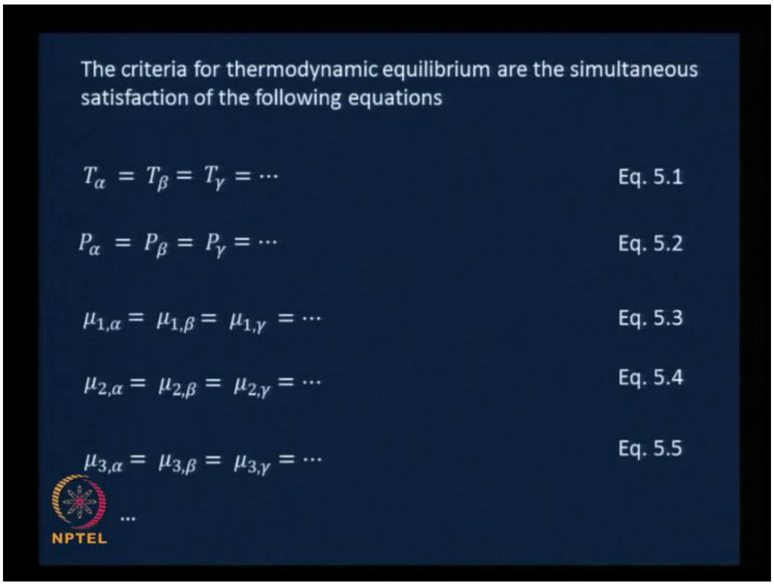
What I mean by this is: consider the evaporation of water. When the liquid water becomes or gets into the vapour phase, there is movement of water molecules from the liquid to the vapour. And let us say under a given set of conditions, that takes place at a particular rate. Here there is no air, by the way. Just water and vapour – a pure substance. So, the liquid water becomes vapour. At the same time you know there is water vapour there, some of those molecules may not have enough energy and they will get back to the liquid phase.

So, there is a rate at which liquid water becomes gaseous water, and there is a rate at which the gaseous water becomes liquid water. What happens at equilibrium is that these two rates match. That is all that happens. There is still continuous motion or movement of liquid water to vapour water, and there is still motion from the vapour phase to the liquid phase. These two rates match, and that is why we call it a dynamic equilibrium.

For the purposes of this course, let the phases be indicated by alpha, beta, gamm,a and so on. Might need more and in a minute we will see why. There could be multiple phases of the same kind; that is why we need more.

For example, we all know that or we may know that proteins are purified, or extracted, through a process called aqueous two phase extraction, where we have two liquid phases, two aqueous liquid phases. So you can call one, alpha, the other one, beta, and so on and so forth. And each of those phases consists of several components. Let the components be indicated as 1, 2, 3 and so on.

(Refer Slide Time: 12:16)



The criteria for thermodynamic equilibrium are the simultaneous satisfaction of the following equations

$$T_\alpha = T_\beta = T_\gamma = \cdots \qquad \text{Eq. 5.1}$$

$$P_\alpha = P_\beta = P_\gamma = \cdots \qquad \text{Eq. 5.2}$$

$$\mu_{1,\alpha} = \mu_{1,\beta} = \mu_{1,\gamma} = \cdots \qquad \text{Eq. 5.3}$$

$$\mu_{2,\alpha} = \mu_{2,\beta} = \mu_{2,\gamma} = \cdots \qquad \text{Eq. 5.4}$$

$$\mu_{3,\alpha} = \mu_{3,\beta} = \mu_{3,\gamma} = \cdots \qquad \text{Eq. 5.5}$$

...

Now, comes the criteria that thermodynamics gives us for thermodynamic equilibrium. And for thermodynamic equilibrium the following equations must be simultaneously satisfied.

The temperature of the alpha phase must equal the temperature of the beta phase must equal the temperature of the gamma phase and so on, which means that the temperature of all the phases has to be equal. That is the first condition for thermodynamic equilibrium, and we will call that equation 5.1.

Secondly, the pressure of the alpha phase, must equal the pressure of the beta phase, must equal the pressure of the gamma phase, and so on. In other words the pressure of all the phases in equilibrium must be the same. Or, in other words, only if the pressures are the same can we call the phases to be in thermodynamic equilibrium; we will call that equation 5.2.

Also, remember the chemical potential that we talked about. The chemical potential of component 1 in the alpha phase, note this, we are talking of a chemical potential of a certain component. And certain component in the alpha phase, mu 1 , alpha, must equal the chemical potential of the same component in the beta phase that must equal the chemical potential of the same component 1 in the gamma phase, and so on and so forth. In other words, the chemical potential of a certain component must be the same in all the phases that are present at equilibrium. We will call this equation 5.3.

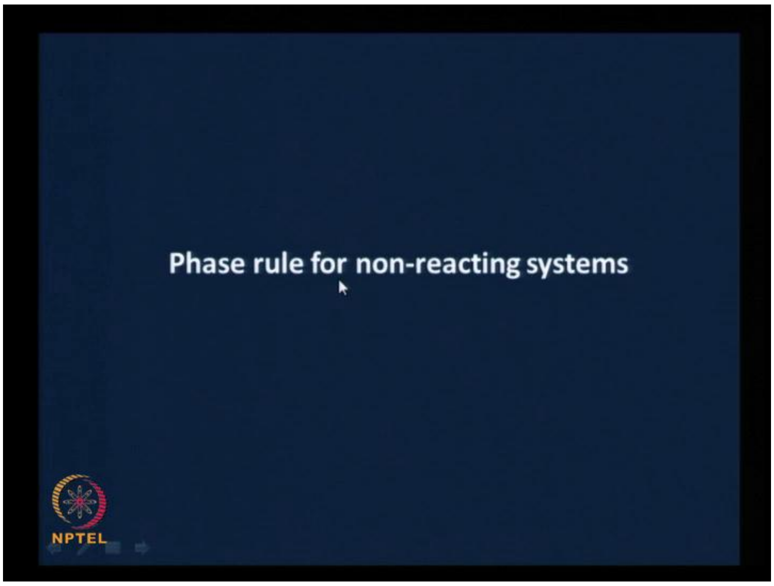
The other things are quite easy to see. The chemical potential of second component must be the same in all the phases: mu 2 alpha must be equal mu 2 beta must be equal mu 2 gamma and so on and so forth. We will call this equation 5.4.

Same thing continued … let me write one more and put dot dot dot later, mu 3 in the alpha phase must equal mu 3 in the beta phase must equal mu 3 in the gamma phase and must be equal to the mu 3 in each of the other phases, we will call this equation 5.5 and so on. … We will have the number of these equations being equal to the number of components that are present in this system, which consists of phases in equilibrium.

To repeat, the temperatures have to be same across the phases. The pressures need to be the same across the phases, as well as the chemical potential of each component must be the same across phases. These are the conditions for equilibrium. We can use it both ways; we can use it to check whether the equilibrium is achieved, we can use it to predict when equilibrium will be achieved.

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.

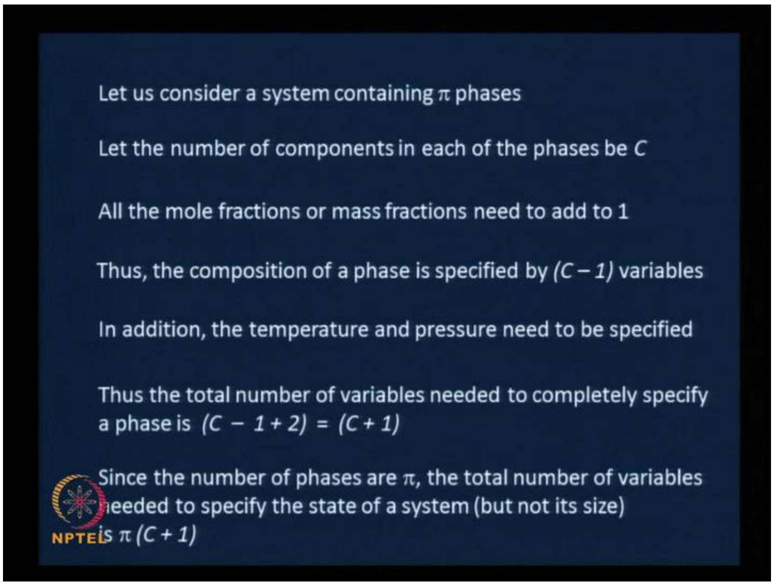
(Refer Slide Time: 15:40)



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.

(Refer Slide Time: 15:53)



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 pi number of phases. You know gas, liquid, vapour and solid and so on, so forth. Let us say in general, it contains pi 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 pi 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.

(no audio 16:43 to 16:48)

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 plus x 2 plus x 3 and so on till plus 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 minus 1 variables.

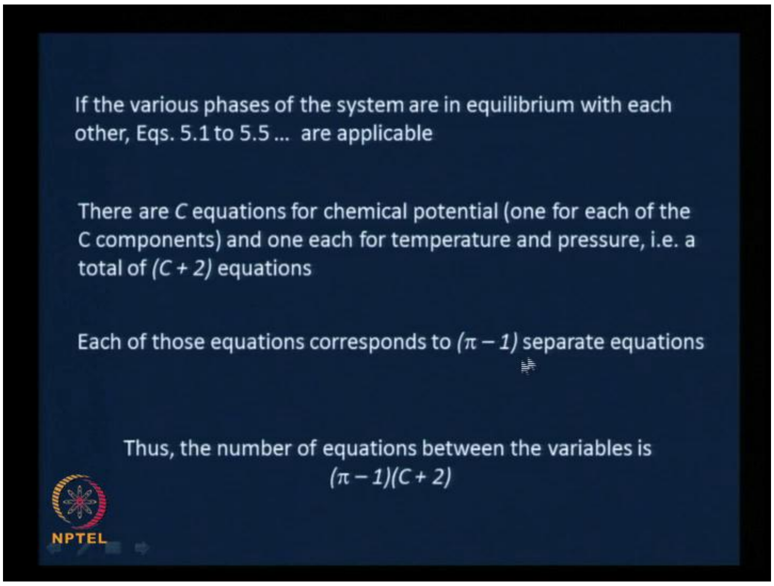
Suppose there are 5 components. We need to know the concentrations of 4 components. The last component, we can always get by adding the mole fractions of these 5 and equating it to 1. Therefore, if we have 4, we can always find the fifth one. Therefore, the composition of a phase is specified by C minus 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 is C minus 1 plus 2 that equals C plus 1. That is C minus 1 variables of compositions, we saw, plus 2 variables, temperature and pressure. You add all these together, you get C plus 1.

We said that each of these component is present at all the phases, and the total number of phases … is pi. Therefore, the total number of variables needed to specify the state of the system, but, not its size, of course, is pi phases times C plus 1 variables that are required to specify in each phase. Therefore, pi into C plus 1.

(no audio 19:04 to 19:08)

(Refer Slide Time: 19:07)



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

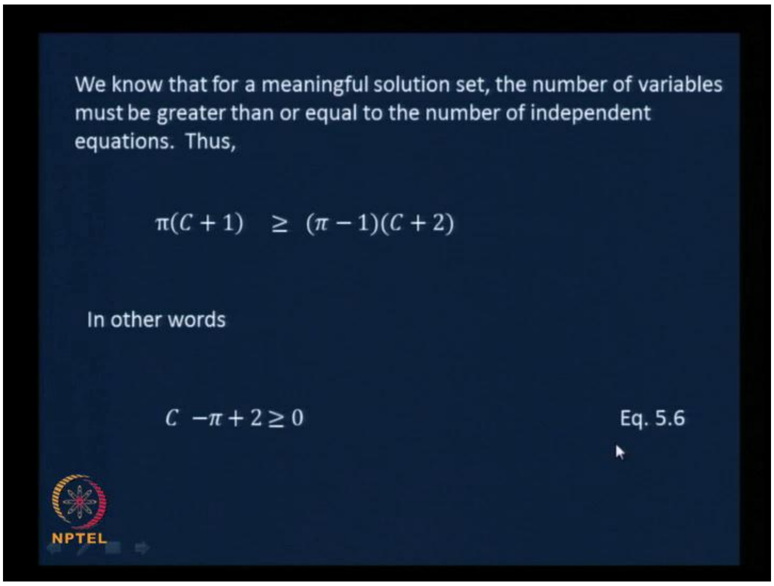
Thus, the number of equations between the variables is $(\pi-1)(C+2)$

If the various phases of the system are at equilibrium with each other, then the conditions of equilibrium can be applied. You know … equations 5.1 to 5.5, which is T alpha equals T beta and so on, P alpha equals P beta equals P gamma, and so on, and the chemical potential of each component in each phase must be the same … of each component in the phases must be the same.

There are C equations for chemical potential, one for each of the C components that are present – that we saw. … We wrote mu 1 alpha equals mu 1 beta equals mu 1 gamma; then, mu 2 alpha equals mu 2 beta equals mu 2 gamma, and so on; mu 3 alpha equals mu 3 beta, and so on. 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, T alpha equals T beta equals T gamma P alpha equals P beta equals P gamma. Therefore, we have a total of C plus 2 equations. And, each of those equations corresponds to pi minus 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 pi minus 1 separate equations. And therefore, the number of equations between the variables is pi minus 1 separate equations into C plus 2 equations.

(Refer Slide Time: 21:00)



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

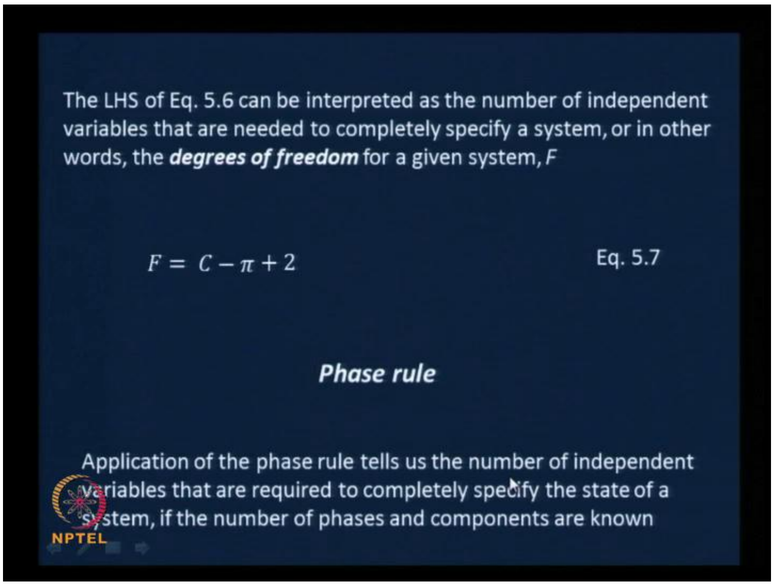
$$C - \pi + 2 \geq 0 \qquad \text{Eq. 5.6}$$

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, pi into C plus 1, you know, number of variables that we saw earlier, must be greater than pi minus 1 into C plus 2 equations, for a general case.

Now we have completely generalized this. We said pi phases and C components, and we got the number of variables as pi into C plus 1. We got the number of independent equations between them as pi minus 1 into C plus 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 into C plus 1 must be greater than or equal to pi minus 1 into C plus 2. In other words, if you transpose this, C minus pi plus 2 must be greater than or equals to 0. You can do the transposition and indeed find that C minus pi plus 2 equals 0, or is greater than or equals to 0. We will call this equation 5.6.

(Refer Slide Time: 22:31)



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

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

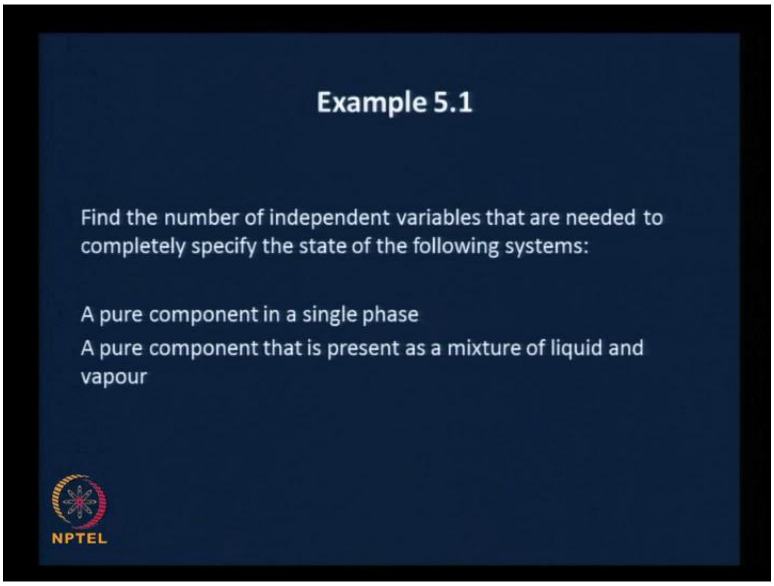
Phase rule

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 this C minus pi plus 2, this 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.

And therefore, F is nothing but C, number of components, minus pi, the number of phases, plus 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.

(Refer Slide Time: 23:54)



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:

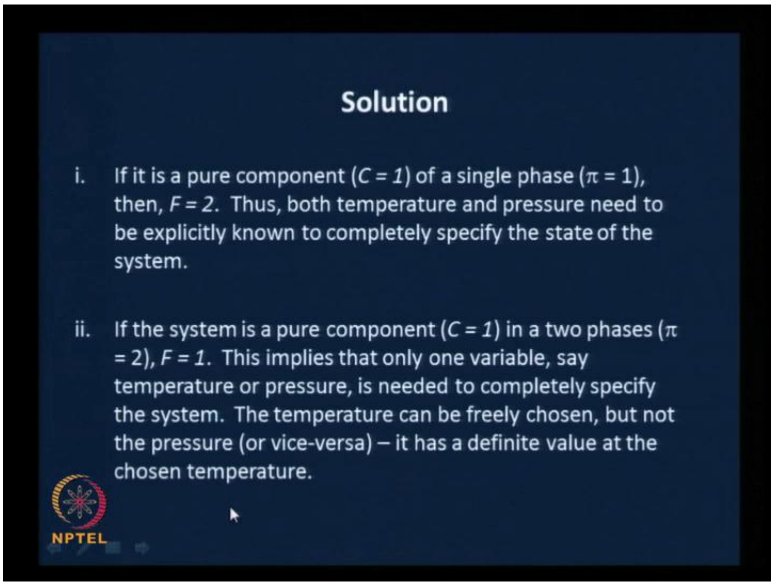
- a pure component in a single phase – that is the first system,
- a pure component that is present as a mixture of liquid and vapour

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.

(No audio 24:37 to 35:08)

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

(Refer Slide Time: 35:18)



Solution

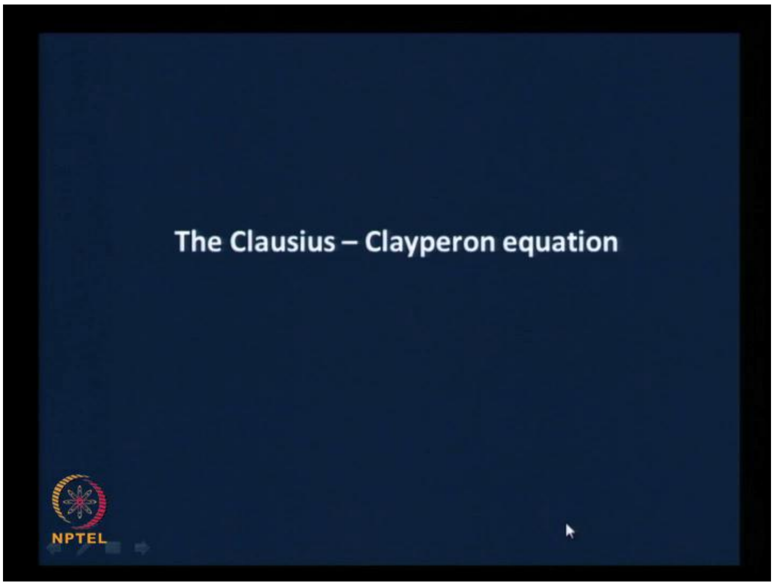
i. If it is a pure component ($C = 1$) of a single phase ($\pi = 1$), then, $F = 2$. Thus, both temperature and pressure need to be explicitly known to completely specify the state of the system.

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.

The solution is as follows, we said the first system is a pure component, which means C is 1 single phase which means pi is 1 and therefore, C minus pi plus 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. And 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 – pi 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.

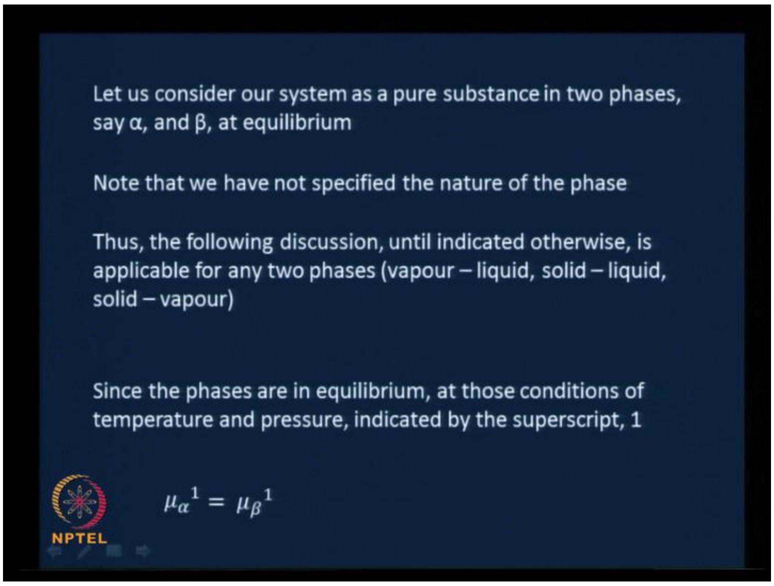
(Refer Slide Time: 37:02)



The Clausius – Clayperon equation

Let us, begin to look at one of the fundamental relationships, when we consider phases in equilibrium, especially, when transitions between phases takes place. That is called the Clausius-Clapeyron equation. We are going to start doing this, and let us see how far we get today.

(Refer Slide Time: 37:37)



Let us consider our system as a pure substance in two phases, say α, and β, at equilibrium

Note that we have not specified the nature of the phase

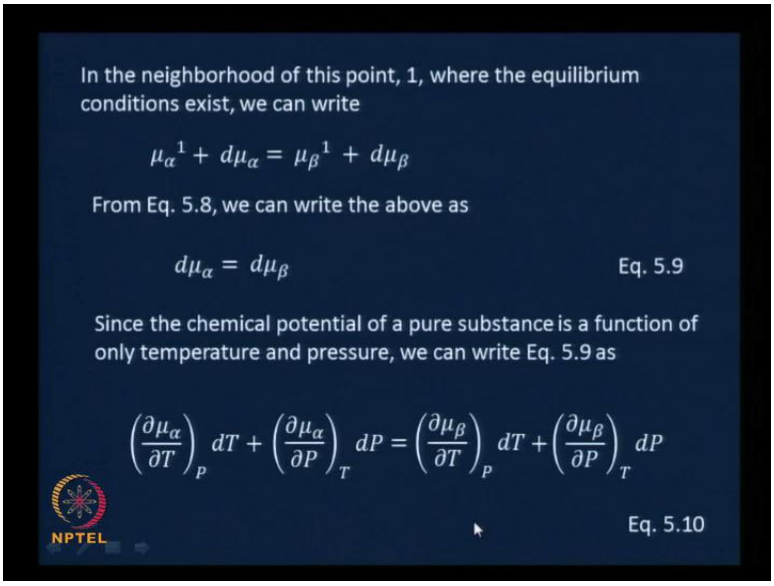
Thus, the following discussion, until indicated otherwise, is applicable for any two phases (vapour – liquid, solid – liquid, solid – vapour)

Since the phases are in equilibrium, at those conditions of temperature and pressure, indicated by the superscript, 1

$$\mu_\alpha{}^1 = \mu_\beta{}^1$$

Let us consider our system as a pure substance. We will start with pure substances. That is a good to understand the basis. Let us consider our system as a pure substance in two phases, say alpha and beta at equilibrium. What I would like you to note is, that we have not specified the nature of the phase. These alpha and beta could be any 2 phases. They could be liquid and vapour phase, liquid and solid phase, vapour and solid phase. That is what is given here: The following discussion, unless indicated otherwise, is applicable for any 2 phases … they could be vapour-liquid, solid-liquid, solid-vapour. Since the phases are in equilibrium at those conditions of temperature and pressure, which we will indicate by the superscript, 1, we can certainly write from the condition of equilibrium, you know the first 5 equations, equations 5.1 to 5.5 and so on, mu alpha at the conditions specified by the temperature and pressure – we will indicate that by 1 – must equal mu beta, which is a chemical potential of a pure component in the other phase, in the beta phase. That is, the chemical potential of the pure component in the alpha phase at certain conditions of temperature and pressure must equal the chemical potential of the same component in the beta phase at the same conditions of temperature and pressure. This automatically comes from the condition of equilibrium. Let us call this equation 5.8.

(Refer Slide Time: 39:28)



In the neighborhood of this point, 1, where the equilibrium conditions exist, we can write

$$\mu_\alpha^{\ 1} + d\mu_\alpha = \mu_\beta^{\ 1} + d\mu_\beta$$

From Eq. 5.8, we can write the above as

$$d\mu_\alpha = d\mu_\beta \qquad \text{Eq. 5.9}$$

Since the chemical potential of a pure substance is a function of only temperature and pressure, we can write Eq. 5.9 as

$$\left(\frac{\partial \mu_\alpha}{\partial T}\right)_P dT + \left(\frac{\partial \mu_\alpha}{\partial P}\right)_T dP = \left(\frac{\partial \mu_\beta}{\partial T}\right)_P dT + \left(\frac{\partial \mu_\beta}{\partial P}\right)_T dP$$

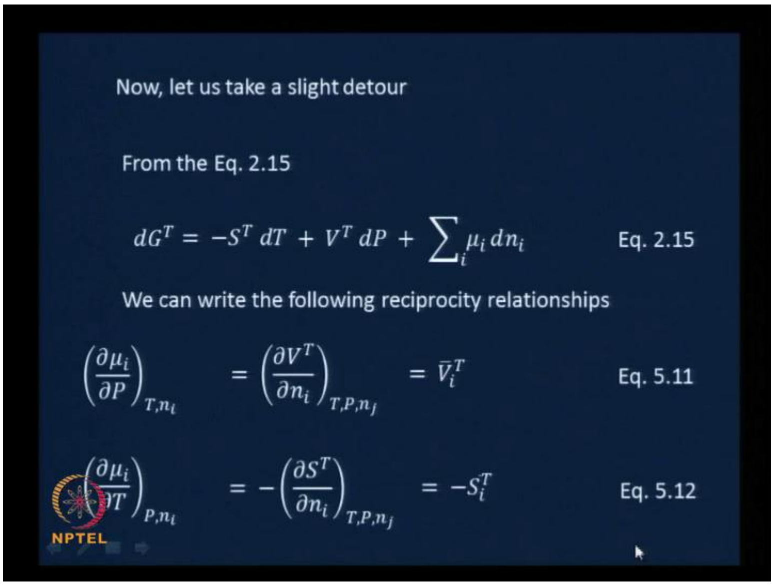
Eq. 5.10

In the neighborhood of this point, which means a very small region around this point, mathematically speaking, where the equilibrium conditions can be considered to exist. You know it is a hypothetical situation here, but, we need the concept of neighborhood to completely develop this particular concept. Therefore, in the neighborhood of this point where the equilibrium conditions can still be considered to exist, we can write mu alpha 1 plus d mu alpha – that is a change from the point 1, in the neighborhood of point 1, equals mu beta 1 plus d mu beta.

Of course, from 5.8 the previous equation, we know that mu alpha 1 equals mu beta 1. Therefore, they can be cancelled. Therefore, d mu alpha equals d mu beta. The differential of mu alpha equals the differential of mu beta. Let us call that equation 5.9.

Since the chemical potential of a pure substance is a function of only temperature and pressure, we can write equation 5.9 in terms of the expanded functionalities. You know this is the total differential; writing it in terms of partial differentials, from the theorem in mathematics, d mu alpha is dou dou T of mu alpha at constant pressure d T, plus dou dou P of mu alpha at constant temperature d P – this is d mu alpha – this equals dou dou T of mu beta at constant pressure d T, plus dou dou P of mu beta at constant temperature d T. Let us call this equation 5.10.

(Refer Slide Time: 41:30)



Now, let us take a slight detour

From the Eq. 2.15

$$dG^T = -S^T\,dT + V^T\,dP + \sum_i \mu_i\,dn_i \qquad \text{Eq. 2.15}$$

We can write the following reciprocity relationships

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_i} = \left(\frac{\partial V^T}{\partial n_i}\right)_{T,P,n_j} = \bar{V}_i^T \qquad \text{Eq. 5.11}$$

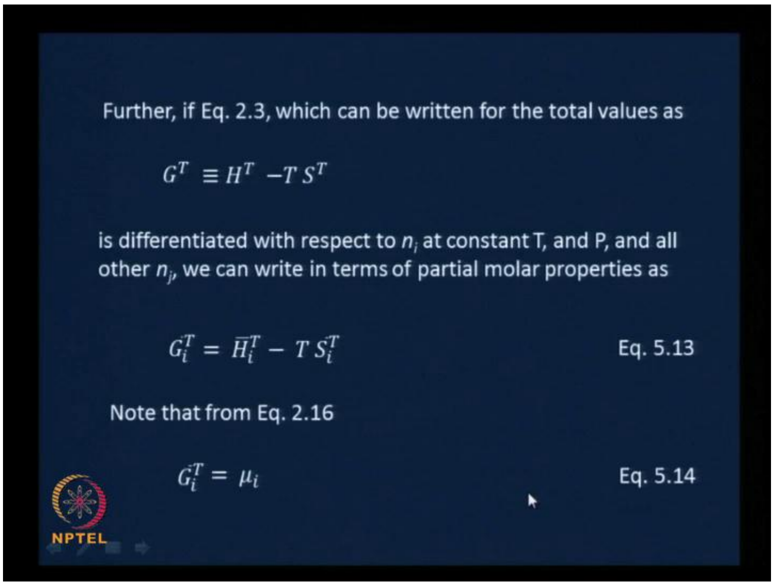
$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_i} = -\left(\frac{\partial S^T}{\partial n_i}\right)_{T,P,n_j} = -S_i^T \qquad \text{Eq. 5.12}$$

Now, let us take a slight detour to establish a few things, and then we will come back to our 2 phases and so on. From equation 2.15, 2 15 that we saw earlier, in the module number 2, d G T equals minus S T d T plus V T d P; you can recall this equation now. By now, you must be familiar with this … since we have seen this so many times, and used it also. Plus, of course, this is a multi-component system. Therefore, sum over all i mu i d n i. This is the equation 2.15 that we saw earlier.

Recall the reciprocity relationships that we, again, saw in the second module? Following the reciprocity relation … rather doing the reciprocity relationship for equation 2.15, the following relationships can be written out. dou mu i dou P at constant T and n i equals dou V T dou n i – now we are doing the reciprocity between these two – dou mu i dou P at a constant T, n i equals … dou V T dou n i at constant T, P, and all other n j, which are different from n i. We can write this, and that equals … you know… this is nothing but the definition of the partial molar of volume V i T hash. Let us call this equation 5.11.

And if we do the reciprocity between this and this we can write dou mu i dou T at constant P, n i, … equals minus dou S T dou n i at constant T, P, and all other n which are different from this I, or all other n j where j is not equal to i. And, what is this is nothing but the partial molar entropy S i T hash – hash is somewhat is missing here – S i T hash. We will call this equation 5.12.

(Refer Slide Time: 44:14)



Further, if Eq. 2.3, which can be written for the total values as

$$G^T \equiv H^T - T\,S^T$$

is differentiated with respect to n_i at constant T, and P, and all other n_j, we can write in terms of partial molar properties as

$$\bar{G}_i^T = \bar{H}_i^T - T\,\bar{S}_i^T \qquad \text{Eq. 5.13}$$

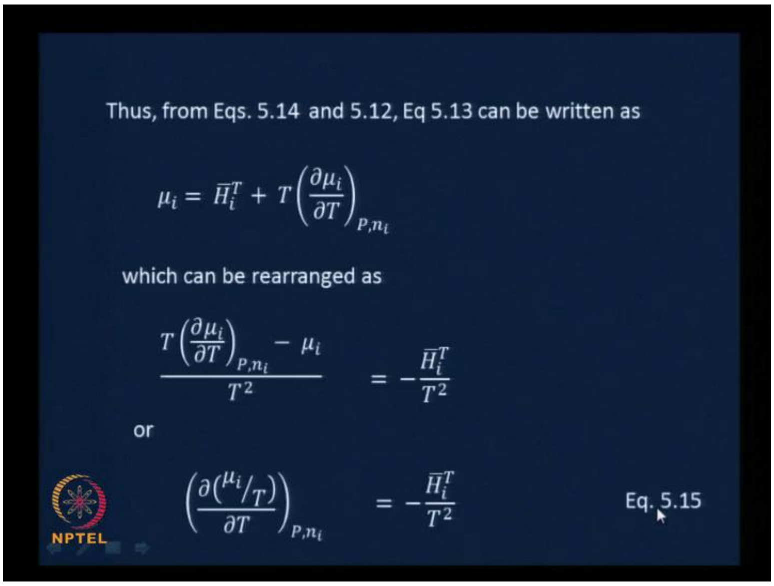
Note that from Eq. 2.16

$$\bar{G}_i^T = \mu_i \qquad \text{Eq. 5.14}$$

Further, if equation 2.3, which can be written for the total values as G T equals H T minus T S T. This is the definition of Gibbs free energy, and we are writing this for the total values … you know … not for a single mole. G T equals H T minus T S T. If this is differentiated, with respect to n i at constant T and P and all other n j s, we can write in terms of partial molar properties as G i T hash equals H i T hash minus T S i T hash.

We are differentiating each term with respect to n i at constant T, P, and n j, and by definition that derivative would be G i T hash. By definition, this derivative would be H i T hash, and this one would be minus T S i T hash. We will call this equation 5.13. And, from equation 2.16, we get G i T hash equals mu i – partial molar property with respect to the single mole there. Therefore, we get it equal to mu i.

(Refer Slide Time: 45:40)



Thus, from Eqs. 5.14 and 5.12, Eq 5.13 can be written as

$$\mu_i = \bar{H}_i^T + T\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_i}$$

which can be rearranged as

$$\frac{T\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_i} - \mu_i}{T^2} = -\frac{\bar{H}_i^T}{T^2}$$

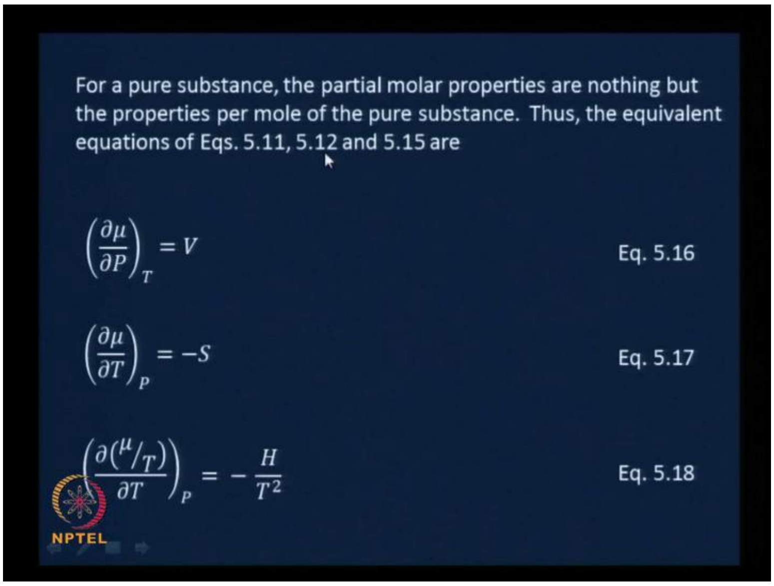
or

$$\left(\frac{\partial(\mu_i/T)}{\partial T}\right)_{P,n_i} = -\frac{\bar{H}_i^T}{T^2} \qquad \text{Eq. 5.15}$$

Therefore, from equations 5.14 and 5.12, equation 5.13; from 5.14 and 5.12; 5.14 is this: G i T hash equals mu i. and 5.12 was this, … which we obtained from the reciprocity relationship. From these two equations, we can write mu i equals H i T hash plus T dou mu i dou T at constant P, n i. Which can be rearranged as … I am just rearranging this by T dou mu i dou T at constant P, n i minus mu i , and I am dividing this by T squared is nothing but, minus H i – now I have taken this to the other side – minus H i T hash by T squared. Just a rearrangement. There is the reason for this rearrangement. … The reason for this rearrangement is this:

This form is nothing but dou dou T of mu i by T, P n i. If you are unable to see this, consider this as u by v, or numerator by denominator. Denominator function into derivative of the numerator function minus the numerator function into derivative the denominator function, which is 1 here, divided by the square of the denominator function and that is the derivative. dou mu i by T dou T at constant P, n i equals minus H i T hash by T squared. We will call this equation 5.15.

(Refer Slide Time: 47:39).



For a pure substance, the partial molar properties are nothing but the properties per mole of the pure substance. Thus, the equivalent equations of Eqs. 5.11, 5.12 and 5.15 are

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V \qquad \text{Eq. 5.16}$$

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -S \qquad \text{Eq. 5.17}$$

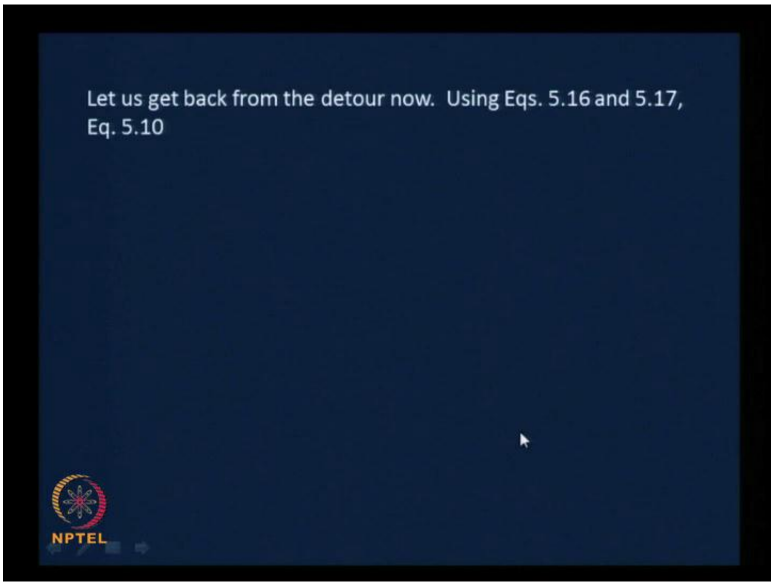
$$\left(\frac{\partial (\mu/T)}{\partial T}\right)_P = -\frac{H}{T^2} \qquad \text{Eq. 5.18}$$

For a pure substance, the partial molar properties are nothing but the properties per mole of the pure substance. You know the kind of coalesce into each other. Thus the equivalent equations of 5.11, 5.12 and 5.15 … you know, when we write down the equations, you can recall those, or you can go back and check what 5.11 5.12 and 5 15 are … dou mu by dou P at constant T equals V, equation 5.16. dou mu dou T at constant P equals minus S, equation 5.17.

And dou mu by T dou T at constant P equals minus H by T squared; equation 5.18. Our 5.11 was when you had i here and V i T hash here. 5.12 was you had a i here and S i T hash here. And you had to take other n also as constant. And here, you had i and H i T hash here, and P and other n s to be constant here.

Therefore, since these are written for a single mole of the pure substance, we can drop all these i s, and hashes, and so on because, the partial molar property becomes the property per mole of the pure substance.

(Refer Slide Time: 49:09)



Let us get back from the detour now. Using Eqs. 5.16 and 5.17, Eq. 5.10

What we will do, when we begin the next class is we will get back from this detour. We essentially wanted to come up with these relationships, and that is why we took a detour. When we begin the next class, we will get back to considering the 2 phases in equilibrium and the process of transfer from one phase, or transition from one phase to another, which is the context of the Clausius-Clapeyron equation. See you in the next class.