Thermodynamics for Biological Systems:
Classical and Statistical Aspects
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Lecture – 40
Clausius Clapeyron Equation (Contd.,)

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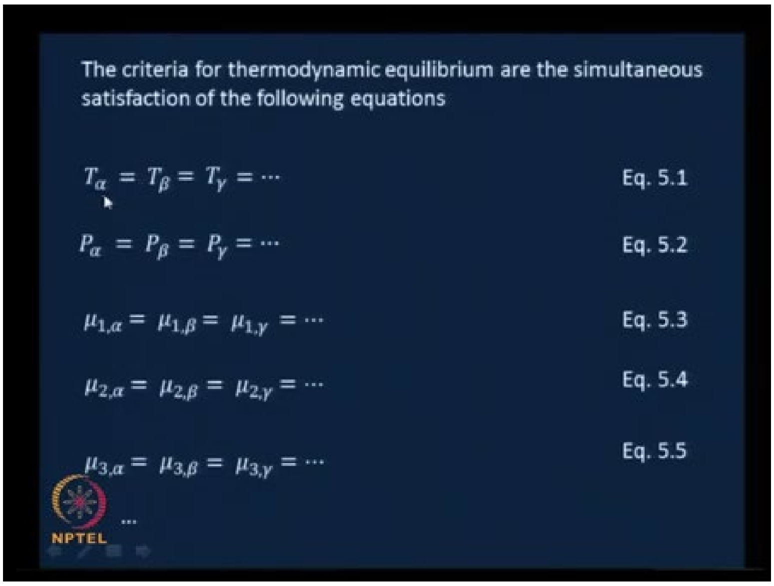

The criteria for thermodynamic equilibrium are the simultaneous satisfaction of the following equations

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

...

Welcome! to this lecture.

In the last lecture, we saw the different criteria for thermodynamic equilibrium across various phases. That is what is given here; this is what saw in the last class. This is the fundamental requirement for thermodynamic equilibrium. If alpha, beta, gamma are various phases in equilibrium, the temperature across the phases or in each of the phases must be equal. In other words, T alpha equals T beta equals T gamma, and so on. This is equation 5.1. The second condition was that the pressures in the various phases must be equal to each other; P alpha equals P beta equals P gamma and so on. The chemical potential of each of the species present in the various phases must be equal to each other. For example, if mu 1 is the chemical potential of the species 1, mu 1 in alpha must equal mu 1 in beta must equal mu 1 in gamma and so on across all the other phases that are present. mu 2, which is a chemical potential of species 2 in the alpha phase must equal mu 2 in the beta phase must equal mu 2 in the gamma phase, and so on.

We can write one such equation for each of the species that are present or each of the components that are present. So, if you look at this, if there are C components that are present, we will have C such equations. Not just that; we also saw that each one these equations is actually a composite of … if π is a total number of phases $(\pi - 1)$ equations. For example, T alpha equals T beta is one equation, T beta equals T gamma is another equation, and so on. Therefore, if there are pi phases, there would be pi minus 1 different equations here. That is valid for each one of these composite equations. This is what we saw in the last class – very fundamental. So, it is good go over it again.

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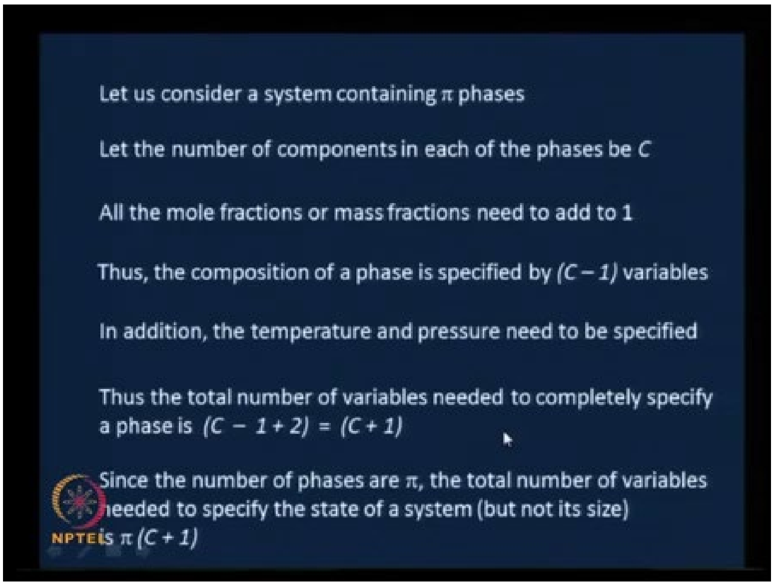

Let us consider a system containing π phases

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 $\pi (C + 1)$

Then, we also saw the phase rule for non-reacting systems. The way we went about deriving the phase rule was if we are considering a system, containing π phases and the number of components is C, then, we saw that the number of equations between variables was $(\pi - 1)$ pi minus 1 into C plus 2.

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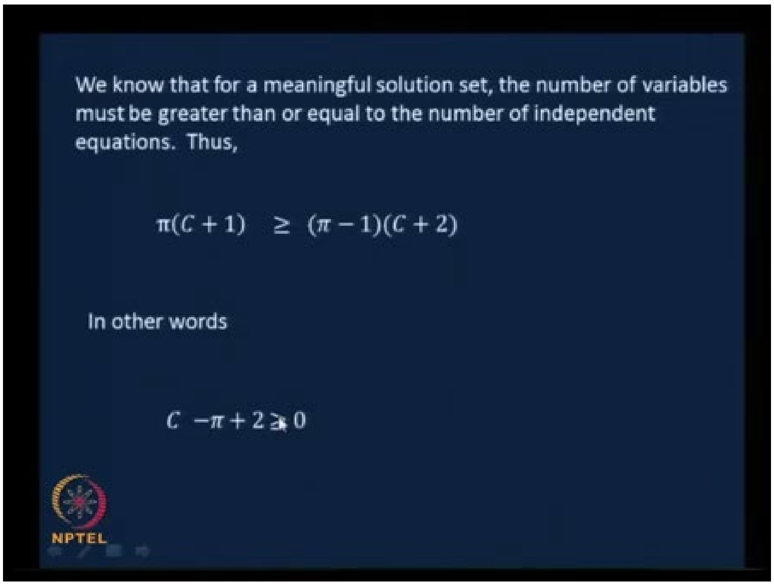

We know that for a meaningful solution set, the number of variables must be greater than or equal to the number of independent equations. Thus,

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

In other words

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

We saw earlier the number of variables was $\pi (C + 1)$. We know from mathematics that, if the number of variables equals the number of independent equations in a system or in a set, then we have a unique solution. Or, at least the number of variables must be greater than the number of independent equations connecting them. Only then will we have a possibility of realistic or meaningful solutions. If the number of variables is less than that … it is not something that we would prefer. Therefore, this is the condition that we looked at: the number of variables $\pi (C + 1)$ in a system that we considering, must be greater than or equal to $(\pi - 1)(C + 2)$, which is the number of independent equations between them. … When we transposed this into getting 0 on the right hand side, then we got $C - \pi + 2 \geq 0$. In other words if we have $C - \pi + 2 = 0$, we have a unique solution set. And, if we have $C - \pi + 2 > 0$, then if we are able to supply that many number of variables, then the system is uniquely defined. This is essentially what this means.

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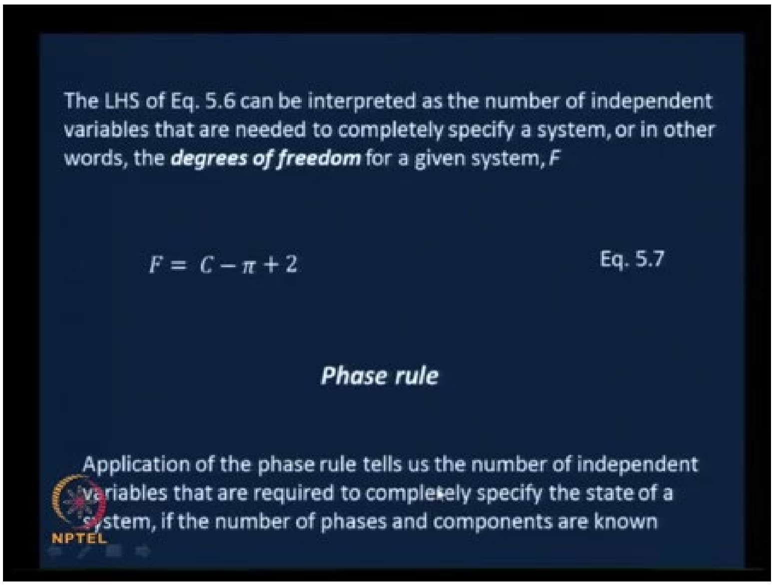

The LHS of Eq. 5.6 can be interpreted as the number of independent variables that are needed to completely specify a system, or in other words, the ***degrees of freedom*** for a given system, F

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

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

This … brought us to the concept of degrees of freedom – this is where it arises from – the degrees of freedom was $C - \pi + 2$ that we saw earlier. This is nothing but the number of variables that are short … in equating the number of variables to the number of independent equations that are available. Therefore, if we supply these variables, the F number of variables, then the system is uniquely defined. Therefore, the application of phase rule tells us the number of independent variables that are required to completely specify the state of the system, if the number of phases and components are known. Then, we worked out an example, and we started looking at the Clausius-Clapeyron equation.

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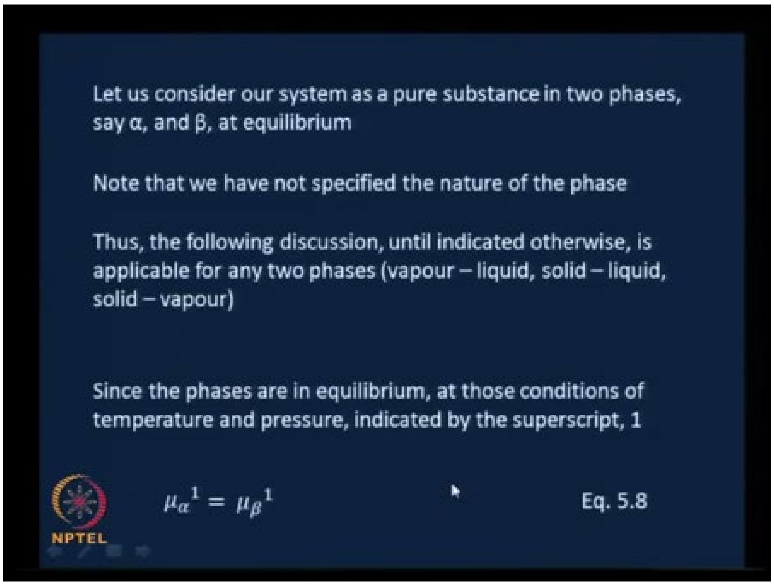

Let us consider our system as a pure substance in two phases, say α, and β, at equilibrium

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

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

We said that the Clausius-Clapeyron equation is valid for any two different phases. We will typically use this when there is a phase change that is occurring – phase change at equilibrium. Therefore, we are looking at vapour-liquid, solid-liquid or solid-vapour phases; these are the three phases that we are look at in this particular course. We said that, at equilibrium, the chemical potential of a certain component between the two phases must be equal. Therefore, we mu alpha 1 must be equal to mu beta 1. This '1' determines the conditions of temperature and pressure that are specified at that particular point. So, ${\mu_\alpha}^1 = {\mu_\beta}^1$ is the basic criterion.

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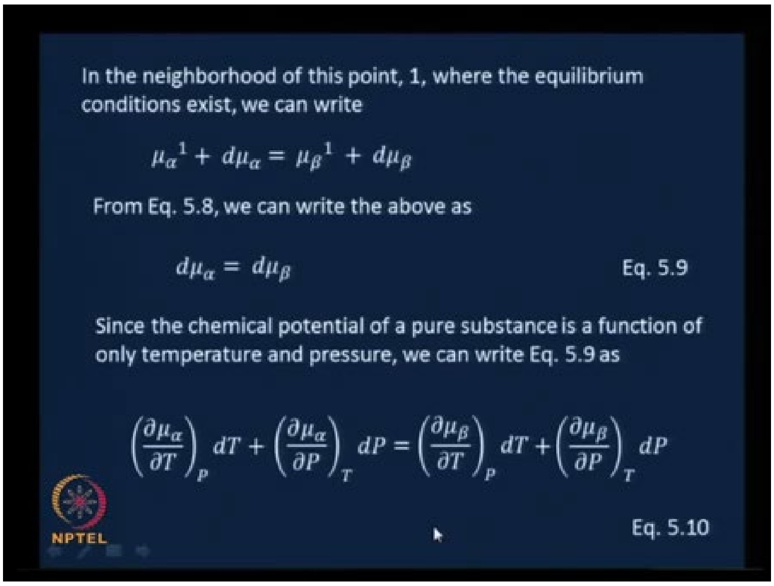

In the neighborhood of this point, 1, where the equilibrium conditions exist, we can write

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

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

Then we went about deriving $d\mu_\alpha = d\mu_\beta$. If we consider mu as a function of temperature and pressure, easily measurable variables, then, this total differential can be written in terms of the partial differentials; that we have already seen.

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

Then we took a detour, and I realized that I have not told you why we took the detour. We took the detour essentially to express the temperature-pressure functionalities of the chemical potential in terms of the other variables, on which we have a better handle. That is a reason, and also, we are going to establish one other relationship, where it becomes easy for our manipulations later on.

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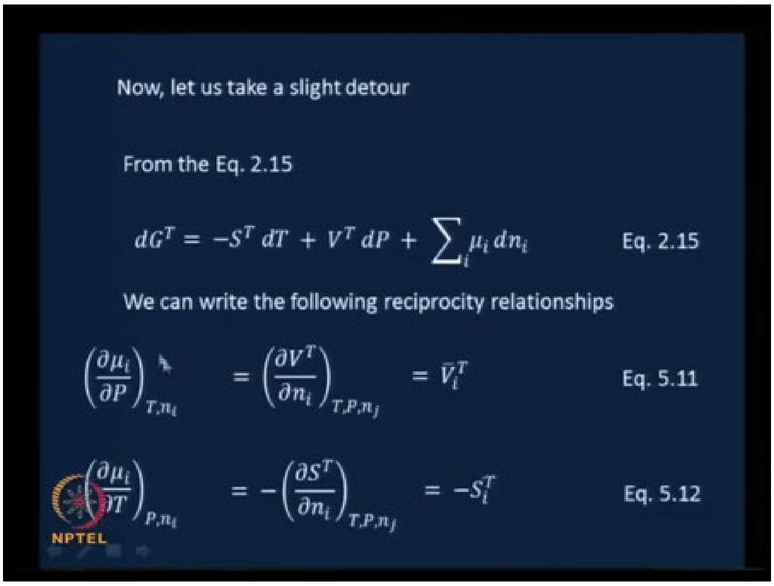

Now, let us take a slight detour

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

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

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

When we took the detour, we … started to consider this equation 2 15:

$$dG^T = -S^T\, dT + V^T\, dP + \sum_i \mu_i\, dn_i$$

Then, when we employed the reciprocity relationships that we picked up in module two over two combinations, I mean two parts of this equation the right hand side at a time, … we got that

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

Similarly, we got the temperature functionality as partial molar entropy. Therefore, these where the terms in the previous equation, if you recall … we will write that again. Therefore, we will take look at that.

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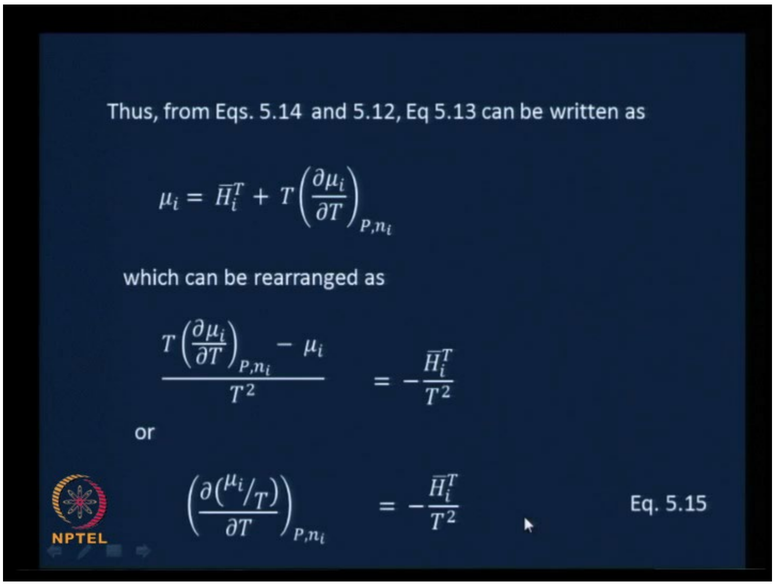

Thus, from Eqs. 5.14 and 5.12, Eq 5.13 can be written as

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

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

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

Then, we also derived

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

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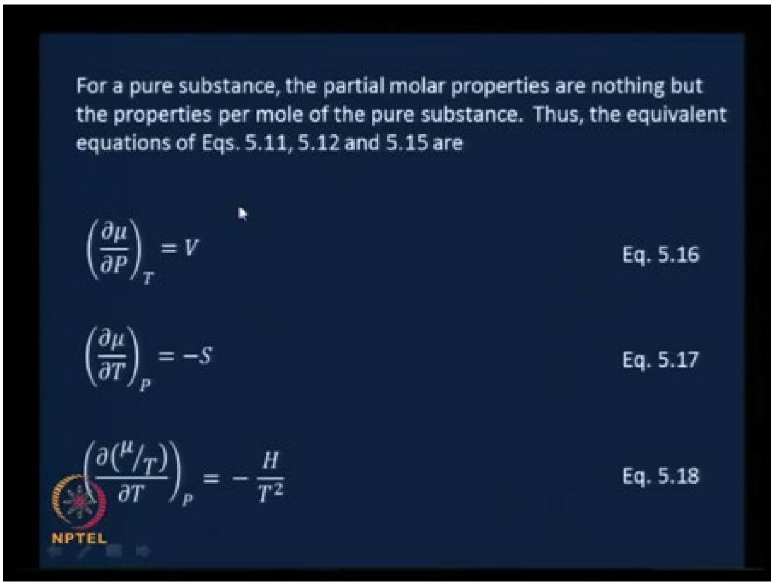

For a pure substance, the partial molar properties are nothing but the properties per mole of the pure substance. Thus, the equivalent equations of Eqs. 5.11, 5.12 and 5.15 are

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

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

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

So, this is where we left off in the last class. The earlier equations that we derived were for a generic system with n number of moles, and so on. Then, we started to consider a pure substance. For a pure substance, we know that the partial molar properties are nothing but the properties per mole of the pure substance. And therefore, the equivalent equations, you know, the temperature, pressure functionalities of mu as well as the dou mu by T expressions that we saw earlier, turn out to be these special equations for 1 mole of a pure substance.

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

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

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

This is where we left off last time, and now what we will do is we will substitute these … remember, this was a detour … we will go back from the detour to … considering the case of equilibrium of a pure substance between two phases.

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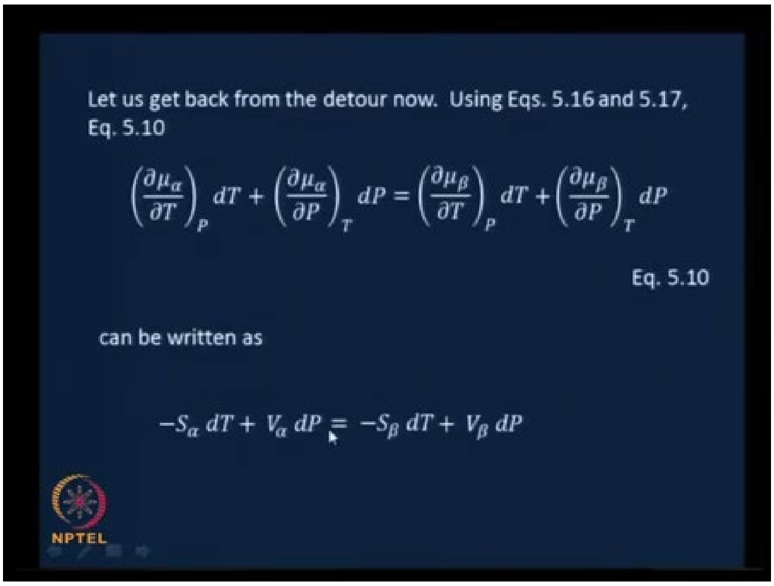

Let us get back from the detour now. Using Eqs. 5.16 and 5.17, Eq. 5.10

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

Eq. 5.10

can be written as

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

This was the equation that we had gotten by equating dmu alpha equals dmu beta;

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

This was equation 5.10, at which point we took a detour. Now we are going to substitute for these expressions in terms of 5 16, 5 17. dou mu alpha douT at constant P was nothing but minus S alpha that we saw for 1 mole a pure substance. Therefore, minus S alpha dT, plus dou mu alpha douP at constant T, we found was V alpha the molar volume in the alpha phase of the pure substance, dP. This equals minus S beta dT plus V beta dP. … Taking dP dT and writing as a derivative – these are differentials and we are getting the derivative from that.

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

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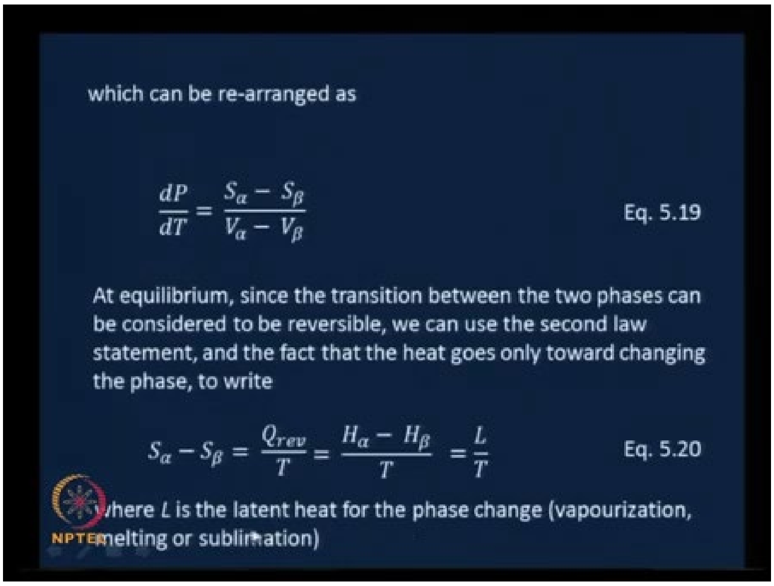

which can be re-arranged as

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

If we do that,

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

Earlier, these were differentials, which can be interpreted as small distances on a graph – a geometrical interpretation. And we know that that (dP dT) can be interpreted as a derivative, as long as the dimensions that are considered are extremely small – in the limit that tends to 0, and so on.

We will call this equation 5.19. This is a nice expression, but this is not very useful. So, we will make it a little more useful. Because P, T, and V are fine; we also have entropies here which are not very easily measurable or as easily measurable as P, T and V are.

To do that, let us consider this. At equilibrium, the transition between the two phases can be considered to be reversible. You know the rate of one process in one direction equals rate of the other process in the other direction, and so on. It is a good assumption to consider that process as reversible. If we consider the process as reversible, we can use the second law statement and the second law definition. Also … we will consider this a little later. Just by considering the second law conditions, we can write

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

This was the statement of the second law, and that we are applying to this particular case of phase change, Q reversible by T. Now let us bring in this fact; the heat goes only towards changing the phase. Therefore, this Q reversible can be replaced by the difference in enthalpy between the two phases. There is nothing else that is happening there, the heat interaction goes directly toward changing the phase.

Therefore, the Q reversible for this particular process can be replaced by the delta H which happens to be H alpha minus H beta. Therefore, S alpha minus S beta becomes equal to H alpha minus H beta by T which can be written as L by T, where L is the latent heat of the phase change. We will call this equation 5 20. Note that this is latent heat for the phase change, and it is not limited only to the liquid to vapour change, which is typically given in textbooks to begin with. This is applicable for the latent heat of vapourisation, latent heat of melting or sublimation.

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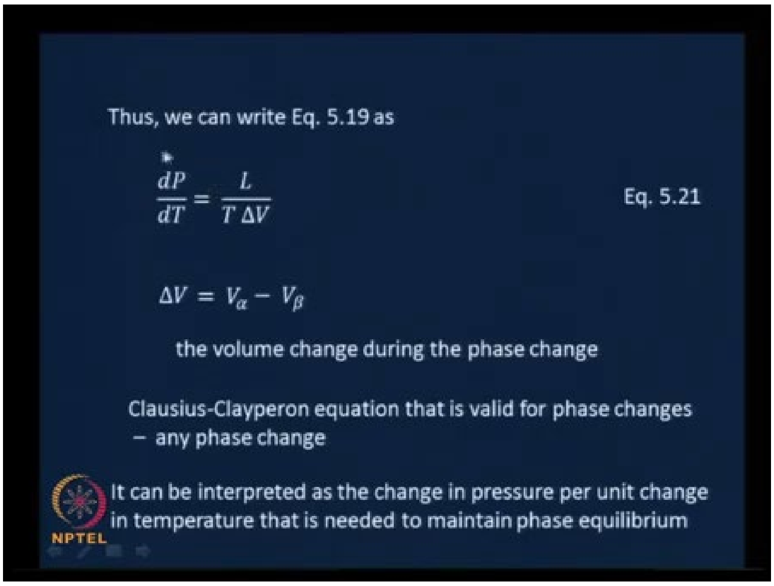

Thus, we can write Eq. 5.19 as

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

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 can write equation 5 19, as

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

delta V was V alpha minus V beta, the change and specific volume between the two phases. Let us call this equation, 5 21. This equation is called the Clausius-Clapeyron equation, and this valid for phase changes, as we had seen, because those were the conditions under which we derived it. We had assumed equilibrium conditions for a phase change and reversible conditions for a phase change and derived this. This is valid for any phase change. Going by the left hand side dP dT, it can be interpreted as the change in pressure per unit change in change in temperature that is needed to maintain equilibrium. Slightly abstract … take a look at it for now, and then it will make sense probably much later.

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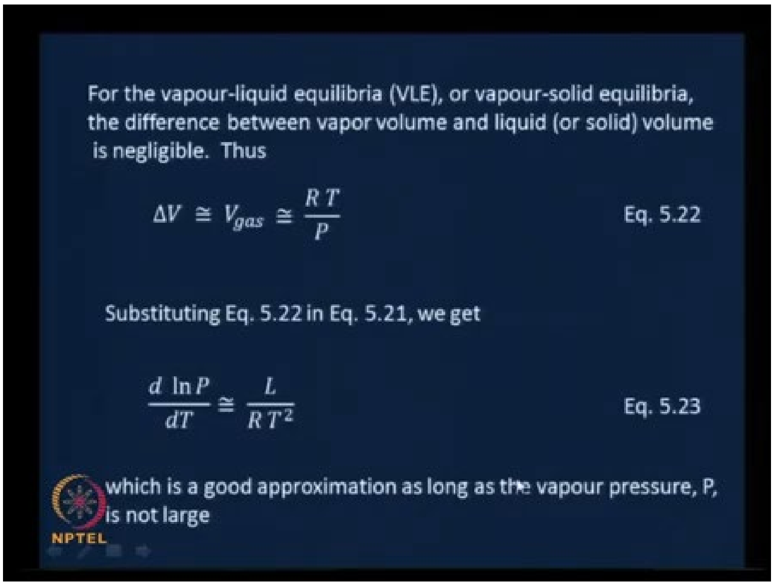

For the vapour-liquid equilibria (VLE), or vapour-solid equilibria, the difference between vapor volume and liquid (or solid) volume is negligible. Thus

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

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

For the vapour-liquid equilibria or vapour-solid equilibrium, the difference between the vapour volume and the liquid or the solid volume is negligible. You know, the vapour volume of a unit amount or a unit mass of a certain substance is typically tens of times the liquid volume; typically about thirty to fifty to eighty times the liquid volume for a unit mass of the substance. And there is a certain ratio here, which is quite large for vapour to solid also. Therefore, this delta V, if you can recall, was nothing but … in the case of vapour-liquid equilibria, V vapour minus V liquid, or V gas minus V liquid. We can replace the delta V by approximately V volume of the gas itself.

We are essentially neglecting the volume of the liquid or the solid here. And volume of the gas can be approximated, if the gas can be considered to behave ideally. You know, under conditions of normal temperature and pressure, this is a reasonably good assumption, except if you are dealing very tricky gases. Therefore, the volume of gas … we are going to use the ideal gas law and express it as RT by P;

$$\Delta V \cong V_{gas} \cong \frac{R\,T}{P}$$

We will call this equation 5 22. And if we substitute this 5 22 into the Clausius-Clapeyron equation, 5 21, we get

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

Let us call this equation 5.23. If you are not able to see this, let us just go back a little bit.

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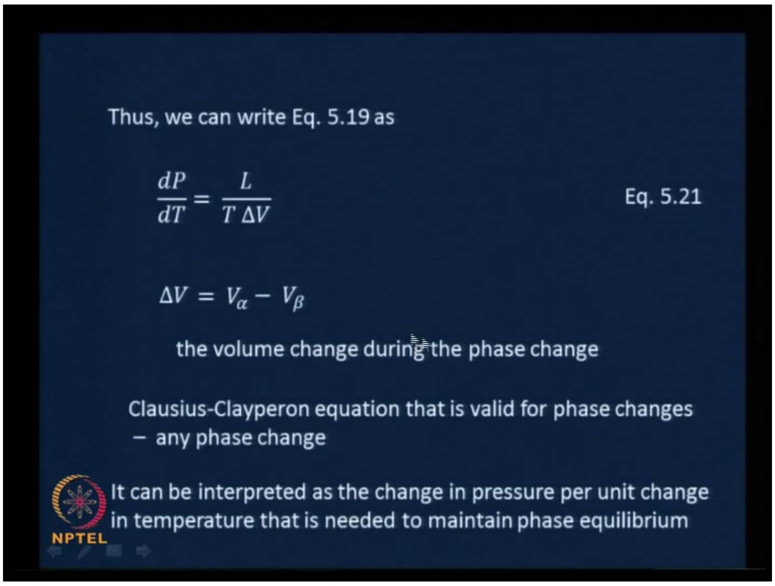

Thus, we can write Eq. 5.19 as

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

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

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

Now, what we have done essentially, here, is replace delta V by V gas; this was RT by P. And therefore, if we combine all Ps together, we get dP by P equals L by TV of the vapour times dT. Integrating that dP by P we get the log term there, and the other terms make sense.

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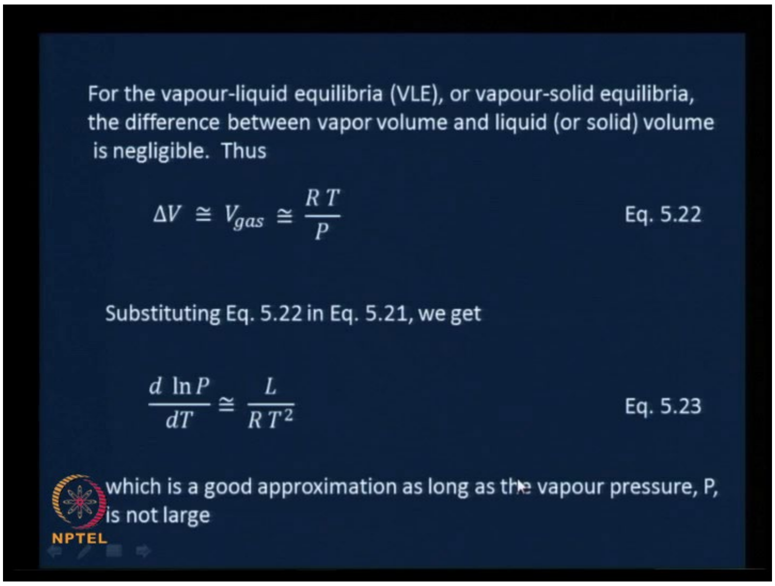

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Substituting Eq. 5.22 in Eq. 5.21, we get

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

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

Therefore, we get dlnP by dT equals L by RT squared. This is typically a very good approximation as long as the vapour pressure is not very large. If vapour pressure is large then be careful in using this approximation.

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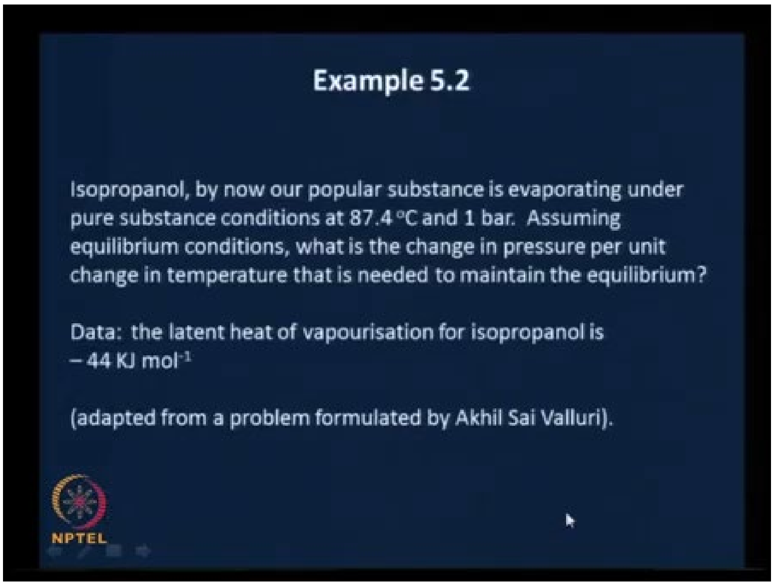

Example 5.2

Isopropanol, by now our popular substance is evaporating under pure substance conditions at 87.4 °C and 1 bar. Assuming equilibrium conditions, what is the change in pressure per unit change in temperature that is needed to maintain the equilibrium?

Data: the latent heat of vapourisation for isopropanol is − 44 KJ mol^{-1}

(adapted from a problem formulated by Akhil Sai Valluri).

We have looked at conditions for equilibrium, the phase rule which are very fundamental aspects. And then we looked at Clausius-Clapeyron equation, for the phase change. Let us work at an example. This example will take time to work out, I will first read out the problem. I will give you say about 15 minutes to think about it and work out the initial aspects. And then I will give you more time with hints to work out the final solution.

Let me read out the problem first. Isopropanol … you know by now … our popular substance, is evaporating under pure substance conditions at 87.4 degree C and 1 bar. It is evaporating under pure substance conditions, which means that the temperature and pressure correspond to points of the vapourisation line in a PT diagram. Assuming equilibrium conditions, what is the change in pressure per unit change in temperature that is needed to maintain equilibrium? And the data that is given here is that, the latent heat of vapourisation for isopropanol is minus 44 kilojoules per mole.

There is a certain background to this. I would like to share that here. I had assigned my students, when I taught this course for the first time to come up with problems, because that is good way of learning the subject itself at a much higher level, and also it will contribute to other aspects such as this. This happens to be a modified form adapted from a problem formulated by one of my students, Akhil Sai Valluri. Please go ahead; take 15 minutes and figure out how you would go about approaching the problem. Then I will give you some hints.

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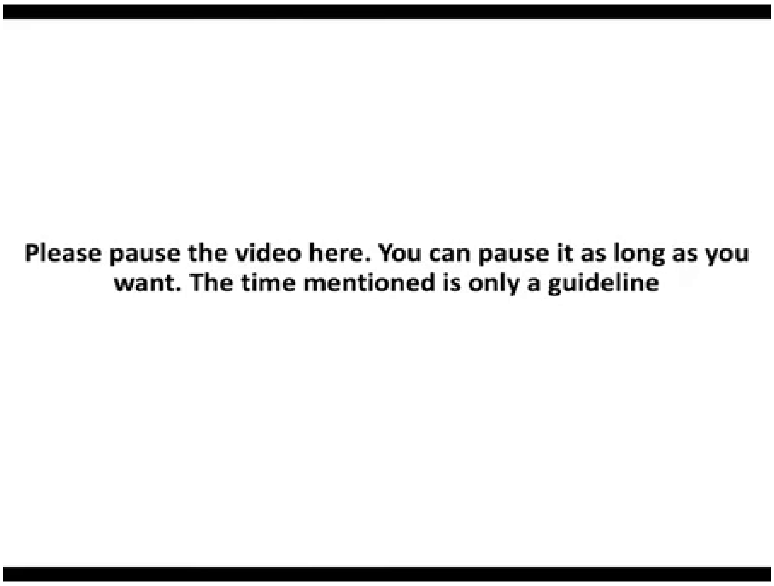

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You would have had time to think through this, and hopefully the thought became focussed towards recognizing that this is a substance evaporating under pure substance conditions, or substance evaporating. Therefore, it is changing its phase from liquid to vapour. Therefore, it is a case of phase change. And what is required is change in pressure per unit change in temperature that is needed to maintain equilibrium. Therefore, the whole process is under equilibrium conditions.

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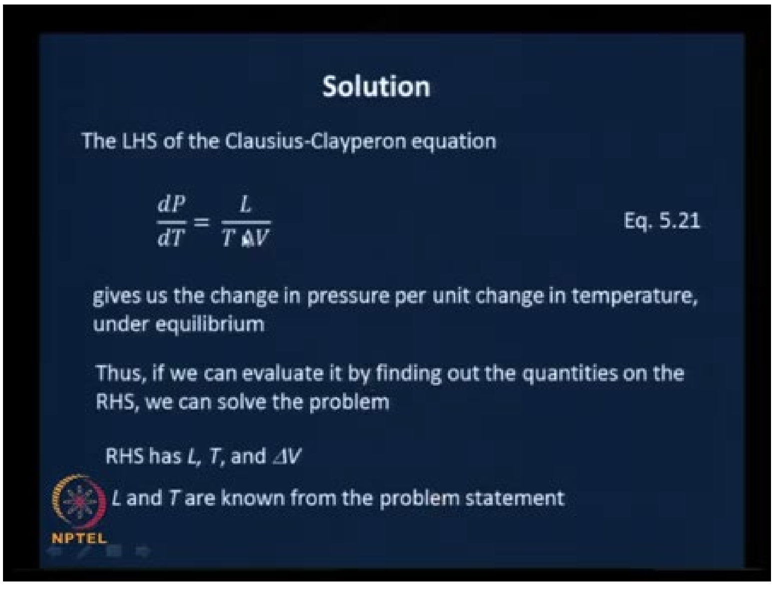

Solution

The LHS of the Clausius-Clayperon 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

So, what does this bring to mind? Definitely the Clausius-Clapeyron equation. In fact, the left hand side of the Clausius-Clapeyron equation

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

… dP dT is what is required to be calculated as a part of this particular problem. If you can find dP dT by evaluating the right hand side… In other words if we know L T delta V, we can substitute the values here and find dP dT, and that is what we need. L is already given – that is the latent heat of vapourisation. So, if we find T delta V … T is also given; it is known from the problem statement. It is the temperature at which the vapourisation is taking place. Therefore, if you find delta V then we are actually done. So, how do you go about finding delta V is the hint that I am going to leave you with for another 15 minutes or so … let us say about 10 minutes, and let us see how you come about with the solution.

Hopefully you would have figured out how to find out delta V. Since we are almost out of time; I am just going to give you some hints, give you time to work it out and show you the complete solution when we meet the next time. delta V is nothing but V of the vapour minus V of the liquid, or V of gas minus V of the liquid.

Therefore, you need to find a way to figure out what the molar volume of the gas phase is, and molar volume of the liquid phase is. What does this bring to mind? Does this bring to mind something to do with equations of state? That is exactly what we are looking at. So, go back to what equations of state are. And this is isopropanol here. See whether you are able to find out the molar volume of the vapour and the molar volume of the liquid under the saturated conditions of the liquid-vapour transition. Please take this as homework. When we meet the next time, when we begin the class, I will give you the solution.

Go ahead please.