Advanced Thermodynamics

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Lecture – 3
Classical Thermodynamics of Phase Equilibria - 2

Welcome to the MOOCs course advanced thermodynamics. The title of this lecture is Classical Thermodynamics of Phase Equilibria part 2. Since it is a continuation of previous lecture, before going into the details of today's lecture, we will be solving a few example problems based on the things what we have discussed in the previous lecture.

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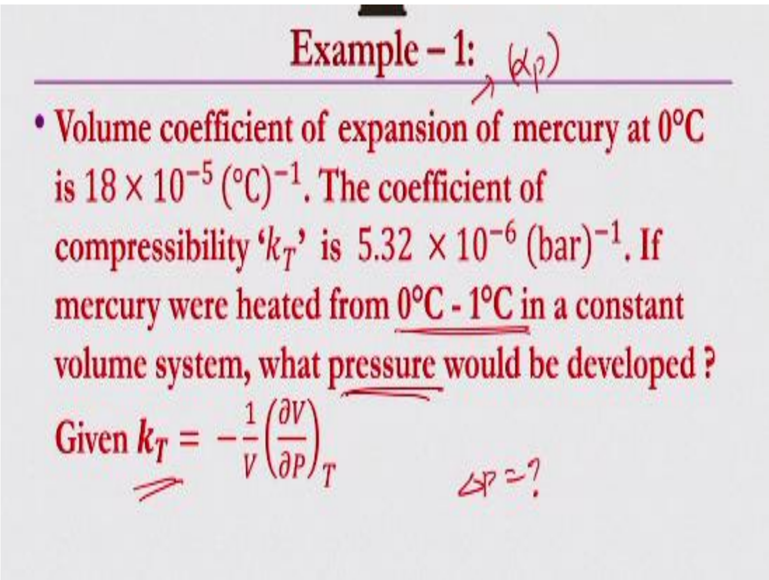

Example – 1: $\rightarrow (\alpha_p)$

- Volume coefficient of expansion of mercury at 0°C is $18 \times 10^{-5}\ (°\mathrm{C})^{-1}$. The coefficient of compressibility 'k_T' is $5.32 \times 10^{-6}\ (\mathrm{bar})^{-1}$. If mercury were heated from 0°C - 1°C in a constant volume system, what pressure would be developed? Given $k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

$\Delta p = ?$

Volume coefficient of expansion of mercury at 0°C is given. The coefficient of compressibility k_T is also given. If mercury were heated up from 0°C to 1°C in a constant volume system, what is the pressure change or how much pressure would be developed? That we have to find out, okay? This coefficient of compressibility is given k_T and then volume coefficient of expansion this α_p is also given, right? So that means, we need to find out Δp, okay? So, that means, $\frac{\partial P}{\partial V}$ we have to find out actually.

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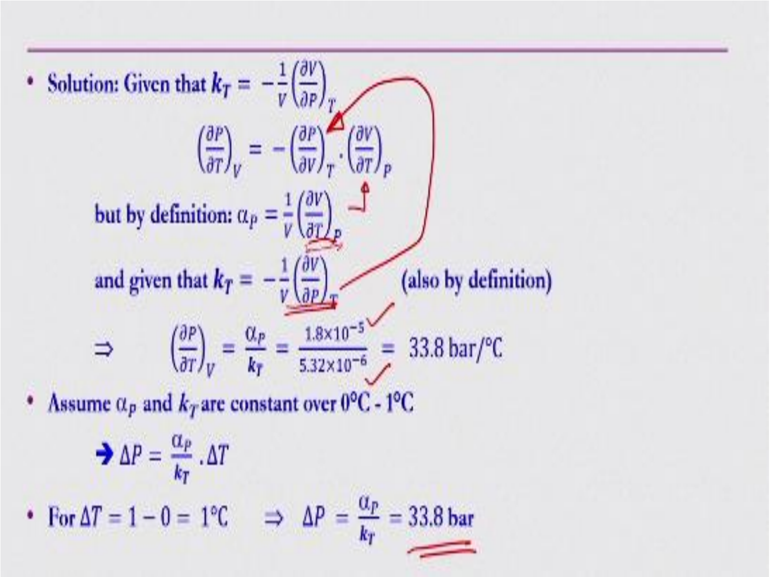

- Solution: Given that $k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_P$$

but by definition: $\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

and given that $k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ (also by definition)

$$\Rightarrow \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha_P}{k_T} = \frac{1.8\times10^{-5}}{5.32\times10^{-6}} = 33.8 \text{ bar/°C}$$

- Assume α_p and k_T are constant over 0°C - 1°C

$$\rightarrow \Delta P = \frac{\alpha_P}{k_T}.\Delta T$$

- For $\Delta T = 1 - 0 = 1$°C $\Rightarrow \Delta P = \frac{\alpha_P}{k_T} = 33.8$ bar

So, given that $k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ that is given. $\left(\frac{\partial P}{\partial T}\right)_V$, we can write it as $-\left(\frac{\partial P}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_P$, right? But further we also know that $\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$. That means this is related to this particular term and then also it is given that you know $k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$. That means this particular term is related to this one.

When we use this one here in this equation, then we have $\left(\frac{\partial P}{\partial T}\right)_V$ is nothing but α_p by k_T. α_p is given in the problem, k_T is given. So, we substitute here this thing, then you will get 33.8 bar/°C. Now, ΔT is 1 °C. So, that means $\Delta P = \left(\frac{\alpha_p}{k_T}\right) . \Delta T$ that is nothing but whatever $\left(\frac{\alpha_p}{k_T}\right)$ is there, that itself would be the pressure that would be developed if you change the temperature from 0 °C to 1 °C.

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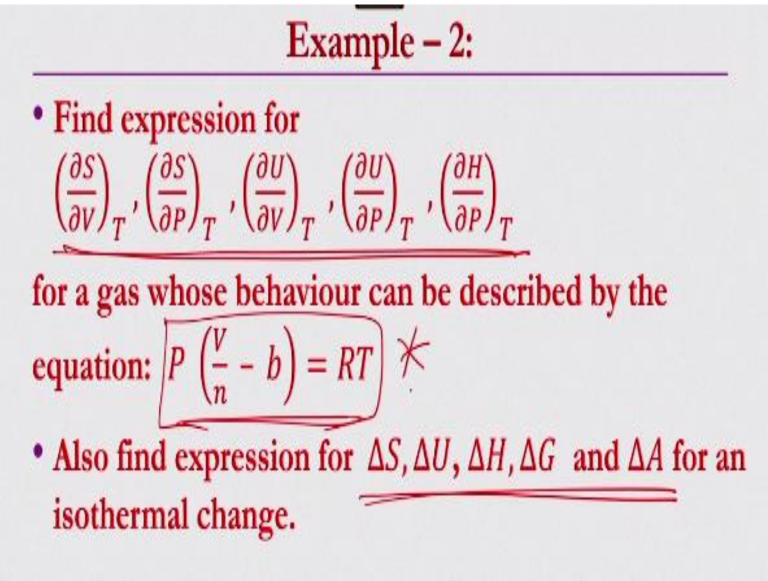

Example – 2:

- Find expression for $\left(\frac{\partial S}{\partial V}\right)_T, \left(\frac{\partial S}{\partial P}\right)_T, \left(\frac{\partial U}{\partial V}\right)_T, \left(\frac{\partial U}{\partial P}\right)_T, \left(\frac{\partial H}{\partial P}\right)_T$ for a gas whose behaviour can be described by the equation: $\boxed{P\left(\frac{V}{n} - b\right) = RT}$ ✱
- Also find expression for $\Delta S, \Delta U, \Delta H, \Delta G$ and ΔA for an isothermal change.

Another example. Find expression for these things for a gas whose behavior can be described by this equation. There is a gas, non-ideal gas is there. So, that equation state of that gas is given by this equation. Then what are the corresponding expressions for these 5 partial derivatives? In addition to those things, also we need to find out the absolute changes, right? Those things we have to find out. So, first we have to make use this equation.

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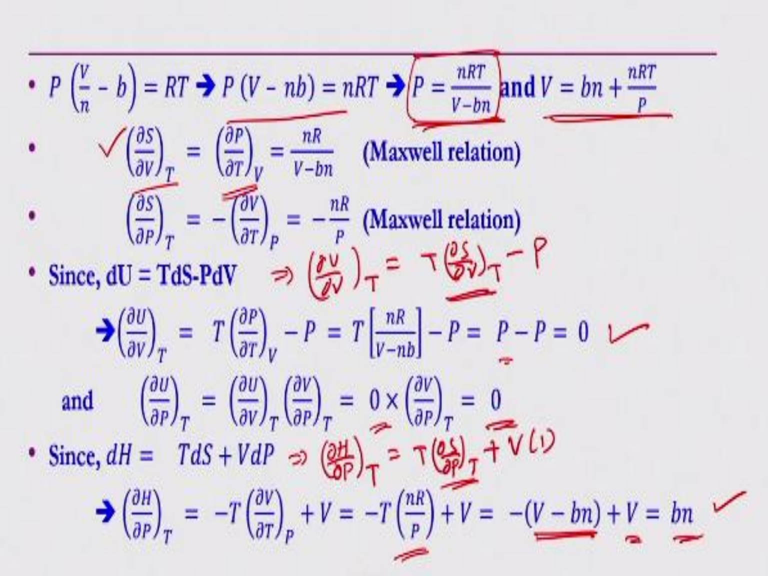

- $P\left(\frac{V}{n} - b\right) = RT \rightarrow P(V - nb) = nRT \rightarrow \boxed{P = \frac{nRT}{V-bn}}$ and $V = bn + \frac{nRT}{P}$
- ✓ $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V-bn}$ (Maxwell relation)
- $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -\frac{nR}{P}$ (Maxwell relation)
- Since, dU = TdS-PdV $\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$

$\rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = T\left[\frac{nR}{V-nb}\right] - P = P - P = 0$ ✓

and $\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T = 0 \times \left(\frac{\partial V}{\partial P}\right)_T = 0$

- Since, $dH = TdS + VdP \Rightarrow \left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V(1)$

$\rightarrow \left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V = -T\left(\frac{nR}{P}\right) + V = -(V - bn) + V = bn$ ✓

So, the equation given is P $\left(\frac{V}{n} - \text{b}\right)$ = R T. So, this equation if you rearrange you can write P = $\frac{\text{nRT}}{\text{V} - \text{bn}}$ and then same equation you can write V = bn +$\frac{\text{nRT}}{\text{P}}$. We are writing this one because we need to find out$\left(\frac{\partial S}{\partial V}\right)_T$, right? But from the Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$. So, that means P is already there. So, this equation if you differentiate with respect to T at constant V then you will get$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\text{nR}}{\text{V} - \text{bn}}$. So, that first one is already found.

Similarly, $\left(\frac{\partial S}{\partial P}\right)_T$ we have to find out and then from the Maxwell relation again $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$. So, V expression we are already having. So, this expression if you differentiate with respect to T at constant P, you will get $\left(\frac{\partial S}{\partial P}\right)_T$. So, $\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$. So, $\left(\frac{\partial S}{\partial P}\right)_T = -\frac{nR}{P}$.

Likewise, you know we can find other properties also because we have dU = TdS - PdV. From this equation, $\left(\frac{\partial U}{\partial V}\right)_T$ can be written as T ∂S. This should be from here actually

$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$. But from the Maxwell relation, $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial V}{\partial T}\right)_V = \frac{nR}{V - bn}$.

So, $\frac{nR}{V - bn}$. T - P. Now, this $\frac{nR}{V - bn}$ is nothing but P from here, equation of state. So, P - P = 0. Third one is also found.

And then next one is $\left(\frac{\partial U}{\partial P}\right)_T$. So, by product rule we can write it as $\left(\frac{\partial U}{\partial V}\right)\left(\frac{\partial V}{\partial P}\right)$

Since $\left(\frac{\partial U}{\partial V}\right)_T = 0$. So this is again going to be 0, forth one is also found.

Another relation that we have dH = TdS + VdP. We need $\left(\frac{\partial H}{\partial P}\right)_T$. So from here, what we can have, $\left(\frac{\partial H}{\partial P}\right)_T$. Then, $T\left(\frac{\partial S}{\partial P}\right)_T + V\left(\left(\frac{\partial P}{\partial P}\right)T = 1\right)$.

But this $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -\frac{nR}{P}$ T + V is here, okay?

So, then we get - $(-V - bn)$ + V because $\frac{nRT}{P}$ nRT = V - bn from the equation of state that is given. And then this V is as it is, so then this bn is there. So these partial differential quantities obtain, so then absolute quantities can be obtained by just by integration.

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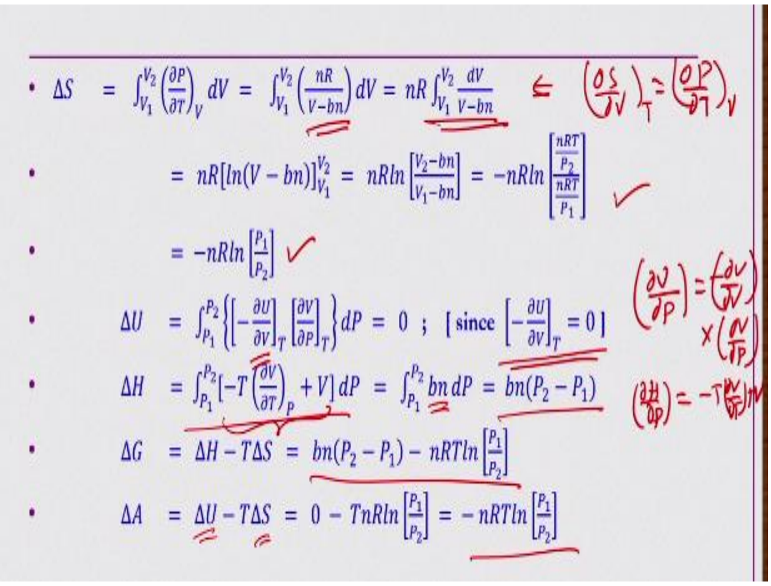

- $\Delta S = \int_{V_1}^{V_2} \left(\frac{\partial P}{\partial T}\right)_V dV = \int_{V_1}^{V_2} \left(\frac{nR}{V-bn}\right) dV = nR\int_{V_1}^{V_2} \frac{dV}{V-bn}$ $\Leftarrow$ $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
- $= nR[\ln(V-bn)]_{V_1}^{V_2} = nR\ln\left[\frac{V_2-bn}{V_1-bn}\right] = -nR\ln\left[\frac{\frac{nRT}{P_2}}{\frac{nRT}{P_1}}\right]$ ✓
- $= -nR\ln\left[\frac{P_1}{P_2}\right]$ ✓
- $\Delta U = \int_{P_1}^{P_2}\left\{\left[-\frac{\partial U}{\partial V}\right]_T \left[\frac{\partial V}{\partial P}\right]_T\right\} dP = 0$; [since $\left[-\frac{\partial U}{\partial V}\right]_T = 0$]
- $\Delta H = \int_{P_1}^{P_2}\left[-T\left(\frac{\partial V}{\partial T}\right)_P + V\right] dP = \int_{P_1}^{P_2} bn\, dP = bn(P_2 - P_1)$
- $\Delta G = \Delta H - T\Delta S = bn(P_2 - P_1) - nRT\ln\left[\frac{P_1}{P_2}\right]$
- $\Delta A = \Delta U - T\Delta S = 0 - TnR\ln\left[\frac{P_1}{P_2}\right] = -nRT\ln\left[\frac{P_1}{P_2}\right]$

$\left(\frac{\partial U}{\partial P}\right) = -\left(\frac{\partial U}{\partial V}\right) \times \left(\frac{\partial V}{\partial P}\right)$

$\left(\frac{\partial H}{\partial P}\right) = -T\left(\frac{\partial V}{\partial T}\right) + V$

From here, ∆S = $\int_{V1}^{V2}\left(\frac{\partial P}{\partial T}\right)$ dV because we know here this $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ from the Maxwell relations, right? So that we have simply written here $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$, $\left(\frac{\partial P}{\partial T}\right)_V$. we already got it as this one. Now, integrate this equation, so, you will get ln V - bn, then V changing from V_1 to V_2, they are not given, so this equation we are having.

So that means, - nR ln $\frac{P1}{P2}$ = ∆ S. Similarly, ∆U, we have seen that ∆U from this equation as you know, we already have this equation $\left(\frac{\partial U}{\partial P}\right) = -\left(\frac{\partial U}{\partial V}\right)\left(\frac{\partial V}{\partial P}\right)$. But $\left(\frac{\partial U}{\partial V}\right) = 0$ that we already derived in the previous slide. So, overall this ∆U = 0. Similarly, ∆H, we have seen that relation, you know $\left(\frac{\partial H}{\partial P}\right)_T$ in the previous slide we derived, $= -T\left(\frac{\partial V}{\partial T}\right) + V$.

So, this equation if you integrate, then you have this one. $\left(\frac{\partial V}{\partial T}\right)=$ bn and then you substitute all these equations here. Whatever this particular expression we found it as bn - $T\left(\frac{\partial V}{\partial T}\right) + V$. We found it as bn dP in previous slide. Integration if we do, $\int_{P1}^{P2}$ bn dP. Then, finally ∆G is nothing but ∆H - T∆S, so that you substitute, so you will get this final delta G expression and then ∆A is nothing but ∆U - T∆S. So, ∆U you already calculated, ∆S you already calculated. So, substitute here, you get ∆A, simple and straightforward.

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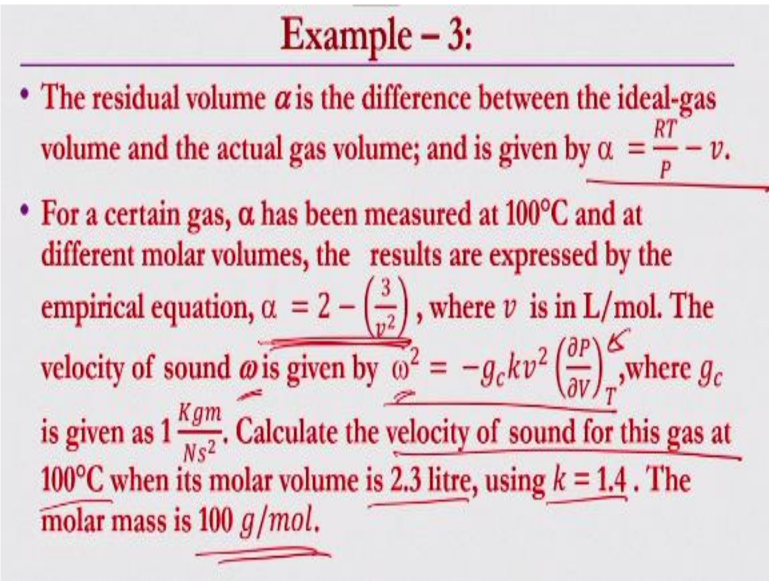

Example – 3:

- The residual volume α is the difference between the ideal-gas volume and the actual gas volume; and is given by $\alpha = \frac{RT}{P} - v$.
- For a certain gas, α has been measured at 100°C and at different molar volumes, the results are expressed by the empirical equation, $\alpha = 2 - \left(\frac{3}{v^2}\right)$, where v is in L/mol. The velocity of sound ω is given by $\omega^2 = -g_c k v^2 \left(\frac{\partial P}{\partial V}\right)_T$, where g_c is given as $1 \frac{Kgm}{Ns^2}$. Calculate the velocity of sound for this gas at 100°C when its molar volume is 2.3 litre, using $k = 1.4$. The molar mass is 100 g/mol.

Example number 3. The residual volume α is the difference between the ideal gas volume and the actual gas volume and is given by $\alpha = \frac{RT}{P} - v$. For a certain gas, α has been measured at 100°C and at different molar volumes. The results are expressed by the emperical equation $\alpha = 2 - \left(\frac{3}{v^2}\right)$ where v is in liter per mol. The velocity of sound omega is given by $\omega^2 = - g_c k v^2 \left(\frac{\partial P}{\partial V}\right)_T$, right?

Calculate the velocity of sound for this gas at 100 °C when its molar volume is 2.3 liters using k = 1.4. The molar mass is also given. So, only thing that if you wanted to know the omega, you should know what is $\left(\frac{\partial P}{\partial V}\right)$. So, α expressions given, 2 expressions are given, we can make use of these equations to get P = function of V and then we can find out $\left(\frac{\partial P}{\partial V}\right)_T$, then substitute here, simple.

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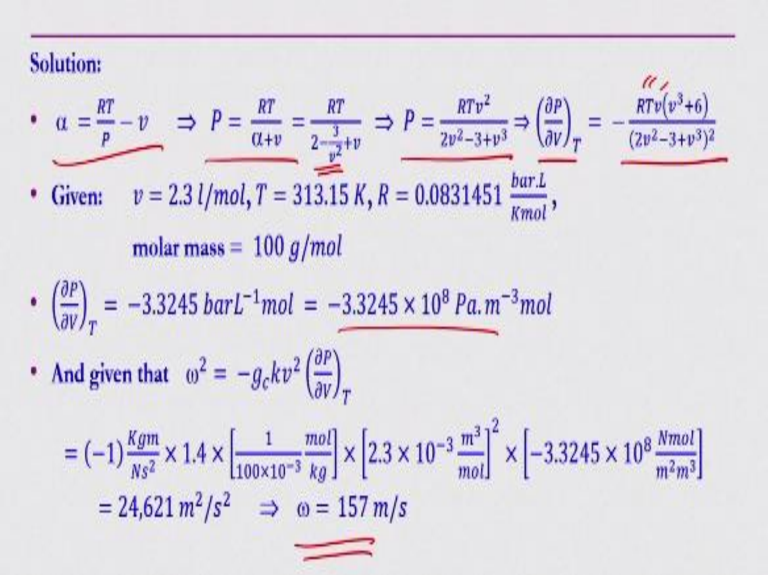

Solution:

- $\alpha = \frac{RT}{P} - v \Rightarrow P = \frac{RT}{\alpha + v} = \frac{RT}{2 - \frac{3}{v^2} + v} \Rightarrow P = \frac{RTv^2}{2v^2 - 3 + v^3} \Rightarrow \left(\frac{\partial P}{\partial V}\right)_T = -\frac{RTv(v^3+6)}{(2v^2-3+v^3)^2}$
- Given: $v = 2.3\ l/mol, T = 313.15\ K, R = 0.0831451\ \frac{bar.L}{Kmol}$,

  molar mass = $100\ g/mol$
- $\left(\frac{\partial P}{\partial V}\right)_T = -3.3245\ barL^{-1}mol = -3.3245 \times 10^8\ Pa.m^{-3}mol$
- And given that $\omega^2 = -g_c k v^2 \left(\frac{\partial P}{\partial V}\right)_T$

$$= (-1)\frac{Kgm}{Ns^2} \times 1.4 \times \left[\frac{1}{100 \times 10^{-3}}\frac{mol}{kg}\right] \times \left[2.3 \times 10^{-3}\frac{m^3}{mol}\right]^2 \times \left[-3.3245 \times 10^8 \frac{Nmol}{m^2 m^3}\right]$$

$$= 24{,}621\ m^2/s^2 \Rightarrow \omega = 157\ m/s$$

So, α is given like this. If you rearrange this equation, P =$\frac{\mathrm{RT}}{\alpha + \mathrm{v}}$. α = 2 - $\left(\frac{3}{v^2}\right)$. You can rearrange this equation, so you will get this one. And then $\left(\frac{\partial P}{\partial V}\right)_T$ if you do, you will get this equation. Now in this equation, R, T, V, etc. everything are know, substitute here. So then you will get because V is given, T is given, R is given, R is known, molar mass is also given.

So, when you substitute all these things $\left(\frac{\partial P}{\partial V}\right)_T$ you will get this value and then we need to know ω but ω^2 expression is given. Here, also g_c is given, k is given, v is known, $\left(\frac{\partial P}{\partial V}\right)$ we just calculated. Substitute all of them, then you will get ω^2 = 24621, that means ω is roughly 157 meter per second, okay? Simply making use of given equation of state to get the required information.

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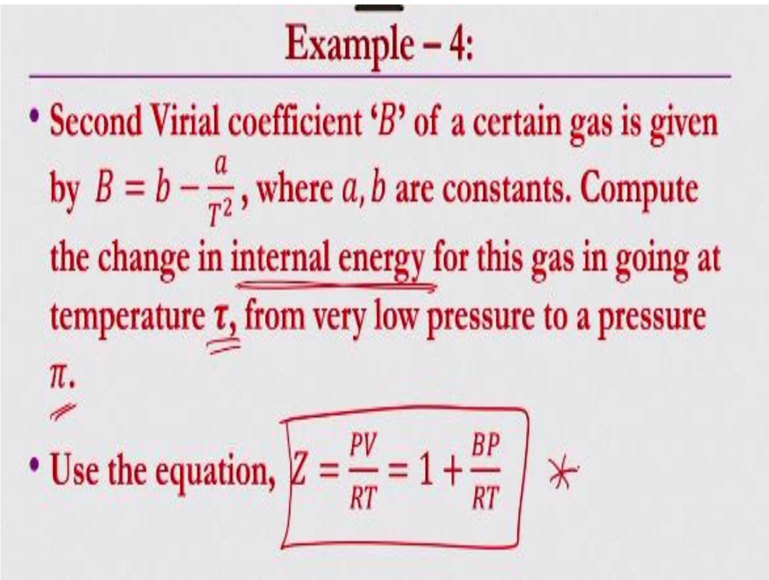

Example – 4:

- Second Virial coefficient 'B' of a certain gas is given by $B = b - \frac{a}{T^2}$, where a, b are constants. Compute the change in internal energy for this gas in going at temperature τ, from very low pressure to a pressure π.
- Use the equation, $\boxed{Z = \frac{PV}{RT} = 1 + \frac{BP}{RT}}$ $*$

Final example problem now. Second Virial coefficient B of a certain gas is given by B =b - $\frac{a}{T^2}$ where a and b are constants. Compute the change in internal energy for this gas in going at temperature τ, the temperature is going to change from certain temperature to τ temperature from very low pressure to air pressure Π. So ΔP is nothing but Π, ΔT is nothing but τ.

Then what is the change in internal energy? ΔU you have to find out, okay? This Virial equation is given Z = $\frac{PV}{RT}$ = 1 + $\frac{BP}{RT}$ is nothing but Virial equation of state, it is given. So, this equation we have to make use.

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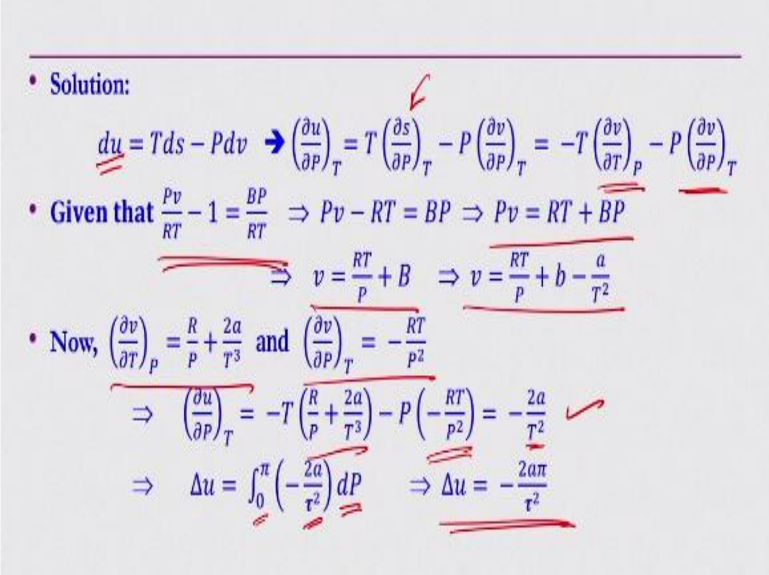

- Solution:

$$du = Tds - Pdv \rightarrow \left(\frac{\partial u}{\partial P}\right)_T = T\left(\frac{\partial s}{\partial P}\right)_T - P\left(\frac{\partial v}{\partial P}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_P - P\left(\frac{\partial v}{\partial P}\right)_T$$

- Given that $\frac{Pv}{RT} - 1 = \frac{BP}{RT} \Rightarrow Pv - RT = BP \Rightarrow Pv = RT + BP$

$$\Rightarrow v = \frac{RT}{P} + B \Rightarrow v = \frac{RT}{P} + b - \frac{a}{T^2}$$

- Now, $\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P} + \frac{2a}{T^3}$ and $\left(\frac{\partial v}{\partial P}\right)_T = -\frac{RT}{P^2}$

$$\Rightarrow \left(\frac{\partial u}{\partial P}\right)_T = -T\left(\frac{R}{P} + \frac{2a}{T^3}\right) - P\left(-\frac{RT}{P^2}\right) = -\frac{2a}{T^2}$$

$$\Rightarrow \Delta u = \int_0^{\pi}\left(-\frac{2a}{\tau^2}\right)dP \Rightarrow \Delta u = -\frac{2a\pi}{\tau^2}$$

So, we need du. So, from here actually du is nothing but Tds - Pdv for the closed system because here exchange of matter nothing has been mentioned. So, then obviously, we can take it as a kind of closed system. So, from here this equation you know at constant temperature, $\left(\frac{\partial u}{\partial P}\right)_T$, you can have $T\left(\frac{\partial s}{\partial P}\right)_T$ - $P\left(\frac{\partial v}{\partial P}\right)_T$. s we do not know but $\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$ from the Maxwell relation, right? This is coming from the Maxwell relation and then this term is already there.

Now, we know from the Virial equation of state that is given $Z = \frac{PV}{RT} = 1 + \frac{BP}{RT}$ is given. From that V you can write as function of you know temperature and pressure and then get the differentiation. So, this is given. Now, this equation you can write like this. So, in terms of V you can write like this and then this $B = b - \frac{a}{T^2}$ that is also given.

So, from here, $\left(\frac{\partial v}{\partial T}\right)$ if you do, you will get this one. $\left(\frac{\partial v}{\partial P}\right)$ If you do, you get this one. So, $\left(\frac{\partial u}{\partial P}\right)_T$ $= - T\left(\frac{\partial u}{\partial T}\right) = \frac{R}{P} + \frac{2a}{T^3} - P\left(\frac{\partial v}{\partial P}\right)$, $\left(\frac{\partial v}{\partial P}\right)_T = -\frac{RT}{P^2}$. So, when you simplify $-\frac{2a}{T^2}$ you will get.
Now, $\Delta P = \Pi$, so $\Delta u = -2a$ here and then temperature is τ, temperature is changing to τ.

Then that means $\frac{2a}{\tau^2}$ and ΔP integral 0 to P. P is changing from very low pressure to Π, the low pressure let us take 0 because it is not given. So, then when you integrate this one $-\frac{2a}{\tau^2}P$, you will get. $P = \Pi - 0$, so that is Π you are getting, so this is the change in internal energy.

We have been discussing classical thermodynamics of phase equilibria. So, how to fix the state of equilibrium for the system that we have taken in which two or more than two phases are co-existing and these phases are equilibrium. So, how to fix the state of equilibria problems, right? So, that can be done using the Gibb's phase rule. The second one is that you know we have been discussing that the chemical potential of each component is equal amongst all co-existing phases' right? Those phases which are at equilibrium, those things we are discussing. So, those derivations we are going to do.

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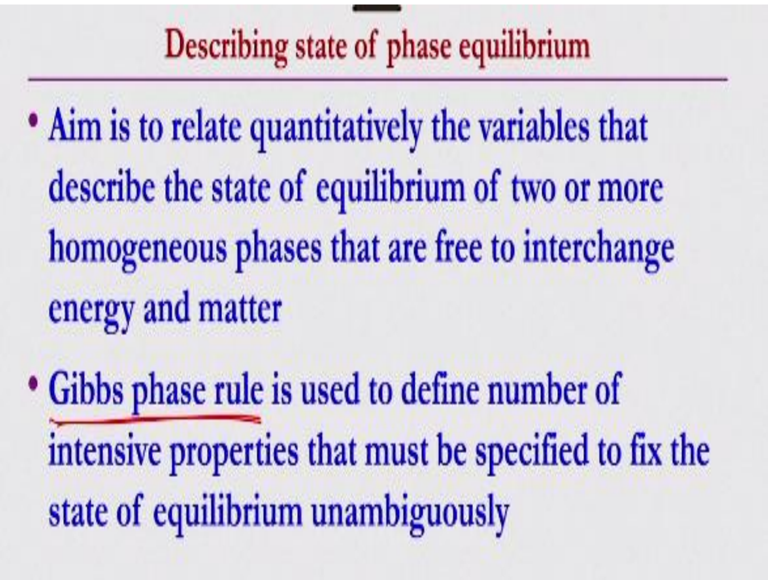

Describing state of phase equilibrium

- Aim is to relate quantitatively the variables that describe the state of equilibrium of two or more homogeneous phases that are free to interchange energy and matter
- Gibbs phase rule is used to define number of intensive properties that must be specified to fix the state of equilibrium unambiguously

Describing state of phase equilibrium. In general in phase equilibrium problem, what is the aim? Aim is to relate quantitatively the variables that describe the state of equilibrium of two or more homogeneous phases that are free to interchange energy and matter. Gibbs phase rule is used to define number of intensive properties that must be specified to fix the state of equilibrium without any ambiguity. So, what is this Gibbs phase rule? This we have to first see, right?

So, then you know how to find out that how many number of intensive variables has to be fixed in order to define the state of equilibrium without any ambiguity, those things that we are going to see in this Gibbs phase rule.

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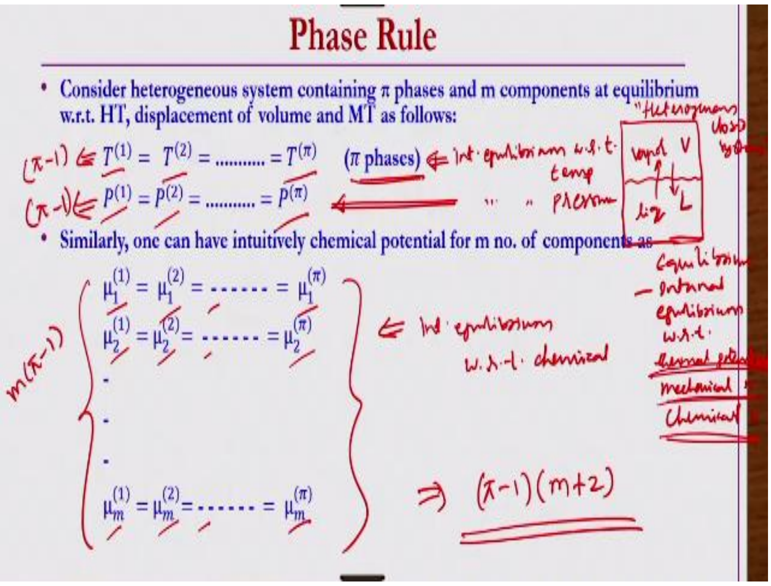

Phase Rule

- Consider heterogeneous system containing π phases and m components at equilibrium w.r.t. HT, displacement of volume and MT as follows:

$$(\pi-1) \Leftarrow T^{(1)} = T^{(2)} = \dots\dots = T^{(\pi)} \quad (\pi \text{ phases}) \Leftarrow \text{Int. equilibrium w.r.t. temp}$$

$$(\pi-1) \Leftarrow P^{(1)} = P^{(2)} = \dots\dots = P^{(\pi)} \longleftarrow \text{" " pressure}$$

- Similarly, one can have intuitively chemical potential for m no. of components as

$$m(\pi-1)\left\{\begin{array}{l} \mu_1^{(1)} = \mu_1^{(2)} = \dots\dots = \mu_1^{(\pi)} \\ \mu_2^{(1)} = \mu_2^{(2)} = \dots\dots = \mu_2^{(\pi)} \\ \cdot \\ \cdot \\ \cdot \\ \mu_m^{(1)} = \mu_m^{(2)} = \dots\dots = \mu_m^{(\pi)} \end{array}\right\} \Leftarrow \text{Int. equilibrium w.r.t. chemical}$$

$$\Rightarrow \underline{\underline{(\pi-1)(m+2)}}$$

So, let us consider a heterogeneous system containing Π number of phases and m number of components at equilibrium with respect to the heat transfer, displacement of volume and mass transfer as follows, right? So, what we have? We have a kind of heterogeneous system which is a closed system because we know that equilibrium processes are you know equal chemical potential behavior whatever we take you know that is valid only for closed system. So, what we do?

We take a heterogeneous closed system, right? But within this one we are having several you know phases, several phases which are homogeneous, right? So, let us say for simplicity we take two phases. We take liquid phase L and then there is a vapor phase V, okay? So, the properties, whatever the density, etc., those properties within the liquid are you know constant, uniform. So, whatever this liquid phase is there that we can take it as a kind of one single homogeneous phase, right?

Then vapor, whatever the properties of the vapor, density, etc., those properties within the vapor are again you know same within that vapor phase, but they are different from vapor to the liquid phase. So, then vapor phase can be taken as a kind of separate homogeneous phase and there exist a kind of equilibrium amongst them. Before attaining the equilibrium obviously, you know the constituents from the liquid may be going to the vapor phase and then similarly constituents of the vapor phase may be coming to the liquid phase depending on the degree of you know transfer of the species.

Once the equilibrium is established, there will not be any kind of tendency to exchange the matter as well. So, here you know within this heterogeneous system, what we have? We have a kind of two homogeneous phases, right? And then there is a kind of an exchange of matter as well, right? So, that is the reason you know within this heterogeneous closed system we can see the equilibrium problem. We can discuss the equilibrium problem. So, as per the definition, as per you know basic equilibrium problem, our phase equilibrium is valid only for the closed system.

So, what we are doing? We are taking a heterogeneous closed system. Within that heterogeneous closed system, we are having different homogeneous phases, okay? Now, here within this heterogeneous system, we have a kind of internal equilibrium. Internal equilibrium with respect to the heat transfer or that is thermal equilibrium. We also have displacement of volume that is also at equilibrium that is you know mechanical equilibrium is there and then with respect to mass transfer as well there is a kind of equilibrium that is chemical equilibrium is also there.

So, this heterogeneous closed system we can say it is at the equilibrium if there is a kind of internal equilibrium with respect to heat transfer that is you know thermal potential with respect to the displacement of volume that is the mechanical potential and then kind of you know with respect to the mass transfer that is you know with respect to the chemical potential. So, that means, you know this thermally equilibrium is established and then mechanically also equilibrium is established and then chemically also equilibrium has been established within this heterogeneous system.

Then we can say that the heterogeneous system is at equilibrium, okay? So now, for this case I have explained this one only for two phases. Now, let us take a common case of Π number of phases and n number of components. So, then what are these relations? What are these equilibrium relations are existing, those things we are going to see now. So, with respect to the heat transfer, what we have you know temperature has to be equal in all the phases if the thermal equilibrium is established.

That means, T of phase 1, T of phase 2, should be equal and then similarly that should be equal to T of phase 3 and so on so T of Π that is temperature in all the phases should be equal, right? Because there are Π number of phases, okay? So, then what we have? $T^{(1)} = T^{(2)} = T^{(3)} ... = T^{(\Pi)}$. So, this is true if there is a kind of internal equilibrium with respect to the heat transfer process. Now, similarly with respect to the internal equilibrium with respect to the displacement of volume or with respect to the mechanical potential if there exist internal equilibrium, then what we have?

We have this $P^{(1)} = P^{(2)} = P^{(3)} \ldots = P^{(\Pi)}$ that is pressure in each phase should be equal that is what the thing that you can understand here if there is a kind of internal equilibrium with respect to the mechanical potential, okay? Now, similarly one can have intuitively chemical potential for m number of components as well. So, that is we know the chemical potential of each component should be equal in phases.

So, let us say for the component 1, the chemical potential of component 1 in phase 1 should be equals to chemical potential of component 1, the same component but in phase 2 that should be equal to chemical potential of the same component 1 in phase 3 and so and so the chemical potential of same component 1 in Π^{th} phase, right? So, that is the chemical potential of first component should be same in all phases 1, 2, 3 and so on so up to Π, right? Similarly, for the second component also, the chemical potential of that particular component should be same in all the phases.

So, that is $\mu_2^{(1)} = \mu_2^{(2)} = \mu_2^{(3)} \dots = \mu_2^{(\Pi)}$, Π number of phases are there, right? So, likewise if you keep on constructing for all m number components like this, so you can have μ_m let us say for the m^{th} component, m number of components are there, so last component let us say m.

So, for the m^{th} component, its chemical potential in phase 1 should be equals to its chemical potential in phase 2 that should be equals to its chemical potential in phase 3 and then likewise that should be equals to chemical potential of that particular m^{th} component in phase Π, right? So, this is how we can see if there is a kind of internal equilibrium with respect to the mass transfer also, okay? So, this relation what it says?

First relation it says you know, system is in internal equilibrium with respect to temperature and then second one, this is the internal equilibrium respect to the pressure, and then this relation says internal equilibrium with respect to you know chemical composition of the mass transfer, okay? So, now how many relations are there here? So, what we can say here? With Π number of phases are there, so we can say Π - 1 relations are there for the heat transfer part. Similarly, you know how many relations are there?

Π - 1 relations are there for the mechanical equilibrium part and then for you know chemical potential point of view or the internal equilibrium with respect to mass transfer point of view, how many relations are there? There are m number of components are there and then Π - 1 relation for each component. So, that is, how many relations are there totally? $(\Pi - 1)(m + 2)$ number of equilibrium relations are existing.

This is very much essential in order to find out the degrees of freedom that are to be fixed in order to fix the state of equilibrium for that given system, okay?

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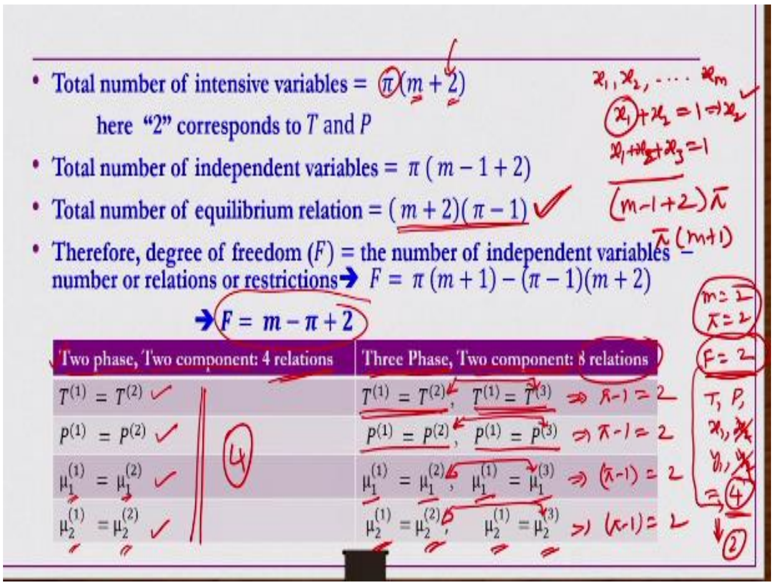

- Total number of intensive variables = $\pi(m+2)$

  here "2" corresponds to T and P
- Total number of independent variables = $\pi(m-1+2)$
- Total number of equilibrium relation = $(m+2)(\pi-1)$ ✓
- Therefore, degree of freedom (F) = the number of independent variables − number or relations or restrictions→ $F = \pi(m+1) - (\pi-1)(m+2)$

  →$F = m - \pi + 2$

Two phase, Two component: 4 relations	Three Phase, Two component: 8 relations
$T^{(1)} = T^{(2)}$ ✓	$T^{(1)} = T^{(2)}$; $T^{(1)} = T^{(3)}$ $\Rightarrow \pi - 1 = 2$
$p^{(1)} = p^{(2)}$ ✓	$p^{(1)} = p^{(2)}$; $p^{(1)} = p^{(3)}$ $\Rightarrow \pi - 1 = 2$
$\mu_1^{(1)} = \mu_1^{(2)}$ ✓ ④	$\mu_1^{(1)} = \mu_1^{(2)}$; $\mu_1^{(1)} = \mu_1^{(3)}$ $\Rightarrow (\pi - 1) = 2$
$\mu_2^{(1)} = \mu_2^{(2)}$ ✓	$\mu_2^{(1)} = \mu_2^{(2)}$; $\mu_2^{(1)} = \mu_2^{(3)}$ $\Rightarrow (\pi - 1) = 2$

$x_1, x_2, \dots x_m$ ✓

$x_1 + x_2 = 1 \Rightarrow x_2$

$x_1 + x_2 + x_3 = 1$

$(m-1+2)\pi$

$\pi(m+1)$

$m = 2$

$\pi = 2$

$F = 2$

$T, P, x_1, \cancel{x_2}, y_1, \cancel{y_2} \Rightarrow 4$

$\downarrow$ ②

Now, total number of intensive variables how many are there? There are m number of components, okay? And there is a temperature, pressure, so m + 2 are there for each phase, and how many phases are there? There are Π number of phases. So, $\Pi\ (m + 2)$ number of intensive variables are there. But all of them are independent that we have to check. Obviously, not all of them are independent because let us say composition wise if you say, let us say x_1, x_2, x_3, etc. that I am doing up to x_m, right? So, m number of components are there, right.

So, let us start with binary measure. If you have x_1 and then x_2. So, $x_1 + x_2 = 1$. So, if you know x_1 obviously, x_2 can be known. So, that means only out of these x_1 and x_2, only one of them is independent variable, other one is not, right? Similarly, let us say if you have a tertiary component measures, then $x_1 + x_2 + x_3 = 1$ that means out of these x_1, x_2, x_3, if you know any two, third one can be found, right?

So, that is the reason all of them are not you know independent variable, out of all of these many intensive variables, not all of them are independent, only $(m - 1)\ \Pi$ those things are independent variable and then m - 1 and then + 2 for the temperature multiplied by Π, so that is Π multiplied by m + 1 number of variables are only independent variable. So, in this relation whatever this 2 is there, that corresponds to temperature and pressure.

So, total number of independent variables are how many? $\Pi\ (m - 1 + 2)$, that is Π into m + 1 are there and then total number of equilibrium relations how many? That we have already seen in the previous slides, they are m + 2 multiplied by Π - 1, right? So, these are we are generally doing, so just for the crosscheck, what we do? We take a system where you know there are 2 phases are there that is $\Pi = 2$ and then 2 components are there that is $m = 2$, then how many relations should be there?

So, according to this equation m is 2 and then Π is also 2. So, $(2 + 2)(2 - 1)$, that is 4, 4 relations should be there. So, what are those four relations? That is T in phase 1 should be equals to T in phase 2 is one relation with respect to the internal equilibrium with respect to the heat transfer. Then, P in phase 1 should be equals to be P in phase 2, that is you know internal equilibrium with respect to the mechanical potential and then there are 2 components.

So, chemical potential of component 1 in phase 1 should be equals to chemical potential of component 1 in phase 2 that is one relation. Then similarly for the second component also, chemical potential of second component in phase 1 should be equals to chemical potential of second component in second phase, so those many relations are there. So, 4 relations are possible here okay. So, that is just to cross check you know whether are we missing any equilibrium relations or are we adding more equilibrium relations like that. For that purpose only this manual crosschecking we are doing.

Let us say if you have 3 phases, that is $\Pi = 3$ and then 2 components are there that is $m = 2$, then 2 + 2 multiplied by 3 - 1. So that is 4 multiplied by 2, 8 relations should be there, right? So, with respect to the temperature, you know with respect to the heat transfer process, $T^{(1)} = T^{(2)}$ that should be one relation and then another one is $T^{(1)} = T^{(3)}$, okay? So, that means $T^{(2)}$ will automatically be equals to $T^{(3)}$, so $T^{(2)} = T^{(3)}$ that will not be a kind of independent relation. It is already established.

If we are writing that one as a kind of traditional relation, so that will be we are counting it two times. If you are saying $T^{(1)} = T^{(2)}$ and $T^{(1)} = T^{(3)}$, obviously it means that $T^{(2)} = T^{(3)}$, okay? Same is for the pressure that is internal equilibrium with respect to the mechanical potential, $P^{(1)} = P^{(2)}$ and then $P^{(1)} = P^{(3)}$. So, that means, obviously, $P^{(2)} = P^{(3)}$. So, that is all you know we can see. So, how many relations are there? $\Pi - 1$ relations are there for the temperature and then $\Pi - 1$ relations are there for the pressure also.

So, Π is here you know, how many more phases are there, 3 phases, so 3 - 1 is 2, so here also 2 and then coming to the chemical potential, the system is you know having 2 components. So, for each component, μ_1 in phase 1 should be equals to μ_1 in phase 2. Similarly, $\mu_1^{(1)} = \mu_1^{(3)}$. So, that means, obviously we are saying $\mu_1^{(2)} = \mu_1^{(3)}$ indirectly, so that we cannot write as a separate relation, otherwise that will be counting one extra relation, okay?

So, $\mu_1^{(1)} = \mu_1^{(2)}$ and $\mu_1^{(1)} = \mu_1^{(3)}$ that implies that $\mu_1^{(2)} = \mu_1^{(3)}$, okay? Same for the second component $\mu_2^{(1)} = \mu_2^{(2)}$ and then $\mu_2^{(1)} = \mu_2^{(3)}$. So, that means $\mu_2^{(2)} = \mu_2^{(3)}$. That means, you know 4 relations are here also, two here that is Π - 1 into 2 components are there, component 1, we are writing 2 and then for component 2 also we are writing Π - 1 is 2 here. So, overall 8 relations are there. So, that you can crosscheck that, here total number of equilibrium relation that we get m + 2 multiplied by Π - 1, right?

So, now Gibbs phase rule what it says? The degree of freedom, degree of freedom in the sense that the minimum number of intensive variables that should be fixed in order to fix the state of equilibrium without any ambiguity that means you know you will not be having any difficulty to find out you know remaining intensive variables if you fix these many intensive variables, right?

So how to find out this intensive variables is nothing but the degree of freedom. So, that should be the number of independent variables - number or relations or restriction that is equilibrium relations, how many equilibrium relations are there? So, we have already seen Π (m + 1) number of independent variables are there. That is not the total number of variables, that is the total independent variables and then number of relations we have seen, (m + 2) (Π – 1).

So, if you subtract these two quantities, you will get degrees of freedom. So, that comes out to be F = m - Π + 2, this is nothing but the Gibb’s phase rule. But it gives information that how many minimum number of intensive variables should be fixed in order to fix the state of equilibrium for the given system, okay?

Let us say if you have a you know binary system and then two phase binary systems, so then number of degrees of freedom F should be how much, m - Π + 2 that is 2. So, what are the total number of variables, intensive variables, temperature and pressure. Let us say these phases are a vapor and liquid phases, then x_1, x_2, and then y_1, y_2 are there. But since these are only 2 components, if x_1 is known, so x_2 is already known, so this is not independent variable. Similarly, if y_1 or y_2 is known, the other one will be obviously known. So, then out of these two, only one is the independent variable, so how many independent variables are there?

Four independent variables, 4 intensive variables are there which are independent. That means, out of these 4 variables if you fix 2 that is degrees of freedom is 2. Out of these 4 variables, if you fix 2, remaining 2 you can find out using the principles of phase equilibrium without any difficulty that is what it means by this Gibb's phase rule that information this Gibb's phase rule will give you.

So, that is, out of these 4 variables, let us say temperature, pressure, x_1, and y_1. If you fix any 2, then remaining 2 you can easily find out without any difficulty using the phase equilibrium principles that is the importance of Gibb's phase rule, okay?

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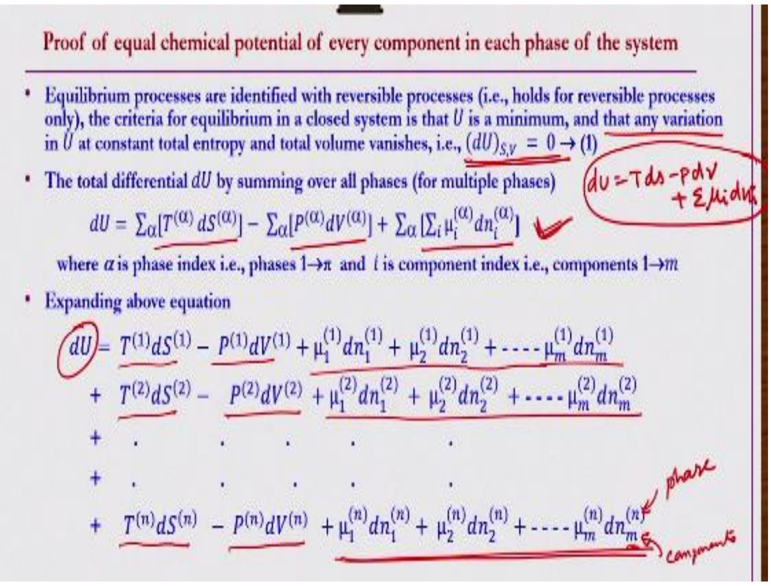

Proof of equal chemical potential of every component in each phase of the system

- Equilibrium processes are identified with reversible processes (i.e., holds for reversible processes only), the criteria for equilibrium in a closed system is that U is a minimum, and that any variation in U at constant total entropy and total volume vanishes, i.e., $(dU)_{S,V} = 0 \rightarrow (1)$
- The total differential dU by summing over all phases (for multiple phases)

$$dU = \sum_\alpha [T^{(\alpha)} dS^{(\alpha)}] - \sum_\alpha [P^{(\alpha)} dV^{(\alpha)}] + \sum_\alpha [\sum_i \mu_i^{(\alpha)} dn_i^{(\alpha)}] \checkmark$$

$du = Tds - pdV + \Sigma \mu_i dn_i$

where α is phase index i.e., phases $1 \rightarrow \pi$ and i is component index i.e., components $1 \rightarrow m$

- Expanding above equation

$$\begin{aligned} dU = {} & T^{(1)} dS^{(1)} - P^{(1)} dV^{(1)} + \mu_1^{(1)} dn_1^{(1)} + \mu_2^{(1)} dn_2^{(1)} + \cdots \mu_m^{(1)} dn_m^{(1)} \\ + {} & T^{(2)} dS^{(2)} - P^{(2)} dV^{(2)} + \mu_1^{(2)} dn_1^{(2)} + \mu_2^{(2)} dn_2^{(2)} + \cdots \mu_m^{(2)} dn_m^{(2)} \\ + {} & \quad . \qquad . \qquad . \qquad . \qquad . \\ + {} & \quad . \qquad . \qquad . \qquad . \qquad . \\ + {} & T^{(n)} dS^{(n)} - P^{(n)} dV^{(n)} + \mu_1^{(n)} dn_1^{(n)} + \mu_2^{(n)} dn_2^{(n)} + \cdots \mu_m^{(n)} dn_m^{(n)} \end{aligned}$$

phase

components

Next we see proof of equal chemical potential of every component in each phase of the system that we have been discussing for a couple of lectures, though we know that you know chemical potential of each component should be equal in each phase, can we prove it? There are you know n number of phases which are coexisting and then these n number of phases are having m number of components let us say.

So, for each component, the chemical potential should be amongst all these m phases whatever the n number of phases are there, in all these phases if you calculate the chemical potential that should be coming out equal, one constant single value for each component, can we prove that one? So, that is what we are going to do in simpler manner. There are you know n number of ways that you can find in different textbooks, but we take a one which is kind of established one.

Equilibrium processes are identified with reversible processes that we know that holds for reversible processes only, and then criteria for equilibrium in a closed system is that U is a minimum or it decreases, okay? And that any variation in U a constant, total entropy and total volume that vanishes. So that means at any variation in U at constant total entropy and total volume vanishes, that is dU at constant S, V should be 0 for reversible processes.

If it is irreversible process, then it should be less than 0, okay? This we know right, so this is true for a closed system, what you have $(dU)_{S, V} = 0$ for reversible process. If the process in the closed system is reversible, then $(dU)_{S, V} = 0$ that means there will not be any change in internal energy of the system, okay? This also we have discussed, we derived this relation in the previous lecture.

The total differential dU by summing over all phases for multiple phases, actually for one single phase what we have seen this relation is nothing but $dU = TdS - PdV + \sum_i(\mu i \; dni)$, this is what we have seen for one single phase in one of our previous lecture this we derived. Let us say there are n number of phases, multiple phases are there. So, then if you write this total derivative for the internal energy of the system, then how do you write? You write $dU = \Sigma_\alpha [T^{(\alpha)} dS^{(\alpha)}] - \Sigma_\alpha [P^{(\alpha)} \; dV^{(\alpha)}] + \Sigma_\alpha [\Sigma_i \mu_i^{(\alpha)} \; dn_i^{(\alpha)}]$.

If you write for only one phase, you will have equation this one that we have already derived in previous lecture. If you have n number of phases are coexisting and a system is a closed system and the process occurring that in the closed system is a kind of reversible process, then we have you know $dU = \Sigma_\alpha [T^{(\alpha)} dS^{(\alpha)}] - \Sigma_\alpha [P^{(\alpha)} \; dV^{(\alpha)}] + \Sigma_\alpha [\Sigma_i \mu_i^{(\alpha)} \; dn_i^{(\alpha)}]$,okay? So, now where here α in this equation is a phase index that may be changing from 1 to Π number of phases and then i stand for the component index and there are m number of components, let us say 1 to m.

Now, let us expand this equation for n number of phases and m number of components. So, for the first phase, phase 1, how you can write this equation $T^{(1)}dS^{(1)} - P^{(1)}dV^{(1)}$ and then the third term in the RHS of this equation, you know it is having several terms. That is $\mu_1^{(1)} dn_1^{(1)} + \mu_2^{(1)} dn_2^{(1)} + \mu_3^{(1)}dn_3^{(1)} + \ldots. + \mu_m^{(1)} dn_m^{(1)}$. That is in phase 1, m number of components are there. In phase 1, the superscript 1 stands for the phase 1.

In the phase 1, m number of components are there, the subscript 1, 2, 3, etc, that is number of components, m components are there. So, all that whatever the $\Sigma_i \mu_i dn_i$ is there that is what this one is for the phase 1.Similarly, if you write for the phase 2, $T^{(2)}dS^{(2)} - P^{(2)}dV^{(2)}$ and then within the second phase, m number of components are there. So, whatever the sigma $\mu_i dn_i$ for the second phase is this one, that is $\mu_1^{(2)} dn_1^{(2)} + \mu_2^{(2)} dn_2^{(2)} + \ldots + \mu_m^{(2)} dn_m^{(2)}$.

So, like that if you keep writing for n number of phases, nth phase let us say you have $T^{(n)}dS^{(n)} - P^{(n)}dV^{(n)}$ + in the nth phase, m number of components are there. Because all these m number of components are distributed among all these n number of phases and these phases are coexisting and this phase is are at equilibrium. So, then further third part is for the nth phase that is $\mu_1^{(n)} dn_1^{(n)} + \mu_2^{(n)} dn_2^{(n)} \ldots + \mu_m^{(n)} dn_m^{(n)}$. So, m stands for this number of components, n stands for the number of phases that are present, nth phase, okay?

Superscript n whatever is there that indicate for the phase okay and then subscript m1 to m etc that indicates for the components. So, this is the dU of the closed system that we have taken, okay?

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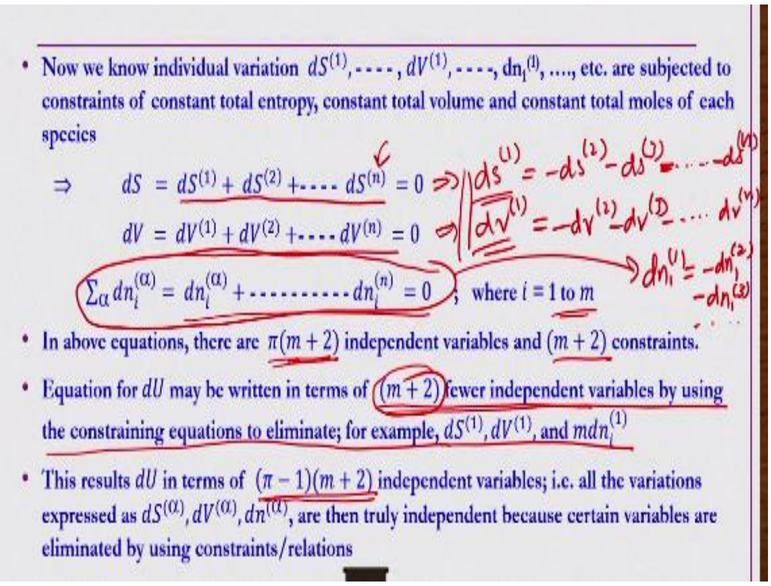

- Now we know individual variation $dS^{(1)}, ----, dV^{(1)}, ----, dn_1^{(1)}, \ldots,$ etc. are subjected to constraints of constant total entropy, constant total volume and constant total moles of each species

$$\Rightarrow \quad dS = dS^{(1)} + dS^{(2)} + \cdots dS^{(n)} = 0 \Rightarrow ds^{(1)} = -ds^{(2)} - ds^{(3)} \cdots - ds^{(n)}$$

$$dV = dV^{(1)} + dV^{(2)} + \cdots dV^{(n)} = 0 \Rightarrow \boxed{dv^{(1)}} = -dv^{(2)} - dv^{(3)} \cdots dv^{(n)}$$

$$\Sigma_\alpha dn_i^{(\alpha)} = dn_i^{(\alpha)} + \cdots\cdots dn_i^{(n)} = 0; \text{ where } i = 1 \text{ to } m \rightarrow dn_1^{(1)} = -dn_1^{(2)} - dn_1^{(3)} \cdots$$

- In above equations, there are $\pi(m+2)$ independent variables and $(m+2)$ constraints.
- Equation for dU may be written in terms of $(m+2)$ fewer independent variables by using the constraining equations to eliminate; for example, $dS^{(1)}, dV^{(1)}$, and $m dn_i^{(1)}$
- This results dU in terms of $(\pi-1)(m+2)$ independent variables; i.e. all the variations expressed as $dS^{(\alpha)}, dV^{(\alpha)}, dn^{(\alpha)}$, are then truly independent because certain variables are eliminated by using constraints/relations

Now we know individual variations that is $dS^{(1)}$, $dS^{(2)}$, etc, $dV^{(1)}$, $dV^{(2)}$, etc., dn_1 in phase 1 dn_1 in phase 2, etc are subjected to constraints of constant total entropy, constant total volume, and constant total number of moles of each species. What does it mean? That means, dS = 0 because constant entropy and then dV = 0 because constant value and then $\Sigma\ dn_i = 0$ because the total number of moles are also constant, right? And then dS is nothing but $dS^{(1)} + dS^{(2)} + dS^{(3)} \ldots + dS^{(n)}$, superscript n again for number of phases. So that should be close to 0.

Similarly for V, $dV = dV^{(1)} + dV^{(2)} \ldots + dV^{(n)} = 0$. So, similarly $\Sigma\, dn_i^{(\alpha)} = 0$ because $dn_i^{(\alpha)} \ldots dn_i^{(m)} = 0$ and then this i stands for 1 to m number of components, right? So, here in above equations, how many independent variables are there? There are m number of components and there is say m for this one and then there is S and V and how many phases are there, Π number of phases are there. So, $(m + 2)\,\Pi$ number of independent variables are there and then how many constraints are there, m + 2 constraints are there. So, because for m number of components m constraints are there like this, this is only for one component I have written like that, m component, m are there, and then two constraints are there for this S and V, so that m + 2 constraints are there, okay? But equation for dU may be written in terms of m + 2 fewer independent variables by using the constraining equations to eliminate for example $dS^{(1)}$, $dV^{(1)}$, and $mdn_i^{(1)}$ like this.

What does it mean? Let us say from here this equation you know, we have you know $dS^{(1)} = -dS^{(2)} - dS^{(3)} \ldots. - dS^{(n)}$ we can write. That means one relation is reduced. Like that you can write for $dS^{(2)}$, $dS^{(3)}$ also you can write, but you can write only for one. Similarly here also you can write let us say if I write for $dV^{(1)}$, so that should be equal to $- dV^{(2)} - dV^{(3)} - dV^{(n)}$ like this we can write, so here also one is reduced, okay?

And then likewise here also, in these relations, how many relations are there? This is nothing but m number of relations are there, from here we have m number of relations are there, okay? So, from each of this relations if you can write like you know for each one $dn_1^{(\alpha)} = - dn_1^{(2)}$ like $dn_1^{(1)} = - dn_1^{(2)} - dn_1^{(3)}$ like this you can write. So, if you count all of those variables, you can have for m number of components, m relations and then for dS, dV 2 relations.

That is m + 2 relations you can reduce, you can define that equation for dU, you can write in terms of m + 2 fewer independent as lesser, m + 2 number of those many less number of independent variables you can use for writing this dU equation by using this constraint equations so that to eliminate $dS^{(1)}$, $dV^{(1)}$, and then $mdn_i^{(1)}$ like that, okay? So, this is important one because based on this relations only whatever the way we are writing these $dS^{(1)}$ and $dV^{(1)}$ we are going to prove that you know or $T^{(1)} = T^{(2)}$, $P^{(1)} = P^{(2)}$ and then $\mu_1^{(1)} = \mu_1^{(2)}$ etc. those kind of things that we are going to prove here.

So, this results in terms of Π - 1 multiplied by m + 2 independent variables, that is, all the variations expressed as $dS^{(\alpha)}$, $dV^{(\alpha)}$, $dn^{(\alpha)}$ then truly independent because certain variables are eliminated by using constraints or relations that we have here, okay?

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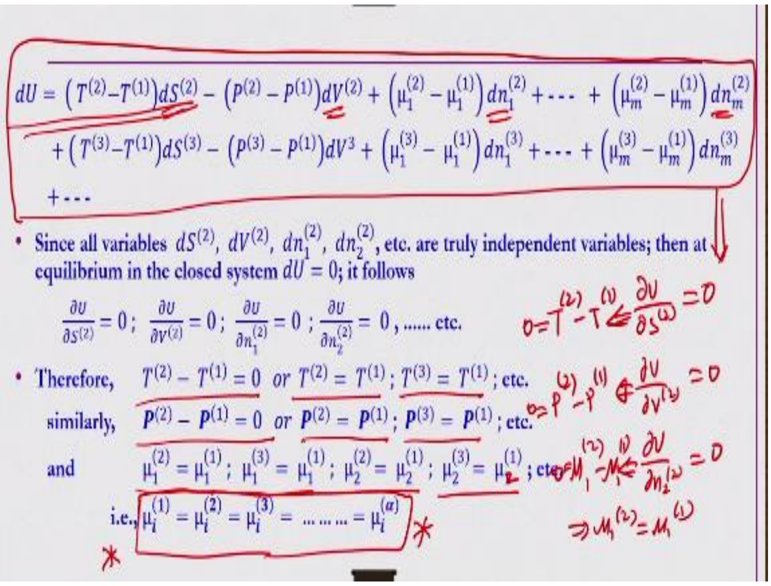

$$dU = \left(T^{(2)}-T^{(1)}\right)dS^{(2)} - \left(P^{(2)}-P^{(1)}\right)dV^{(2)} + \left(\mu_1^{(2)}-\mu_1^{(1)}\right)dn_1^{(2)} + \cdots + \left(\mu_m^{(2)}-\mu_m^{(1)}\right)dn_m^{(2)}$$
$$+ \left(T^{(3)}-T^{(1)}\right)dS^{(3)} - \left(P^{(3)}-P^{(1)}\right)dV^{3} + \left(\mu_1^{(3)}-\mu_1^{(1)}\right)dn_1^{(3)} + \cdots + \left(\mu_m^{(3)}-\mu_m^{(1)}\right)dn_m^{(3)}$$
$$+ \cdots$$

- Since all variables $dS^{(2)}$, $dV^{(2)}$, $dn_1^{(2)}$, $dn_2^{(2)}$, etc. are truly independent variables; then at equilibrium in the closed system $dU = 0$; it follows

$$\frac{\partial U}{\partial S^{(2)}} = 0;\ \frac{\partial U}{\partial V^{(2)}} = 0;\ \frac{\partial U}{\partial n_1^{(2)}} = 0;\ \frac{\partial U}{\partial n_2^{(2)}} = 0, \ldots\ldots \text{etc.}$$

$0 = T^{(2)} - T^{(1)} \Leftarrow \frac{\partial U}{\partial S^{(2)}} = 0$

- Therefore, $T^{(2)} - T^{(1)} = 0$ or $T^{(2)} = T^{(1)}$; $T^{(3)} = T^{(1)}$; etc.

  similarly, $P^{(2)} - P^{(1)} = 0$ or $P^{(2)} = P^{(1)}$; $P^{(3)} = P^{(1)}$; etc.

  and $\mu_1^{(2)} = \mu_1^{(1)}$; $\mu_1^{(3)} = \mu_1^{(1)}$; $\mu_2^{(2)} = \mu_2^{(1)}$; $\mu_2^{(3)} = \mu_2^{(1)}$; etc.

  i.e., $\boxed{\mu_i^{(1)} = \mu_i^{(2)} = \mu_i^{(3)} = \ldots\ldots\ldots = \mu_i^{(\alpha)}}$ *

$0 = P^{(2)} - P^{(1)} \Leftarrow \frac{\partial U}{\partial V^{(2)}} = 0$

$0 = \mu_1^{(2)} - \mu_1^{(1)} \Leftarrow \frac{\partial U}{\partial n_1^{(2)}} = 0$

$\Rightarrow \mu_1^{(2)} = \mu_1^{(1)}$

So, let us make use of these reduced independent variables of the eliminating certain variables by using these relations whatever the benefit is there, that benefit we make use in writing this dU. Whatever dU that we have written previously is this one, right? This is dU relation that we have written in the expanded form previously without eliminating $dS^{(1)}$, $dV^{(1)}$, etc., okay? Now what we do? We have this relation dS = 0 and $dS = dS^{(1)} + dS^{(2)} \ldots + dS^{(n)}$.

So what we can get from here $dS^{(1)} = - dS^{(2)} - dS^{(3)} \ldots - dS^{(n)}$. This dU is nothing but whatever we have done $\Sigma_\alpha T^{(\alpha)} dS^{(\alpha)} - \Sigma_\alpha P^{(\alpha)} dV^{(\alpha)} + \Sigma_\alpha \Sigma_i \mu_i^{(\alpha)} dn_i^{(\alpha)}$, this expression whatever we have for n number of phases, so that we expanded like this in one of the previous slides. So, the same thing I have written here. Now, what I am going to do in this relation, in place of $dS^{(1)}$, I am going to use this expression, okay? So, $T^{(1)} (- dS^{(2)} - dS^{(3)} \ldots - dS^{(n)})$, right?

So, first let us concentrate only temperature terms. So, then what I do now here? Already there is a $T^{(2)} dS^{(2)}$ right? $T^{(2)} dS^{(2)}$ is here and then now here $T^{(1)} (- dS^{(2)})$ is there. So, this I can write $(T^{(2)} - T^{(1)}) dS^{(2)}$, this I can write it now, right? Because now $dS^{(1)}$ is replaced by $- dS^{(2)} - dS^{(3)}$ and so on so. So, $- dS^{(2)} (T^{(1)})$ is $- T^{(1)} dS^{(2)}$. There is already $T^{(2)} dS^{(2)}$ is there. If I take $dS^{(2)}$ as common, $dS^{(2)} (T^{(2)} - T^{(1)})$ I can write. Same thing I can write for you know wherever this $T^{(3)}$ etc. are there, okay?

So, that is how we can do, okay? Now, in place of $P^{(1)}dV^{(1)}$ what I do? I will do the same thing. So, in place of $dV^{(1)}$, now I use this relation because dV = 0 that is constant volume, right? When I use this one - $dV^{(2)}$ - $dV^{(3)}$ and so on so - $dV^{(n)}$ that is what we are having. Now, already there is a $P^{(2)}$ $dV^{(2)}$, right? So, what I do you know $P^{(2)}$ $dV^{(2)}$ is there and now this $P^{(1)}$ multiplied by - $dV^{(2)}$ and there is a - 1 here. So, + $P^{(1)}$ $dV^{(2)}$, so - $P^{(2)}$ + $P^{(1)}$ $dV^{(2)}$ like this I can write, okay?

So, similarly, for the first component since the number of moles of each component are also constant in the system, so in place of $dn_1^{(1)}$ I can write - $dn_1^{(2)}$ - $dn_1^{(3)}$ and so on so - $dn_1^{(n)}$, right? So, that means, here what I do in place of this $\mu_1^{(1)}$ this is multiplied by $dn_1^{(1)}$. So, in place of $dn_1^{(1)}$ I can write - dn_1 in phase 2 - dn_1 in phase 3 and so on so - dn_1 in phase n, let us say n number of phases. So, now here, what I can say, out of these two you know, there is already $\mu_1^{(2)}$ $dn_1^{(2)}$ that I write it here.

Out of these two what I do, $\mu_1^{(2)}$ multiplied by $dn_1^{(2)}$ and then here - μ_1 $dn_1^{(2)}$ two is there, so that I can write - $\mu_1^{(1)}$ $(dn_1^{(2)})$, this is how I can write. Like this if I write for all other variables also, all other remaining terms also, then I write together them like this I will be having like this one as I proved here $T^{(2)}$ - $T^{(1)}$ $dS^{(2)}$ – $(P^{(2)}$ - $P^{(1)})dV^{(2)}$ or $(P^{(1)}$ - $P^{(2)})dV^{(2)}$ either way you can write.

So, - $(P^{(2)}$ - $P^{(1)})dV^{(2)}$ and then for the first component also μ_1 in phase 2 - μ_1 in phase 1 $(dn_n^{(2)})$ and so on so. For the m^th^ component $\mu_m^{(2)}$ - $\mu_m^{(1)}$ $dn_m^{(2)}$ like this you can write, right? So, like this if you keep on writing you know for other terms also like this, the series will continue until you write for all the terms which correspond to all the variables that are present in this system that including the number of phases and number of components, okay?

Now, what I do? The same equation I have rewritten here, whatever the equation that we have simplified in the previous slide, I have written like this. Now, dU is 0 at constant entropy, constant value, and then constant composition. That means what? Let us say $\frac{\partial U}{\partial S(2)}$ = 0 and then similarly $\frac{\partial U}{\partial \mathrm{V}(2)}$ = 0 because at the constant volume and then $\frac{\partial U}{\partial \mathrm{n}(2)}$ = 0 and then $\frac{\partial U}{\partial S(2)}$ from this relation what you get? You will get $T^{(2)}$ - $T^{(1)}$. Similarly, using the same relation if you do $\frac{\partial U}{\partial \mathrm{V}(2)}$ what you will get? You will get $P^{(2)}$ - $P^{(1)}$ and likewise if you $\frac{\partial U}{\partial \mathrm{n}(2)}$, then you will get $\mu_1^{(2)}$ -

$\mu_1^{(1)}$, this is what you get. So, since this is 0, so this should also be 0, this should also be 0 and this should also be 0. So, that means, if $T^{(2)} - T^{(1)} = 0$ that meant $T^{(2)} = T^{(1)}$. Similarly, you will get $T^{(3)} = T^{(1)}$, $T^{(4)} = T^{(1)}$ like that you get so many relations for all the terms and then since $P^{(2)} - P^{(1)} = 0$, you will get $P^{(2)} = P^{(1)}$.

Likewise if you do for other terms, $P^{(3)}$ also you will get as equals to $P^{(1)}$ and then $P^{(4)}$ will also be equals to $T^{(1)}$, like that you will get so many other equilibrium relations, right? Similarly, μ_1 in 2 should be equals to μ_1 in 1 that you will get because from here μ_1 in 2 is nothing but μ_1 in 1 from here from this relation. Similarly, μ_1 in 3 should be equals to μ_1 in 1, phase 1.

Similarly, like that other components also if you do the μ_2 in phase 2 = μ_2 in phase 1 and then μ_2 in phase 3 = μ_2 in phase 1 and so on so like that so many relations you will get depending on the number of components and number of phases that are present in the system. So, what does it mean? That means here from this relations, you can get μ_i in phase 1 = μ_i in phase 2 = μ_1 in phase 3 = and so on so μ_i in phase α if there exists α number of phases or Π number of phases or n number of phases whatever you call.

Now it says that you know chemical potential of each component is same in all the phases which are coexisting and are at equilibrium. So, that we have proved it. In addition to this one, we have also proved that you know if the processes in internal equilibrium with respect to heat transfer, temperature in all the phases is equal and then also if the process is at internal equilibrium with respect to the displacement of volume, that is mechanical equilibrium is existing then pressure in all phases should also be equal, that is also we have proved here.

In addition to that, whatever the chemical potential of each component in all the phases should be equal. So, other thermal equilibrium and mechanical equilibrium relations are also proved. So, at equilibrium, whatever the thermal equilibrium, mechanical equilibrium, and chemical equilibrium relations are there, all of them are proved here. So, now, it is no ambiguity or there is no confusion that the chemical potential of each component in all phases which are coexisting should be equal. So, that we have proved.

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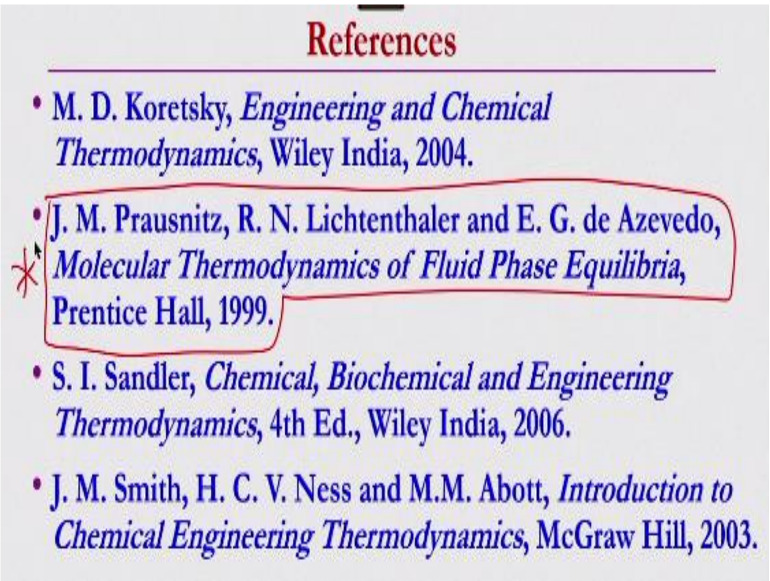

References

- M. D. Koretsky, *Engineering and Chemical Thermodynamics*, Wiley India, 2004.
- * J. M. Prausnitz, R. N. Lichtenthaler and E. G. de Azevedo, *Molecular Thermodynamics of Fluid Phase Equilibria*, Prentice Hall, 1999.
- S. I. Sandler, *Chemical, Biochemical and Engineering Thermodynamics*, 4th Ed., Wiley India, 2006.
- J. M. Smith, H. C. V. Ness and M.M. Abott, *Introduction to Chemical Engineering Thermodynamics*, McGraw Hill, 2003.

The references for this lecture are you know Engineering and Chemical Thermodynamics by Koretsky. Then, Molecular Thermodynamics of Fluid Phase Equilibrium by Prausnitz et al. and Chemical, Biochemical and Engineering Thermodynamics by Sandler. An introduction to Chemical Engineering Thermodynamics by Smith et al. However, the details that are present in this lecture can be found in this particular reference that is Prausnitz et al.

Thank you.