Chemical Principles II
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Tutorial Problem-16

Okay. So we will continue solving the thermodynamic relations problem.

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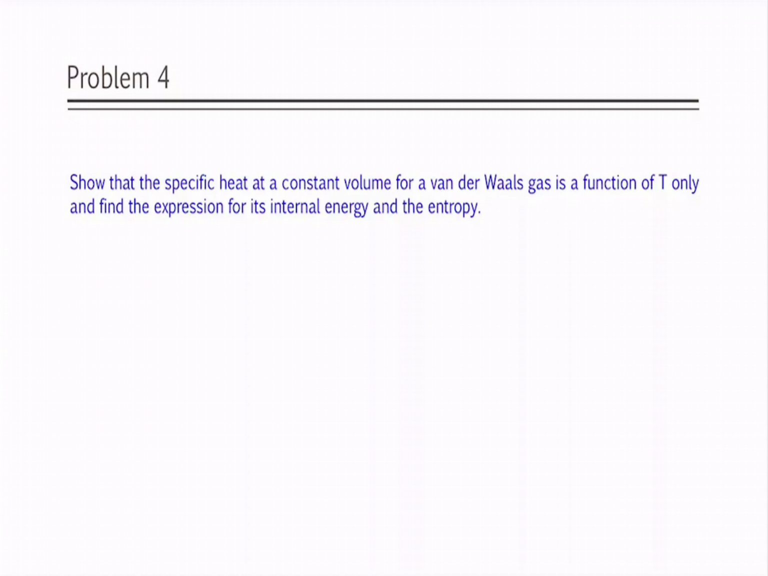

Problem 4

Show that the specific heat at a constant volume for a van der Waals gas is a function of T only and find the expression for its internal energy and the entropy.

And the next problem that we are going to do is show that the specific heat at a constant volume for a van der waal gas is a function of T only and find the expression of its internal energy and entropy. So we have to show that specific heat at a con specific heat at a constant volume for Van der waal gas.

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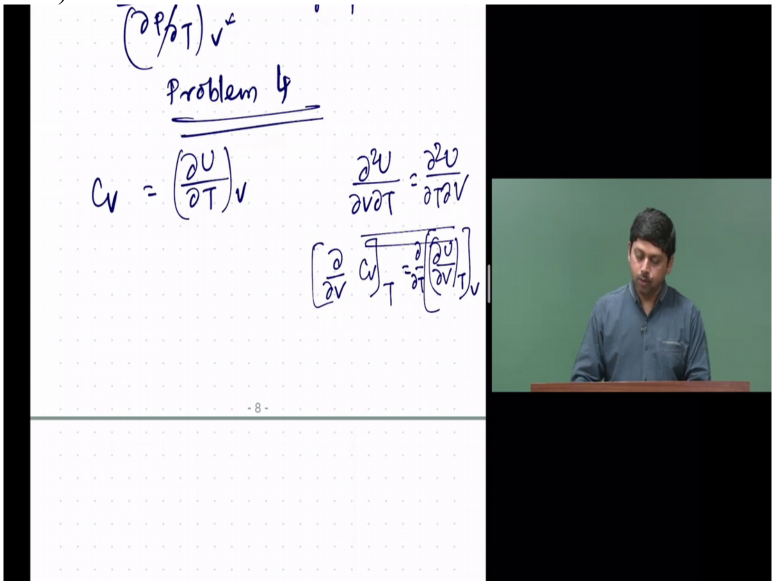

$\left(\partial P/\partial T\right)_V$

Problem 4

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad \frac{\partial^2 U}{\partial V \partial T} = \frac{\partial^2 U}{\partial T \partial V}$$

$$\left[\frac{\partial}{\partial V} C_V\right]_T = \frac{\partial}{\partial T}\left[\left(\frac{\partial U}{\partial V}\right)_T\right]_V$$

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Now the problem 4. Now you see specific heat at a constant volume is CV which is Dell U by Dell T at a constant V by definition. Right? So we need to see how to do that. But there is a trick here that you need to use it. You need to use the functionality of U as an exact differential. So meaning we need to exercise this quality of U as an exact differential which means that you know exact differential is when D2U at DV DT is = D2U at DT DV.

That is when the exact differential characteristics comes. Which means that first you take the derivative with respect to T at a constant V which is nothing but CV. So which means that Del Del V of CV at a constant T is Del U by Del V at a constant T. And derivative of that with respect to T at a constant V. So we are going to exercise that.

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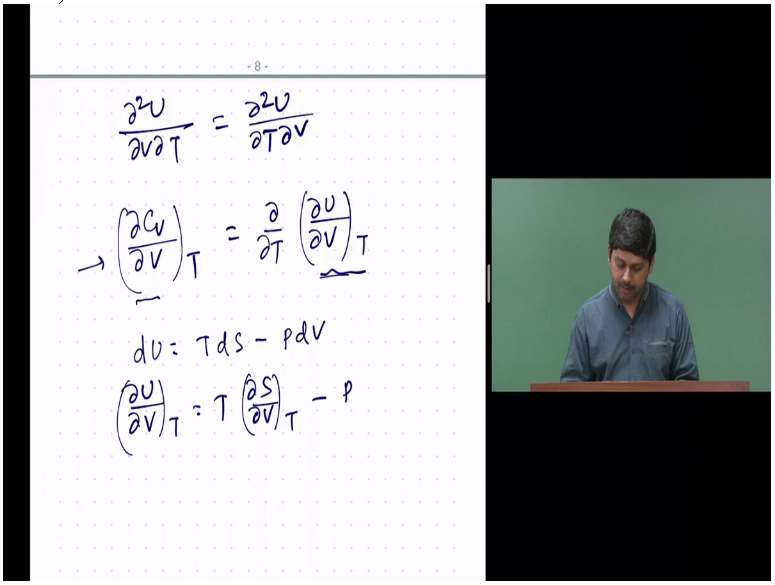

$$\frac{\partial^2 U}{\partial V \partial T} = \frac{\partial^2 U}{\partial T \partial V}$$

$$\rightarrow \underline{\left(\frac{\partial C_v}{\partial V}\right)_T} = \frac{\partial}{\partial T}\underline{\left(\frac{\partial U}{\partial V}\right)_T}$$

$$dU = TdS - pdV$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p$$

So let us write that that D2U by DV DT is = D2U by DT DV. Now how **how** did they even think of that first of all? It will be clear why did we even think of that. So we are writing that Del Del V of CV at a constant temperature or or or let us write the way we are normally writing. Del CV by Del V at a constant T is = Del Del T of Del U by Del V at a constant T. The reason we are writing that because having familiar with this particular thing that we discussed during the joules expansion thing that how the internal energy changes with respect to volume at a fixed temperature.

So that is the reason that we have done that. Another reason is that these variables U is a function of 2 variables, sorry the the the thermodynamic potential uses the function of 2 variables, S and V or T and V and things like that. So therefore, CV is also a function of 2 variables, it could be a function of 2 variables, V and T and we need to show it is a function of one variable, T. So therefore we need to show that if it varies with respect to V or not.

If it does not vary with respect to V, then we can see it is a function of T alone because that is what we have to prove. So if is if something is a function of 2 variables and then it does not depend on one, that means it is a function of one variable only. So that is the reason we need to do Del CV by Del VT. if we show these to be zero, then we know that it does not vary with V anymore. And that is the reason we wrote Del Del V. And then it gives me this particular quantity Del U by Del V at a constant T.

Another reason of writing this way because we have shown you that this can be converted to something of P and T. For example, you know that DU is = TDS - PDV. Ya but if you do DU by DV, I do not get the T here. Okay. Fine, no problem but we can write that and then we can take the differentiation with respect to V at a constant T will give us T Del S by Del V at a constant T - P.

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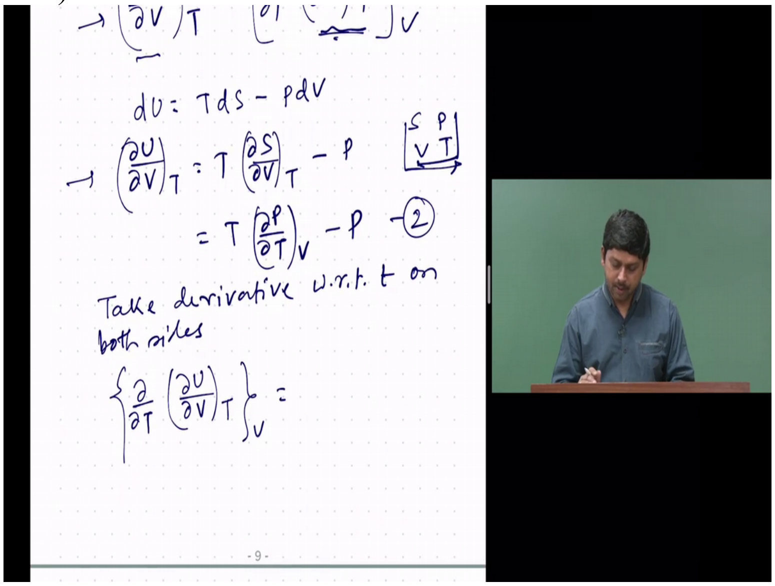

$$dU = TdS - PdV$$

$$\rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P \qquad \boxed{\begin{matrix} S & P \\ V & T \end{matrix}}$$

$$= T\left(\frac{\partial P}{\partial T}\right)_V - P \quad - ②$$

Take derivative w.r.t T on both sides

$$\left\{\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right\}_V =$$

And Maxwell's relation showed us that Del S by Del V at a constant T is nothing but Del P by Del T at a constant V. So this is the thing that we get relation we get. For this particular thing, this we have to do at a constant V. So therefore, if I now take okay let us call that a equation 1, let us that we equation 2 and then take derivative with respect to T on both sides so that we get the equation 1. What we get is Del Del T of this particular quantity Del U by Del V at a constant T is okay so we will not okay we will not do that right away because that will be complicated. We can do a simpler approach. We can calculate what this quantity is. We can calculate what this quantity is for van der waal gas.

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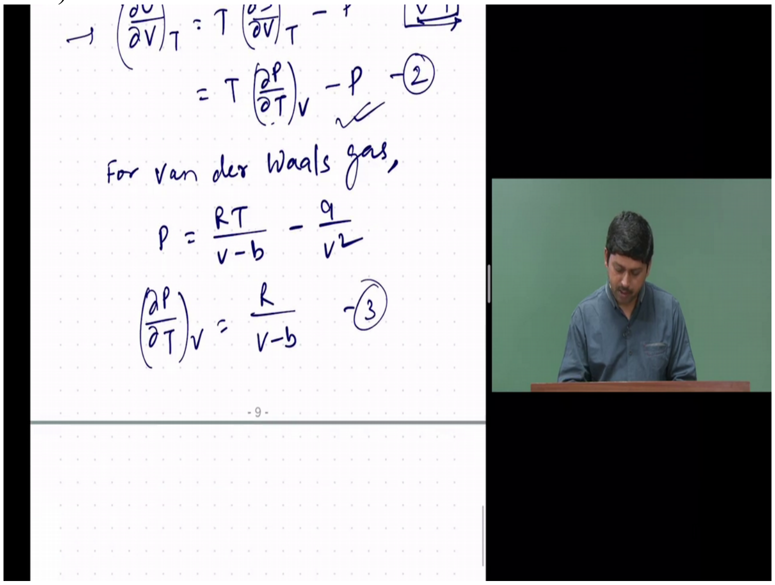

$$\rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

$$= T\left(\frac{\partial P}{\partial T}\right)_V - P$$ —②

For van der Waals gas,

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

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$ —③

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If we have to say for for van der waal's gas, we know that P = RT by V - B - A by V square. We discussed about that. We will just continue. Del P Del T at a constant V is nothing but R by V - B. Equation 3.

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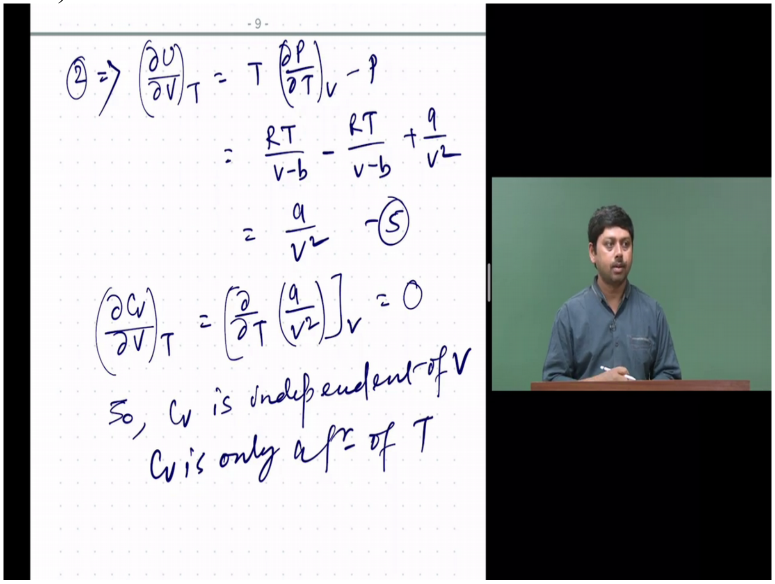

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② ⇒ $$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

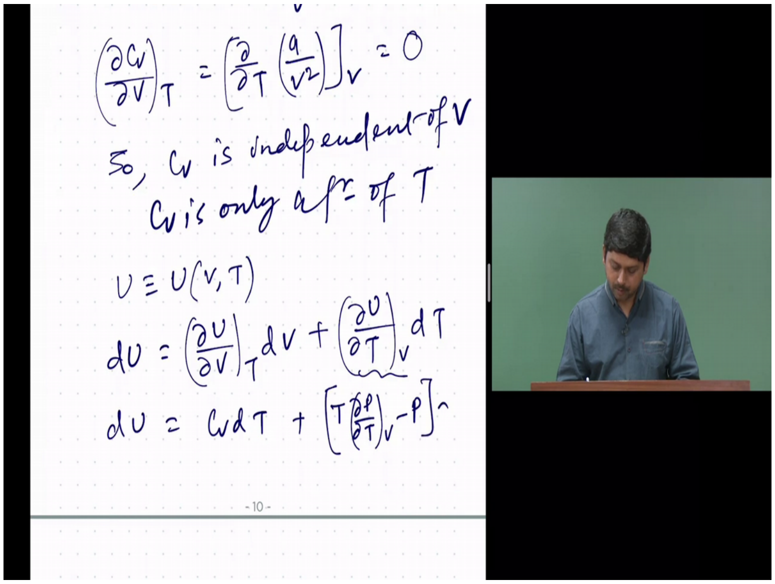
$$= \frac{RT}{V-b} - \frac{RT}{V-b} + \frac{a}{V^2}$$

$$= \frac{a}{V^2}$$ —⑤

$$\left(\frac{\partial C_v}{\partial V}\right)_T = \left[\frac{\partial}{\partial T}\left(\frac{a}{V^2}\right)\right]_V = 0$$

So, C_v is independent of V

C_v is only a fn of T



$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left[\frac{\partial}{\partial T}\left(\frac{a}{V^2}\right)\right]_V = 0$$

So, C_V is independent of V

C_V is only a fn of T

$$U \equiv U(V,T)$$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \underline{\left(\frac{\partial U}{\partial T}\right)_V} dT$$

$$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]^\wedge$$

So now equation from equa from equation 2 we get Del U by Del V at a constant T is T Del P Del T V - P, right? So I should put that as equation 4. So we are going to use both. So T into Del P Del T at a constant V will be as you know that it will be RT by V - B - this particular quantity RT by V - B + A by V square which is nothing but A by V square. So we got that as equation 5. So now we go back to equation 1 and we write Del CV by Del V at a constant T is Del T A by V square at a constant V. Since it does not depend on temperature, it will be zero.

So therefore, CV is independent of V. So since CV since CV come from U and U depends on T and V, so then CV is only a function of T at least and therefore van der waal gas. So now we have to find the expression of internal energy and entropy. Now we will go for that this particular equation that for internal energy and entropy, we can write U as a function of V and T. okay. So we can write Del U or DU as Del U by Del V TDV + Del U by Del T V DT.

So that means DU because we need to get the expression of U, so we need to write DU term only and we need to write in such a way that we can get the other terms. For example, you can see here, Del U by Del TV is nothing but CV. So it is CVDT + Del U by Del V TDV. So Del U by Del V TDV, Del U by Del V T is we have got this one, right? T Del P Del T V - P. okay. So you got that.

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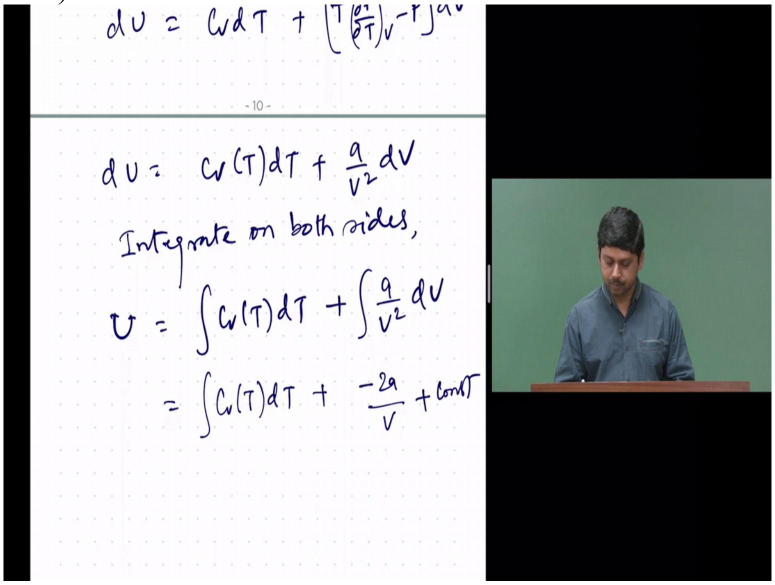

$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV$

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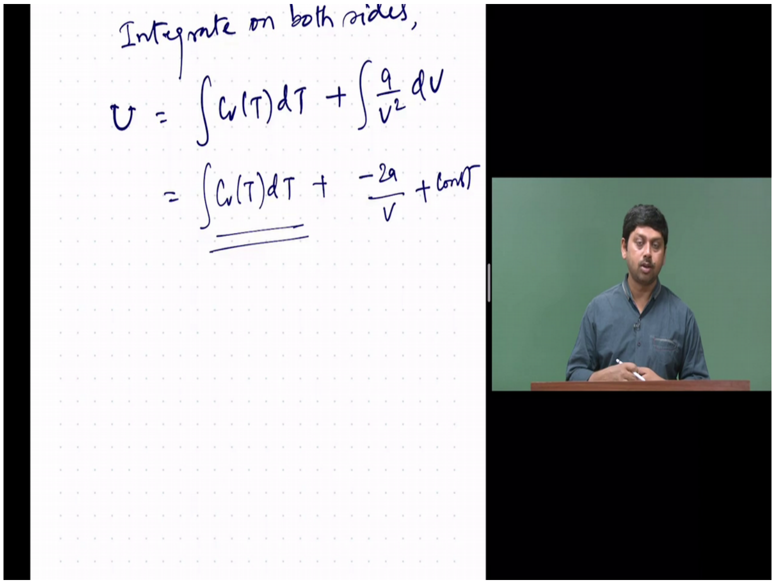
$dU = C_V(T)dT + \frac{a}{V^2}dV$

Integrate on both sides,

$U = \int C_V(T)dT + \int \frac{a}{V^2}dV$

$= \int C_V(T)dT + \frac{-2a}{V} + \text{const}$



Integrate on both sides,

$U = \int C_V(T)dT + \int \frac{a}{V^2}dV$

$= \underline{\underline{\int C_V(T)dT}} + \frac{-2a}{V} + \text{const}$

Now DU is, now CV depends on temperature. So we should write CV DT + this quantity which is T Del P Del T V - P is nothing but A by V square DV. Now integrate on both sides. It will give you U as integration of CVT DT. So without knowing how CV depends on T, we cannot integrate this. We have to keep it this form + integration of A by V square DV and so CVT DT + now this will give us - 2 A - 2 + 1 Uhh by B + constant. So that is how we can express U in terms of…

So we cannot do this integration because we need to know the expression of capital CV as a function of A. If you know that, then you can do that because we have already shown that it depends on T. If it is a constant, then CV will just come out and typically it is assumed to be constant in cases then you can, especially for ideal gas you know it is a constant. We can take it out and it will be a simple T. Sorry, so it should be it should be A by V not - 2. It will be - A by V. So if I write again, CV DT - A by B + constant, integration constant.

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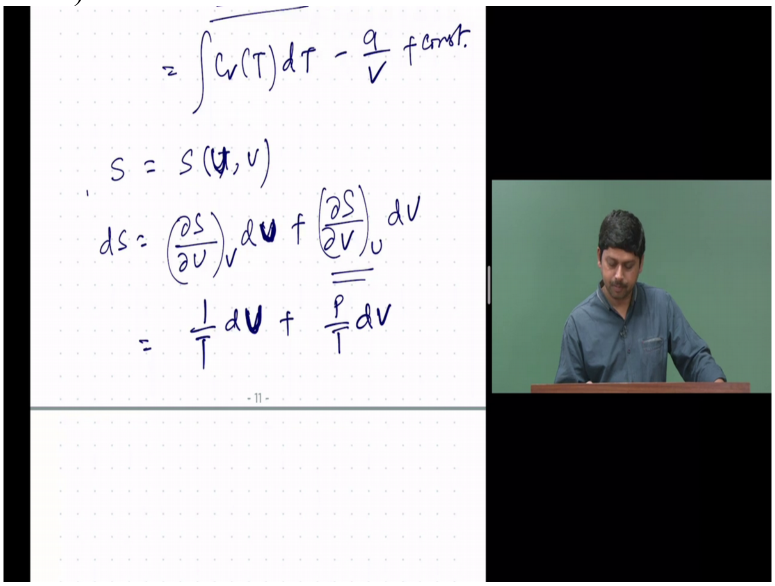
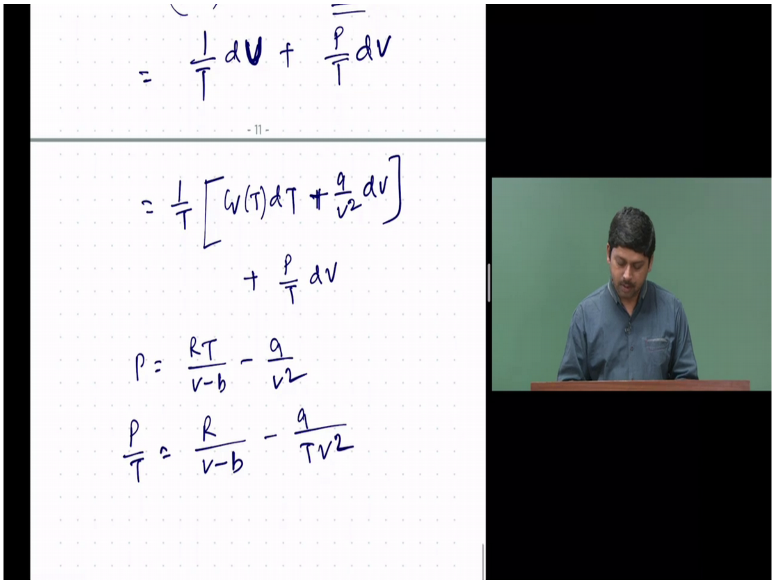


$$= \int C_v(T)\,dT - \frac{a}{V} + \text{const.}$$

$$S = S(U, V)$$

$$dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$$

$$= \frac{1}{T}\,dU + \frac{P}{T}\,dV$$



$$= \frac{1}{T}\,dU + \frac{P}{T}\,dV$$

$$= \frac{1}{T}\left[C_v(T)\,dT + \frac{a}{V^2}\,dV\right] + \frac{P}{T}\,dV$$

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

$$\frac{P}{T} = \frac{R}{V-b} - \frac{a}{TV^2}$$

So now similarly we can write S also as a function of let us say T and V. And we can write DS as Del S by or S is a function of U and V. So we can write as U and V as well. okay. So let us write that. So Del U by Del V so Del S by Del U at a constant V DV + Del S by Del V U at a and DV. So now Del S by Del U at a constant V is nothing but P by T. You can show that. How do you show that? That you have to figure it out and Del S by Del V T is Uhh no sorry so this is U right? So this is U, I was confused. So this is U.

So this is nothing but 1 by T and this is P by T DV. So you can you can you can figure it out whether it is + P by T or not. So you see now you got DU and DU we already know as this quantity. So 1 by T CV TDT + A by V square DV + P by T DV. And what is P by T? So if we see P by T, it is P is RT by V - B - A by V square. So P by T is R by B - B square - A by TV Square.

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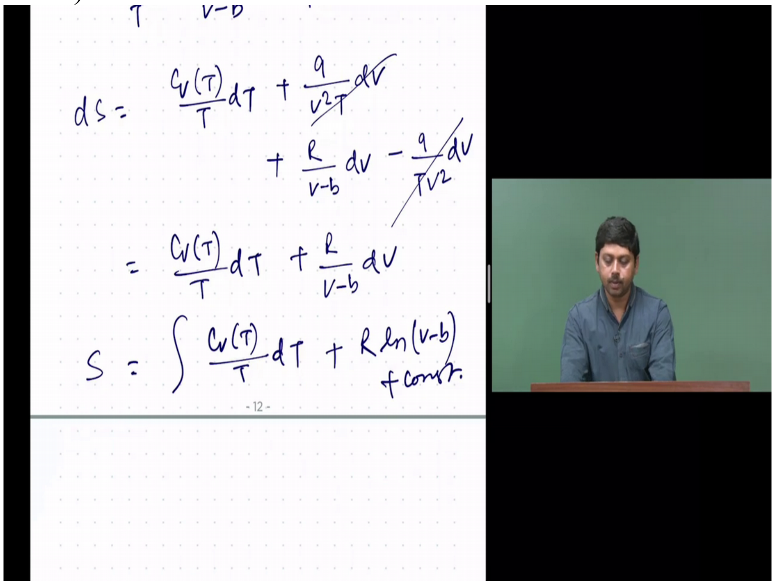

$$ds = \frac{C_v(T)}{T}dT + \cancel{\frac{a}{V^2T}dV} + \frac{R}{V-b}dV - \cancel{\frac{a}{TV^2}dV}$$

$$= \frac{C_v(T)}{T}dT + \frac{R}{V-b}dV$$

$$S = \int \frac{C_v(T)}{T}dT + R\ln(V-b) + \text{const.}$$

So DS is CVT by T DT + A by V square T DV + R by V - B DV - A by TV Square DV which is CVT by T DT and this quantity cancels leaving us R by V - B DV. And integrate both sides, you will get S = you cannot do the integration because you do not know the form for CV. And here we can get R Ln V - B + constant. So that will be the expression of entropy. Okay. So that finishes this problem. Now we will go to the next problem.

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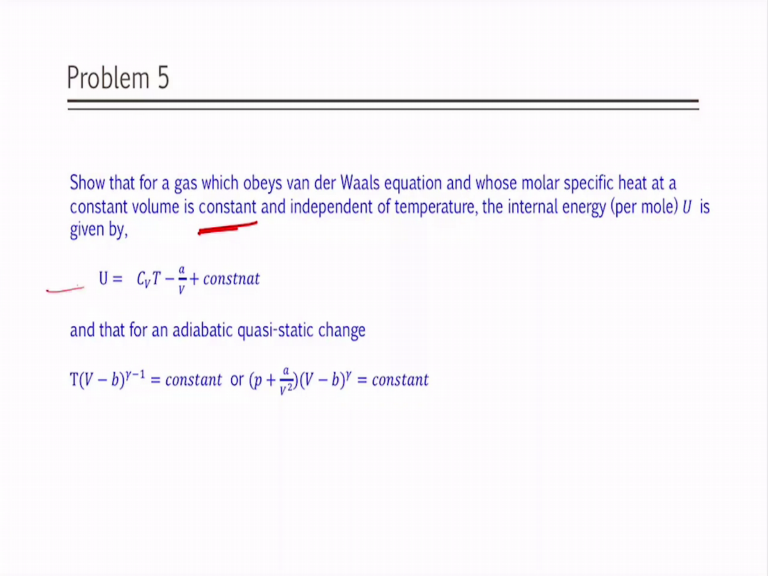

Problem 5

Show that for a gas which obeys van der Waals equation and whose molar specific heat at a constant volume is constant and independent of temperature, the internal energy (per mole) U is given by,

$$U = C_V T - \frac{a}{V} + constnat$$

and that for an adiabatic quasi-static change

$$T(V-b)^{\gamma-1} = constant \text{ or } \left(p + \frac{a}{V^2}\right)(V-b)^{\gamma} = constant$$

So let us do the problem number 5. And problem number 5 is, show that for a gas which are based van der waals equation and whose molar specific heat at a constant volume is constant and independent of temperature, the internal energy U can begin by this.

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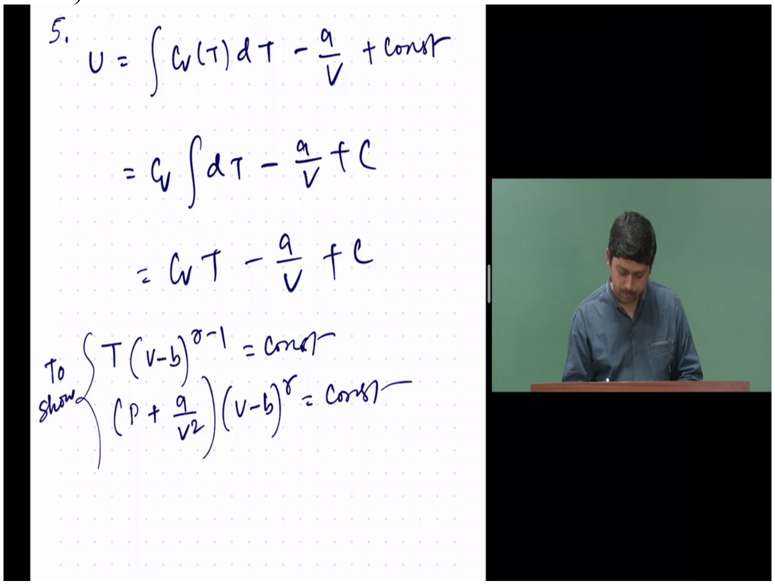

5.

$$U = \int C_V(T)\,dT - \frac{a}{V} + Const$$

$$= C_V \int dT - \frac{a}{V} + C$$

$$= C_V T - \frac{a}{V} + C$$

To show

$$\begin{cases} T(V-b)^{\gamma-1} = Const \\ \left(P + \frac{a}{V2}\right)(V-b)^{\gamma} = Const \end{cases}$$

Now we have seen that for the same system we can write U as integration CV TDT - A by B + constant. So that is the equation for van der waal gas. We have shown that. Now in this particular problem, it is specified that CV is independent of temperature. It can be a constant. So we can take the CV out and we can do DT - A by V + constant C which is CVT - A by V + constant and that is what proves this. And this this this expression I am writing from the previous problem that we did.

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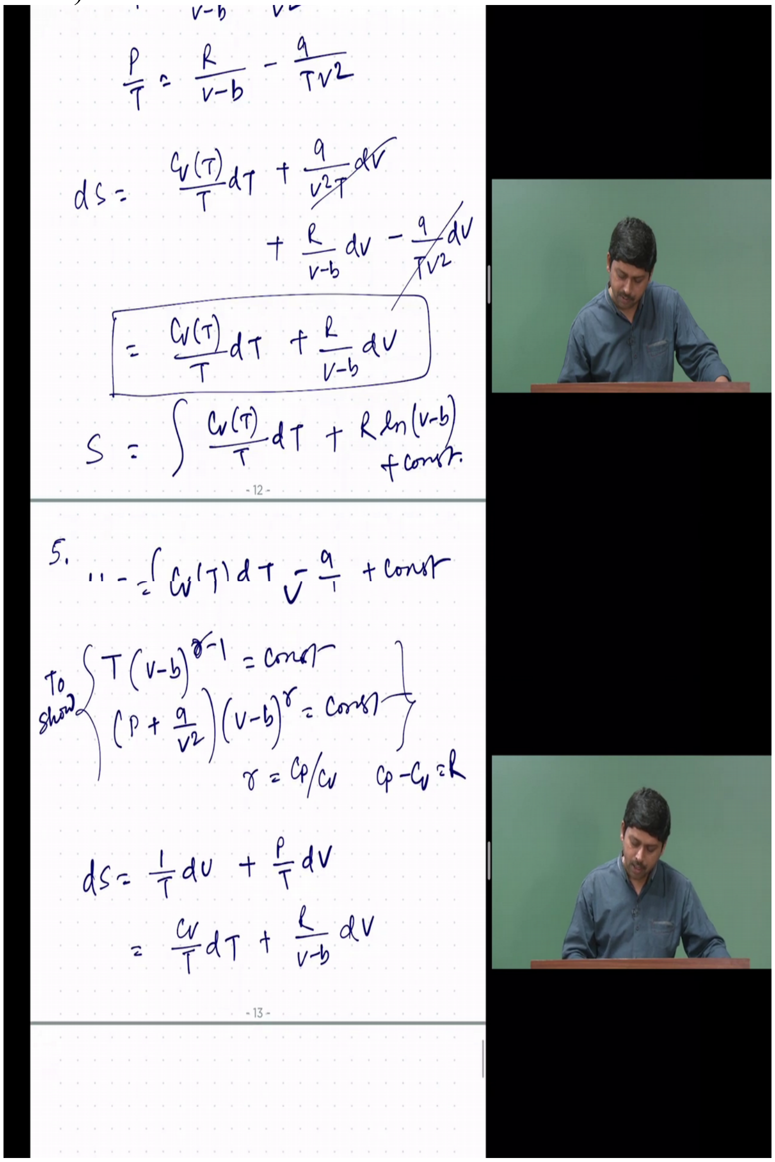

$$\frac{P}{T} = \frac{R}{V-b} - \frac{a}{TV^2}$$

$$dS = \frac{C_V(T)}{T}dT + \cancel{\frac{a}{V^2T}dV} + \frac{R}{V-b}dV - \cancel{\frac{a}{TV^2}dV}$$

$$\boxed{= \frac{C_V(T)}{T}dT + \frac{R}{V-b}dV}$$

$$S = \int \frac{C_V(T)}{T}dT + R\ln(V-b) + \text{const.}$$

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5. $U = \int C_V(T)\,dT - \frac{a}{V} + \text{const}$

To show

$$T(V-b)^{\gamma-1} = \text{const}$$

$$\left(P + \frac{a}{V^2}\right)(V-b)^{\gamma} = \text{const}$$

$\gamma = C_P/C_V$ $C_P - C_V = R$

$$dS = \frac{1}{T}dU + \frac{P}{T}dV$$

$$= \frac{C_V}{T}dT + \frac{R}{V-b}dV$$

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Now it says that and that for an adiabatic versus static change, for adiabatic versus static change, show that T V - B to the power gamma - 1 is constant or T + A by V square V - B to the power gamma is constant. That we need to show. So now we have to show that this quantity holds and since we are talking about this gamma, CP by CV, so actually this can be only done if we assume that gamma by definition is CP - CV and we have to assume that CP - CV is = R which is only true for ideal gas but we need to assume that for van der waal's gas also taking into account that it is a very diluted gas. So if we do that, then again we can write the expression of S, D as 1 by T DU + P by T DV.

Now 1 by T 1 by T DU we already know what it is or we already got that expression of that. We can we can write this one as you can see as DS. So CV by T DT + R by V - B DV. So CV by T DT + R by V - B DV. Okay. So this we already got without any approximation for van der waal gas.

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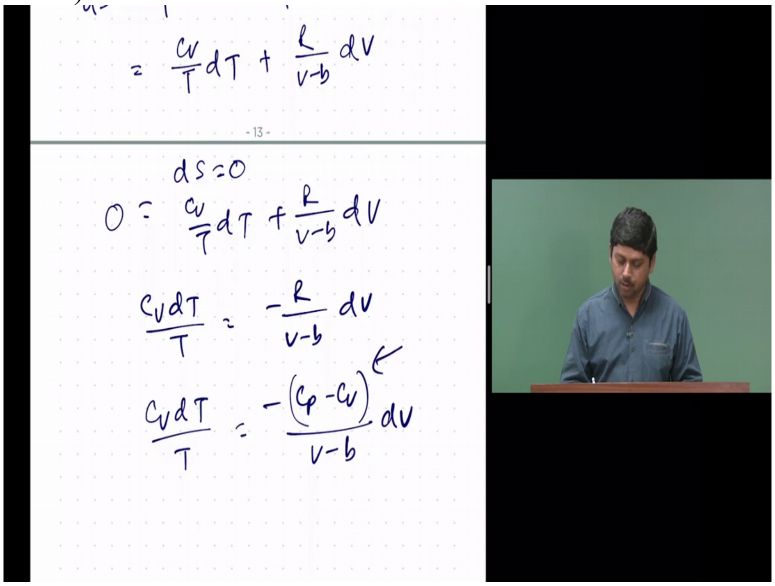


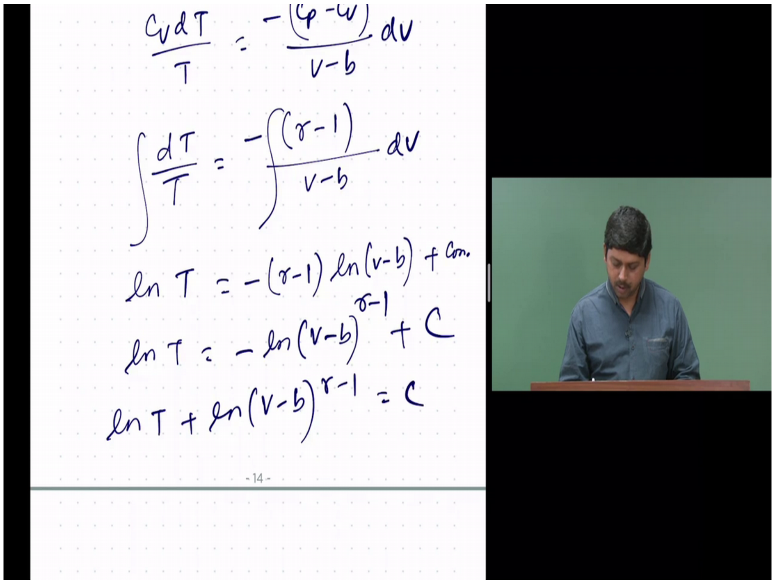
$$= \frac{C_v}{T}dT + \frac{R}{V-b}dV$$

$$dS = 0$$

$$0 = \frac{C_v}{T}dT + \frac{R}{V-b}dV$$

$$\frac{C_v dT}{T} = -\frac{R}{V-b}dV$$

$$\frac{C_v dT}{T} = -\frac{(C_p - C_v)}{V-b}dV$$



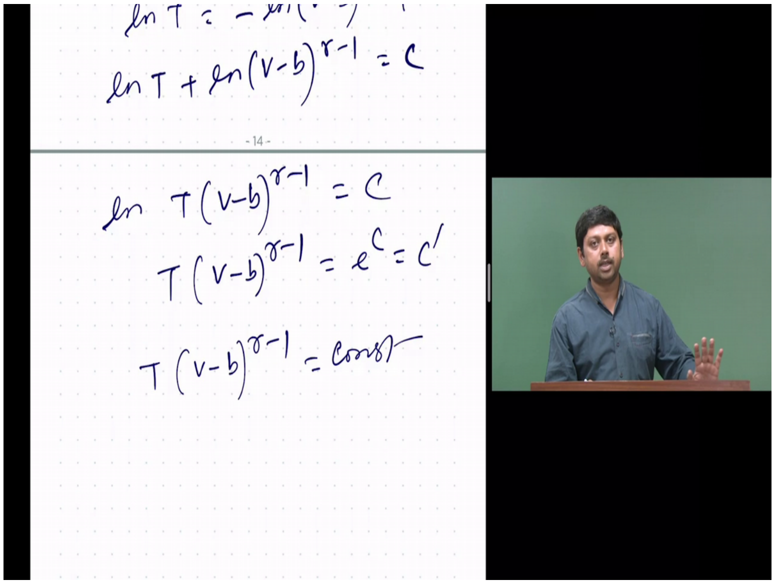
$$\frac{C_v dT}{T} = -\frac{(C_p - C_v)}{V-b}dV$$

$$\int\frac{dT}{T} = -\int\frac{(\gamma-1)}{V-b}dV$$

$$\ln T = -(\gamma-1)\ln(V-b) + \text{Con.}$$

$$\ln T = -\ln(V-b)^{\gamma-1} + C$$

$$\ln T + \ln(V-b)^{\gamma-1} = C$$



$\ln T = -\ln($

$\ln T + \ln(V-b)^{\gamma-1} = C$

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$\ln T(V-b)^{\gamma-1} = C$

$T(V-b)^{\gamma-1} = e^{C} = C'$

$T(V-b)^{\gamma-1} = \text{Const}$

Now in order to introduce the gamma and and we know that for adiabatic reversible adiabatic process, DS = 0. So 0 = CV by T DT + R by V - B DV. Okay. So now we can write CV DT by T is - R by V - B DV. Now you see that we can write R for an ideal gas as CP - CV and that is not true for van der waal gas but we are assuming that because otherwise we will not get the gamma. So DT by T = - now we divide by CV. So we will get gamma - 1 by V - B DV. Okay.

So now once we get that, you see we can get integrate on both sides and we can get Ln T = - gamma - 1 or 1 -, you could have done Ln V - B + constant. So Ln T is - Ln V - B to the power gamma - 1 + constant as C. So now you can see I can bring it to the left-hand side. Ln V - B to the power gamma - 1 = C.

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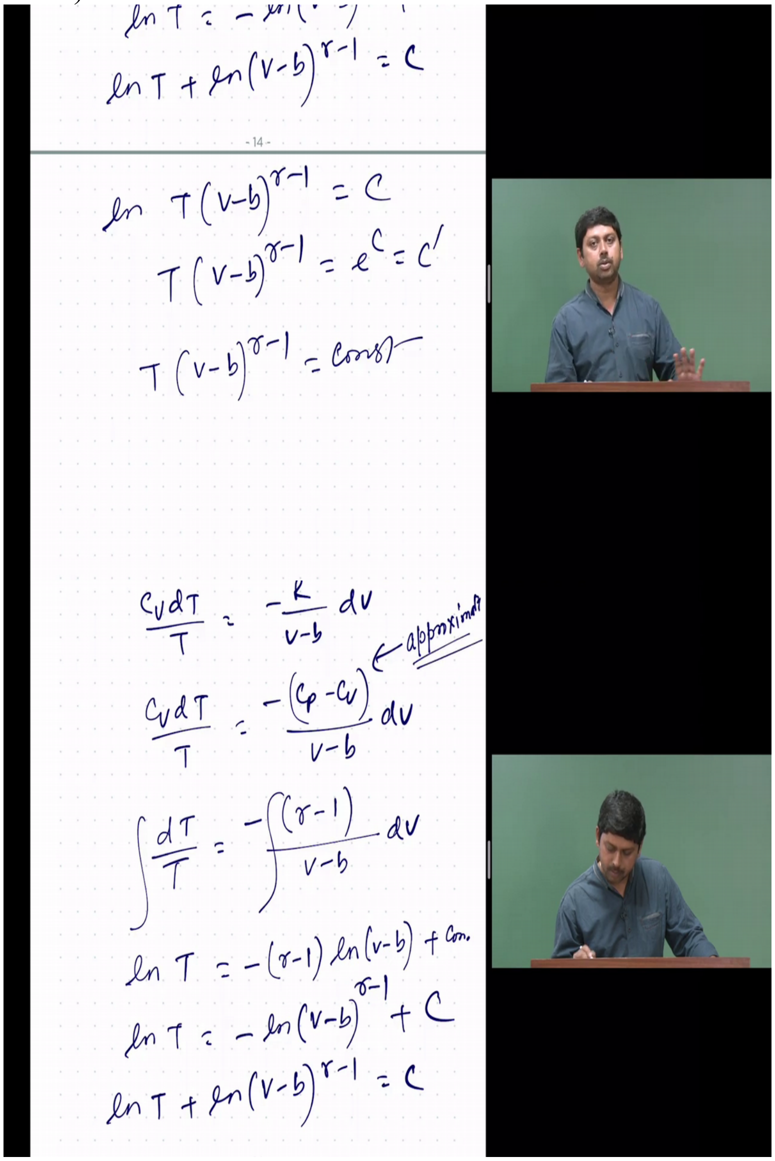

$\ln T + \ln(V-b)^{\gamma-1} = C$

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$\ln T(V-b)^{\gamma-1} = C$

$T(V-b)^{\gamma-1} = e^{C} = C'$

$T(V-b)^{\gamma-1} = \text{Const}$

$\frac{C_v dT}{T} = -\frac{R}{V-b} dV$

$\leftarrow$ approximate

$\frac{C_v dT}{T} = -\frac{(C_p - C_v)}{V-b} dV$

$\int \frac{dT}{T} = -\int \frac{(\gamma-1)}{V-b} dV$

$\ln T = -(\gamma-1)\ln(V-b) + \text{Con.}$

$\ln T = -\ln(V-b)^{\gamma-1} + C$

$\ln T + \ln(V-b)^{\gamma-1} = C$

Or Ln T into V - B to the power gamma - 1 is = C or T into V - B to the power gamma - 1 is e to the power C or let us say another constant, C prime. So we can see that T into V - B to the power - 1 is a constant for quasi-static adia reversible adiabatic changes. We just took DS = 0 and we just take took R to be CP - CV approximately. So that is like an approximate changes that we have done here. Approximation. That is why we got the gamma. Okay. So this we have shown.

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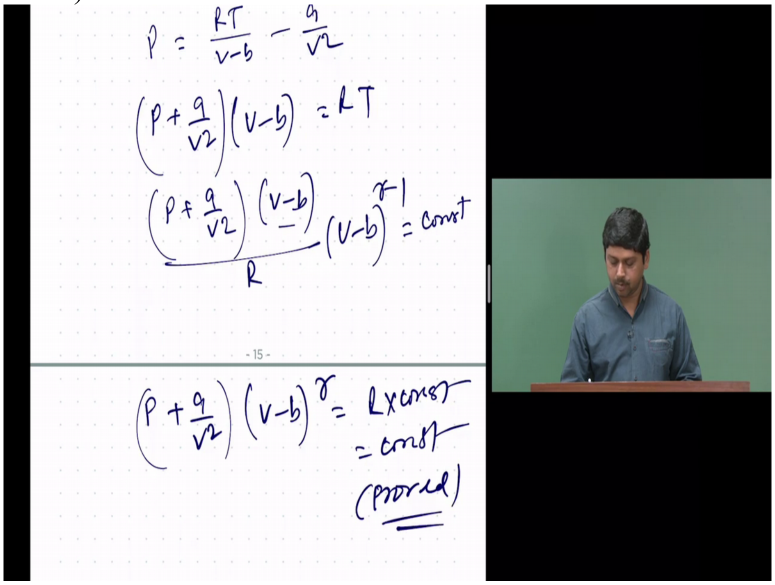

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

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

$$\underbrace{\frac{\left(P + \frac{a}{V^2}\right)(V-b)}{R}}(V-b)^{\gamma-1} = \text{const}$$

$$\left(P + \frac{a}{V^2}\right)(V-b)^{\gamma} = R \times \text{const}$$

$$= \text{const}$$

(proved)

And now and that is same as showing that, you can so the last part, same as showing that same as showing that it is P + A by V square V - B to the power gamma. We know that P = RT by V - B + A by V square - A by V square. So P + A by V square into V - B is RT. That you know. Therefore we can write the same equation 1 as we just replace the T by P + A by V square V - B by R into V - B to the power gamma - 1 is a constant. And then we can write P + A by V square V - B and V - B gamma to the power 1 is V - B to the power gamma is = R into constant which is another constant. That is also proved.

Okay. So that brings us to all the tutorial problems that we have decided for the thermodynamic relations and also that brings us to the end of all the lectures of this chemical principles II. So I would like to mention to you is that we have used first law of thermodynamics, 2nd law of thermodynamics from classical approaches, 2nd law of thermodynamics from statistical approaches and then we have used the fundamental equations of thermodynamics and derived all the thermodynamic relations, Maxwell's relations and everything.

We have talked about heat engines, their efficiencies and also we have shown that different principles, different statements of 2nd law for example efficiency cannot be 1 is in turn related to the efficiency the entropy of the universe is increasing. And entropy from the statistical point of view means nothing but the possibilities. So I hope that you will you will be able to apply these principles in different situations in in both you know experimental, when we are observing when you are observing something or when you are doing some experiments or or any any other situations in day-to-day life one can you can you will be able to associate the changes from the fact that the entropy of the universe is changing or if you only look at the object that you are looking at and then you can find out whether the free energy, Helmoge free energy or Gibbs free energy or other free other quantities are changing or not.

So in short that any change that we observe, that will be governed by these principles of thermodynamics. So I hope that you will get benefited from this course and and it will be helpful in whatever you want to apply it for or learn it for. Okay. Thank you.