

Course on Phase Equilibrium Thermodynamics

By Professor Gargi Das

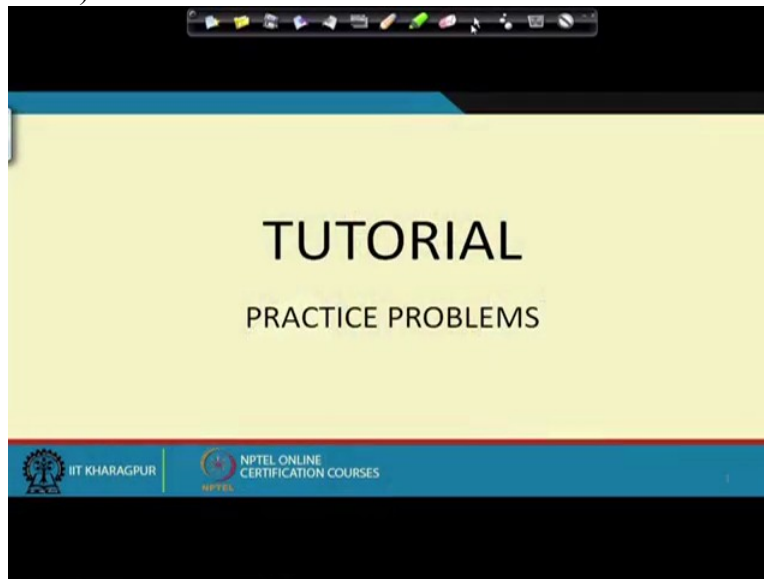
Department of Chemical Engineering

Indian Institute of Technology Kharagpur

Lecture 25

Tutorial

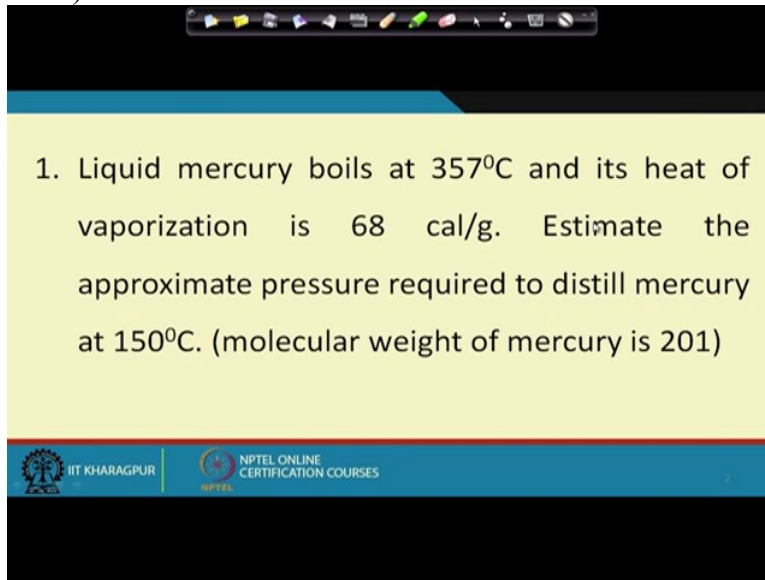
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Well, so today we have come to the to the tutorial after the 4th week. So we are already halfway through the thermodynamics course. I believe you must have faced quite a number of doubts and we have also got some very interesting clarification and doubts and questions from your side. We welcome much more questions on this. In fact, we would also welcome suggestions from you regarding **(ex)** explaining once more some portions which were not very clear or maybe certain portions which you think had become more difficult and you would like to have, like me to explain it once more.

It will be good if you can put up all the suggestions on the portal. We will try to accommodate them as much as possible. Now coming to the tutorial after the end of the 4th week. Means we are already halfway through and this is the tutorial particularly pertaining to the next week.

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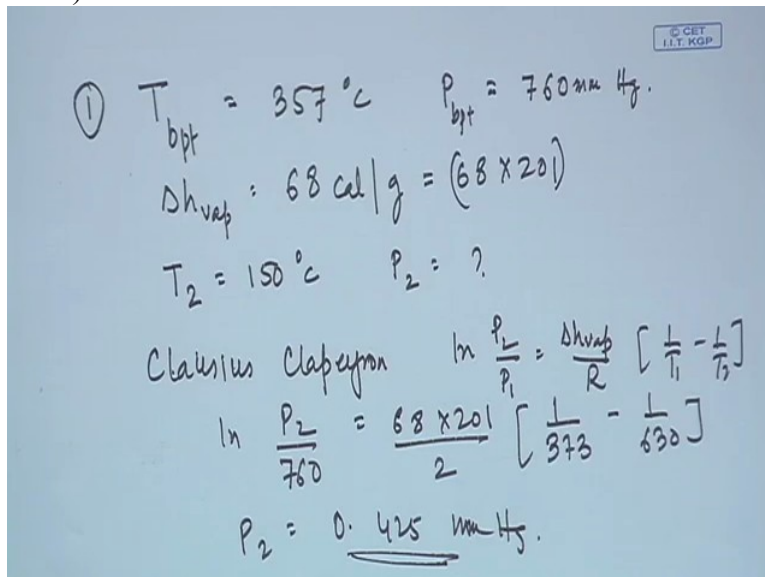


1. Liquid mercury boils at 357°C and its heat of vaporization is 68 cal/g. Estimate the approximate pressure required to distill mercury at 150°C. (molecular weight of mercury is 201)

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So in this particular, the 1st problem is that let us say **this** this problem how **how** do we handle this particular problem? What does it say? It says that liquid mercury it boils at about 357 degree centigrade.

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① $T_{bpt} = 357^{\circ}\text{C}$ $P_{bpt} = 760 \text{ mm Hg}$
 $\Delta h_{vap} = 68 \text{ cal/g} = (68 \times 201)$
 $T_2 = 150^{\circ}\text{C}$ $P_2 = ?$
Clausius Clapeyron $\ln \frac{P_2}{P_1} = \frac{\Delta h_{vap}}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$
 $\ln \frac{P_2}{760} = \frac{68 \times 201}{2} \left[\frac{1}{373} - \frac{1}{423} \right]$
 $P_2 = \underline{0.425 \text{ mm Hg}}$

So therefore the problem 1, the boiling point of mercury that is given as 357 degree centigrade. Heat of vaporisation is also given in calories per gram, mind it. So therefore **it is not it** just note that this particular heat of vaporisation which is given, this is given as the specific latent heat of vaporisation and not the molar latent heat. So therefore you have to keep it in mind that you are

going to convert this to the **latent to the** molar latent heat of vaporisation by multiplying it with the molecular weight of mercury which is 201.

And then it is given, it is required that the pressure which is required to distill mercury at 150 degrees centigrade. So therefore we know that at the boiling point of mercury, naturally it is going to have the saturated vapour pressure, right? So therefore, at the P at this particular boiling point, this is nothing but equal to 760 millimetres mercury and we want to distill mercury not at the boiling point but at 150 degree centigrade.

So therefore T2 that is 150 degrees centigrade and we would like to find out what is the approximate pressure required for this particular distillation. Now you know that from the data which is given, you are given the boiling point, the corresponding saturation vapour pressure which is known to you, your latent heat of vaporisation is given. If you assume that the latent heat of vaporisation does not change from 150 degrees centigrade to 357 degrees centigrade which is definitely as we have already discussed is quite a drastic assumption but nevertheless, we make this assumption to for simpler calculations.

Then in that case, we find that the Clausius–Clapeyron equation can be quite suitable for it. What is the Clausius–Clapeyron equation let us recall. We **had, I** had already discussed the Clausius–Clapeyron equation in the class. It was $\ln P_2 \text{ by } P_1 \text{ is equal to } \Delta H \text{ vaporisation by } R \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$. Is not it? So therefore if we use this, we find that we are required to find out P2. We know T1 right?

ΔH vaporisation, this has to be 68 into 201 and this is given in calories. So therefore the corresponding R also has to be taken in calories. So therefore this is 2 and 1 by T1 is 1 by 373 minus 1 by 630 right? So therefore if you solve this out, then what do you find? On solving this out what do we find? We find that we get P2 as 0.425 millimetres mercury. So therefore we find that this is the required pressure which is required to distil mercury at 150 degrees centigrade.

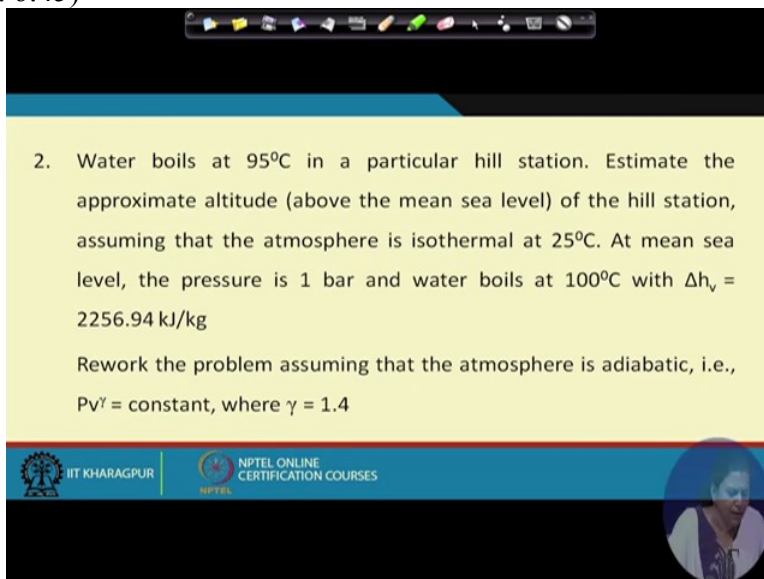
This was quite a direct Clausius–Clapeyron equation and let me tell you **that** that you will be given some such direct applications of Clausius–Clapeyron equation in assignments and then possibly will be evaluated also on the basis of these particular problems which are done in the class. I would like to mention that whatever evaluation process we take up, that is at the final

semester exam or the final test that we take, more or less you will be dealing with whatever problems have been done in the class, the problems or the questions which are asked in the assignments.

One more thing also I would like to tell you that in the course of phase equilibrium thermodynamics for the last 4 weeks, you must have faced problems by because **you** you had to deal with a large number of formulae for estimation of properties and maybe several gas laws and several other equations. Now **we would be** you will be required definitely to remember certain simple equations. For example, Clausius–Clapeyron equation you are supposed to remember all or it is not very difficult to derive it.

Ideal gas equation, Vander Wal's equation you have been doing for a very long time. I suppose you already know these equations by heart. But all the difficult equations, say Maxwell's equations and several such equations, they **they** will be posted before your test and you can refer to those particular equations when during a test season but it is not a bad practice to remember some of these equations for your future usage of thermodynamics right? So therefore this was one particular application of Clausius–Clapeyron equation.

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2. Water boils at 95°C in a particular hill station. Estimate the approximate altitude (above the mean sea level) of the hill station, assuming that the atmosphere is isothermal at 25°C. At mean sea level, the pressure is 1 bar and water boils at 100°C with $\Delta h_v = 2256.94 \text{ kJ/kg}$

Rework the problem assuming that the atmosphere is adiabatic, i.e., $Pv^\gamma = \text{constant}$, where $\gamma = 1.4$

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②a. $T_2 = 95^\circ\text{C}$
 $T_1 = 100^\circ\text{C}$

P_2
 P_1] ρgh
 $(P_2 - P_1)A = \rho gh$

$P_v = \text{constant}$ $P_2 V_2$ at the altitude $= P_1 V_1$ sea level.

$\ln \frac{P_2}{P_1} = \frac{\Delta h_{\text{vap}}}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] = \frac{2256.96 \times 10^3 \text{ J/kg}}{8.314} \left(\frac{1}{373.15} - \frac{1}{368.15} \right)$

$= -0.1778$

Now let us go to the next problem. A slightly more involved problem. What does it tell you? It tells you that water boils at 95 degrees centigrade in a particular hill station, right? We know that at the mean sea level, water boils at 100 degrees centigrade. So therefore, definitely the pressure on the top of the hill station is quite high as compared to the sorry it is quite low as compared to the pressure at the sea level., right?

So therefore, we know that at the sea level, the pressure the water boiling point, this is 100 degrees centigrade and here, the boiling point is 95 degrees centigrade. Why does this happen? Why is the boiling point difference? Naturally because the pressure here has to be lower as compared to the pressure here. What makes the difference in pressure between the 2 places? It is naturally the difference in height between the 2 places.

So definitely, between P_1 and P_2 , there is a difference in height which brings about the difference in pressure, isn't it? So therefore, this arises due to ρgh of the air column between the 2, is not it? So therefore, from here we know that P_2 minus P_1 into A will should definitely be equal to ρgh right? So therefore due to this particular altitude difference, there is a pressure difference which brings about the difference in the boiling points.

And **you are** here the question which is there, you are asked to estimate the approximate altitude and the 2 conditions. What are the 2 conditions? 1st condition is atmosphere is isothermal. What does it imply? It implies that in the atmosphere, PV equals to constant. Or in other words, that V

is this molar volume or in other words, your P_2V_2 at the altitude is equal to say P_1V_1 at the sea level. So this one information is given.

Possibly if we are going to use this information in order to express P_2 in terms of P_1 and then relate this particular equation to from the basic force balance equation to find out H . This is problem 1 and the problem 2 is to repeat the whole thing if the atmosphere is adiabatic. Let us deal with problem 2 part A first and then we go to part B, right? So here again use the same equation $\ln P_2$ by P_1 this is equal to $\Delta H_{\text{vaporisation}}$ by R I had already written it down earlier $\frac{1}{T_1} - \frac{1}{T_2}$, fine?

Now here we know everything except P_2 . This is the only unknown that we have. You find other than that, we know everything. What is P_1 equals to? P_1 is at this P_1 it is the atmospheric pressure. So therefore, from here we know and $\Delta H_{\text{vaporisation}}$ it is also given. It is given as 2256.94. In this case, just note that it is given in kilojoules per kg right? So it is better you convert it to joules because we know R in terms of joules.

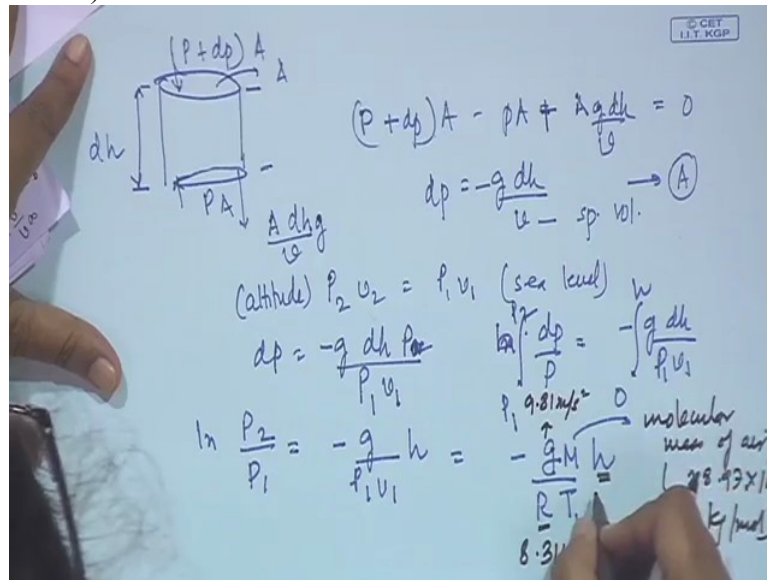
So therefore, this becomes into 10 to the power 3 joules per kg, right? So therefore this is 2256.96 into 10 to the power 3 joules per kg. Accordingly your R this is going to be 8.314. Again in this case, you note that the latent heat of vaporisation is the specific latent heat, it is not the molar latent heat. But in this case, you note that it is the substance or the fluid in between it is air.

So therefore what do we do? We simply multiply it with the molecular weight, the average molecular weight we assume and from here I am just substituting T_1 and T_2 minus 1 by 368.15. Just note certain things, when you are doing these problems, firstly T_1 and T_2 even when they are given degrees centigrade, they have to be converted to Kelvin, the absolute scale temperature.

Next thing is please note the unit in which $\Delta H_{\text{vaporisation}}$ is expressed. If it is expressed as per kg, we are required to convert it to per mole. If it is and also note the unit in which $\Delta H_{\text{vaporisation}}$ is expressed, you are required to express R also in the same units, right? So from here you know that $\ln P_2$ by P_1 this is equals to minus 0.1778, right?

What are you required to find out? You are required to find out the height difference when you know the **the** ratio of the pressures or the pressure difference between the 2 right? So you need one more equation to relate the pressure difference to the altitude of that particular place. From physics, we know how we are supposed to these.

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We take an infinitesimal volume element say. From the infinitesimal volume element, this is say the infinitesimal volume element right? And in this infinitesimal volume element the cross-sectional area is say A , the small height is say dh , here the **the** pressure suppose it is say P plus DP into A . Here the pressure is P into A . And this pressure is acting here. And we find that **the** the weight of the fluid which is **which is** acting downwards what is it? It is Adh , the volume into divided by the specific volume into g right?

So therefore for **for** this particular volume we know that since there is no acceleration, so from force balance what we get? From force balance, we get, this is going to be P plus dP minus P into A , this is equals to $Agdh$ by V . Or in other words, it is better you write it down in this way. This is equal to 0. Is not it? So P plus dP into A minus PA plus this, this is the pressure force and this is the gravitational force, this equals to 0.

From where we **we** get, dP is nothing but minus gdh by V . Please note that V is nothing but the specific volume, right? Now for isothermal conditions, what do we know? We know as I have

told you, P_2V_2 equals to P_1V_1 where P_1V_1 refers **to this** to the sealevel, this refers to the sea level and this refers to the height above the altitude. Agreed? So therefore can we not write down this particular equation, say equation A if we can substitute dP , we find that this equation dP , this gives you as this is gdh by or rather gdh by P_1V_1 is not it?

From where, we find that sorry this is $P \cdot L$ or dP by P this is nothing but equal to minus gdH by P_1V_1 integral from 0 to H and this integral extends from P_1 at the sea level to P_2 at the altitude h ? So from here what do we get? We get $\ln P_2$ by P_1 this is equals to minus g by P_1V_1 into h agreed? And we know that P_1V_1 since it is since for this particular case, **we can** we can easily write express it as g by RT_1 , the temperature here into M into h where we know what is M .

M is nothing but the molecular mass of air right? It is the molecular weight or the molecular mass of air. What is this equal to? 28.97 into 10 to the power minus 3 kg per mole. This is the molecular weight of air right? g also you know it is the acceleration due to gravity. In SI units, this is going to be 9.81 metre per second square fine? You are supposed to find out h . R accordingly you have to substitute R in the variant equations.

So therefore in this particular case, R is going to be 8.314 in terms of joules and your molar mass I have said, so therefore now equating $\ln P_2$ by P_1 we have already obtained $\ln P_2$ by P_1 in this particular case if you see.

(Refer Slide Time: 17:12)

$P_v = \text{constant}$ at the altitude

$$\ln \frac{P_2}{P_1} = \frac{\Delta h_{\text{vap}}}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] = \frac{2256 \times 10^3 \times 18 \times 10^{-3}}{8.314} \left(\frac{1}{373.15} - \frac{1}{368.15} \right)$$

$$= -0.1778$$

$$-0.1778 =$$

$$\ln \frac{P_2}{P_1} = -\frac{g}{P_1 v_1} h = -\frac{g M}{R T_1} h$$

molecular mass of air $(28.97 \times 10^{-3} \text{ kg/mol})$

②a. $T_2 = 95^\circ\text{C}$
 $T_1 = 100^\circ\text{C}$

$\frac{P_2}{P_1} = \frac{P_2}{P_1} = \frac{P_2}{P_1} = \frac{P_2}{P_1}$

$P_v = \text{constant}$ at the altitude

$$\ln \frac{P_2}{P_1} = \frac{\Delta h_{\text{vap}}}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] = \frac{2256 \times 10^3 \times 18 \times 10^{-3}}{8.314} \left(\frac{1}{373.15} - \frac{1}{368.15} \right)$$

$$= -0.1778$$

$$-0.1778 = -\frac{9.81 \times 28.97 \times 10^{-3} \times h}{8.314 \times 298.15}$$

$h = 1550.8$

$$\begin{aligned}
 T_1 &= 100^\circ\text{C} & P_1 &= P_2 \\
 (P_2 - P_1)A &= \rho g h \\
 P_0 &= \text{constant} & P_2 u_2 &= P_1 u_1 \text{ (at the altitude)} \\
 \ln \frac{P_2}{P_1} &= \frac{\Delta h_{\text{vap}}}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] = \frac{2256 \times 10^3 \text{ J/kg}}{8.314} \left(\frac{1}{373.15} - \frac{1}{368.15} \right) \\
 &= -0.1778 \\
 -0.1778 &= \frac{9.81 \times 28.97 \times 10^{-3} \times h}{8.314 \times 298.15} \quad | h = 1550.8 \text{ m}
 \end{aligned}$$

This is equals to minus 0.1778. So we can relate the 2. Minus 0.1778 this will be equal to this particular portion here, so we can substitute all the terms here. This is equals to 9.81 into 28.97 into 10 to the power minus 3 into h divided by 8.314 into the temperature 298.15. So from here, what do you get? You get h equals to 1550.8 metres. Well I will **I I will I will I will** write it slightly more.

This is 1550.8 meters, right? So therefore what did you do in this case? In this particular case, basically using Clausius–Clapeyron equation you found out what should be $\ln P_2$ by P_1 equals to right? And then what you did? You perform the force balance here. From the force balance, equating the forces which is acting on this particular infinitesimal volume of air of cross-sectional area A and height dh, the forces which are acting on it are the pressure forces which act due to the pressure difference and this is balanced by the force of gravity on this particular volume element.

(Refer Slide Time: 18:50)

Diagram of a fluid element of height dh and cross-sectional area A . The forces acting on it are pressure P at the bottom, pressure $(P+dp)$ at the top, and weight $A \rho dh g$ acting downwards.

$$(P+dp)A - PA + \frac{A \rho dh g}{\rho} = 0$$

$$dp = -\frac{g dh}{\frac{1}{\rho} - \text{sp. vol.}} \rightarrow (A)$$

(altitude) $P_2 V_2 = P_1 V_1$ (see level)

$$dp = -\frac{g dh P \rho}{P_1 V_1}$$

$$\ln \frac{P_2}{P_1} = -\frac{g}{P_1 V_1} h = -\frac{g M}{R T_1} h$$

where $g = 9.81 \text{ m/s}^2$, $M = \text{molecular mass of air} = 28.97 \times 10^{-3} \text{ kg/mol}$, and $R = 8.314 \text{ J/mol}\cdot\text{K}$.

So accordingly, from this particular force balance, you get this equation. And then the only thing which is given to you connecting dP and V is that the air column or the atmosphere behaves as **an I be its** it is in under isothermal conditions. So from there, you get this particular equation for relating dP and V . Accordingly you make the relationships and from here, you get this particular equation.

(Refer Slide Time: 19:21)

Diagram of a fluid element of height dh and cross-sectional area A . The forces acting on it are pressure P at the bottom, pressure $(P+dp)$ at the top, and weight $A \rho dh g$ acting downwards.

$$(P+dp)A - PA + \frac{A \rho dh g}{\rho} = 0$$

$$dp = -\frac{g dh}{\frac{1}{\rho} - \text{sp. vol.}} \rightarrow (A)$$

(altitude) $P_2 V_2 = P_1 V_1$ (see level)

$$dp = -\frac{g dh P \rho}{P_1 V_1}$$

$$\ln \frac{P_2}{P_1} = -\frac{g}{P_1 V_1} h = -\frac{g M}{R T_1} h$$

where $g = 9.81 \text{ m/s}^2$, $M = \text{molecular mass of air} = 28.97 \times 10^{-3} \text{ kg/mol}$, and $R = 8.314 \text{ J/mol}\cdot\text{K}$.

$h \approx 1550.8 \text{ m}$

Handwritten derivation on a whiteboard:

Diagram of a fluid element of height dh and area A . Forces shown: $(P+dp)A$ (top), PA (bottom), and $A \cdot dh \cdot g$ (weight).

$$(P+dp)A - PA + \frac{A \cdot dh \cdot g}{g} = 0$$

$$dp = -\frac{g \cdot dh}{v_{sp}} \quad \text{--- sp. vol. ---} \quad \text{--- (A) ---}$$

(altitude) $P_2 v_2 = P_1 v_1$ (sex level)

$$dp = -\frac{g \cdot dh \cdot P}{P_1 v_1}$$

$$\ln \frac{P_2}{P_1} = -\frac{g}{P_1 v_1} h = -\frac{g \cdot M}{R \cdot T_1} h$$

Annotations: $P_1 = 9.81 \text{ m/s}^2$, $M = \text{molecular mass of air} = 28.97 \times 10^{-3} \text{ kg/mol}$, $R = 8.314$.

Final result: $h = 1550.8 \text{ m}$

Now this I have find, you have 2 equations for $\ln P_2$ by P_1 . One is this equation, one is this equation. Simply equate the 2 equations and you get h . Now this was for the 1st part of the problem. What about the 2nd part? The 2nd part, it is slightly involved.

(Refer Slide Time: 19:36)

2. Water boils at 95°C in a particular hill station. Estimate the approximate altitude (above the mean sea level) of the hill station, assuming that the atmosphere is isothermal at 25°C . At mean sea level, the pressure is 1 bar and water boils at 100°C with $\Delta h_v = 2256.94 \text{ kJ/kg}$

Rework the problem assuming that the atmosphere is adiabatic, i.e., $Pv^\gamma = \text{constant}$, where $\gamma = 1.4$

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Qa. $T_2 = 95^\circ\text{C}$ P_2
 $T_1 = 100^\circ\text{C}$ P_1 $\left. \begin{matrix} P_2 \\ P_1 \end{matrix} \right\} \rho g h$
 $(P_2 - P_1)A = \rho g h$

$P_v = \text{constant}$ $P_2 v_2 = P_1 v_1$ at the altitude $P_1 v_1$ (sea level).

$\ln \frac{P_2}{P_1} = \frac{\Delta h_{\text{vap}}}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] = \frac{2256 \times 10^3 \text{ J/kg}}{8.314} \left[\frac{1}{373.15} - \frac{1}{368} \right]$
 $= -0.1778$ $\left(\frac{1}{373.15} - \frac{1}{368} \right)$

$-0.1778 = - \frac{9.81 \times 28.97 \times 10^{-3} \times h}{8.314 \times 299.15}$ $h = 1550$

It is said that the atmosphere instead of behaving isothermally, it behaves adiabatically and the gamma is given. So therefore in this particular case, we find that the relationship between, the Clausius–Clapeyron equation, that particular equation it is **it is** applicable in this case, no matter whether the atmosphere behaves under isothermal or adiabatic conditions. So for part B, definitely we can take up this particular portion.

(Refer Slide Time: 20:09)

Diagram: A cylinder of cross-section A and height dh . The top surface is at pressure $(P + dp)$ and the bottom surface is at pressure P . The weight of the cylinder is $A dh \rho$.

$(P + dp)A - PA + \frac{A dh \rho}{\rho} = 0$
 $\Rightarrow dp = -g dh$ \rightarrow (A)
 $\frac{dp}{P} = - \frac{g dh}{\frac{P}{\rho}}$ $\frac{dp}{P} = - \frac{g dh}{\frac{P}{\rho}}$ $\frac{dp}{P} = - \frac{g dh}{\frac{P}{\rho}}$

(altitude) $P_2 v_2 = P_1 v_1$ (sea level)
 $dp = - \frac{g dh P}{P_1 v_1}$ $\frac{dp}{P} = - \frac{g dh}{P_1 v_1}$ $\frac{dp}{P} = - \frac{g dh}{P_1 v_1}$

$\ln \frac{P_2}{P_1} = - \frac{g}{P_1 v_1} h$ $\frac{dp}{P} = - \frac{g dh}{P_1 v_1}$ $\frac{dp}{P} = - \frac{g dh}{P_1 v_1}$ $\frac{dp}{P} = - \frac{g dh}{P_1 v_1}$

$h \approx 1550.8 \text{ m}$

(b) $\ln \frac{P_2}{P_1} = -0.1778$ (Clausius-Clapeyron eqn)
 $dp = -\frac{g dh}{v}$
 $P_1 V_1^\gamma = P_2 V_2^\gamma$
 $dp = P_1 V_1^\gamma (-\gamma) V_1^{-(\gamma+1)} dV \rightarrow$
 $\rightarrow P_1 V_1^\gamma V_1^{-(\gamma+1)} dV = -\frac{g dh}{v}$
 $V^{-\gamma} dV = \frac{g dh}{P_1 V_1^\gamma}$
 $\left(\frac{P_1}{P_2}\right)^{\frac{\gamma-1}{\gamma}} = 1 + \left(\frac{-\gamma}{\gamma}\right) \frac{g h}{P_1 V_1^\gamma}$

And we can write down for part B, $\ln P_2$ by P_1 equals to minus 0.1778 this we have obtained from Clausius–Clapeyron equation right? This we already know. Now for force balance, the in the same way that we had done the force balance here, in the same way we can perform the force balance, same approach and we get this equation as well. So we write down this equation also, this equation is dP equals to minus gdh by V .

The only thing comes that when you want to relate P and V , then in the last problem you had tried to relate them assuming the atmosphere to be isothermal, now you will be trying to relate them assuming the atmosphere to be under adiabatic condition. So in the previous problem, the relationship was $P_2 V_2$ equals to $P_1 V_1$, in this particular case, the relationship is as you know, it is $P_1 V_1^\gamma$ equals to $P_2 V_2^\gamma$ right?

This is the only equation that you are going to use. This is the only difference from the previous problem but naturally, the calculations become slightly involved in this particular case. So therefore if we if you are proceeding in the same way, we find that in this particular case, dP equals to $P_1 V_1^\gamma$ the power γ minus γ V to the power minus γ plus 1 into dV , just the same way that we had **we we had** proceeded in the previous case, we do it and then we substitute this particular equation in this equation right?

When we substitute, just substitute it and then you see what you get. The equation is going to be something of minus γ $P_1 V_1$ to the power γ V to the power minus γ plus 1 dV

will be equal to minus dh by V . Or we can write it down as V the power minus γ dV equals to gdh $\gamma P_1 V_1$ to the power γ , right? So you **can you** can keep on expanding it and finally when you expand it, you find that V_2 by V_1 to the power 1 minus γ , this is equal to 1 plus 1 minus γ by γgh by $P_1 V_1$.

You can again elaborate it **for** further. This V_2 by V_1 to the power γ we can always write it write it down as P_1 by P_2 to the power γ minus 1 by γ , these are all adiabatic equations. This can be written down then as 1 plus 1 minus γ by $drama$, the same thing that I have written down here gh by $P_1 V_1$ right? So therefore from here, what do we get?

(Refer Slide Time: 23:31)

$$\frac{P_2}{P_1} = \left[1 + \left(\frac{1-\gamma}{\gamma} \right) \frac{gh}{P_1 V_1} \right]^{\frac{\gamma}{\gamma-1}}$$

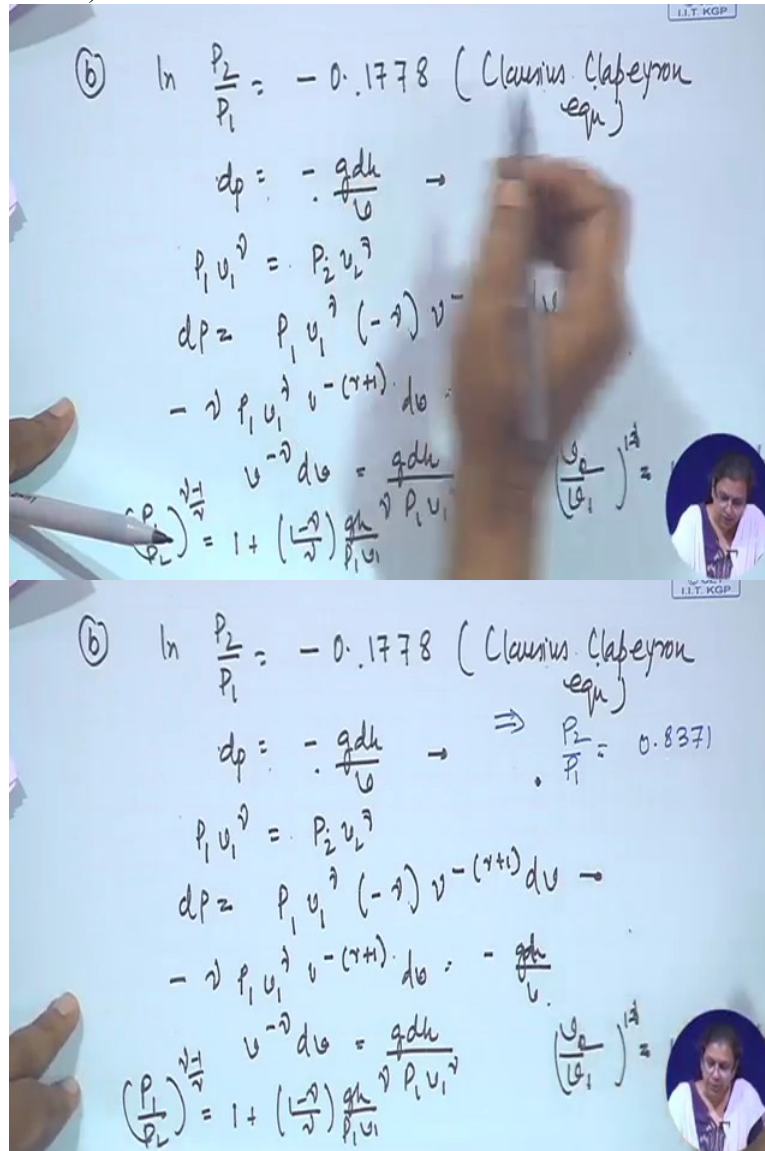
$\rightarrow RT_1/M$

$$\frac{P_2}{P_1} = 1 - \frac{0.4 \times 9.81 \times 28.97 \times 10^3}{1.4 \times 8.314 \times 298.15}$$

We get from here that P_2 by P_1 , this is simply 1 plus the reciprocal of the thing which I had written down there, gh by $P_1 V_1$ whole to the power γ by γ minus 1 right? And from there, I get $\ln P_2$ by P_1 . I can **I can** very well substitute everything here. Now **instead of P** just like I had done in the previous case, instead of $P_1 V_1$ I can substitute it with RT_1 . For 1 mole, this is going to be RT_1 by M . And therefore I can **I can** from here I can very well write, this I will write later. From here, I can very well write this down as P_2 by P_1 equals to substituting all the values we are going to get 1 minus γ is 0.4 because γ is 1.4 as it is mentioned.

g is equal to 9.81 just like the previous case, molecular mass is 28.97 into 10 to the power minus 3 into h this divided by gamma which is 1.4 into R 8.314 into T which is 298.15, the room temperature. So simply substitute it and this we know, this is $\ln P_2$ by this is P_2 by P_1 .

(Refer Slide Time: 25:17)



⑥ $\ln \frac{P_2}{P_1} = -0.1778$ (Clausius-Clapeyron eqn)

$$dp = - \frac{g dh}{v}$$

$$P_1 v_1^\gamma = P_2 v_2^\gamma$$

$$dp = P_1 v_1^\gamma (-\gamma) v^{-\gamma-1} dv$$

$$-\gamma P_1 v_1^\gamma v^{-\gamma-1} dv = - \frac{g dh}{v}$$

$$v^{-\gamma} dv = \frac{g dh}{\gamma P_1 v_1^\gamma}$$

$$\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} = 1 + \left(\frac{\gamma-1}{\gamma} \right) \frac{g h}{P_1 v_1^\gamma}$$

⑥ $\ln \frac{P_2}{P_1} = -0.1778$ (Clausius-Clapeyron eqn)

$$dp = - \frac{g dh}{v} \Rightarrow \frac{P_2}{P_1} = 0.8371$$

$$P_1 v_1^\gamma = P_2 v_2^\gamma$$

$$dp = P_1 v_1^\gamma (-\gamma) v^{-\gamma-1} dv$$

$$-\gamma P_1 v_1^\gamma v^{-\gamma-1} dv = - \frac{g dh}{v}$$

$$v^{-\gamma} dv = \frac{g dh}{\gamma P_1 v_1^\gamma}$$

$$\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} = 1 + \left(\frac{\gamma-1}{\gamma} \right) \frac{g h}{P_1 v_1^\gamma}$$

Handwritten derivation on a whiteboard showing the Clausius-Clapeyron equation and its application to find altitude h .

$$\frac{P_2}{P_1} = \left[1 + \left(\frac{1-\gamma}{\gamma} \right) \frac{g h}{P_1 v_1} \right]^{\gamma/(\gamma-1)}$$

Below the equation, a note indicates $R T_1 / M$ is the value for $\frac{g h}{P_1 v_1}$.

$$\frac{P_2}{P_1} = 1 - \frac{0.4 \times 9.81 \times 28.97 \times 10^{-3} \times h}{1.4 \times 8.314 \times 298.15}$$

$$0.8371 = \left[1 - 3.2755 \times 10^{-5} h \right]^{3.5}$$

The final result is boxed:

$$h = 1512.3 \text{ m}$$

And from Clausius–Clapeyron we had obtained $\ln P_2$ by P_1 equals to this. From here, we get P_2 by P_1 this is equals to 0.8371. So I can very well equate this P_2 by P_1 with the value which I have got here, I can equate both the values, this is equals to 1 minus 3.2755 into 10 to the power minus 5 into h whole to the power 3.5 right? So from here, I get h equals to 1512.3 metres.

So you find in order to find the altitude, it depends upon if the atmosphere is behaving isothermally or if the atmosphere is behaving adiabatically, it is this portion simply matters when we try to relate the pressure and the specific volume. And for this particular equation, it is important to consider the atmosphere in one particular state but other than that, the rest of the problem is same for part 2A and 2B. We need to perform a force balance in order to relate your height with the pressure and then we need to perform or rather we need to find out the ratio between the pressures from Clausius–Clapeyron.

And equating the Clausius–Clapeyron equation with the force balance equation where we have made necessary corrections **as** by considering the atmosphere 1st as isothermal and then as adiabatic and after that equating, we find out the altitude. So therefore, this is one particular way by which you can find out the altitude provided the altitude is high enough to bring about a reasonable difference in the boiling point of water right?

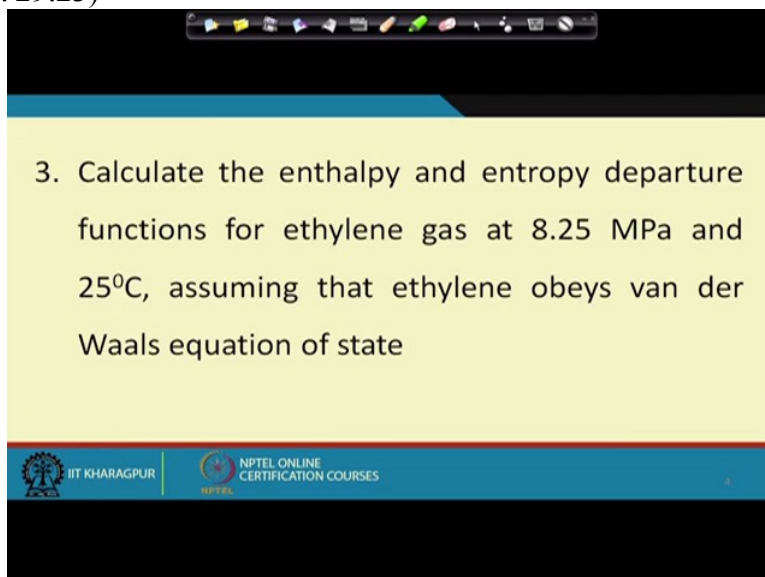
So now we go to the next problem. We had enough of Clausius–Clapeyron. So at the moment, we would go for some property estimations. Now in this regard, I would like to tell you that we have already discussed property estimations and we found out that there are several equations

and when we do not know exactly which equation the gas obeys, then under that condition, we either refer to the compressibility factor chart or we refer to the reduced coordinate charts which expressed ΔH^* and ΔS^* in terms of a unique function of reduced temperature and pressure.

Now mostly in industries, we find that the charts, they are **very** very much used but since it is difficult for us to provide chart etc, so therefore we will be considering primarily on finding out these departure functions from equations of state. Now since for example purpose, using Redlich Kwong and Peng Robinson which is again mostly used in industries. Particularly the Redlich Kwong equation is very much used in the hydrocarbon industries.

The procedure is the same but since the calculations become slightly involved and we are all dealing with hand calculations for the purpose of this class, **I** we would primarily like to be rather primarily like to keep our problem within simpler equations of state. It can be a Vander Waal's equation of state, it can be a Berthelot equation of state which is also a very simple equation of state or some particular equation of state which is much less involved, just to simplify calculations but it is important for you to remember that usually in industries, we **I** either go for the generalised charts, charts which have been provided by **by** various workers or we use, usually we use the Redlich Kwong equation of state.

(Refer Slide Time: 29:23)



3. Calculate the enthalpy and entropy departure functions for ethylene gas at 8.25 MPa and 25°C, assuming that ethylene obeys van der Waals equation of state

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$$(h - h^0)_{T,P} = \int_{P=0}^P \left(\frac{\partial h}{\partial P} \right)_T dP = \int_{P=0}^P \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right]_T dP$$

$$(s - s^0)_{T,P} = \int_{P=0}^P \left[\left(\frac{\partial s}{\partial P} \right)_T + \frac{R}{P} \right] dP = - \int_{P=0}^P \left[\left(\frac{\partial v}{\partial T} \right)_P - \frac{R}{P} \right] dP$$

$$v dP = d(Pv) - P dv$$

$$\left[\left(\frac{\partial v}{\partial T} \right)_P dP \right]_T = - \left[\left(\frac{\partial P}{\partial T} \right)_v dv \right]_T$$

Handwritten red notes: Pv , $\int d(Pv) - \int P dv$, RT , v

So if you remember, when I was taking the class, I had derived the expressions for enthalpy and entropy departure functions right? And I had also mentioned **if you** if you recall, I had also mentioned that these departure functions, they are expressed in the terms of PVT where you require V to be a function of P. We had found that most of the equations, the cubic and the real equations, it is often more useful for us if we can express the functions in terms of P as a function of V and T.

So therefore we have to make some particular modifications of this equation such that we could express the enthalpy and entropy departure in terms of dV instead of dP. I do not know whether you remember this or not but we had in order to change these particular expressions, what did we do? VdP is nothing but equals to be known that V, PV equals to RT, right? So from there we found out VdP this is nothing but equals to dPV minus PdV. This is true not only for ideal gas, this is true for every gas obeying any particular equation of state.

So instead of VdP, we can we can make the substitute as dPV minus PdV. What happens then? Then what are the limits of dPV? When P equals to 0, we know the gas behaves as an ideal gas. So PV becomes equal to RT under this particular condition, right? So **so** therefore we make this following substitution. If we make this following substitution, then instead of VdP we write it down as dPV minus PdV, right?

Now when we write this as dPV minus integral PdV fine? The limits are from P equals to 0 to P equals to P . For P equals to 0, we know the gas behaves as an ideal gas. The gas behaves an ideal gas at P equals to 0, what is the corresponding PV equals to? For ideal gas, we know PV is nothing but equals to RT for 1 mole of the gas. And for P equals to P , naturally this is going to be PV , right? And we know that for an ideal gas, the volume can be approximated as V infinity or V_0 fine?

And volume here, it is V . So instead of this 1st term, we can substitute it with the 2 terms. And then if you recall, we had mentioned that from the cyclic rule, we can write $\Delta V / \Delta T$ at constant P , this particular term, we can very well replace it with $\Delta P / \Delta T$ at constant V . How?

(Refer Slide Time: 32:17)

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

$$\Delta h^* = \int_{P=0}^P \left[V - T \left(\frac{\partial V}{\partial T}\right)_P \right] dP = \int_{P=0}^P V dP - T \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$= (P_V - RT) + \int_{V=\infty}^V \left[T \left(\frac{\partial P}{\partial T}\right)_V - P \right] dV$$

$$= RT (Z-1) + \int_{V=\infty}^V \left[T \left(\frac{\partial P}{\partial T}\right)_V - P \right] dV$$

$$(h - h^0)_{T,P} = \int_{P=0}^P \left(\frac{\partial h}{\partial P} \right)_T dP = \int_{P=0}^P \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right] dP$$

$$(s - s^0)_{T,P} = \int_{P=0}^P \left[\left(\frac{\partial s}{\partial P} \right)_T + \frac{R}{P} \right] dP = - \int_{P=0}^P \left[\left(\frac{\partial v}{\partial T} \right)_P - \frac{R}{P} \right] dP$$

$$v dP = d(Pv) - P dv$$

$$\left[\left(\frac{\partial v}{\partial T} \right)_P dP \right]_T = - \left[\left(\frac{\partial P}{\partial T} \right)_v dv \right]_T$$

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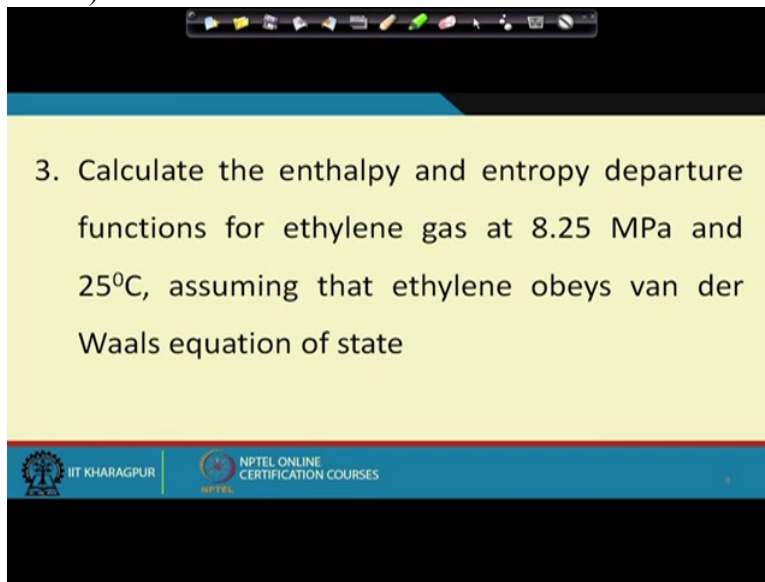
From the cyclic rule, Del V Del T at constant P into dP constant T this can be very well written down substituted as minus Del P Del T at constant V into dV at constant T. So therefore from the cycling rule, we have gone there. So therefore instead of this particular term, we can very well substitute it in this particular fashion fine? By doing this, **what do** what have we actually achieved?

By making these particular substitutions, we find that the equations which we had obtained here, this particular equation, we can write it down, I will just write down the equation once more for your convenience. V minus T Del V Del T at constant P whole thing as dP which can be written down as P equals to 0 to PVdP minus T integral P equals to 0 to P Del V Del T at constant PdP right? So instead of VdP, what do we do?

We substitute it just the way I have written down, we substitute it with PV and then integration, what does it give? It gives this PV minus RT. So therefore from this particular term, we get PV minus RT and for the next substitution, what do we get? It is V equals to infinity to V T Del P Del T at constant V minus PdV this is at constant T, fine? Or else we can write it down as in terms of Z if you want to write, RT into Z minus 1 plus integral V equals to infinity to V T Del P Del T at constant V minus P into dV.

So if you observe this equation, you find that you can find out the enthalpy departure function for any particular equation which expresses P as a function of T and V . Now let us see what was the what was the problem **which has been** which was given, the previous problems which we were dealing with.

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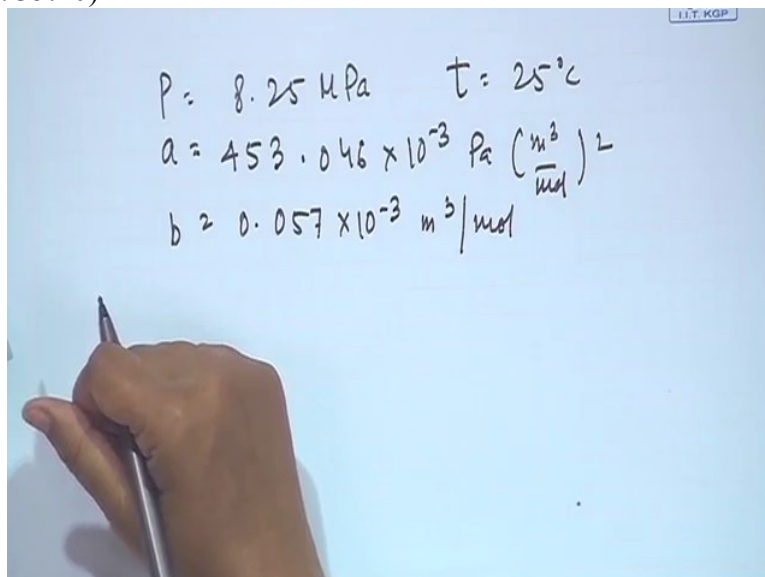


3. Calculate the enthalpy and entropy departure functions for ethylene gas at 8.25 MPa and 25°C, assuming that ethylene obeys van der Waals equation of state

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This particular problem, this was to calculate the enthalpy and entropy departure function of what? For an ethylene gas, right? Now for this particular ethylene gas, the gas is at 8.25 MPa pressure.

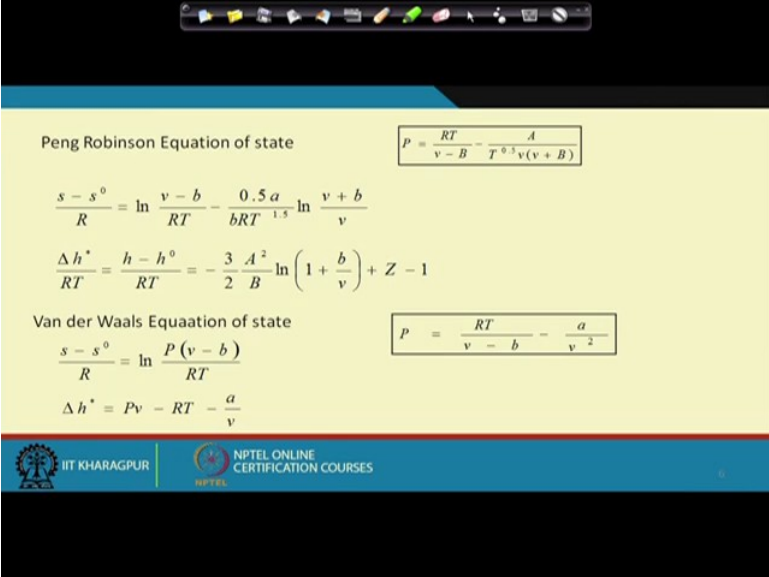
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$P = 8.25 \text{ MPa}$ $T = 25^\circ\text{C}$
 $a = 453.046 \times 10^{-3} \text{ Pa} \left(\frac{\text{m}^3}{\text{mol}}\right)^2$
 $b = 0.057 \times 10^{-3} \text{ m}^3/\text{mol}$

So P is given 8.25 MPa and the temperature is given, T small T is given as 25 degrees centigrade. It is given that the gas obeys Vander Waal's equation of state. The a of the, a and b are not given, you can note it down. It is 453.046 into 10 to the power minus 3 Pascal metre cube per mole whole square, b is 0.057 into 10 to the power minus 3 metre cube per mole. This is given, right? So once these 2 are given, then in that case, what you need to do.

(Refer Slide Time: 36:11)



Peng Robinson Equation of state

$$P = \frac{RT}{v - B} - \frac{A}{T^{0.5}v(v + B)}$$

$$\frac{s - s^0}{R} = \ln \frac{v - b}{RT} - \frac{0.5a}{bRT^{1.5}} \ln \frac{v + b}{v}$$



$$\frac{\Delta h^*}{RT} = \frac{h - h^0}{RT} = -\frac{3}{2} \frac{A^2}{B} \ln \left(1 + \frac{b}{v} \right) + Z - 1$$

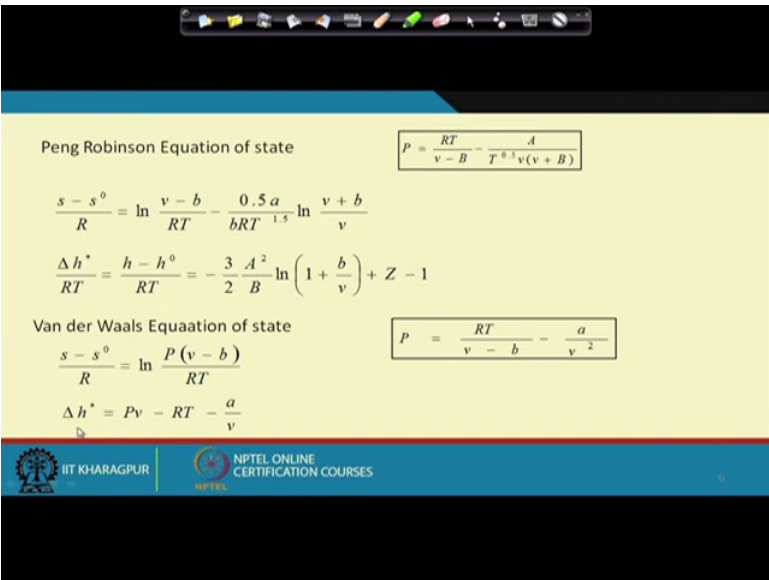
Van der Waals Equation of state

$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

$$\frac{s - s^0}{R} = \ln \frac{P(v - b)}{RT}$$

$$\Delta h^* = Pv - RT - \frac{a}{v}$$

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Peng Robinson Equation of state

$$P = \frac{RT}{v - B} - \frac{A}{T^{0.5}v(v + B)}$$

$$\frac{s - s^0}{R} = \ln \frac{v - b}{RT} - \frac{0.5a}{bRT^{1.5}} \ln \frac{v + b}{v}$$



$$\frac{\Delta h^*}{RT} = \frac{h - h^0}{RT} = -\frac{3}{2} \frac{A^2}{B} \ln \left(1 + \frac{b}{v} \right) + Z - 1$$

Van der Waals Equation of state

$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

$$\frac{s - s^0}{R} = \ln \frac{P(v - b)}{RT}$$

$$\Delta h^* = Pv - RT - \frac{a}{v}$$

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Just in this particular case you know that here in this equation, you can substitute the the for the Vander Waal's equation if you see, this is the Vander Waal's equation. This is the Vander Waal's

equation and till this particular equation, it was a home assignment. If you if you make **this the** the necessary substitutions here, then in that case the final equation which you arrive at is this. Once you arrive at this equation, find, finding out Delta h star is no problem.

T and V are known, RT are known, A is already given, so you can find out Delta h star. Same way, you can find out Delta S star as well. Right?

(Refer Slide Time: 36:54)

The slide displays two equations of state. The top section is for the Peng Robinson Equation of state, showing the pressure equation and the entropy change equation. The bottom section is for the Van der Waals Equation of state, showing the pressure equation and the enthalpy change equation.

Peng Robinson Equation of state

$$P = \frac{RT}{v - B} - \frac{A}{T^{0.5} v(v + B)}$$

$$\frac{s - s^0}{R} = \ln \frac{v - b}{RT} - \frac{0.5 a}{bRT^{1.5}} \ln \frac{v + b}{v}$$

$$\frac{\Delta h^*}{RT} = \frac{h - h^0}{RT} = -\frac{3}{2} \frac{A^2}{B} \ln \left(1 + \frac{b}{v} \right) + Z - 1$$

Van der Waals Equation of state

$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

$$\frac{s - s^0}{R} = \ln \frac{P(v - b)}{RT}$$

$$\Delta h^* = P_v - RT - \frac{a}{v}$$

Logos for IIT KHARAGPUR and NPTEL ONLINE CERTIFICATION COURSES are visible at the bottom.

Handwritten derivations for the Van der Waals equation of state. The first line shows the enthalpy change equation. The second line shows the value of b. The third line shows the pressure equation. The fourth line shows the derivative of pressure with respect to volume. The fifth line shows the enthalpy change equation with the pressure derivative substituted.

$$= RT (Z - 1) + \int_{\infty}^v \left[T \left(\frac{\partial P}{\partial T} \right)_v - P \right] \frac{dv}{T}$$

$$b = 0.057 \times 10^{-3} \text{ m}^3/\text{mol}$$

$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

$$\left(\frac{\partial P}{\partial T} \right)_v = \frac{R}{v - b}$$

$$\Delta h^* = RT \left(\frac{P_v}{RT} - 1 \right) + \int_{\infty}^v \left(\frac{RT}{v - b} - \frac{RT}{(v - b)} + \frac{a}{v^2} \right) dv$$

$$= (P_v - RT - \frac{a}{v})$$

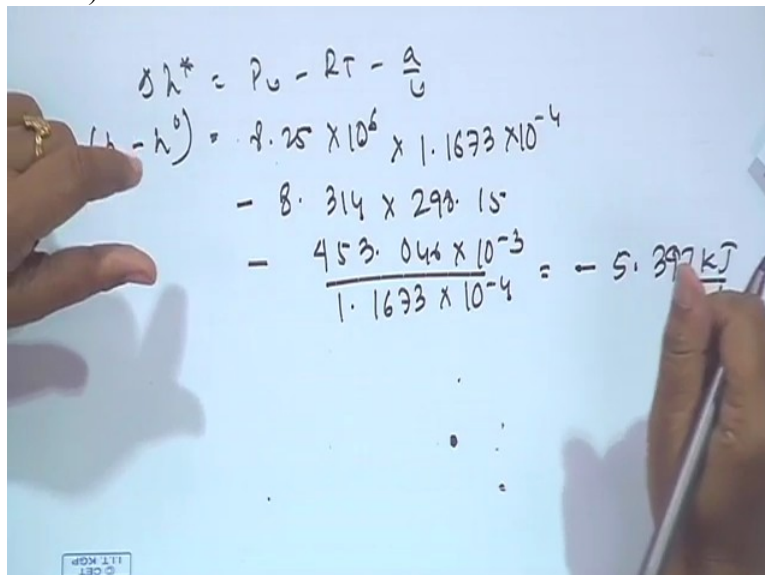
And if you wish a slightly more elaboration on this on the substitution, then I would like to tell you that well P is RT by V minus b minus a by V square. Just to tell you how we arrived **at this**

at this particular equation **this particular equation** from this equation. This was your home assignment. I believe that most of you have done it already. In case you have got stuck up, I will just like to do it once more.

P is given, $\Delta P \Delta T$ at constant V is very simple. R by V minus b. So therefore Δh^* I have already found out. This is PV minus RT. So P is already given, so PV minus RT is very simple for you to find out. This is going to be equal to RT into PV by RT minus 1 right? And that if you substitute $\Delta P \Delta T$ at constant V here then what do you get? You get integral V equals to infinity to V, this is going to be RT by V minus b from here if you observe, minus again RT by V minus b plus a by V square dV fine for V equals to V to infinity.

From here, what do we get? We get from here, RT RT cancels out, so you get PV minus RT and here these 2 cancels out. So therefore minus a by V. You just make the necessary substitutions and you are going to get the answer for this particular equation.

(Refer Slide Time: 38:48)



Handwritten calculation on a whiteboard:

$$\Delta h^* = P_0 - RT - \frac{a}{V}$$

$$(h - h^0) = 8.25 \times 10^6 \times 1.1673 \times 10^{-4}$$

$$- 8.314 \times 298.15$$

$$- \frac{453.046 \times 10^{-3}}{1.1673 \times 10^{-4}} = -5.397 \text{ kJ}$$

The answer for this particular equation is...for this particular equation P, T, everything is given. So therefore **for** this particular equation, your ΔH^* if you make all these substitutions, then in that case, I will just make the substitutions for you. 1st term is PV minus RT minus a by V. What is P equals to it is given? It is given 8.25 mega Pascals. So into 10 to the power 6 into 1.1673 into 10 to the power minus 4, this is V.

One thing I would like to remind that this V you have to find out from the basic Vander Waal's equation you are required to find out V under this pressure temperature conditions. To find it out, you find V to be equals to 1.673 into 10 to the power minus 4. It might happen that in some problems just to reduce the calculation time and all, we might be providing you the volume but normally under conditions, you are supposed to find out the specific volume, right?

Minus RT? What is minus RT? R in this case is 8.314, T is 298.15 minus a by V. a is already given, 453.046 into 10 to the power minus 3 divided by 1.1673 into 10 to the power minus 4, right? Make the calculations, you find that the Delta h star which is nothing but the actual value h minus the ideal gas value, this is going to be minus 5.397 kilojoules per mole. Make the calculation and find it out for yourself.

(Refer Slide Time: 40:39)

$$(h - h^0)_{T,P} = \int_{P=0}^P \left(\frac{\partial h}{\partial P} \right)_T dP = \int_{P=0}^P \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right] dP$$

$$(s - s^0)_{T,P} = \int_{P=0}^P \left[\left(\frac{\partial s}{\partial P} \right)_T + \frac{R}{P} \right] dP = - \int_{P=0}^P \left[\left(\frac{\partial v}{\partial T} \right)_P - \frac{R}{P} \right] dP$$

$$v dP = d(Pv) - P dv$$

$$\left[\left(\frac{\partial v}{\partial T} \right)_P dP \right]_T = - \left[\left(\frac{\partial P}{\partial T} \right)_v dv \right]_T$$

In the same way you are supposed to proceed for s minus s0. This also if you recall, this part also we had derived. Again here, we have Del V Del T at constant PdP. Substitute it with this. And we have R by P dP right? So therefore in this case also, **you** you can substitute it. If you make the necessary substitutions, then what do you get? Once you make the necessary substitutions, I will just write it down once more.

(Refer Slide Time: 41:13)

$$\begin{aligned}
 \Delta S^* &= - \int_{P_0}^P \left[\left(\frac{\partial U}{\partial T} \right)_P - \frac{R}{P} \right] dP \\
 &= \int_{V=\infty}^V \left(\frac{\partial P}{\partial T} \right)_V dV + R \int_{P_0}^P \frac{dP}{P} \\
 &= \int_{V=\infty}^V \left(\frac{\partial P}{\partial T} \right)_V dV + R \left[\int_{RT}^{P_0V} \frac{d(PV)}{PV} - \int_{V=\infty}^V \frac{dV}{V} \right] \\
 &= R \ln \left(\frac{P_0}{RT} \right) + \left[\int_{V=\infty}^V \left(\frac{\partial P}{\partial T} \right)_V dV - \int_{V=\infty}^V \frac{R}{V} dV \right] \\
 &= R \ln 2 + \int_{V=\infty}^V \left[\left(\frac{\partial P}{\partial T} \right)_V - \frac{R}{V} \right] dV
 \end{aligned}$$

$$\begin{aligned}
 &= R \ln 2 + R \ln \frac{V-b}{V_{\infty}-b} - R \ln \frac{V}{V_{\infty}} \\
 &= R \ln 2 + R \ln \frac{V-b}{V_{\infty}-b} - R \ln \frac{2RT}{P} \left(\frac{P^0}{RT} \right) \\
 &= R \ln \left(\frac{V-b}{V_{\infty}-b} \right) + R \ln \frac{P}{P^0} = R \ln \frac{P(V-b)}{P^0(V_{\infty}-b)} \\
 \Delta S^* &= R \ln \frac{P(V-b)}{RT} \\
 &= 8.314 \ln \frac{8.25 \times 10^4 (1.1633 \times 10^{-4} - 0.053 \times 10^{-3})}{-13.431 \text{ J/mol K} \cdot 298.15}
 \end{aligned}$$

Your Delta s star then becomes equal to, in this case it is minus Del V Del T at constant P integral P equals to 0 to P minus R by P dP at constant T fine? So this if you make **make** the substitution, you get V equals to infinity to V Del P Del T at constant VdV plus R dP by P integral P equals to 0 to P. How to make this? This is already substituted, so you have V equals to infinity to V Del P Del T at constant VdV.

For this case, what do you write? For this case, you write integral dPV by PV you simply write down the equation, then you make the **you** you just write it down and divide by V, you get this as

$R \int \frac{dP}{P} = R \ln \frac{P}{P_0}$ by $PV = nRT$ right? Here here **again** you are going to put the limits, what are the limits? This is T to P . What are the limits for this? V equals infinity to V .

So what do you get finally? Finally the things which you get is $R \ln \frac{P}{P_0}$ by T which is again nothing but z . This **this** particular thing is nothing but z . So you can also write it down as $R \ln z$. Plus you get V equals to infinity to V integral $\frac{dP}{P}$ at constant T minus $R \ln \frac{P}{P_0}$ by V I will just write it down. Integral V equals to infinity to V this is dV , this is dV is not it? I have taken this term out and I have combined these 2 terms because both of them are in terms of dV . So therefore what do I get here?

This is $R \ln z$ plus integral V equals to infinity to V $\frac{dP}{P}$ at constant T minus $R \ln \frac{P}{P_0}$ by V dV which gives me on slightly little more substitution, it gives me $R \ln z$ plus $R \ln$ if you observe, this particular case, we get dV by V , so $R \ln V$ minus b by V infinity minus V minus $R \ln V$ by V infinity. Agreed? So therefore, from here **we can** you can make the substitutions. Or in other words, you can also write it down as $R \ln z$ slightly more substitution, V minus b by V infinity minus B minus $R \ln z$ by P into P_0 by T .

Can we now do it? Because V infinity is the ideal gas volume right? V is zRT by P . I have just made some substitutions. So therefore this gives me as $R \ln$ because $R \ln z$ $R \ln z$ they are going to cancel out and finally what I get, $R \ln V$ by B by V minus b plus $R \ln P$ by P_0 . Agreed? Which is nothing but $R \ln P$ into V minus b by P_0 into V infinity minus b . Or in other word, this is nothing but $R \ln P$ into V minus b by RT . is not it?

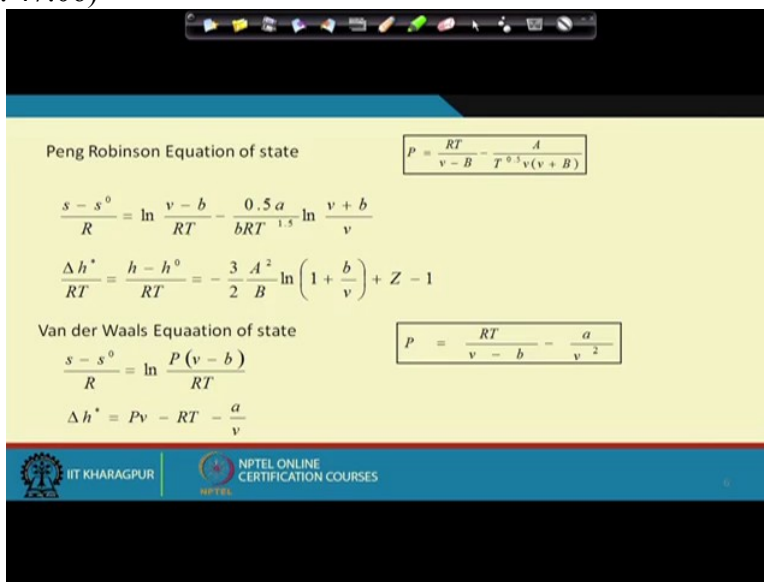
So therefore you find Δs^* from a very simple equation. Again **if you** if you refer to the previous problem which was there, if you **if you** go to the previous problem you find that in this particular equation you know R , what is R ? $8.314 \ln P$ you already know 8.25 into 10 to the power 6 right V minus b fine? This is 1.1673 into 10 to the power minus 4 minus b 0.057 to 10 to the power minus 3 divided by R 8.314 into 298.15 .

You can find it. This is nothing but minus 13.431 joules per mole Kelvin. Please try it out for yourself and see if you can get this particular equation or not, right?

So so this is we have found out enthalpy and entropy departure functions, we have assumed that it obeys the Vander Waal's equation of state. So therefore we have expressed it in terms of a

(pre) from a pressure to of volume explicit form that is we have **expressed** is expressed it as P as a function of V and T. We have used that equation and we have found out the enthalpy and entropy departure functions.

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Peng Robinson Equation of state

$$P = \frac{RT}{v - B} - \frac{A}{T^{0.5}v(v + B)}$$

$$\frac{s - s^0}{R} = \ln \frac{v - b}{RT} - \frac{0.5a}{bRT^{1.5}} \ln \frac{v + b}{v}$$

$$\frac{\Delta h^*}{RT} = \frac{h - h^0}{RT} = -\frac{3}{2} \frac{A^2}{B} \ln \left(1 + \frac{b}{v} \right) + Z - 1$$

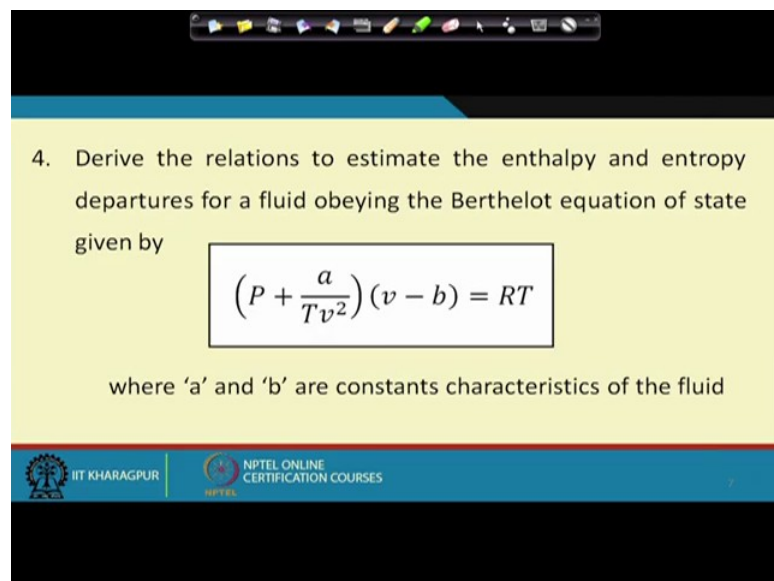
Van der Waals Equation of state

$$P = \frac{RT}{v - b} - \frac{a}{v^2}$$

$$\frac{s - s^0}{R} = \ln \frac{P(v - b)}{RT}$$

$$\Delta h^* = Pv - RT - \frac{a}{v}$$

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4. Derive the relations to estimate the enthalpy and entropy departures for a fluid obeying the Berthelot equation of state given by

$$\left(P + \frac{a}{Tv^2} \right) (v - b) = RT$$

where 'a' and 'b' are constants characteristics of the fluid

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Now suppose it is not a Vander Waal's equation of state, suppose I say that well, it obeys some other equation of state which is not a Vander Waal's equation of state but it is more or less it is it shows that instead of a by V square, there is also a temperature term there. Quite expectedly because intermolecular force of attraction depends on the temperature as well right? So for this case, just proceeding in the

similar manner, can we not find out the Delta h star and the Delta s star, the enthalpy and entropy departure functions just the way we have done it for the Vander Waal's equation of state.

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$$(h - h^0)_{T,P} = \int_{P=0}^P \left(\frac{\partial h}{\partial P} \right)_T dP = \int_{P=0}^P \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right]_T dP$$

$$(s - s^0)_{T,P} = \int_{P=0}^P \left[\left(\frac{\partial s}{\partial P} \right)_T + \frac{R}{P} \right] dP = - \int_{P=0}^P \left[\left(\frac{\partial v}{\partial T} \right)_P - \frac{R}{P} \right] dP$$

$$v dP = d(Pv) - P dv$$

$$\left[\left(\frac{\partial v}{\partial T} \right)_P dP \right]_T = - \left[\left(\frac{\partial P}{\partial T} \right)_v dv \right]_T$$

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We start in the same particular manner, this is our basic equations. This and this are our basic equations. We make this and this substitutions just the way we had done for the Vander Waal's equation and then what do we get?

(Refer Slide Time: 48:10)

4. Derive the relations to estimate the enthalpy and entropy departures for a fluid obeying the Berthelot equation of state given by

$$\left(P + \frac{a}{T v^2} \right) (v - b) = RT$$

where 'a' and 'b' are constants characteristics of the fluid

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$$\begin{aligned}
 \Delta h^* &= RT(z-1) + \int_{V=\infty}^V \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV \\
 &= (P_V - RT) + \int_{V=\infty}^V \frac{2a}{TV^2} dV = (P_V - RT) - \frac{2a}{TV} \\
 P &= \frac{RT}{V-b} - \frac{a}{TV^2} \\
 \left(\frac{\partial P}{\partial T} \right)_V &= \frac{R}{V-b} \\
 &= \frac{RT}{V-b} - \frac{a}{TV} - RT - \frac{2a}{TV} \\
 &= \boxed{\frac{bRT}{V-b} - \frac{3a}{TV}}
 \end{aligned}$$

We get Delta h star equals to RT into z minus 1. Just same equation I am writing down. Infinity to V T Del P Del T at V minus P into dV just the equation we had obtained. This can be written down as PV minus RT as you know plus integral V equals to infinity to V, this is 2A if if you make the necessary substitutions, then in that case, if you write the Berthelot equation, I will just go to the equation once more for you to see it.

If you go to this particular equation, what does it give you? It gives you P equals to RT by V minus b minus a by TV square, right? So therefore and then from here you can also find out what is Del P Del T at constant V? This is nothing but equals to R by V minus b right? So therefore we can very well substitute that whatever we have obtained, and so therefore here in this particular case what do we get?

We get this as 2a by TV square dV fine? And then this becomes equals to PV minus RT minus 2a by TV which gives you RTV by V minus b minus a by TV minus RT minus 2a by TV. On further simplification, we get bRT by V minus b minus 3a by TV. You can compare this with the Vander Waal's expression that we had obtained. In the same way, you can proceed for in order to find out the entropy departure function as well.

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$$\begin{aligned}
 \Delta S^* &= R \ln 2 + \int_{V=\infty}^V \left[\left(\frac{\partial P}{\partial T} \right)_V - \frac{R}{V} \right] dV \\
 &= R \ln 2 + \int_{V=A}^V \left[\frac{R}{V-b} - \frac{a}{T^2 V^2} - \frac{R}{V} \right] dV \\
 &= R \ln 2 + R \ln \frac{V-b}{V-\infty-b} - R \ln \frac{V}{V-\infty} - \frac{a}{T^2 b} \\
 \Delta S^* &= R \ln 2 + R \ln \frac{V-b}{V} - \frac{a}{T^2 b}
 \end{aligned}$$

In the entropy departure function also, again I start with the same equations which I had derived right? Equation was $R \ln z$ plus V equals to infinity to V $\Delta P / \Delta T$ at constant V minus R by V constant $T dV$ which can be written down as in this particular case if you substitute all these things, you get V equals to infinity to V we get R by V minus b minus a by $T^2 V^2$ minus R by V to dV , right?

So here what do we get? We get $R \ln Z$ plus $R \ln V$ minus b by V infinity minus b minus $R \ln V$ by V infinity minus a by $T^2 V$ which can further be substituted as plus $R \ln$. With all the simplifications you get V minus b by V minus a $T^2 V$, right? So therefore if you know or rather if you can express your enthalpy and entropy departure function then in that case whatever be the equation of state, you can substitute it and accordingly **we can** you can find out the enthalpy and entropy departure functions for any particular cubic equation of state.

The same is true for the Vander Waal's equation of state as well. If you do not know whether the gas obeys the any particular equation of state, then definitely we have to resort to the generalised charts to find out the enthalpy and entropy departure functions. So this completes our assignment or rather our tutorial for the 4th week. I would welcome much more questions from you so that for the tutorial of the next week, we can include all those doubts and we can address whatever concerns you have. Thank you very much.