Thermodynamics for Biological Systems:
Classical and Statistical Aspects
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Lecture – 45
Review of module 5

Welcome back!

In this lecture, let us review whatever we did in module 5 under phase equilibrium. As you know, there could be various phases - the three major phases that we are looking at in this particular course are the solid, liquid, and the vapour phase.

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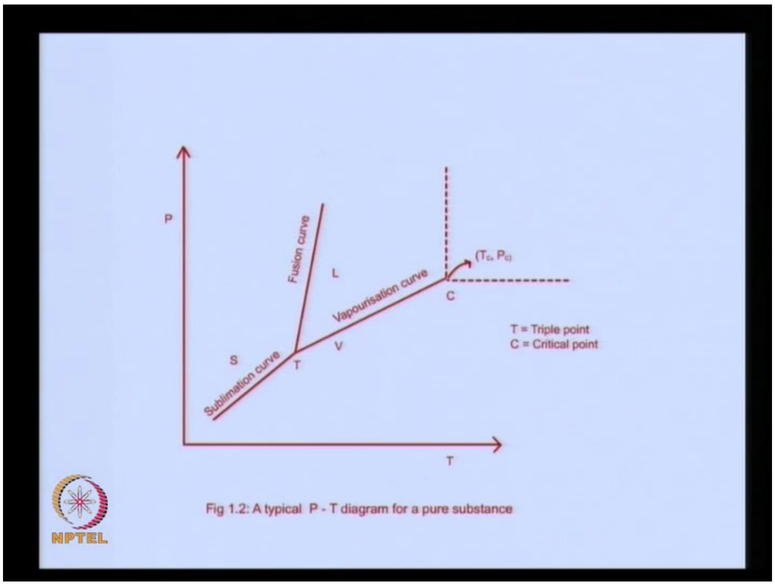

Fig 1.2: A typical P - T diagram for a pure substance

… If they exist in equilibrium or any two phases existing in equilibrium or all three phases exiting in equilibrium with each other – how do we handle such situations, is what we are going to look at … or what is the formalism for handling such situations is what we are going to look at in this course.

We had initially seen the P T diagram, the pressure versus temperature diagram for a pure substance to set the base for the kind of systems that we will be interested in. We said that in this region, you know region essentially means the combinations of temperature pressure, T comma P, is each point here; the combinations of temperature and pressure in which the solid would exist, in which the liquid would exist here, and here the vapour exist. This is the sublimation curve across which the solid to vapour transition takes place, which means along these combinations of temperature and pressure, you have solid co existing with vapour.

This is the vaporization curve, which is easier to imagine. We have the liquid co exiting with the vapour across this line or across the pressures and temperature conditions that are given by this line. This is the fusion curve across which or on which you have coexistence of both the solid phase, and the liquid phase. We also said that beyond or above the critical pressure critical pressure – critical temperature critical pressure point is this. Above the critical temperature here, and above the critical pressure we have the supercritical phase which we are not going to consider in this particular course.

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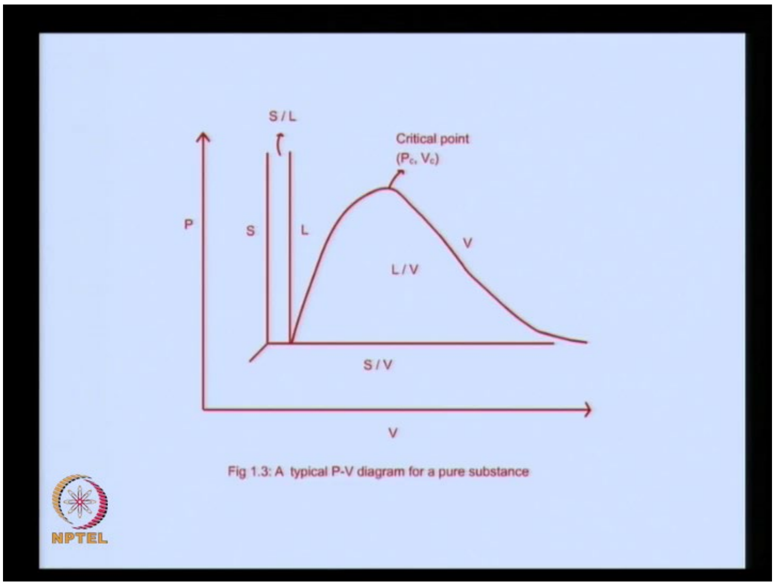

Fig 1.3: A typical P-V diagram for a pure substance

The same information can also be obtained in a P versus V diagram, the pressure verses specific volume diagram. This is again for a pure substance. We saw that the lines in the previous graph get represented somewhat as regions in this particular graph. Here we have the solid phase in these combinations of specific volumes, and pressure; in these combinations of specific volume and pressure, you have the liquid phase, and in these combinations of specific volume and pressure we have the vapour phase. This is the critical point here, Vc, Pc. In this region we have the coexistence of both the solid, and liquid phase; in this region we have the coexistence of solid and vapour phase, and underneath this dome in this region we have the coexistence of liquid and vapour phases.

So, these are the kind of systems that we are looking at we have the coexistence of 2 or more phases together at the same time. Initially we looked at the pure substance and then extended it to a multi component system .

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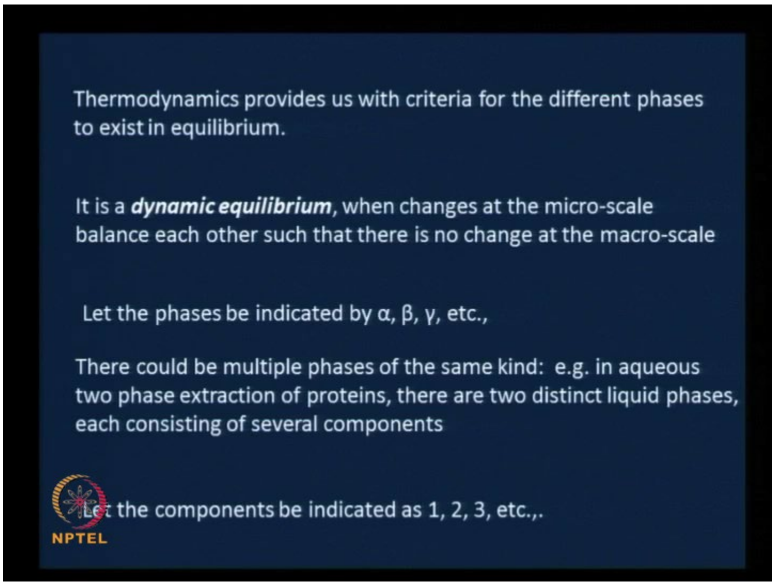

Thermodynamics provides us with criteria for the different phases to exist in equilibrium.

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.,.

The take home message from this particular module is this exact slide – the conditions that thermodynamics provides with … as criteria for different phases to exist in equilibrium. As we had seen … before we look at the conditions, we need to understand that it is a dynamic equilibrium, which means that there are changes occurring at the micro scale. Those changes occurring at the micro scale balance each other, so that there is no change at the macro scale. We had given the example of a substance going from the liquid phase to a vapour phase.

For example, water, just pure water, going from the liquid phase, H_2O that we know of, to the vapour phase; we said that there is a rate at which the water molecules move from the liquid phase to the vapour phase, and at the same time there is a rate at which the water molecules move from the vapour phase to the liquid phase. If the rate in one direction equals the rate in the other direction that is the condition of equilibrium that we are looking at. What we mean by dynamic equilibrium is that these are taking place at all the time – it is just that the rates balance, so that we are not able to see any changes at the macro scale.

We said that we are going to indicate phases by alpha, beta, gamma, and so on. There could be multiple phases of the same kind such as 2 distinct liquid phases, and things like that. … Also the components we are going … to indicate by 1, 2, 3, and so on.

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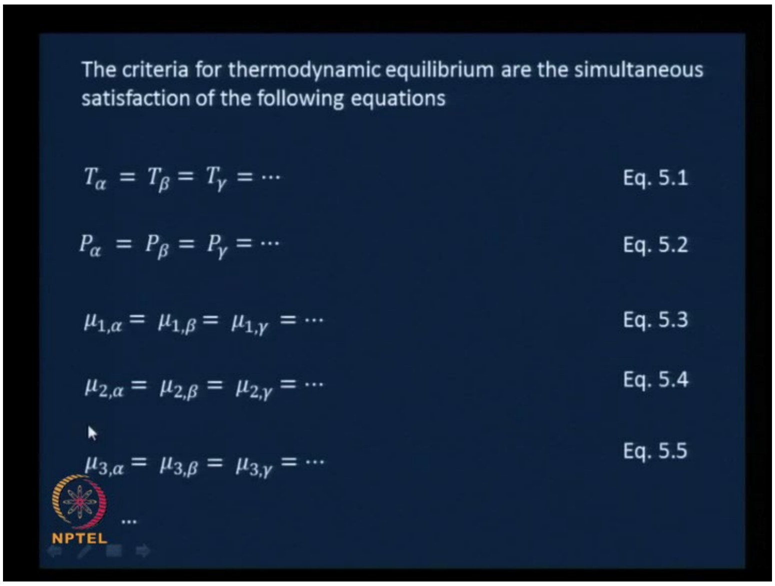

The criteria for thermodynamic equilibrium are the simultaneous satisfaction of the following equations

$T_\alpha = T_\beta = T_\gamma = \cdots$ Eq. 5.1

$P_\alpha = P_\beta = P_\gamma = \cdots$ Eq. 5.2

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

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

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

...

Now, we come to the criteria for thermodynamic equilibrium. If a system is said to be in thermodynamic equilibrium, it needs to satisfy simultaneously the following equations. That is,

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

Therefore, the temperatures in all the phases must be equal equation 5.1. This is the condition for thermal equilibrium.

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

The equality of pressures across the various phases, equation 5.2, is the condition for mechanical equilibrium. This is thermal equilibrium, mechanical equilibrium, and the condition for the chemical equilibrium is given by all these equations that follow. Which is the chemical potential of any component in any phase must be equal. Or, in other words, chemical potential of a certain component i, in all the phases must be equal.

In other words,

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

We call this equation 5.3.

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

The chemical potential of component 2 in the various phases alpha, beta and gamma – they must all be equal; equation 5.4. We wrote one more equation, and then we said we need to write as many equation as there are components.

For the third component,

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

This was equation 5.5, and we could write as many equations as there are components. So, all these put together are the conditions that need to be simultaneously satisfied for chemical equilibrium. Thermal equilibrium, mechanical equilibrium, chemical equilibrium – all three put together is thermodynamic equilibrium.

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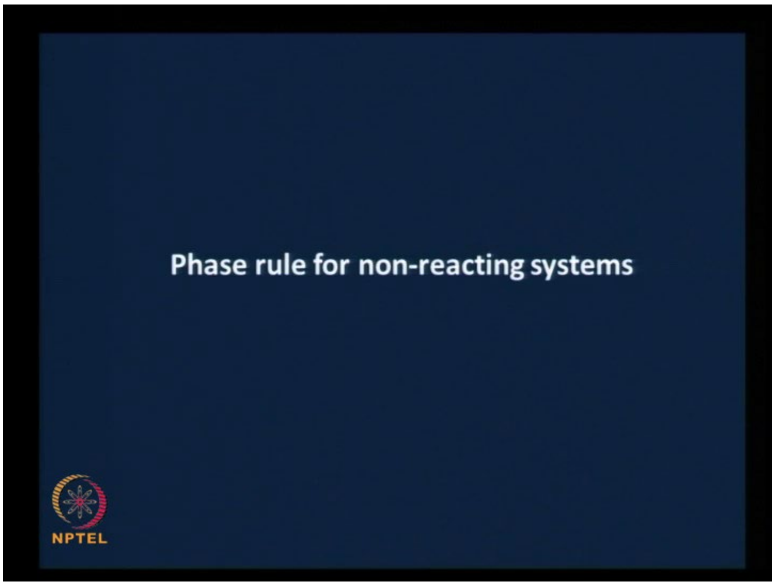

Phase rule for non-reacting systems

Then we derived what is called the phase rule for non reacting system. There are no reactions in the system that we going to consider, and for such systems this phase rule will be valid.

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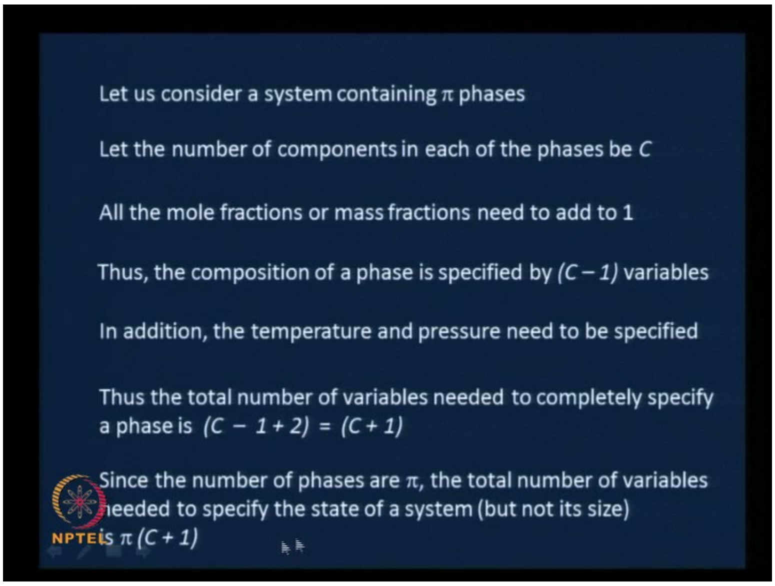

Let us consider a system containing π phases

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 $\pi(C+1)$

And the bases for this was something like this: if the system contains pi phases, solid, liquid, vapour, and so on. Or it could be liquid 1, liquid 2 and so on and so forth. If the number of … or for simplicity, let us say solid, liquid, vapour phases, and the number of components in each phase is C. Then we said that the number of variables needed to specify the state of the system is $\pi(C+1)$. This is the number of variables.

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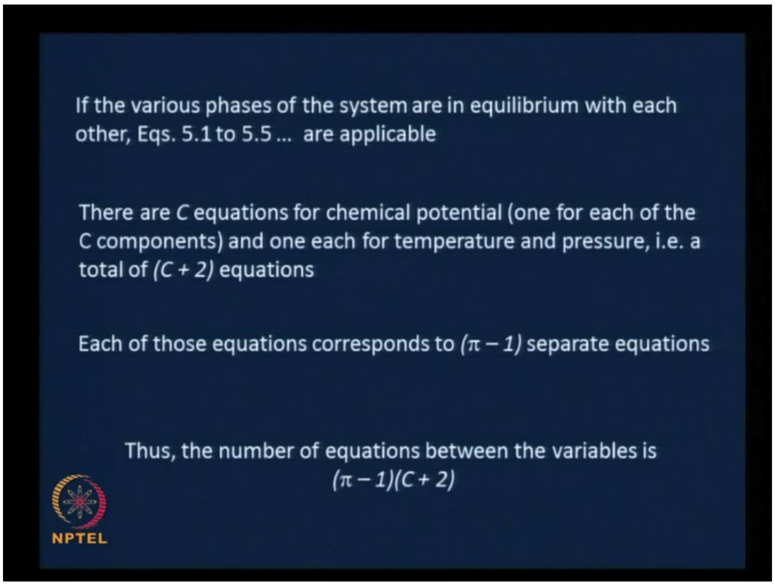

If the various phases of the system are in equilibrium with each other, Eqs. 5.1 to 5.5 … are applicable

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

And we saw that the number of equations between the variables by the arguments … we can go back and see the arguments again … is $(\pi-1)(C+2)$. Therefore, the … number of equations between the variables is $(\pi - 1)(C + 2)$. And, the number of variables was $\pi(C + 1)$. We know that for a set of mathematical equations, if there are certain variables and certain equations, the number of variables is typically equal to or more than the number of independent equations between them for a meaningful solution to arise. If it is equal, fine, we have a unique set of solution. If it is not equal, probably we need to supply some information, so that the number of variables becomes equal to the number of equations, and then we can get a unique solution. This was the basis for the phase rule, as follows.

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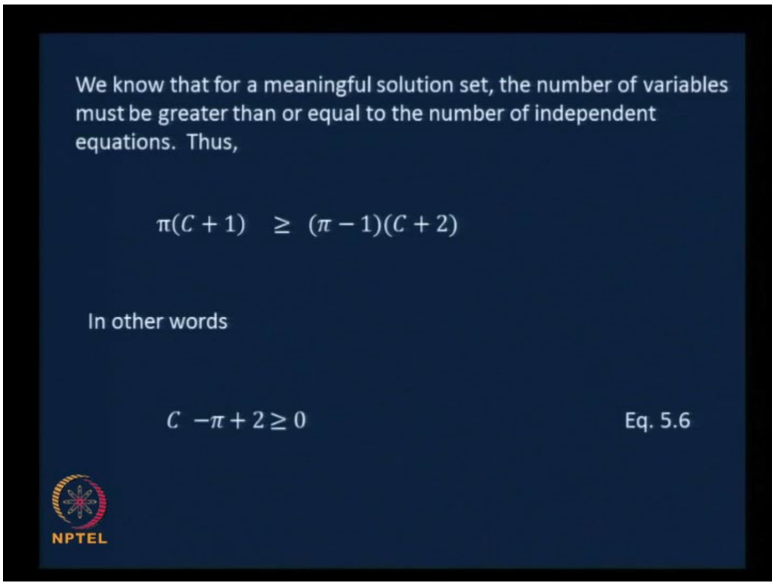

We know that for a meaningful solution set, the number of variables must be greater than or equal to the number of independent equations. Thus,

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

In other words

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

This is the number of variables, $\pi(C + 1)$, must be greater than the number of equations, $(\pi - 1)(C + 2)$. In other words, if you multiply, and then group these appropriately and transpose this, we saw that $(C - \pi + 2) \geq 0$. If it is equal to 0 we get a unique solution set, if it is greater than 0 then we need to supply that many variables, or we need to specify that many variables for a unique solution to arise.

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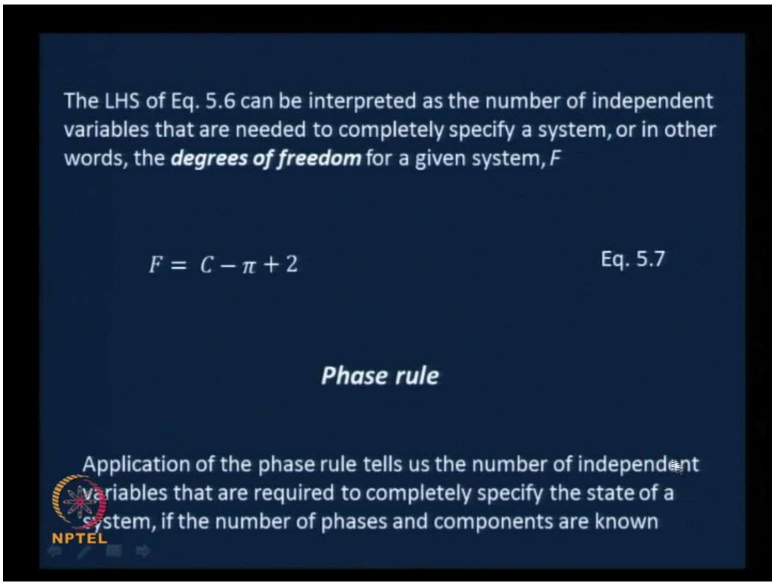

The LHS of Eq. 5.6 can be interpreted as the number of independent variables that are needed to completely specify a system, or in other words, the ***degrees of freedom*** for a given system, F

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

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 number of variables that we needed to supply is what we designated as the number of degrees of freedom, or F; $F = (C - \pi + 2)$. This is called the phase rule. The number of separate variables that need to be specified to completely describe or completely specify this system or any given system is called the number of degrees of freedom of that particular system. Typically, the variables that we choose are pressure, temperature, and the specific volume in that order of importance; or temperature, pressure, specific volume.

This is worth repeating. Application of the phase rule tells us that the number of in 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: π phases and C components, $F = (C - \pi + 2)$. Again, this is valid when there are no reactions that take place in the system. Then we worked out an example to calculate the degrees of freedom in a couple of systems.

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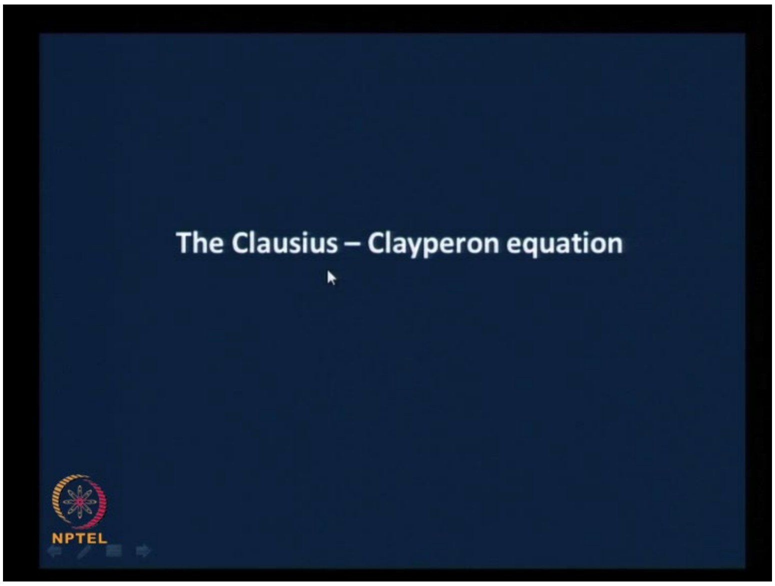

The Clausius – Clayperon equation

Then, we looked at the so-called, Clausius-Clayperon equation. To remind you, the Clausius-Clapeyron equation is valid for any two phases in equilibrium. It could be a solid-liquid phase, a liquid-vapour phase, solid-vapour phase and so on.

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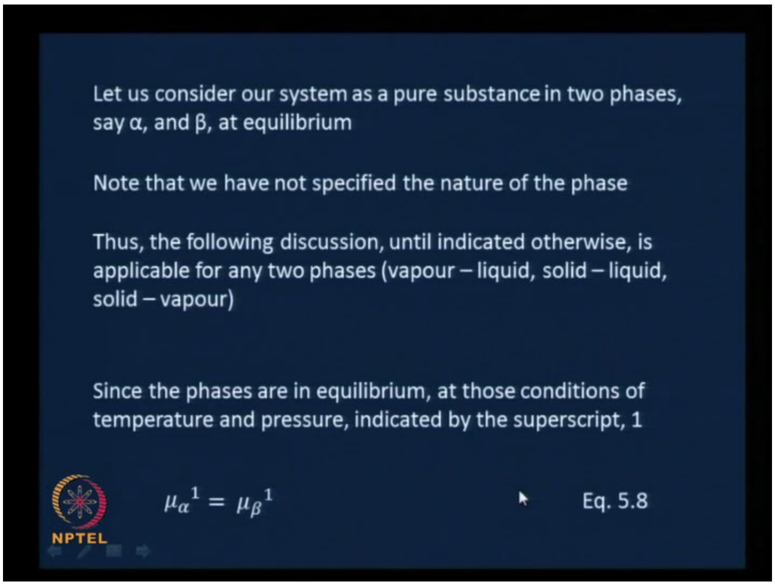

Let us consider our system as a pure substance in two phases, say α, and β, at equilibrium

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

$$\mu_{\alpha}{}^{1} = \mu_{\beta}{}^{1} \qquad \text{Eq. 5.8}$$

… the vapour solid; the solid liquid and the solid vapour phase – there should be 2 distinct phases actually.

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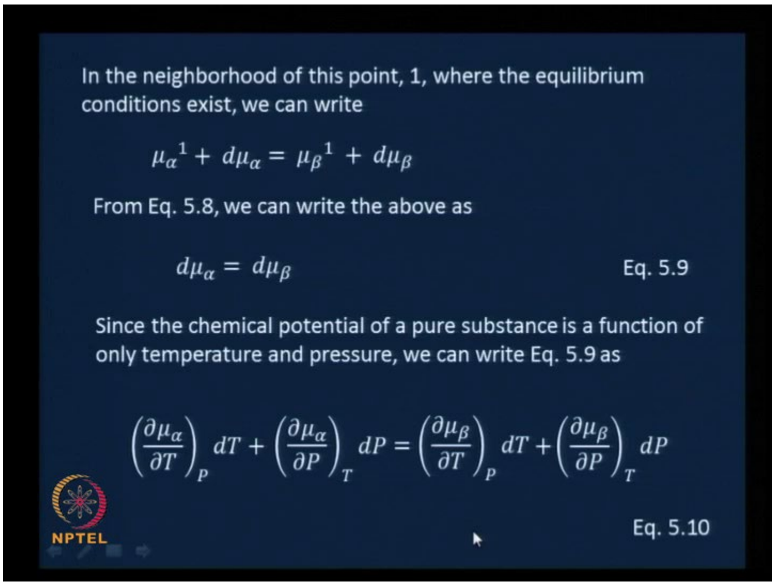

In the neighborhood of this point, 1, where the equilibrium conditions exist, we can write

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

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

We went about deriving the Clausius-Clapeyron equation by using the condition that those 2 phases are in equilibrium; and therefore, the chemical potentials have to be equal – that is where we started. Then, we expressed the differentials of the chemical potential or equated the differentials of the chemical potential, and we expressed them as functions of temperature and pressure, because they are easily measurable.

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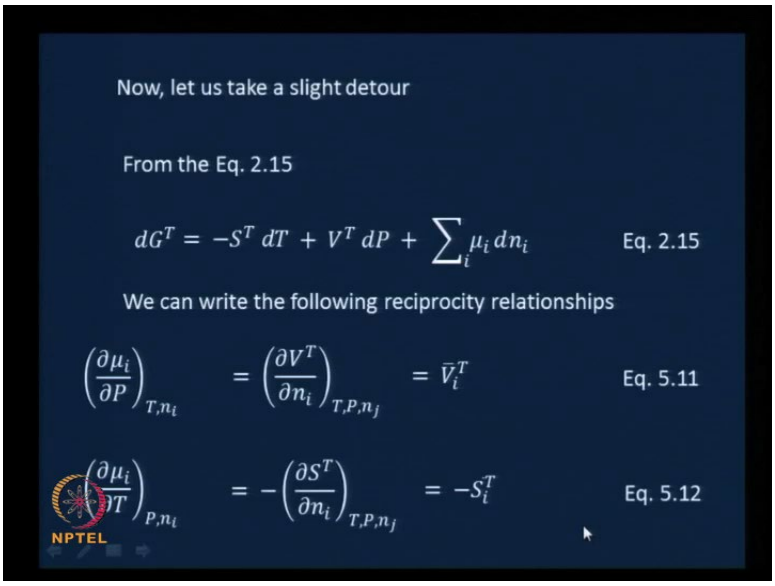

Now, let us take a slight detour

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

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

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

Then we took a detour to essentially get expressions that are useful for the temperature derivative of the chemical potential, and the pressure derivative of the chemical potential at constant pressure, and temperature, respectively.

We also got one more equation that was useful. This is the way we went about doing at. We started with the equation 2. 15, we applied the reciprocity relationship between 2 of these things taken together. I think we took these two first, and then these two to get

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

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

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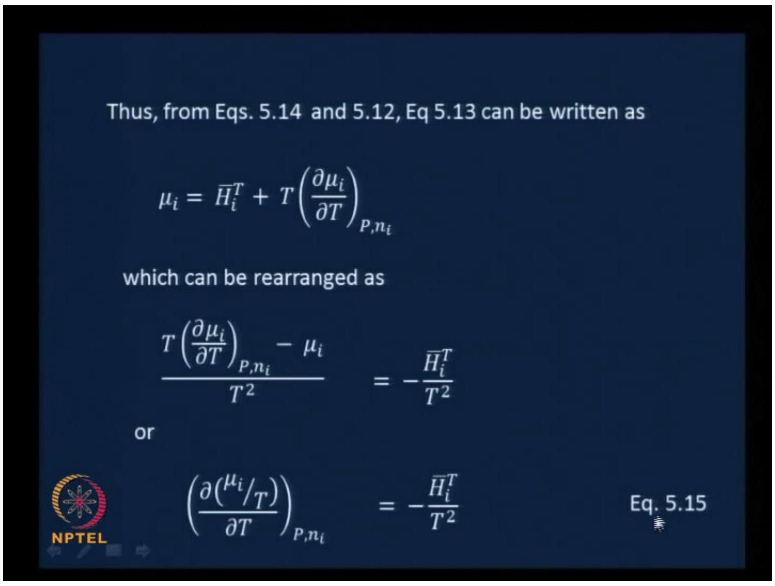

Thus, from Eqs. 5.14 and 5.12, Eq 5.13 can be written as

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

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

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

We got this, and then it is quite interesting when we went about the derivation. This was the additional equation that we got.

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

This we will use later that is what we said.

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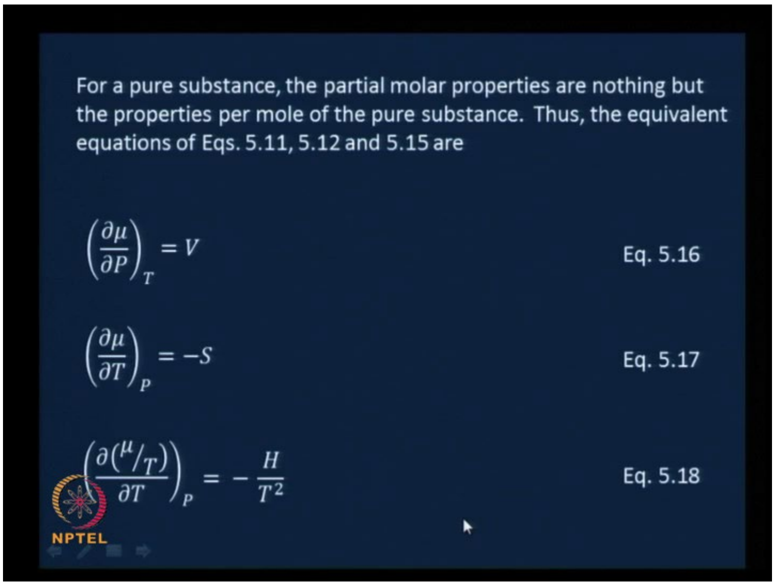

For a pure substance, the partial molar properties are nothing but the properties per mole of the pure substance. Thus, the equivalent equations of Eqs. 5.11, 5.12 and 5.15 are

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

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

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

And those were equations that are valid for multi components systems, and since we are looking initially at pure components while deriving the Clausius-Clayperon equation, we wrote equivalent expressions for the pure components.

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V$$

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial (\mu/T)}{\partial T}\right)_P = -\frac{H}{T^2}$$

Using these, we substituted into the equality of the chemical potential differential expression.

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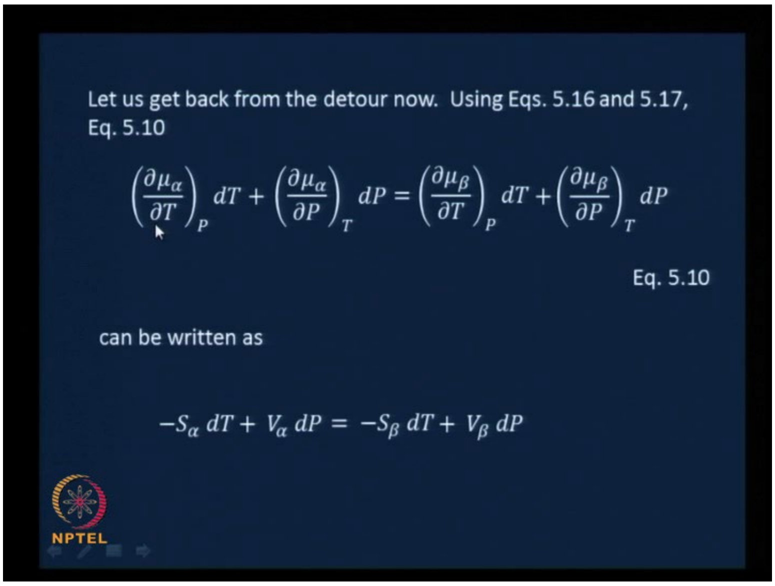

Let us get back from the detour now. Using Eqs. 5.16 and 5.17, Eq. 5.10

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

Eq. 5.10

can be written as

$$-S_\alpha\, dT + V_\alpha\, dP = -S_\beta\, dT + V_\beta\, dP$$

… which is 5.10 … which is given here;

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

Then we substituted these, we could write this in terms of molar entropies, and molar volumes.

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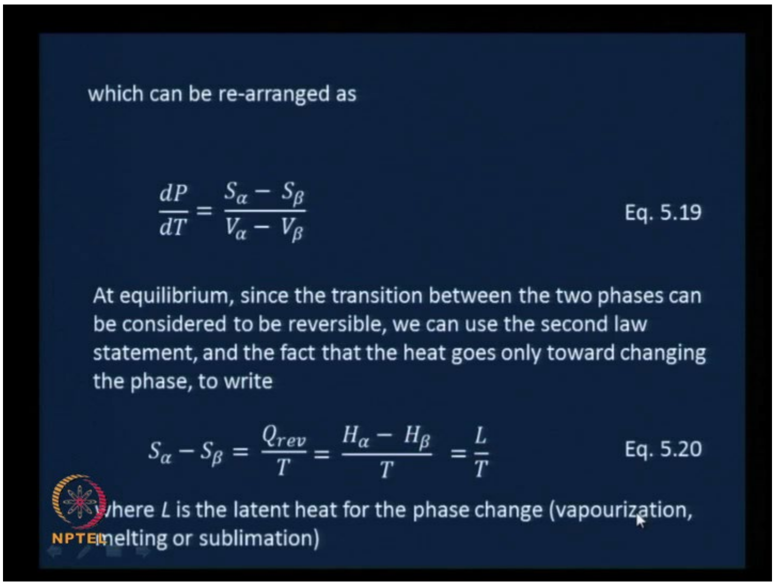

which can be re-arranged as

$$\frac{dP}{dT} = \frac{S_\alpha - S_\beta}{V_\alpha - V_\beta}$$

Eq. 5.19

At equilibrium, since the transition between the two phases can be considered to be reversible, we can use the second law statement, and the fact that the heat goes only toward changing the phase, to write

$$S_\alpha - S_\beta = \frac{Q_{rev}}{T} = \frac{H_\alpha - H_\beta}{T} = \frac{L}{T}$$

Eq. 5.20

where L is the latent heat for the phase change (vapourization, melting or sublimation)

Just by rearranging that we could get

$$\frac{dP}{dT} = \frac{S_\alpha - S_\beta}{V_\alpha - V_\beta}$$

the difference in entropies divided by the difference in specific volumes. Then, we had utilized the condition or the special case that the transition between the 2 phases, between the liquid and vapour phase – that process can be considered to be a reversible process. Therefore, we could apply the second law statement for writing entropies in terms of the heat interaction, Q reversible by T. Since the only heat interaction is going towards the change of phase we could replace that with the change in enthalpy between the 2 phases, and which is nothing but the latent heat of the phase transition. In this case latent heat of the phase transition between alpha to beta given as L – L by T.

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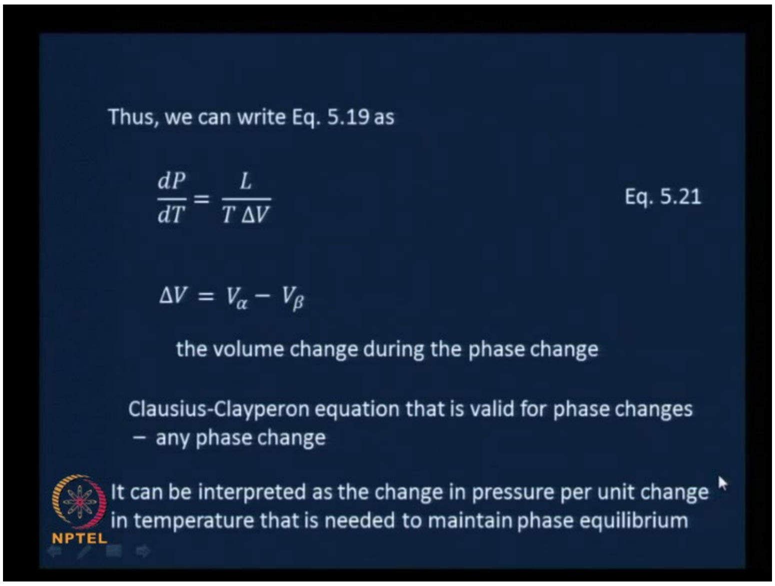

Thus, we can write Eq. 5.19 as

$$\frac{dP}{dT} = \frac{L}{T\,\Delta V} \qquad \text{Eq. 5.21}$$

$$\Delta V = V_\alpha - V_\beta$$

the volume change during the phase change

Clausius-Clayperon equation that is valid for phase changes
– any phase change

It can be interpreted as the change in pressure per unit change in temperature that is needed to maintain phase equilibrium

Therefore, we could write

$$\frac{dP}{dT} = \frac{L}{T\,\Delta V}$$

This was the Clausius-Clayperon equation where delta V, the volume change in the phase change, is V alpha minus V beta. And then as mentioned earlier, Clausius-Clayperon equation is valid for phase changes, for any phase change not necessarily liquid to vapour. It is also valid for liquid to vapour phase change, and it can be interpreted as the change in pressure per unit change in temperature; that is needed to maintain phase equilibrium.

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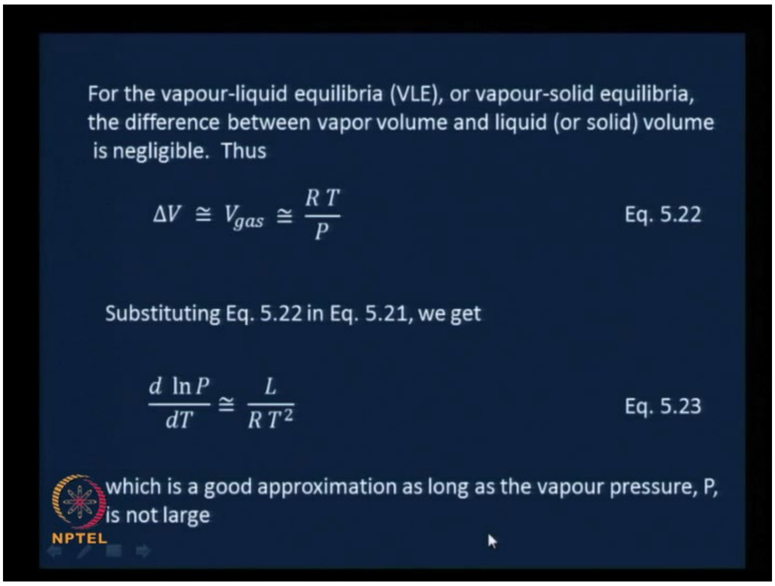

For the vapour-liquid equilibria (VLE), or vapour-solid equilibria, the difference between vapor volume and liquid (or solid) volume is negligible. Thus

$$\Delta V \cong V_{gas} \cong \frac{R\,T}{P} \qquad \text{Eq. 5.22}$$

Substituting Eq. 5.22 in Eq. 5.21, we get

$$\frac{d\,\ln P}{dT} \cong \frac{L}{R\,T^2} \qquad \text{Eq. 5.23}$$

which is a good approximation as long as the vapour pressure, P, is not large

Then we brought in this approximation; that for vapour liquid equilibria, or vapour solid equilibria, the difference between the vapour volume, and the liquid or the solid volume or rather, I should say that the liquid volume or the solid volume is negligible compared to the vapour volume. Therefore, the difference between those specific volumes is nothing but … that equal to the vapour volume itself. Therefore, delta V is approximately equal to … the vapour volume or V gas. If we use an ideal gas relationship, we can write that as equal to R T by P. If we do that, we get

$$\frac{d\,\ln P}{dT} \cong \frac{L}{R\,T^2}$$

which is a good approximation to use for the Clausius-Clayperon equation as long as the vapour pressure, P, is not large; this is what we had said.

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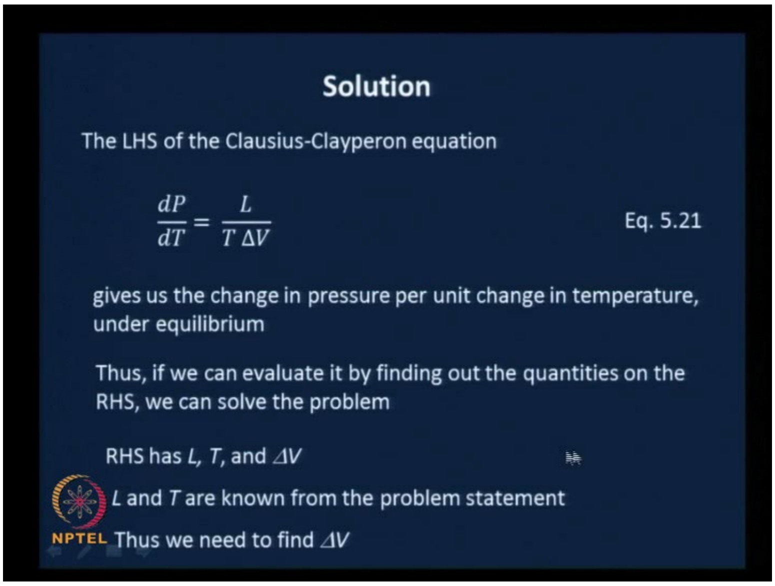

Solution

The LHS of the Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{L}{T\,\Delta V} \qquad \text{Eq. 5.21}$$

gives us the change in pressure per unit change in temperature, under equilibrium

Thus, if we can evaluate it by finding out the quantities on the RHS, we can solve the problem

RHS has L, T, and ΔV

L and T are known from the problem statement

Thus we need to find ΔV

Then, we worked out a problem involving iso-propanol, our popular substance, which is going from the vapour phase to the liquid phase. The solution was detailed. … It was quite simple; we had to find $\frac{dP}{dT}$, and we said that we could find that by using … the values of these variables – L and T, where given in the problem itself, and delta V was the one that we needed to find out. Turned out to be a little lengthy, because it involved an iterative solution for both the volumes. I had shown you how to set up an iteration in a standard spreadsheet, and go about getting the value. It was very simple way of doing that. Once you set it up, it’s simple. It just takes time to describe it, but the process itself, if you do it yourself, is quite fast.

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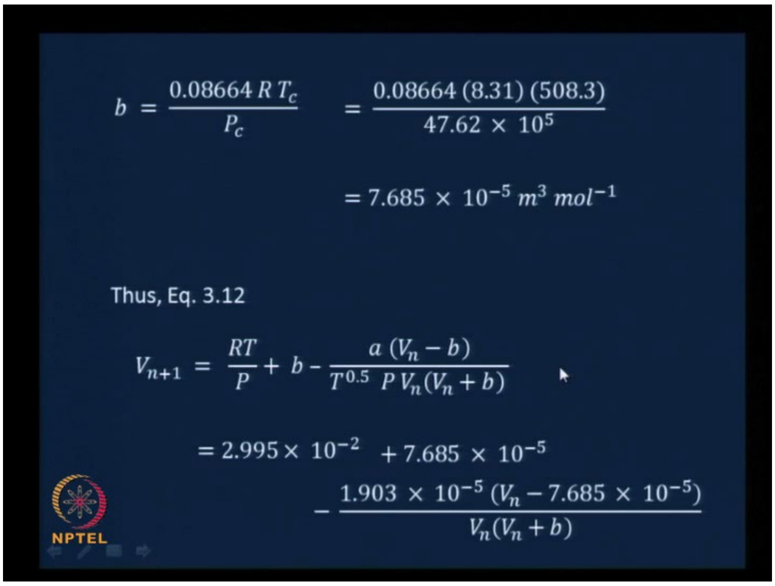

$$b = \frac{0.08664\,R\,T_c}{P_c} = \frac{0.08664\,(8.31)\,(508.3)}{47.62 \times 10^5}$$

$$= 7.685 \times 10^{-5}\ m^3\ mol^{-1}$$

Thus, Eq. 3.12

$$V_{n+1} = \frac{RT}{P} + b - \frac{a\,(V_n - b)}{T^{0.5}\ P\,V_n(V_n + b)}$$

$$= 2.995 \times 10^{-2} + 7.685 \times 10^{-5} - \frac{1.903 \times 10^{-5}\,(V_n - 7.685 \times 10^{-5})}{V_n(V_n + b)}$$

We saw that we had used different formulations of the Redlich Kwong equation to get estimates of first, the vapour volume, by starting with the ideal gas volume as the initial guess. Then, a different formulation for the liquid volume, in which we started with the value of b as the initial guess; the volume of molecules as the initial guess for liquid volumes.

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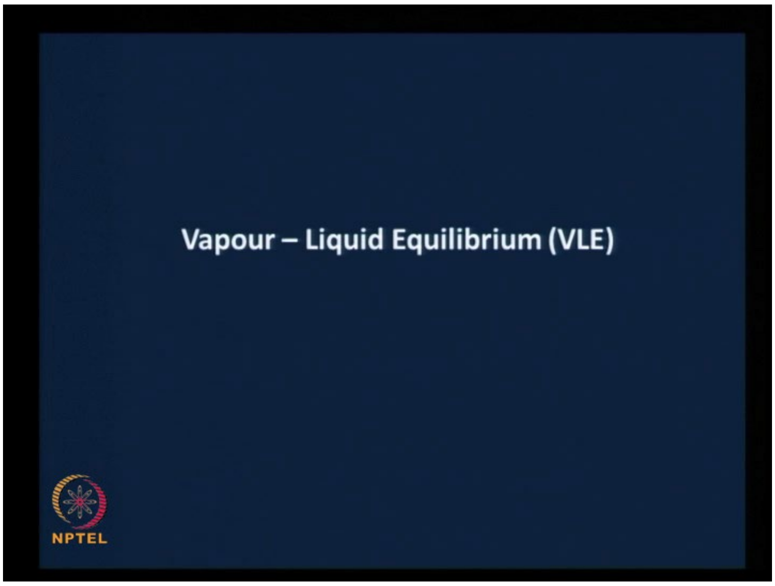

Vapour – Liquid Equilibrium (VLE)

Then, we started looking at the various equilibria or the specific governing equations for various equilibria. We had looked at vapour liquid equilibrium in some detail.

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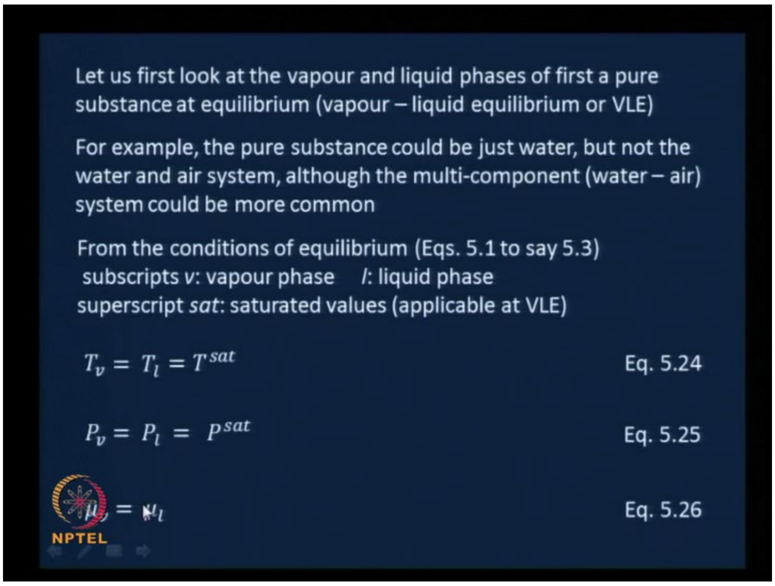

Let us first look at the vapour and liquid phases of first a pure substance at equilibrium (vapour – liquid equilibrium or VLE)

For example, the pure substance could be just water, but not the water and air system, although the multi-component (water – air) system could be more common

From the conditions of equilibrium (Eqs. 5.1 to say 5.3)
subscripts *v*: vapour phase *l*: liquid phase
superscript *sat*: saturated values (applicable at VLE)

$$T_v = T_l = T^{sat} \qquad \text{Eq. 5.24}$$

$$P_v = P_l = P^{sat} \qquad \text{Eq. 5.25}$$

$$\mu_v = \mu_l \qquad \text{Eq. 5.26}$$

The basis is quite simple: the temperatures, and pressures have to be equal, and the chemical potentials have to be equal. We said we are going to take these as given – that is thermal equilibrium and mechanical equilibrium as given. We will typically concentrate on the chemical equilibrium part is what we said. $\mu_v = \mu_l$ is what arises as a part of writing the chemical equilibrium in the liquid vapour equilibrium case.

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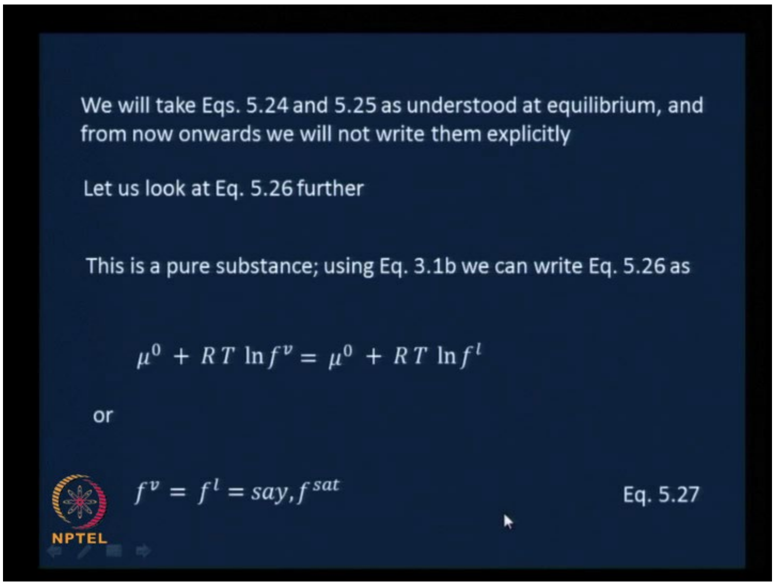

We will take Eqs. 5.24 and 5.25 as understood at equilibrium, and from now onwards we will not write them explicitly

Let us look at Eq. 5.26 further

This is a pure substance; using Eq. 3.1b we can write Eq. 5.26 as

$$\mu^0 + RT\ln f^v = \mu^0 + RT\ln f^l$$

or

$$f^v = f^l = say, f^{sat} \qquad \text{Eq. 5.27}$$

Then, we had if it is a pure substance, we said we could write

μ_v as $\mu^0 + \ RT\ ln\, f^v$, and μ_l can be written as $\mu^0 + \ RT\ ln\, f^l$. So, cancelling the terms, we could get the fugacity of the pure component in the vapour phase, must equal the fugacity of the pure component in the liquid phase. And, we said that must say, equal f sat because saturated conditions exist when there is a liquid to vapour or a vapour to liquid transition.

$$f^v = f^l = say,\ f^{sat}$$

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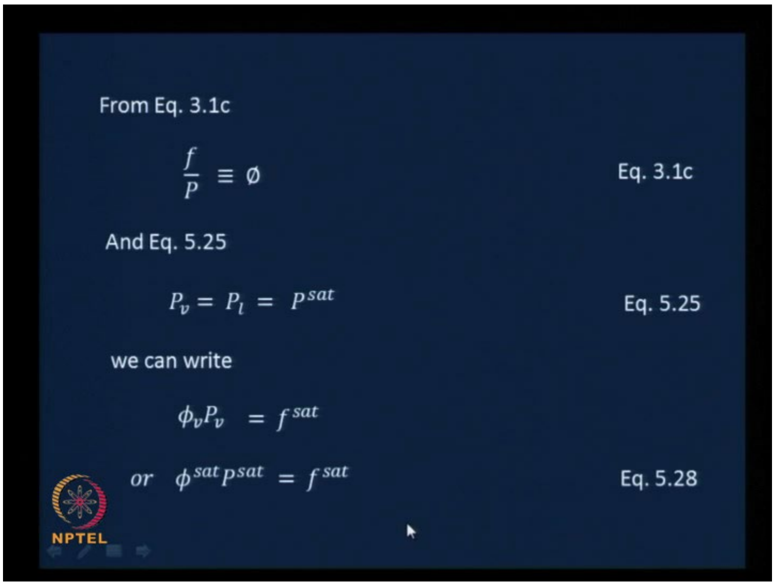

From Eq. 3.1c

$$\frac{f}{P} \equiv \emptyset \qquad \text{Eq. 3.1c}$$

And Eq. 5.25

$$P_v = P_l = P^{sat} \qquad \text{Eq. 5.25}$$

we can write

$$\phi_v P_v = f^{sat}$$

$$or\ \ \phi^{sat} p^{sat} = f^{sat} \qquad \text{Eq. 5.28}$$

… Using the fugacity coefficient, and the fact that the pressure would turn out to be the saturated pressure, we could write the fugacity coefficient of the pure component,

$$\frac{f}{P} \equiv \emptyset$$

$$P_v = P_l = P^{sat}$$

$$\phi_v P_v = f^{sat}$$

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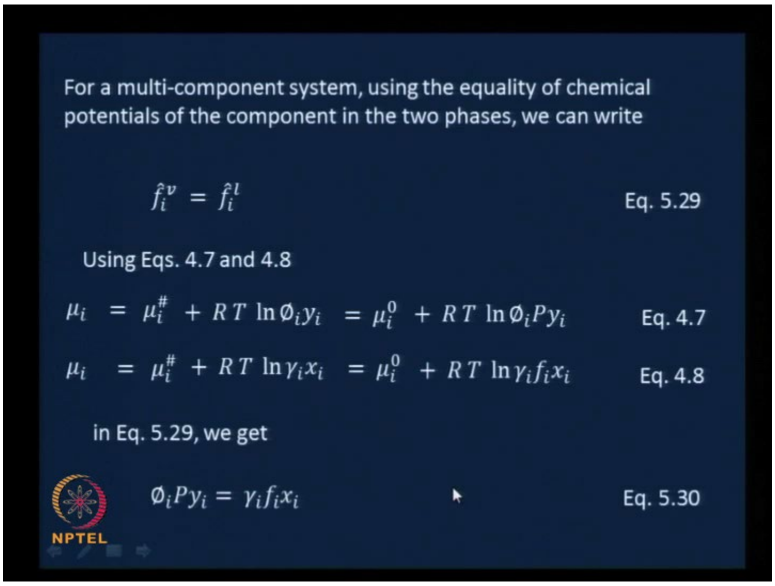

For a multi-component system, using the equality of chemical potentials of the component in the two phases, we can write

$$\hat{f}_i^v = \hat{f}_i^l \qquad \text{Eq. 5.29}$$

Using Eqs. 4.7 and 4.8

$$\mu_i = \mu_i^{\#} + RT\ \ln \emptyset_i y_i = \mu_i^0 + RT\ \ln \emptyset_i P y_i \qquad \text{Eq. 4.7}$$

$$\mu_i = \mu_i^{\#} + RT\ \ln \gamma_i x_i = \mu_i^0 + RT\ \ln \gamma_i f_i x_i \qquad \text{Eq. 4.8}$$

in Eq. 5.29, we get

$$\emptyset_i P y_i = \gamma_i f_i x_i \qquad \text{Eq. 5.30}$$

… This was for a pure component, $\phi^{sat}P^{sat} = f^{sat}$. For a multi component system, we used the equality of the chemical potentials of the component in the 2 phases, and we could write

$$\hat{f}_i^v = \hat{f}_i^l$$

Then, using the detailed expressions of the chemical potentials,

$$\mu_i = \mu_i^{\#} + RT\ ln\,\emptyset_i y_i = \mu_i^0 + RT\ ln\,\emptyset_i P y_i$$

This is for the vapour phase, and this is for the liquid phase,

$$\mu_i = \mu_i^{\#} + RT\ ln\,\gamma_i x_i = \mu_i^0 + RT\ ln\,\gamma_i f_i x_i$$

f i is the pure component fugacity. If we equate the two, then we could write

$$\emptyset_i P y_i = \gamma_i f_i x_i$$

This is the condition for equilibrium in the vapour liquid equilibrium case. This was equation 5.30.

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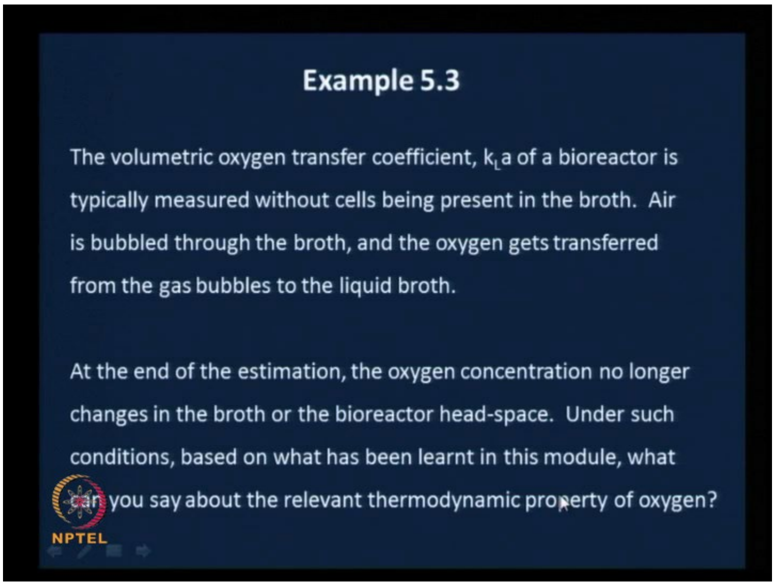

Example 5.3

The volumetric oxygen transfer coefficient, k_La of a bioreactor is typically measured without cells being present in the broth. Air is bubbled through the broth, and the oxygen gets transferred from the gas bubbles to the liquid broth.

At the end of the estimation, the oxygen concentration no longer changes in the broth or the bioreactor head-space. Under such conditions, based on what has been learnt in this module, what can you say about the relevant thermodynamic property of oxygen?

Then we worked out a problem which involved K_La, the volumetric mass transfer coefficient.

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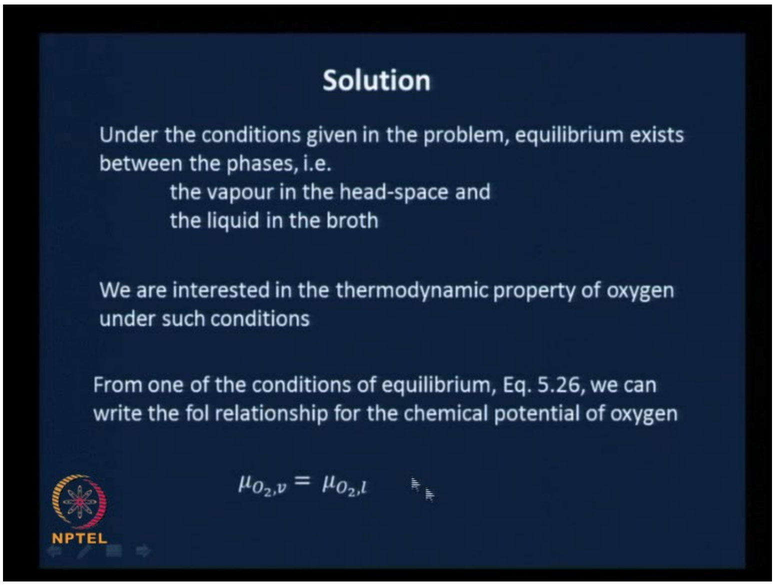

Solution

Under the conditions given in the problem, equilibrium exists between the phases, i.e.
the vapour in the head-space and
the liquid in the broth

We are interested in the thermodynamic property of oxygen under such conditions

From one of the conditions of equilibrium, Eq. 5.26, we can write the fol relationship for the chemical potential of oxygen

$$\mu_{O_2,v} = \mu_{O_2,l}$$

The solution was quite simple – that is the chemical potential of oxygen in the vapour phase must equal the chemical potential of oxygen in the liquid phase under the conditions in the problem, which that of equilibrium.

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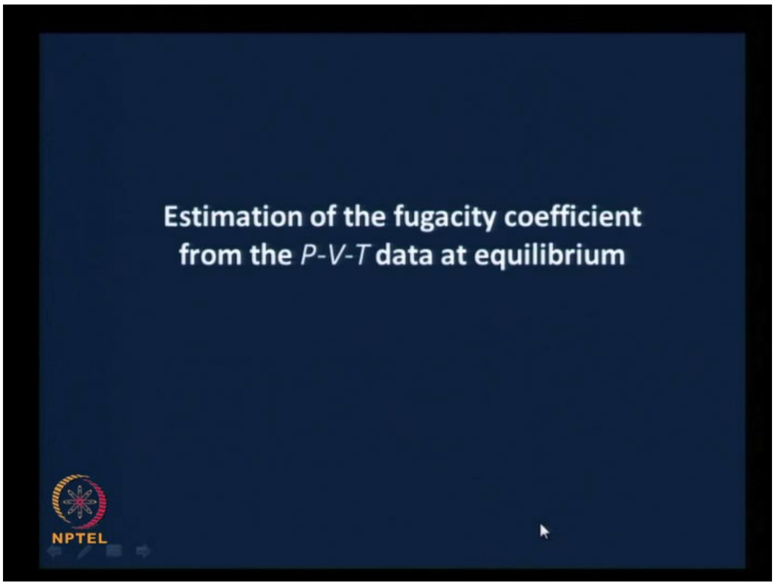

Estimation of the fugacity coefficient from the *P*-*V*-*T* data at equilibrium

Then we looked at using the vapour liquid equilibrium case, and estimating the fugacity coefficient from the P-V-T data at equilibrium, which is the vapour liquid equilibrium.

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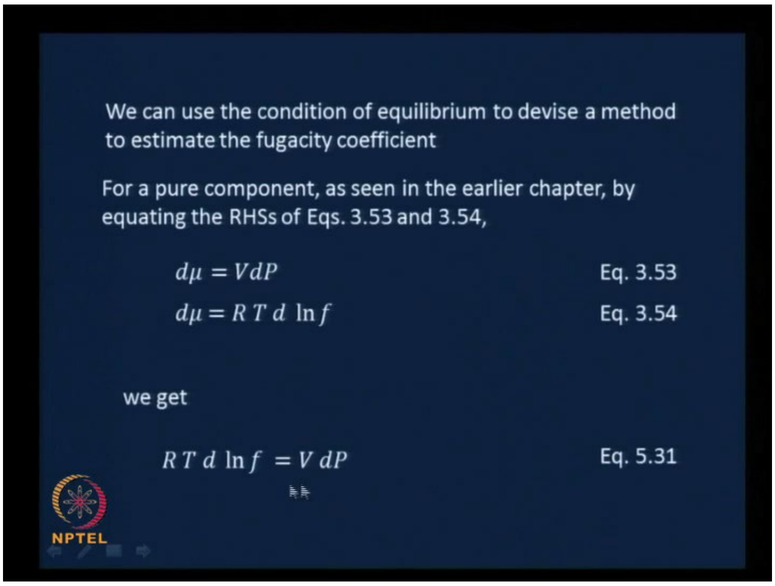

We can use the condition of equilibrium to devise a method to estimate the fugacity coefficient

For a pure component, as seen in the earlier chapter, by equating the RHSs of Eqs. 3.53 and 3.54,

$$d\mu = V dP \qquad \text{Eq. 3.53}$$

$$d\mu = R\,T\,d\,\ln f \qquad \text{Eq. 3.54}$$

we get

$$R\,T\,d\,\ln f = V\,dP \qquad \text{Eq. 5.31}$$

This was essentially a different method of getting the fugacity coefficient. We had derived this by starting out with some expressions in module 3. We got

$$R\,T\,d\,\ln f = V\,dP$$

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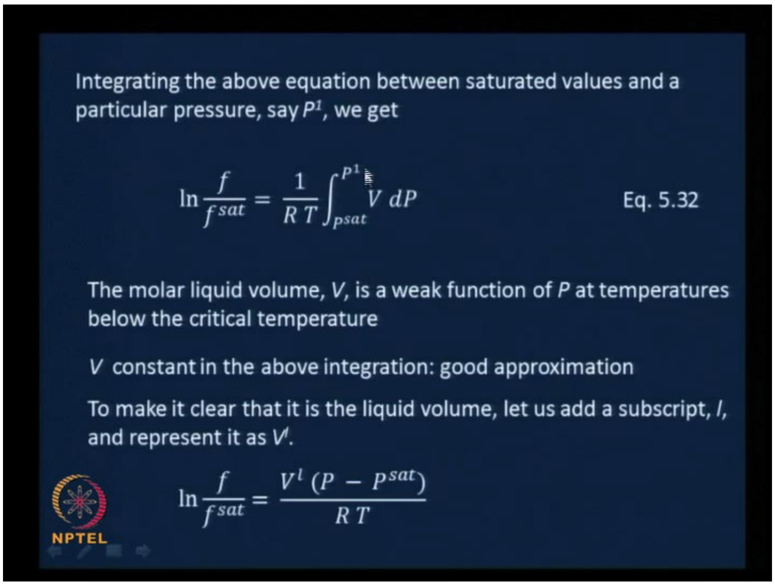

Integrating the above equation between saturated values and a particular pressure, say P^1, we get

$$\ln \frac{f}{f^{sat}} = \frac{1}{R\,T}\int_{P^{sat}}^{P^1} V\, dP \qquad \text{Eq. 5.32}$$

The molar liquid volume, V, is a weak function of P at temperatures below the critical temperature

V constant in the above integration: good approximation

To make it clear that it is the liquid volume, let us add a subscript, l, and represent it as V^l.

$$\ln \frac{f}{f^{sat}} = \frac{V^l\,(P - P^{sat})}{R\,T}$$

We had integrated that expression, and we had identified that the molar liquid volume V is a weak function of pressure at temperatures below the critical temperature. Therefore, this V, molar volume, can be considered a constant in this integration. It comes out, and that is a very good approximation. If it comes out, then we could write

$$\ln \frac{f}{f^{sat}} = \frac{1}{R\,T}\int_{P^{sat}}^{P^1} V\, dP$$

Then the integral will be the definite integral between P sat and P 1 – we are going to drop 1 – becomes

$$\ln \frac{f}{f^{sat}} = \frac{V^l\,(P - P^{sat})}{R\,T}$$

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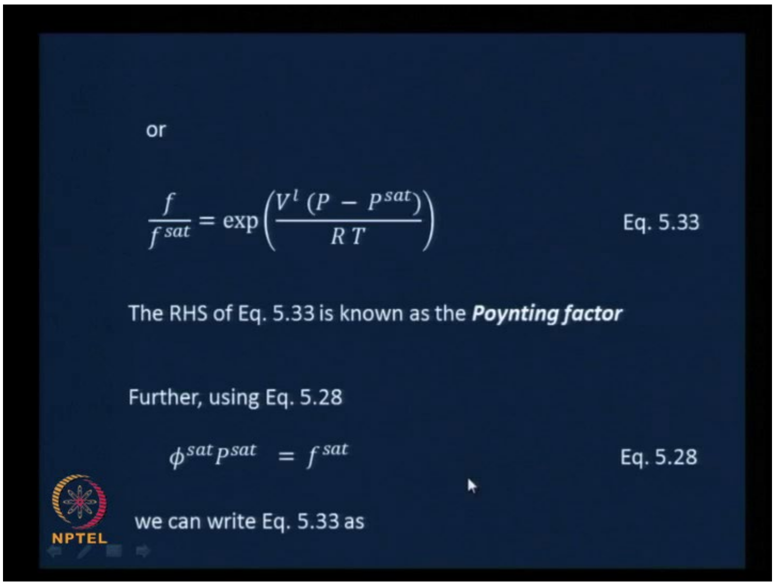

or

$$\frac{f}{f^{sat}} = \exp\left(\frac{V^l\,(P - P^{sat})}{R\,T}\right) \qquad \text{Eq. 5.33}$$

The RHS of Eq. 5.33 is known as the ***Poynting factor***

Further, using Eq. 5.28

$$\phi^{sat} P^{sat} = f^{sat} \qquad \text{Eq. 5.28}$$

we can write Eq. 5.33 as

Or, f by f sat equals what we call the Poynting factor,

$$\frac{f}{f^{sat}} = exp\left(\frac{V^l\,(P - P^{sat})}{R\,T}\right)$$

Then we had invoked equation 5.28,

$$\phi^{sat} P^{sat} = f^{sat}$$

in the case of vapour liquid equilibrium.

$\emptyset_i P y_i = \gamma_i f_i x_i$

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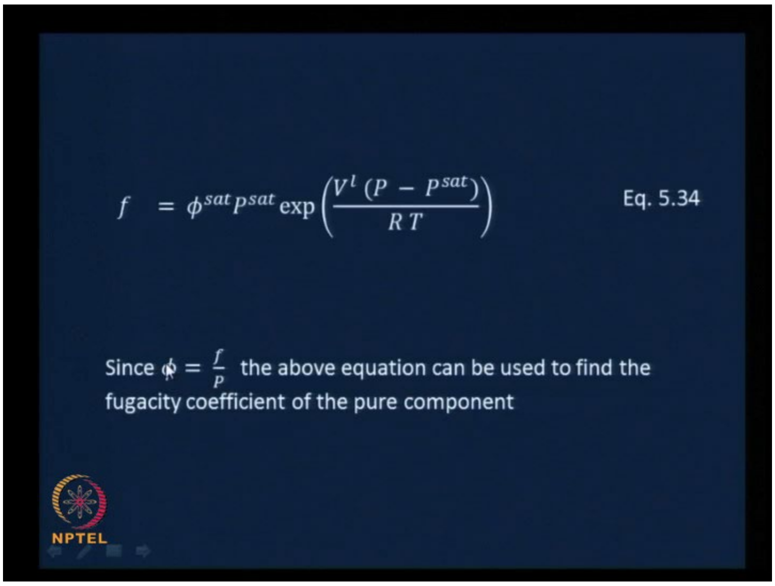

$$f = \phi^{sat} p^{sat} \exp\left(\frac{V^l (P - p^{sat})}{RT}\right) \qquad \text{Eq. 5.34}$$

Since $\phi = \frac{f}{P}$ the above equation can be used to find the fugacity coefficient of the pure component

And, we could write, by expressing one in terms of the other, and recognizing that phi is nothing but f by P,

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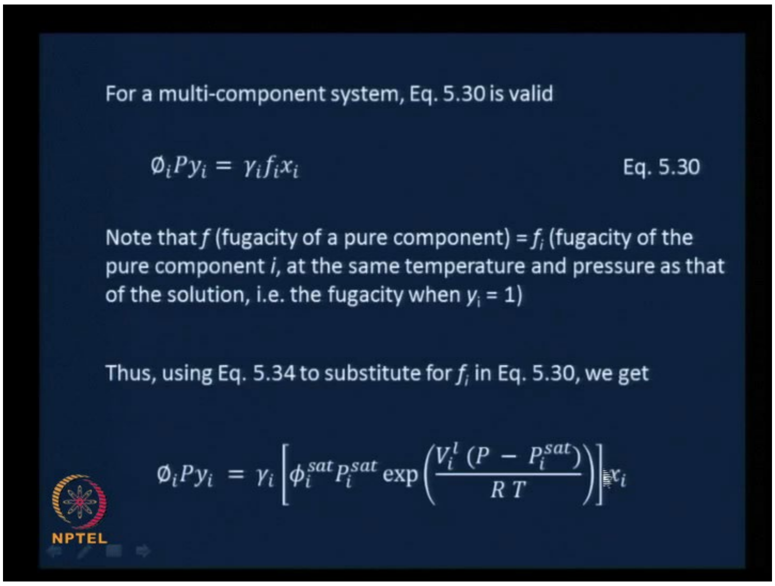

For a multi-component system, Eq. 5.30 is valid

$$\emptyset_i P y_i = \gamma_i f_i x_i \qquad \text{Eq. 5.30}$$

Note that f (fugacity of a pure component) = f_i (fugacity of the pure component i, at the same temperature and pressure as that of the solution, i.e. the fugacity when $y_i = 1$)

Thus, using Eq. 5.34 to substitute for f_i in Eq. 5.30, we get

$$\emptyset_i P y_i = \gamma_i \left[\phi_i^{sat} P_i^{sat} \exp\left(\frac{V_i^l (P - P_i^{sat})}{RT}\right)\right] x_i$$

We could write

$\emptyset_i P y_i = \gamma_i f_i x_i$

This is the condition for a equilibrium in a multi components systems. This was for the pure component; we could write fugacity as

$$\emptyset_i P y_i \ = \ \gamma_i \left[\phi_i^{sat} P_i^{sat} \, exp\left(\frac{V_i^l \, (P - P_i^{sat})}{R\,T}\right)\right] x_i$$

This is the Poynting factor. Then, for a multi component system, this is valid, is what we saw earlier in equation 5.30. When we used this expression for fi that we had developed –

$$\emptyset_i P y_i \ = \ \gamma_i \left[\phi_i^{sat} P_i^{sat} \, exp\left(\frac{V_i^l \, (P - P_i^{sat})}{R\,T}\right)\right] x_i$$

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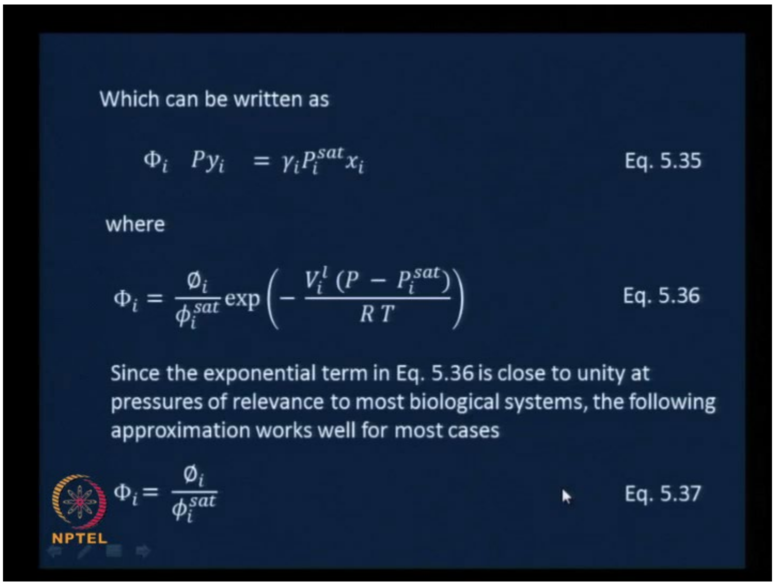

Which can be written as

$$\Phi_i \quad P y_i \ = \gamma_i P_i^{sat} x_i \qquad \text{Eq. 5.35}$$

where

$$\Phi_i = \frac{\emptyset_i}{\phi_i^{sat}} \exp\left(-\ \frac{V_i^l \ (P \ - \ P_i^{sat})}{R\,T}\right) \qquad \text{Eq. 5.36}$$

Since the exponential term in Eq. 5.36 is close to unity at pressures of relevance to most biological systems, the following approximation works well for most cases

$$\Phi_i = \frac{\emptyset_i}{\phi_i^{sat}} \qquad \text{Eq. 5.37}$$

$$\Phi_i \quad P y_i \ = \ \gamma_i P_i^{sat} x_i$$

This is the useful equation in this particular case for estimating the activity coefficient, where fi i, we had said, was nothing but

$$\Phi_i \ = \ \frac{\emptyset_i}{\phi_i^{sat}} \, exp\left(-\ \frac{V_i^l \, (P - P_i^{sat})}{R\,T}\right)$$

We also recognized that for most biological systems at pressures that are normal, this term pretty much becomes 1. Therefore,

$$\Phi_i = \frac{\emptyset_i}{\phi_i^{sat}}$$

Therefore, you could substitute it back under this to get gamma i from VLE data; VLE is vapour liquid equilibrium data.

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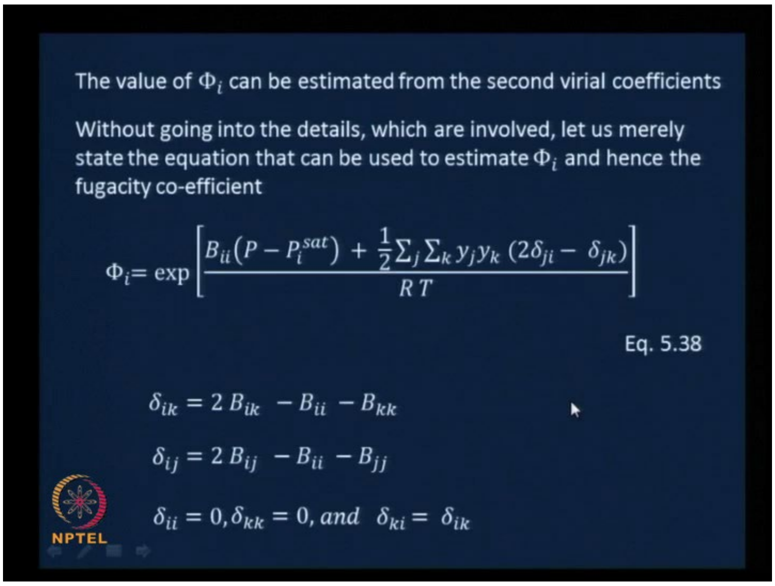

The value of Φ_i can be estimated from the second virial coefficients

Without going into the details, which are involved, let us merely state the equation that can be used to estimate Φ_i and hence the fugacity co-efficient

$$\Phi_i = \exp\left[\frac{B_{ii}(P - P_i^{sat}) + \frac{1}{2}\Sigma_j \Sigma_k y_j y_k (2\delta_{ji} - \delta_{jk})}{RT}\right]$$

Eq. 5.38

$$\delta_{ik} = 2\,B_{ik} - B_{ii} - B_{kk}$$

$$\delta_{ij} = 2\,B_{ij} - B_{ii} - B_{jj}$$

$$\delta_{ii} = 0, \delta_{kk} = 0, and \;\; \delta_{ki} = \delta_{ik}$$

We also saw that phi can be estimated from the second virial coefficients. We did not derive this. I said that I am just going to give you expressions, so that you … could use this if these values become available in terms of tables, and so on.

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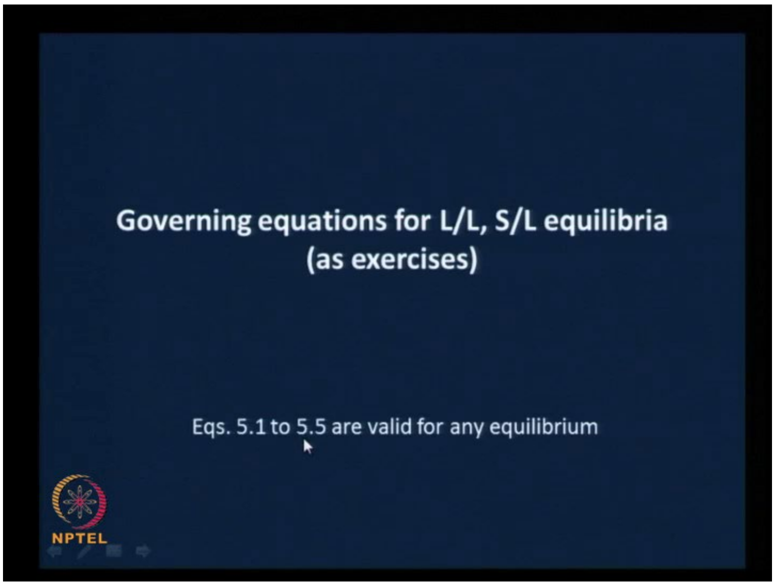

Governing equations for L/L, S/L equilibria (as exercises)

Eqs. 5.1 to 5.5 are valid for any equilibrium

Then, we went about deriving the governing equations for solid-liquid, liquid-liquid and solid-liquid equilibria. In fact, you derived this and we just checked it. … The basal equations that we used were the conditions of thermal equilibrium, mechanical equilibrium and chemical equilibrium, predominantly chemical equilibrium.

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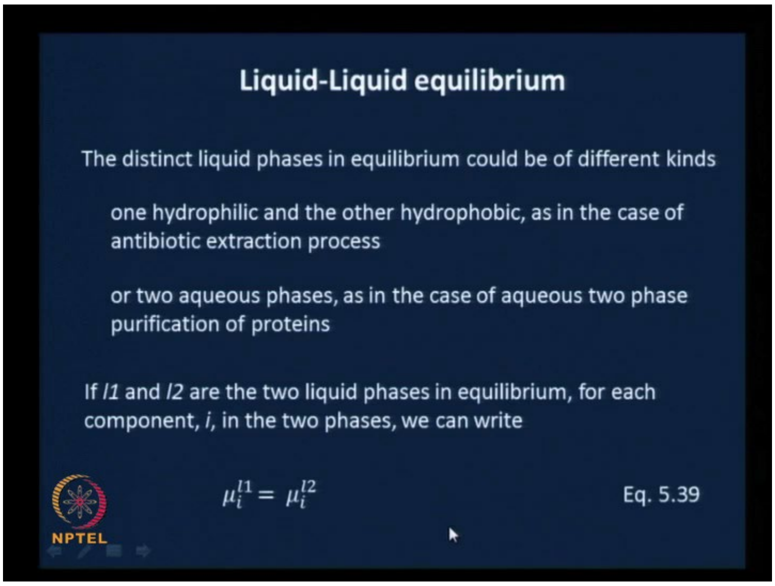

Liquid-Liquid equilibrium

The distinct liquid phases in equilibrium could be of different kinds

one hydrophilic and the other hydrophobic, as in the case of antibiotic extraction process

or two aqueous phases, as in the case of aqueous two phase purification of proteins

If *l1* and *l2* are the two liquid phases in equilibrium, for each component, *i*, in the two phases, we can write

$$\mu_i^{l1} = \mu_i^{l2} \quad \text{Eq. 5.39}$$

We had seen where this becomes relevant; in the case of liquid-liquid equilibrium, we said that you could have two different liquid phases – one being hydrophobic, the other one being hydrophilic, or both could be hydrophilic. The hydrophobic-hydrophilic pair is used in say, antibiotic extraction. The hydrophilic-hydrophilic pair – two distinct hydrophilic phases – is used in the extraction of proteins to maintain their activity by maintaining their conformation. … If l 1 and l 2 are the 2 liquid phases in equilibrium, and for each component we could write the equality of chemical potentials.

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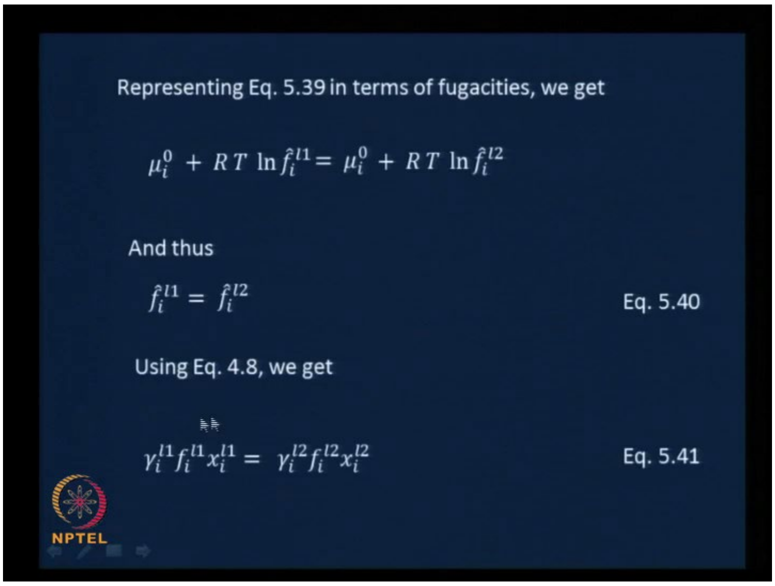

Representing Eq. 5.39 in terms of fugacities, we get

$$\mu_i^0 + RT \ln \hat{f}_i^{l1} = \mu_i^0 + RT \ln \hat{f}_i^{l2}$$

And thus

$$\hat{f}_i^{l1} = \hat{f}_i^{l2} \qquad \text{Eq. 5.40}$$

Using Eq. 4.8, we get

$$\gamma_i^{l1} f_i^{l1} x_i^{l1} = \gamma_i^{l2} f_i^{l2} x_i^{l2} \qquad \text{Eq. 5.41}$$

… From this expansion comes the equality of the fugacities of the component i between these two phases. Utilising equation 4.8 in module 4, you could write the fugacity in terms of pure component fugacity;

$$\gamma_i^{l1} f_i^{l1} x_i^{l1} = \gamma_i^{l2} f_i^{l2} x_i^{l2}$$

This is the governing equation for liquid-liquid equilibrium. We had also worked out a problem after this, an example that of ampicillin extraction.

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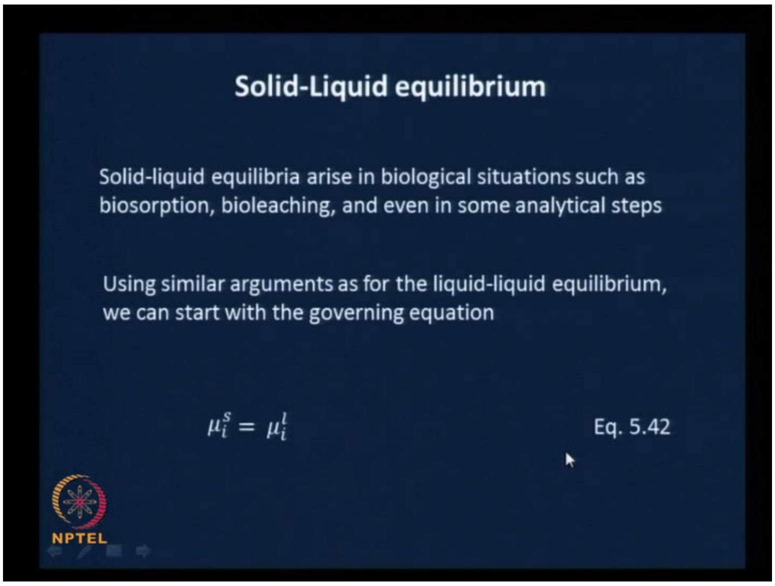

Solid-Liquid equilibrium

Solid-liquid equilibria arise in biological situations such as biosorption, bioleaching, and even in some analytical steps

Using similar arguments as for the liquid-liquid equilibrium, we can start with the governing equation

$$\mu_i^s = \mu_i^l \qquad \text{Eq. 5.42}$$

And the ratio of the activity coefficients in those two phases. Then, we looked at solid liquid equilibrium in some sort of hurry. We said that you could have a solid phase and a liquid phase, and let us say a component distributing between the solid phase and liquid phase in equilibrium. I had given some examples such as biosorption. For example, when there are toxic trace metals that are present in say an effluent, one of the ways by which they can be removed effectively is by contacting the liquid phase with the metal – you contact this liquid phase with the metal, with another solid phase into which the metal can partition.

Therefore, there is a huge reduction in the volume that contains the metal, and therefore better processing capabilities later. The solid phase could be let us say dried self cells; dried cells from even brewing industries could be used as the material which can be utilized to remove the toxic trace metals such as chromium, copper, cadmium; chromium as you all know is quite toxic – chromium's VI is very toxic, and so on. So this can be used to remove all such things. Bioleaching is a similar phenomenon, where there is contact between a solid and a liquid phase and there is a distribution of a metal say, between these 2 phases. … Even in some analytical steps you come across situations where a solid is contacted with a liquid, and there is distribution of a certain component or some components. In such cases, we could utilize the same arguments for equilibrium – equations 5.1 to 5.5, and so on, need to be valid in any case. They are basal conditions of equilibrium.

Even if we concentrate from 5.3 onwards – we are going to take thermal and mechanical equilibrium as given – the chemical equilibrium, the equality of chemical potentials of each component across the phases … of a certain component across phases. … If we use that then, we come across the condition that the chemical potential of the component i in the solid phase must equal the chemical potential of the same component in the liquid phase. This could be for example, chromium or cadmium that is distributing between the waste water, and the bio sorbent that is used to remove this particular metal. So mu i in the solid phase equals mu i in the liquid phase.

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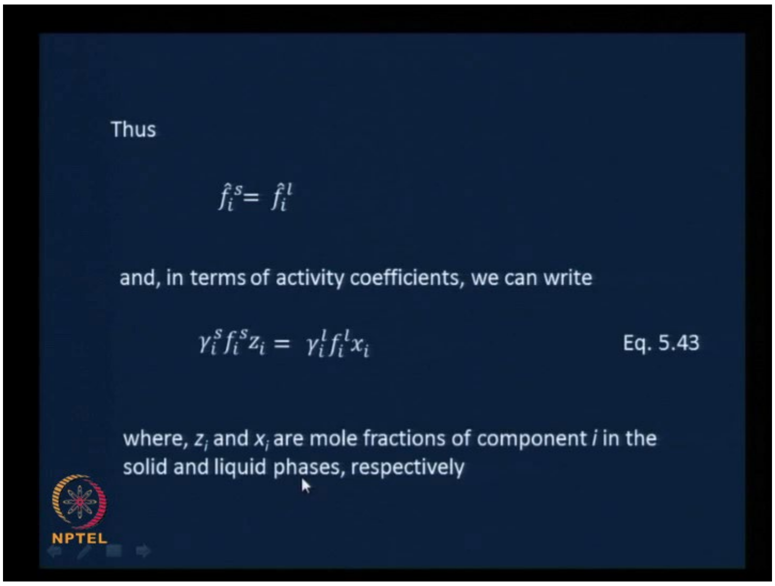

Thus

$$\hat{f}_i^s = \hat{f}_i^l$$

and, in terms of activity coefficients, we can write

$$\gamma_i^s f_i^s z_i = \gamma_i^l f_i^l x_i \qquad \text{Eq. 5.43}$$

where, z_i and x_i are mole fractions of component *i* in the solid and liquid phases, respectively

And if we take that into account, and expand it in terms of the fugacities, the terms will cancel, and what we are left with is the fugacity of the component i in the solid phase, equals the fugacity of the component in the liquid phase.

$$\hat{f}_i^s = \hat{f}_i^l$$

In terms of the activity coefficients, we can write for the solid phase, gamma i s, the activity of the component i in the solid phase, the pure component fugacity in the solid phase, times the mole fraction in the solid phase, z i, equals the activity coefficient in the liquid phase, times … the pure component fugacity, times the mole fraction in the liquid phase.

$$\gamma_i^s f_i^s z_i = \gamma_i^l f_i^l x_i$$

This becomes the governing equation for equilibrium in the solid-liquid case. z i and x i are mole fractions of component i in the solid and liquid phases, respectively. So, we had essentially seen the conditions of equilibrium - chemical equilibrium particularly, and then phase rule, and then we had taken up specific cases of vapour-liquid equilibrium, VLE, liquid-liquid equilibrium, LLE, and solid-liquid equilibrium, SLE. We had also shown one of the ways of estimating the activity coefficient from the conditions of vapour-liquid equilibrium. That is essentially what we did in module 5, and when we come to the next class, we will start out the last module of this particular course, module 6 on reaction equilibrium. See you then.