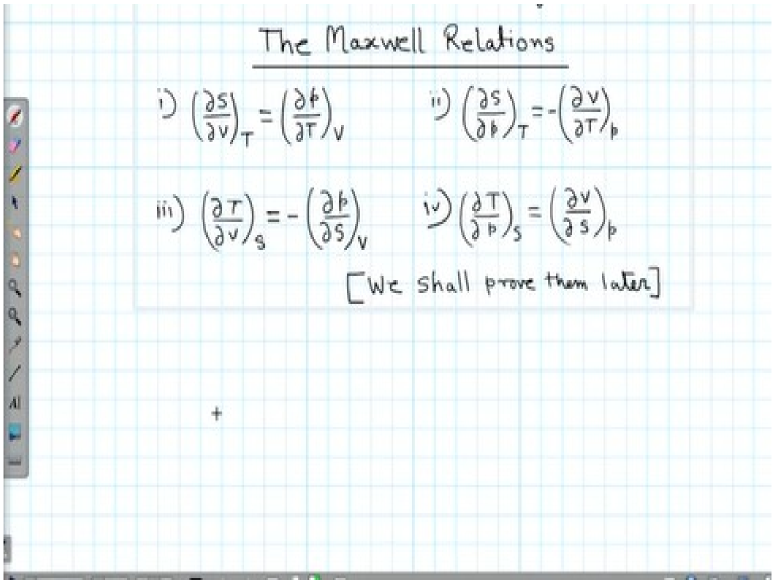
Thermal Physics
Prof. Debamalya Banerjee
Department of Physics
Indian Institute of Technology, Kharagpur

Lecture - 47
Application of Thermodynamic Relations

Hello and welcome back to another lecture of this NPTEL lecture series on thermal physics. Now in the last lecture we talked about thermodynamic relations and we talked about the applications of those relations and in order to find T ds equation, energy equation and also, we have applied those in order to compute the internal energy of Van der Waals gas. Now so today we will continue from where we have left in the last class.

(Refer Slide Time: 00:56)



The Maxwell Relations

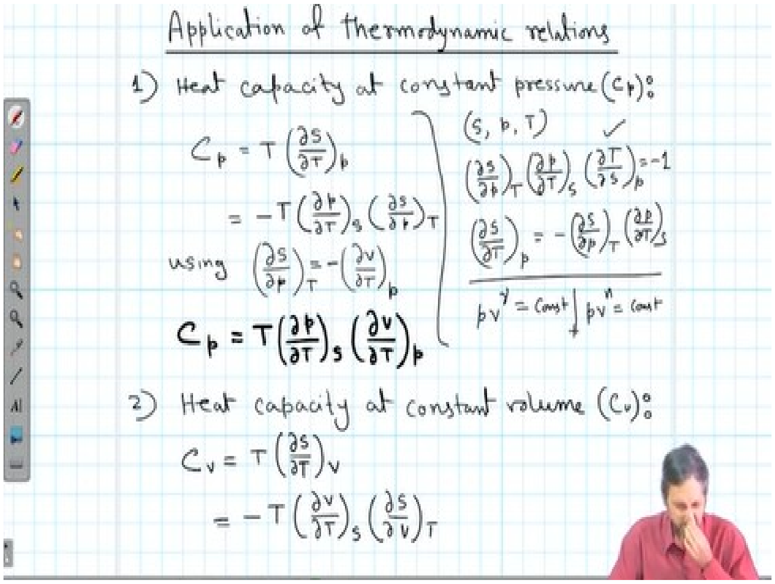
i) $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$ ii) $\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$

iii) $\left(\frac{\partial T}{\partial v}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$ iv) $\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial v}{\partial s}\right)_p$

[We shall prove them later]

So, let us quickly recap the thermodynamic relations with the Maxwell's relations. So, these are the four relations we have talked about relation one, two, three and four.

(Refer Slide Time: 01:11)



Application of thermodynamic relations

1) Heat capacity at constant pressure (C_p):

$$C_p = T\left(\frac{\partial s}{\partial T}\right)_p$$

$$= -T\left(\frac{\partial p}{\partial T}\right)_s\left(\frac{\partial s}{\partial p}\right)_T$$

using $\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$

$$C_p = T\left(\frac{\partial p}{\partial T}\right)_s\left(\frac{\partial v}{\partial T}\right)_p$$

(s, p, T) ✓

$$\left(\frac{\partial s}{\partial p}\right)_T\left(\frac{\partial p}{\partial T}\right)_s\left(\frac{\partial T}{\partial s}\right)_p = -1$$

$$\left(\frac{\partial s}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T\left(\frac{\partial p}{\partial T}\right)_s$$

$pv^\gamma = \text{Const}$ | $pv^n = \text{Const}$

2) Heat capacity at constant volume (C_v):

$$C_v = T\left(\frac{\partial s}{\partial T}\right)_v$$

$$= -T\left(\frac{\partial v}{\partial T}\right)_s\left(\frac{\partial s}{\partial v}\right)_T$$

And without further delay we will directly go to the application of these relations. So, the first applications we have listed many applications in this lecture. So, the first application is the heat capacity at constant pressure. So, far what we know about C p, C p is equal to T del s del T p. Now if what we can do is we can slightly modify this relation using the fact so basically, we can substitute del s del P T with del P del T s times del s del P T with a minus sign.

Now what is the origin of this equation? If we choose S, P and T as my three independent parameters I am just putting a running node here. So, what we can do is? We can write del S del P T times del P del so it will be del P del T S times del T del S P will be equal to minus 1. So, this is a general formulation that we have proved in one of our previous classes and if this is the case then we can so, if this is the case then we can write del S delta.

So, if I basically take this particular term to this side, it will be del S del T P and this will be equal to - of del S del P T del P del T S. Because this is the first occurrence of this such relation I have just did it explicitly for you. But next time onwards I will directly put this substitution relation. I think you will understand what I mean. So, if not just do these few steps and then you will realize that something like del S del P T can be expressed as minus del P del T S times del S del P T.

So, that is exactly what we have substituted here. Now once again from the Maxwell's relation del S del P T is equal to minus del V del T. So, again Maxwell's relation you might think that how do I remember all these Maxwell's relations that will be discussed in the next lecture. How to remember this Maxwell's relation and then we have C p is equal to minus del P del T S times del V delta P. Now what is the advantage of writing C p in this particular form over this parent form which is T del S del T P?

The advantage is if we have the equation of state then we can directly compute del V del T P from there. And what is del P del T S? del P del T S is calculated when I say S constant that means it is calculated along an adiabatic path. For a ideal gas we know P, V to the power gamma is equal to constant that is for an ideal gas and even for a non-ideal gas generally an adiabatic process follows a polytroph P v to the power n = constant where n the value of n is something that we have to determine.

It is somewhere close to gamma but not exactly equal to gamma. So, once we know this polytroph or once we know this know the adiabatic path so this is only, I mean of course I have just written in in terms of P and V but we can also express it in terms of V and T or P and T. So, basically any combination of these three parameters P, V and T. So, if we know such a combination from there, we have to compute del P del T S.

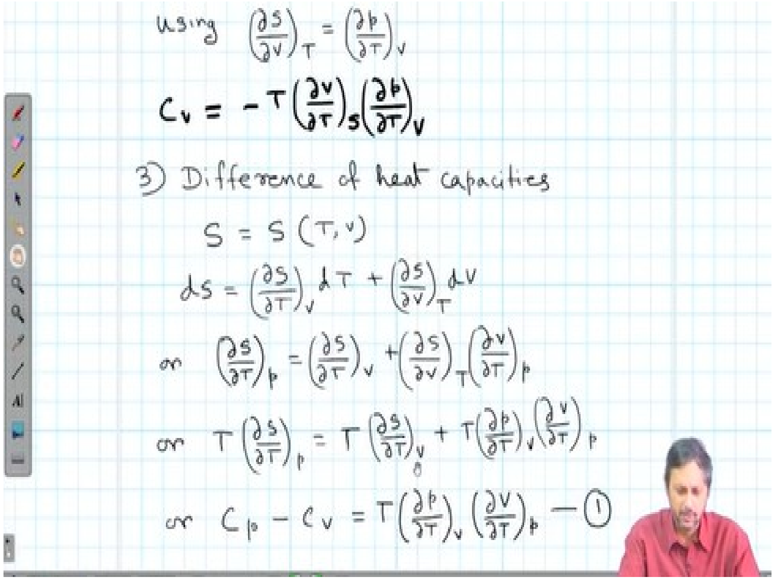
So, and then we just have to multiply these two which gives us C p directly. Now what is the advantage? Look at this del S del T P is something that we cannot compute directly from the equation of state. But from this if we focus on this particular form, we can compute both this parameter and both this function sorry, both this quantity directly from either equation of state. One from equation of state and the other one is from the polytroph along which the adiabatic process takes place.

And also, that polytroph is determined by this one the equation of state itself. So, basically this allows us to compute C p directly from the equation of state. And this is what we have a tremendous advantage because previously so far whatever we have done we have not. So, internal energy is one example that we got in the last lecture that so far, we have not discussed I mean before this particular discussion.

We have not discussed anything about the functional form, functional dependence of internal energy or functional dependence of heat capacity, how it is correlated directly with the equation of state. Now we are trying to correlate those with the equation of state of a system. Similarly for C v the heat capacity at constant volume which is T del S del T v once again can be written as minus T del V del T S del S del V T. So, once again we have to use a similar formalism here.

So, instead of S, T and P in the previous case we have to take S, T and V as three independent parameters and compute a relation similar to this instead of pressure you have to put volume and you get to this relation.

(Refer Slide Time: 07:12)



using $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$

$$C_v = -T\left(\frac{\partial v}{\partial T}\right)_s\left(\frac{\partial p}{\partial T}\right)_v$$

3) Difference of heat capacities

$$S = S(T, v)$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$$

or $\left(\frac{\partial s}{\partial T}\right)_p = \left(\frac{\partial s}{\partial T}\right)_v + \left(\frac{\partial s}{\partial v}\right)_T\left(\frac{\partial v}{\partial T}\right)_p$

or $T\left(\frac{\partial s}{\partial T}\right)_p = T\left(\frac{\partial s}{\partial T}\right)_v + T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p$

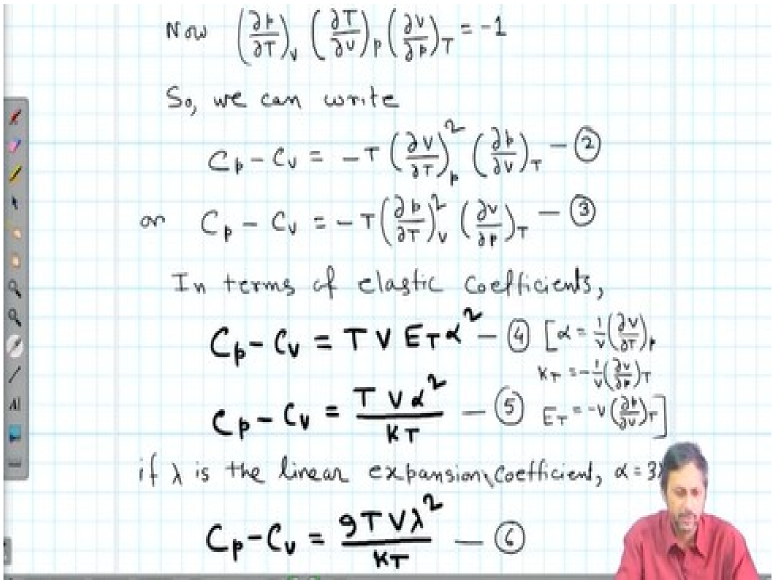
or $C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p$ — ①

Simplifying further we get C v is equal to and once again we have to use the Maxwell relation that del S del V T is equal to del V del T v and we get C v is equal to minus T del V del T S times del P del T v. So, the same argument goes the second term del P del T v is directly computed from the equation of state whereas the first term is along calculated along an adiabatic path. Now next comes the difference in heat capacities.

So, we write start by writing S is equal to S, T and V. So, dS is equal to del S del T v dT plus del S del V T dV. So, if I just take this dP like so if I divide it by delta T at constant pressure so we have del S del T P is equal to del S del T v plus del S del V T del V del T. Multiplying by T we can write C p minus C v is equal to T del so there is the modification so we have this is C p this is C v. Now we simply substitute this del V del T del S del V T with del P del T v.

And we have C p minus C v is equal to T times del P del T v del V del T P. The advantage once again is once we know the equation of state you can try it if you can put, for example, ideal gas equation and see if this goes to zero or not.

(Refer Slide Time: 08:56)



Now $\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_p \left(\frac{\partial v}{\partial p}\right)_T = -1$

So, we can write

$$C_p - C_v = -T\left(\frac{\partial v}{\partial T}\right)_p^2 \left(\frac{\partial p}{\partial v}\right)_T \quad — ②$$

or $$C_p - C_v = -T\left(\frac{\partial p}{\partial T}\right)_v^2 \left(\frac{\partial v}{\partial p}\right)_T \quad — ③$$

In terms of elastic coefficients,

$$C_p - C_v = T V E_T \alpha^2 \quad — ④$$

$$C_p - C_v = \frac{T V \alpha^2}{K_T} \quad — ⑤$$

$\left[\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p\right.$

$K_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T$

$\left.E_T = -v\left(\frac{\partial p}{\partial v}\right)_T\right]$

if λ is the linear expansion coefficient, $\alpha = 3$

$$C_p - C_v = \frac{9 T V \lambda^2}{K_T} \quad — ⑥$$

Next what we can do is once again we have this relation between pressure volume and temperature. So, this is not U but this is V so careful. So, we have this relation between pressure, volume and temperature and we can write C p minus C v is equal to minus T del V del T square del P del V T or we can also write so I mean I have not shown you all the intermediate steps. But from there if you substitute for del P del T v you get del V del T P whole square times del P del V T.

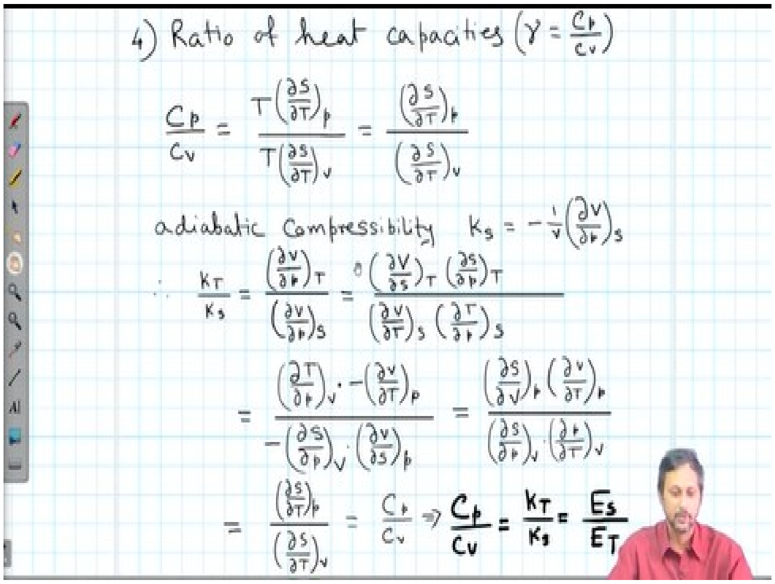
Similarly, you can also do another substitution I mean instead of substituting for del P del T v if you substitute for del V del T P then you get sorry if you substitute once for del P del T v and another time for del V delta P once you get this one the second time you get this one. So, both are equivalent relations, just another way of writing, we call it equation 2 and 3. Now why we; do that because we want to write everything in terms of the elastic coefficients.

What are the elastic coefficients? We have alpha which is 1 over V del V del T P that is the coefficient of volume expansion. We have isothermal compressibility k which is minus 1 over V del V del P T and we have isothermal elasticity E T which is minus V del P del V T. So, everything in terms of this bulk modulus. So, we have C p minus C v, we can either express from this relation. Relation 2 can be represented as T v E T alpha square or relation 3 can be represented as C p minus C v is equal to T v alpha square by K T.

Now if lambda is the linear expansion coefficient, then we have alpha is equal to 3 lambda. So, then we can substitute for this one here substitute for alpha here l. For example, in this relation so we have 9 alpha square and sorry 9 lambda square and we have C p minus C v is equal to 9 T v lambda square by K T. So, these are all different forms of heat capacity differences. Why we do that? Because as I am keep saying this; it is sometimes not possible to determine the equation of state for a given substance or non-ideal gas.

But it is somewhat easy to measure this bulk elastic modulus in a direct experimental way. So, once we know this elastic modulus, we can simply plug this in and we can get the difference in heat capacity. So, this is just for the sometimes these forms are just convenient to use.

(Refer Slide Time: 12:02)



4) Ratio of heat capacities $\left(\gamma = \frac{C_p}{C_v}\right)$

$$\frac{C_p}{C_v} = \frac{T\left(\frac{\partial S}{\partial T}\right)_p}{T\left(\frac{\partial S}{\partial T}\right)_v} = \frac{\left(\frac{\partial S}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial T}\right)_v}$$

adiabatic Compressibility $K_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$

$$\therefore \frac{K_T}{K_S} = \frac{\left(\frac{\partial V}{\partial P}\right)_T}{\left(\frac{\partial V}{\partial P}\right)_S} = \frac{\left(\frac{\partial V}{\partial S}\right)_T\left(\frac{\partial S}{\partial P}\right)_T}{\left(\frac{\partial V}{\partial T}\right)_S\left(\frac{\partial T}{\partial P}\right)_S}$$

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

$$= \frac{\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial S}{\partial T}\right)_V} = \frac{C_p}{C_v} \Rightarrow \frac{C_p}{C_v} = \frac{K_T}{K_S} = \frac{E_S}{E_T}$$

Also, we can compute the ratio of this heat capacity which is given as C p by C v which is T del S del T del S del T P, at time divided by T del S del T v. So, del S del T P divided by del S del T v. Now I can directly prove like after a lot of manipulation I can show that this is directly equal to K T by k S. Instead, what we do is I start from defining adiabatic compressibility which is k S so minus 1 over V del V del P S.

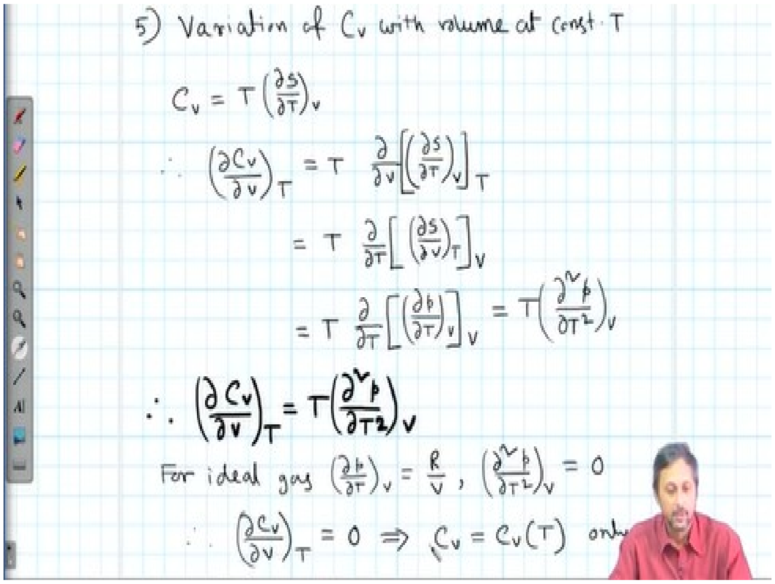
Please remember the adiabatic sorry isothermal compressibility is K T is equal to minus 1 over V del V del P T and this is del V 1 over V del V del P S that means it is happening in an adiabatic manner. So, that this ratio once again goes through lots of manipulation here. So, we start with del V del P T del V del P S and now what we do is we write this del V del P T as del V del S T del S del P T. Here also we write del V del T S del T del P S.

And then we apply Maxwell's relation into this one and this one. So, del S del P T is equal to minus del P del T P whereas this one del V del T S is equal to minus del S del P V. So, sometimes this is directly from the Maxwell's relation, sometimes we have to take the Maxwell's relation and invert both sides. Just go through it once you will realize and then what do we do? Basically, we take the ones which are keeping the same parameter constant.

For example, these two are keeping P constant, this one is P constant, this one is P constant. So, if I just invert this one it will be del in the numerator it will be del S del V P constant and times of course there is a minus sign here which cancels. So, del S del V P constant, del V del T P constant. Similarly, it will be del S del P V constant and del P del T v constant. So, once again we simplify and get del S del T P divided by del S del T v which is nothing but C p by C v.

So, we see C p by C v is equal to K T by k s. But once again the elasticity is nothing is the opposite of compressibility. So, we have K T which is the compressibility and E T which is elasticity. So, similarly we can define adiabatic elasticity then K T by k s will be equal to E s by E T. So, C p by C v is equal to either K T by k s or is equal to E s by E T. So, this final relation we have to keep in mind.

(Refer Slide Time: 15:04)



5) Variation of C_v with volume at const. T

$$C_v = T\left(\frac{\partial s}{\partial T}\right)_v$$

$$\therefore \left(\frac{\partial C_v}{\partial v}\right)_T = T\frac{\partial}{\partial v}\left[\left(\frac{\partial s}{\partial T}\right)_v\right]_T$$

$$= T\frac{\partial}{\partial T}\left[\left(\frac{\partial s}{\partial v}\right)_T\right]_v$$

$$= T\frac{\partial}{\partial T}\left[\left(\frac{\partial p}{\partial T}\right)_v\right]_v = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v$$

$$\therefore \left(\frac{\partial C_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v$$

For ideal gas $\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v}$, $\left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0$

$\therefore \left(\frac{\partial C_v}{\partial v}\right)_T = 0 \Rightarrow C_v = C_v(T)$ onl

Now another thing is variation of C v with volume at constant temperature. Now what do you mean by that? So, we all know that there are two types of heat capacity, one is measured at constant volume and the other one is measured at constant pressure. But then let us assume we confine some amount of gas in a very tiny one cc container. So, one centimetre by one centimetre by one centimetre container and we measure.

We do some experiment measure the heat capacity of that gas. Now the same gas goes into a 1 litre container which is 1 cc to 1 litre is 1000 times. So, thousand times more diluted and we repeat the measurement once again. Next, we put this gas into a 1 meter cubed container which is

10 to the power 6 times diluted as compared to the first one and even more actually one centimetre cubed, one meter cube.

Whatever there is a large factor could be six, could be nine I do not remember offhand, but whatever it is. Now after this volume is one meter cube the same volume which was initially contained in one centimetre cube. Now if it is in one meter cube what is the heat capacity? So, ideally for an ideal gas all these three cases the heat capacity should be same. But is it the case every time we do that? So, let us look into it in a from a thermodynamic perspective.

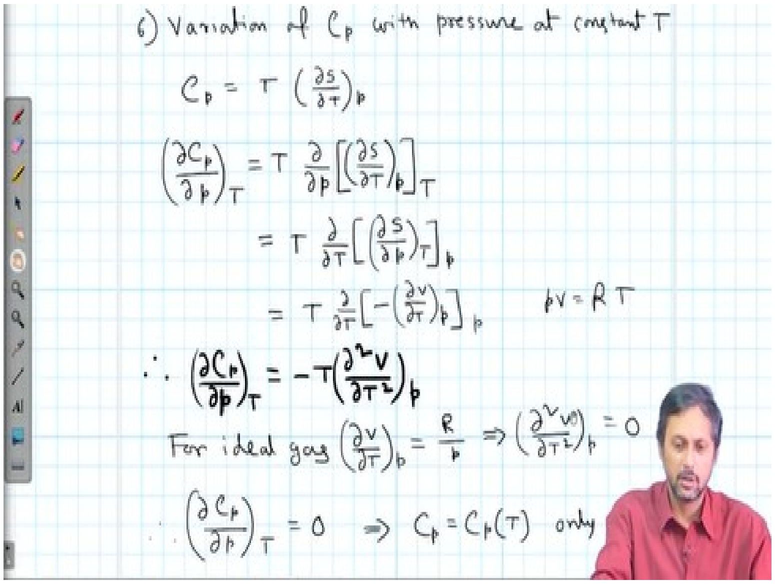
So, C v is equal to T del S del T v. Now del C v del V T is equal to T del V of so del del V of del S del T v with T constant. Now because these are even in dS is a state sorry S is a state function these two integrations can be interchanged and we can have T del del T of at V constant of del S del V T. Now from Maxwell's relation we can substitute del S del V T by del P del T v and we get T. So, once again these two are the same like del P del T v also has V constant and we have a del del T with also V constant.

So, basically so it will be a double derivative of P with V constant. So, we have T is equal to del 2 P del T 2 with V constant. So, del C v del T is equal to T del 2 P del T square is equal to V. So, for ideal gas we have del P del T v is equal to R by V or just now I remember I just said by mistake that this should be zero for ideal gas, now it should be R actually. So, T del P del T v times del V del T P you can start from PV is equal to RT and you will find that this will give you R.

So, the difference is C p - C v = R. You can do the same thing from here or here you should get the same result. It is just for convenience we modify those to get this in terms of the bulk modulus. Anyway, so for ideal gas we have PV = RT. So, once again del P del T v is R by V del 2 P del T 2 with V constant will be equal to 0. Because this is only a function of V there is no temperature anymore.

So, this is equal to 0 so we have del C v del T is equal to 0 that means for an ideal gas there is no change of C v as a function of volume and C v remains a function of temperature only.

(Refer Slide Time: 19:03)



6) Variation of C_p with pressure at constant T

$$C_p = T\left(\frac{\partial s}{\partial T}\right)_p$$

$$\left(\frac{\partial C_p}{\partial p}\right)_T = T\frac{\partial}{\partial p}\left[\left(\frac{\partial s}{\partial T}\right)_p\right]_T$$

$$= T\frac{\partial}{\partial T}\left[\left(\frac{\partial s}{\partial p}\right)_T\right]_p$$

$$= T\frac{\partial}{\partial T}\left[-\left(\frac{\partial v}{\partial T}\right)_p\right]_p \qquad pv = RT$$

$$\therefore \left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p$$

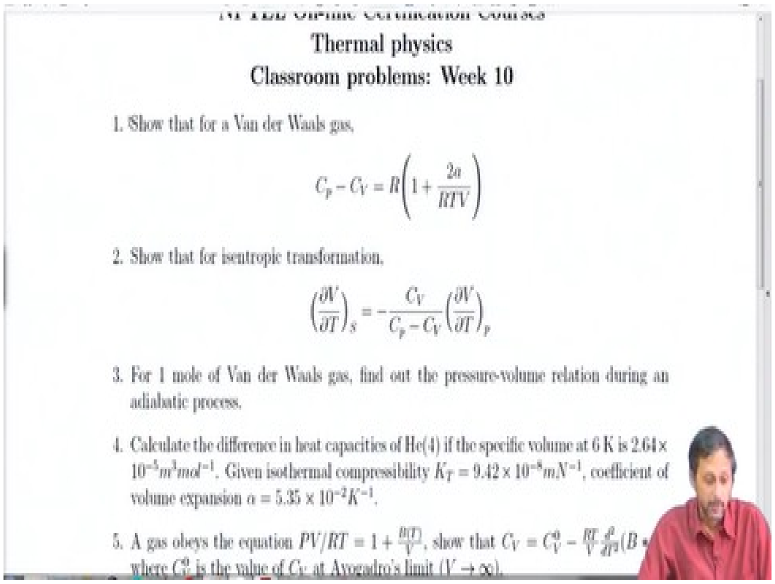
For ideal gas $\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} \Rightarrow \left(\frac{\partial^2 v}{\partial T^2}\right)_p = 0$

$$\therefore \left(\frac{\partial C_p}{\partial p}\right)_T = 0 \Rightarrow C_p = C_p(T) \text{ only}$$

Similarly for pressure sorry heat capacity at constant pressure we can do very similar manipulation and get so the same question persist. We have a big large amount of gas. Let us say we measure the heat capacity at constant pressure. We compress it substantially by a factor of 10 to the power 3 or so measure the heat capacity. We again do some more compression and measure heat capacity at constant pressure.

So, every time we do, we compress the gas does the heat capacity change. So, that is given finally by this equation which is del C p del P at constant temperature is equal to minus T del 2 V del T 2. Once again for ideal gas this quantity becomes 0 and C becomes a function of temperature only.

(Refer Slide Time: 19:59)



Thermal physics

Classroom problems: Week 10

1. Show that for a Van der Waals gas,

$$C_p - C_V = R\left(1 + \frac{2a}{RTV}\right)$$

2. Show that for isentropic transformation,

$$\left(\frac{\partial V}{\partial T}\right)_S = -\frac{C_V}{C_p - C_V}\left(\frac{\partial V}{\partial T}\right)_p$$

3. For 1 mole of Van der Waals gas, find out the pressure-volume relation during an adiabatic process.

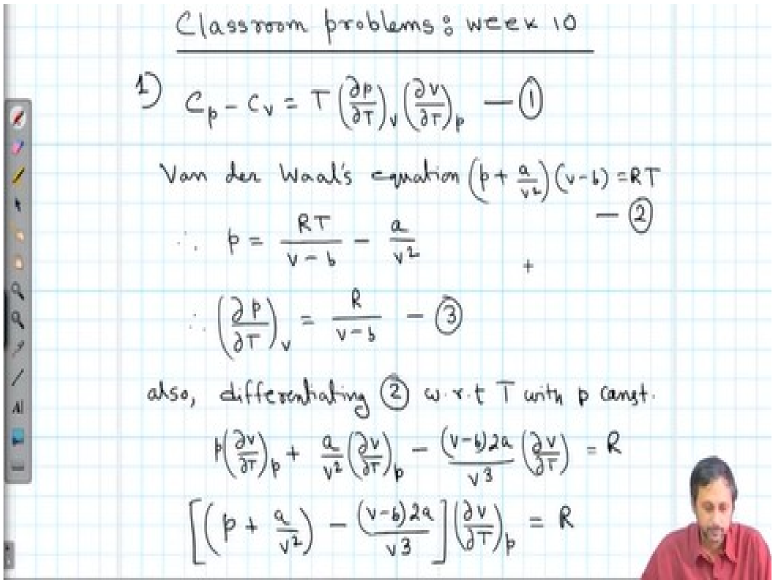
4. Calculate the difference in heat capacities of He(4) if the specific volume at 6 K is $2.64 \times 10^{-5} m^3 mol^{-1}$. Given isothermal compressibility $K_T = 9.42 \times 10^{-8} m N^{-1}$, coefficient of volume expansion $\alpha = 5.35 \times 10^{-2} K^{-1}$.

5. A gas obeys the equation $PV/RT = 1 + \frac{B(T)}{V}$, show that $C_V = C_V^0 - \frac{RT}{V}\frac{d^2}{dT^2}(B$

where C_V^0 is the value of C_V at Avogadro's limit ($V \to \infty$).

So, now we move to solve some classroom problems. So, we have a problem set for week 10 and there we have many problems. Out of that we will be doing the first four problems in today's lecture. So, the first problem is that show that for a Van der Waals gas C p minus C v is equal to R 1 plus 2 a R divided by RTV. I mean ideally there should be an approximate sign so I will change that because this is an approximate relation as we will see so I have to change this symbol here. So, let us look into it.

(Refer Slide Time: 20:37)



Classroom problems : week 10

1) $C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p$ — ①

Van der Waal's equation $\left(p + \frac{a}{v^2}\right)(v-b) = RT$ — ②

$\therefore \quad p = \frac{RT}{v-b} - \frac{a}{v^2}$

$\therefore \quad \left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-b}$ — ③

also, differentiating ② w.r.t T with p const.

$$p\left(\frac{\partial v}{\partial T}\right)_p + \frac{a}{v^2}\left(\frac{\partial v}{\partial T}\right)_p - \frac{(v-b)2a}{v^3}\left(\frac{\partial v}{\partial T}\right) = R$$

$$\left[\left(p + \frac{a}{v^2}\right) - \frac{(v-b)2a}{v^3}\right]\left(\frac{\partial v}{\partial T}\right)_p = R$$

So, what we have seen? We have already seen that C p minus C v is equal to T del P delta V del V delta P and as I have discussed during the when we derived this also, we have I have mentioned that the advantage of having this relation is both del V del T v and del V del T P are directly derivable from the equation of state. So, once we know the equation of state, we can directly compute the C p C v relation using this.

And it could be any equation of state. I mean it does not matter if we have a simple or complicated equation of state. In principle we can always we will be able to compute del P del T v. So, let us do it for this Van der Waals equation which is P plus a by V square times V minus b is equal to RT. So, we call it equation two. So, we can rearrange this one and write P is equal to RT by V minus b minus a by V square then it will give you del P del T v is equal to R by V minus b.

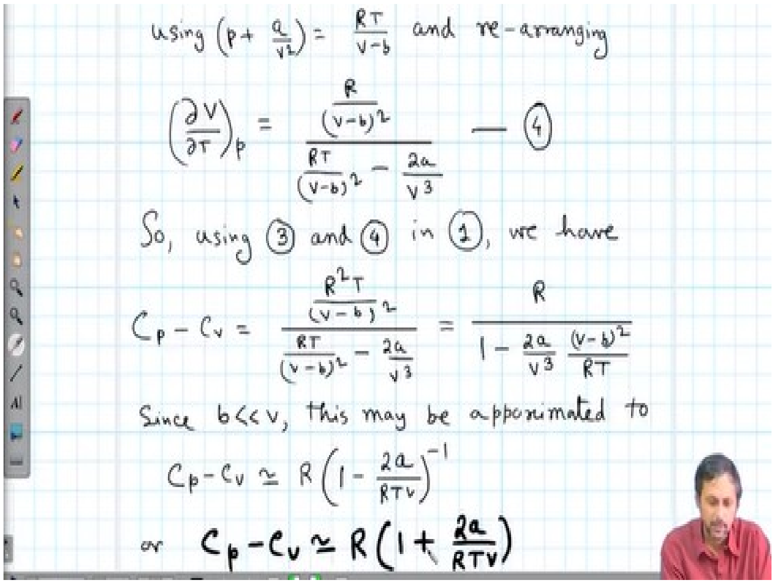
So, let us call it equation 3 and once again we can differentiate this relation 2 with respect to T with keeping P constant. So, what will happen to that? So, let us open this bracket so we have v minus b here. So, we take we write this as P times v minus b plus a times v minus b divided by v square. So, if I do this differential the first term will give you P del V del T P because P remains constant during this process.

So, the second term will be basically a sorry second term will be a by V square times v minus b so there is no P here. So, basically if I take del del T on this so there will be the first term will be minus a by v cubed v minus b and the second term will be plus a by v square times it will be simply del V del T. So, this term whole multiplied by del V delta. Anything else, did I miss anything? a by v cubed not exactly yes there is a factor of 2 here.

So, exactly these two terms we will have here. So, just to show you I have this I have done it here. But finally, what we will get is this relation. And if we take del V del T P out then we can write this as P plus a by v square minus v minus b times 2 a divided by v cubed whole multiplied by del V del T P is equal to R. So, from there we can write also we can use that P plus a by v square is equal to RT divided by v minus b.

So, if we use that we get del V del T P is equal to R by v minus b whole square divided by RT by v minus b whole square minus 2 a by V cubed. Just to get rid of this v minus b from here so we have divided. So, we first simplified this relation so we wrote it as R divided by this will be p plus a by v square will be RT by v minus b minus R divided by v minus b minus v minus b 2 a by v cubed. So, just to get rid of this v plus b from here so, we have modified this slightly and wrote it in this form.

(Refer Slide Time: 24:44)



using $\left(p+\frac{a}{v^2}\right) = \frac{RT}{v-b}$ and re-arranging

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{\frac{R}{(v-b)^2}}{\frac{RT}{(v-b)^2} - \frac{2a}{v^3}} \quad — ④$$

So, using ③ and ④ in ①, we have

$$C_p - C_v = \frac{\frac{R^2T}{(v-b)^2}}{\frac{RT}{(v-b)^2} - \frac{2a}{v^3}} = \frac{R}{1 - \frac{2a}{v^3}\frac{(v-b)^2}{RT}}$$

Since $b \ll v$, this may be approximated to

$$C_p - C_v \simeq R\left(1 - \frac{2a}{RTv}\right)^{-1}$$

or $$C_p - C_v \simeq R\left(1 + \frac{2a}{RTv}\right)$$

So, from using 3 and 4 in 1 so basically, we have del P del T v and del P del T P so if we use that in the original C p C v relation we get C p - C v = R square T divided by v minus b whole square divided by RT by v minus b whole square minus 2 a by v cubed. Now once again what we can do is we see T by v minus b whole square is common in these two terms. So, we can get rid of that and we can write this as R divided by 1 minus 2 a by v cubed v minus b whole square divided by R T.

Now up to this point this is an exact relation. So, C p minus C v is equal to that for a Van der Waals gas. Now what we have in the problem is essentially an approximation of this relation which we have mentioned here. So, all we have to do is we have to make some assumption. The first assumption which not exactly sorry this not assumption is make some approximation. The first approximation is because b is much smaller than v we can substitute this v minus b square with b square.

So, that means we can write this as R times 1 minus 2 a by v cubed. So, you see this will be v square there will be a v cubed here. So, it will be 2a divided by RT times V. So, this is an approximate relation whole to the power minus 1. Once again, a is also small because a is one of the Van der Waals constants and we have already seen that Van der Waals constants have smaller dimension I mean it is much, much less than 0.

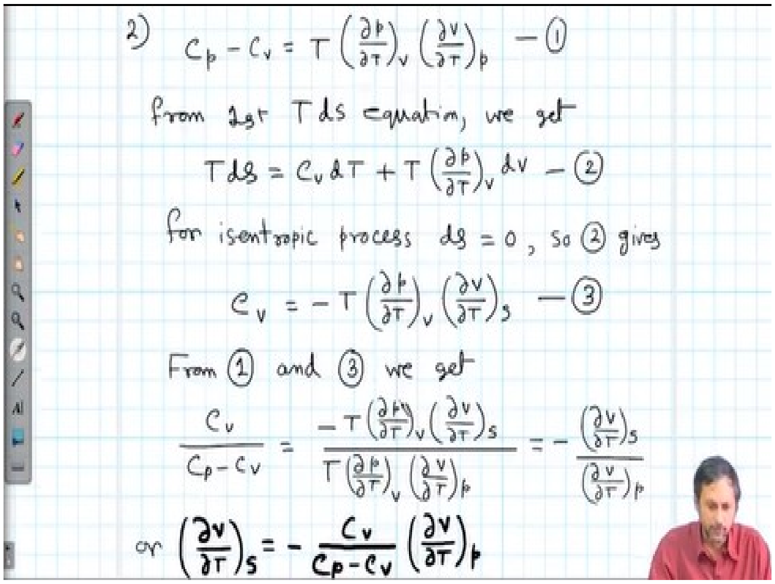
So, what we can do is we can approximate this relation as so it is a basically a binomial expansion. So, this is approximated as R times 1 plus 2 a divided by RTV. So, this is my final relation final answer but this is remember that this is an approximate relation. And this is nothing but the binomial expansion it is 1 minus x whole to the power minus 1 is approximately is equal to 1 plus x plus x square and higher order terms.

So, this is only the binomial expansion and given that x is small we can keep only up to the first non-zero I mean first term, first degree of x. So, that is exactly what we have done here and finally we have this answer. So, let us move to the second problem. Second problem is show that for isentropic transformation del V del T s is equal to minus C v divided by C p minus C v del V del T p. Now this is a very important relation because as we have discussed already in the thermodynamic relations.

There are certain cases where the derivative is taken with respect to entropy constant. Now entropy can not a part of the equation of state but using this relation what we have derived here. We can actually transform this in differential into a differential which is directly deliverable from the equation of state. And of course, C v C p minus C v the difference in heat capacity everything is derivable from the equation of state.

So, basically what we are going to do here is we are going to transform an equation or transform a derivative which is not directly achievable from the equation of state into a form in which we can derive it directly from the equation of state of a system.

(Refer Slide Time: 28:50)



2) $C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p$ — ①

from 1st T ds equation, we get

$$T\,ds = C_v\,dT + T\left(\frac{\partial p}{\partial T}\right)_v dv \quad \text{— ②}$$

for isentropic process $ds = 0$, so ② gives

$$C_v = -T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_s \quad \text{— ③}$$

From ① and ③ we get

$$\frac{C_v}{C_p - C_v} = \frac{-T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_s}{T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p} = -\frac{\left(\frac{\partial v}{\partial T}\right)_s}{\left(\frac{\partial v}{\partial T}\right)_p}$$

or $\left(\frac{\partial v}{\partial T}\right)_s = -\frac{C_v}{C_p - C_v}\left(\frac{\partial v}{\partial T}\right)_p$

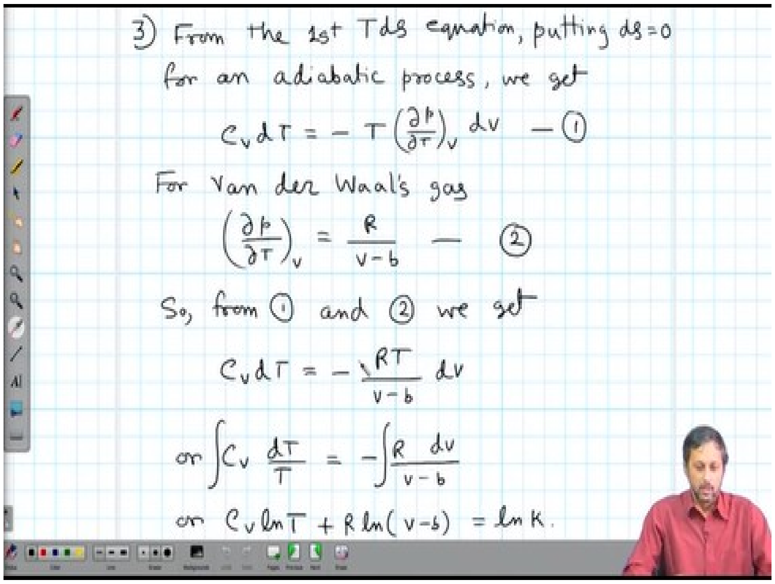
So, for this one we start again with this relation that C p minus C v is equal to T del P del T v times del V del T p. Now from the first T dS equation we get T dS is equal to C v dT plus T del P del T v dv. Now for an isentropic process or adiabatic process we have d S is equal to 0. So, this term goes to 0 and this equation can be rearranged as C v is equal to minus T del P del T v times del V del T s. So, what happens is this there is a del V here, d V here, there is a dT here.

Under the condition that dS = 0 we can rewrite this as del V divided by del T at s constant. So, we have relation 1 and we have relation 3. So, we can compute the ratio C v divided by C p minus C v which is minus T del P sorry so which is - T del P del T v divided by multiplied by del V del T s divided by so which is from equation 3 divided by T del P del T v del V delta p. We see del P del T v cancels from the numerator and denominator leaving and T and T cancels leaving us with minus del V del T s divided by del P del T p.

So, del V del T s is equal to minus C v divided by C p minus C v del V del T p. So, which is a very powerful result and we see that using simple mathematics of thermodynamic relation actually enables us to calculate all the important properties of a system starting from the equation of state. Problem three for one mole of Van der Waals gas find out the pressure volume relation during an adiabatic process.

We know that for an ideal gas the adiabatic pressure volume relation is p V to the power gamma is equal to constant. So, basically, we have to derive a similar relation but this time for Van der Waals gas.

(Refer Slide Time: 31:14)



3) From the 1st TdS equation, putting dS = 0 for an adiabatic process, we get

$$C_v dT = -T\left(\frac{\partial p}{\partial T}\right)_v dv \quad — ①$$

For Van der Waal's gas

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-b} \quad — ②$$

So, from ① and ② we get

$$C_v dT = -\frac{RT}{v-b} dv$$

$$\text{or} \int C_v \frac{dT}{T} = -\int \frac{R\, dv}{v-b}$$

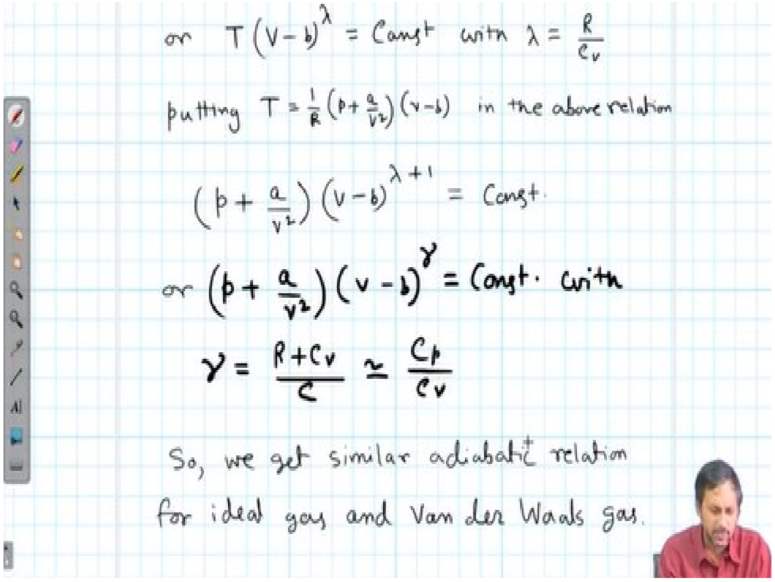
$$\text{or} \quad C_v \ln T + R \ln(v-b) = \ln K.$$

So, once again from the first radius equation putting dS = 0 we can rewrite this. So, exactly the way we did it in I mean very similar to sorry not exactly what very similar to this equation. But here we are not writing C v in terms of these two derivatives instead we are writing C v dT is equal to minus T del P del T v d v. Now from the Van der Waals equation we can directly compute del P del T v which is R by v minus b which we did in the first problem itself.

So, I am not repeating it again. So, from 1 and 2 we can basically we can substitute for R by v minus b here and we can rearrange to write C v dT is equal to minus RT by v minus b d v which is C v. So, rearranging we get integration C v dT by T is equal to minus R d v by v minus b which gives you C v ln R plus R ln C v ln T plus R ln v minus b is equal to some constant ln K where this is K is actually a constant. So, any constant we do not care what is this constant.

So, this in the same time what we can do is we can divide this by C v this relation. So, we can write ln T plus R by v ln v minus b is equal to some other constant K prime ln K prime.

(Refer Slide Time: 32:48)



or $T(v-b)^{\lambda} = \text{Const}$ with $\lambda = \frac{R}{C_v}$

putting $T = \frac{1}{R}\left(p+\frac{a}{v^2}\right)(v-b)$ in the above relation

$$\left(p+\frac{a}{v^2}\right)(v-b)^{\lambda+1} = \text{Const.}$$

or $\left(p+\frac{a}{v^2}\right)(v-b)^{\gamma} = \text{Const.}$ with

$$\gamma = \frac{R+C_v}{C} \simeq \frac{C_p}{C_v}$$

So, we get similar adiabatic relation for ideal gas and Van der Waals gas.

And which can further be simplified as T times v minus b whole to the power lambda is equal to constant. We can of course compute the constant if we know K for sorry if we know K, we can write this constant in terms of K but we are not willing to do that we are just putting this as constant. So, where lambda is equal to R by C v. Now what we have to do is we need to get the relation in terms of pressure and volume. So, we need to substitute for this temperature.

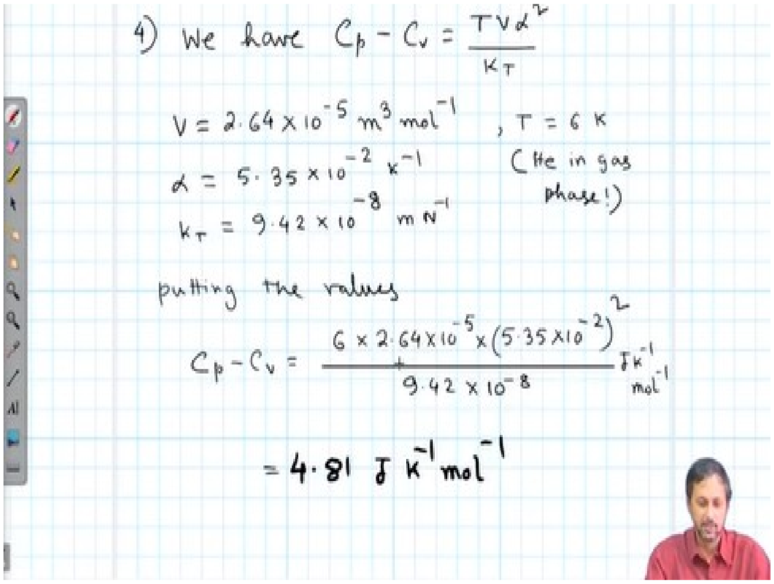
So, if we put now go back to the Van der Waals equation which we have used in the first problem. Where is it? See this is my Van der Waals equation here. So, if I write we have to substitute for temperature we have to write T is equal to 1 over R P plus a by v square times v minus b that exactly what we have done here. So, we have written T is equal to 1 over R P lpus a by v square v minus b into this relation. So, it becomes P lpus a by v square times v minus b whole to the power lambda plus 1.

Because there is a v minus b coming here which is a constant. So, our final relation is P plus a by v square times P minus v whole to the power gamma is equal to constant. Here we define gamma as R divided by C v by sorry it should be C v which is approximately equal to C p minus C v. Because even for Van der Waals gas we see we what we have derived here. We see a is a small constant and if the volume is somewhat large then this term actually vanish, the second term.

And then C p minus C v approximately becomes equal to R. So, what I am trying to tell you here that even for a Van der Waals gas the adiabatic relation the or the adiabatic constant gamma will be I mean I should not probably call it gamma exactly because gamma is defined as C p minus C v. Probably, I should put a gamma dash which will be approximately equal to gamma for ideal gas. Now it for with this we come to the last problem which is basically a numerical problem.

Calculate the difference in heat capacities for helium 4 if the specific volume at 6 kelvin is 2.64 into 10 to the power minus 5 meter cube per mole. Given isothermal compressibility K T is equal to 9.42 into 10 to the power minus 8 in proper unit and coefficient of volume expansion alpha is 5.35 into 10 to the power minus 2 Kelvin inverse.

(Refer Slide Time: 35:49)



4) We have $C_p - C_v = \frac{TV\alpha^2}{\kappa_T}$

$V = 2.64 \times 10^{-5}\ m^3\ mol^{-1}$, $T = 6\ K$

$\alpha = 5.35 \times 10^{-2}\ K^{-1}$

$\kappa_T = 9.42 \times 10^{-8}\ m\ N^{-1}$

(He in gas phase!)

putting the values

$$C_p - C_v = \frac{6 \times 2.64 \times 10^{-5} \times (5.35 \times 10^{-2})^2}{9.42 \times 10^{-8}}\ J K^{-1} mol^{-1}$$

$$= 4.81\ J\ K^{-1}\ mol^{-1}$$

So, basically in this problem we simply have to use the relation that C p minus C v is equal to T v alpha square divided by K T. T is given 6 K that means at 6 K helium is in gas phase. So, boiling point for helium 4 is 4.2 kelvin so at 6 kelvin in under normal atmospheric pressure condition it will be in gas phase. So, the specific volume V is given, alpha is given, K T is given, all we have to do is we have to put these constants in here and we get C p minus C v is equal to 4.81 joules per kelvin inverse per mole inverse.

Which is hugely deviated which is actually approximately equal to R by 2 given that R is equal to 8.3. So, this is slightly less than R by 2 sorry slightly greater than R by 2 but somewhere close to R by 2. So, we see which is a huge deviation from the ideal gas behaviour and that is the beauty of this expression. This particular expression that we do not care whether what is the equation of state here.

Maybe the equation of state is so complicated that we cannot even you know compute the differentials from directly from the equation of state or maybe an equation of state is not even defined. But as long as this elastic coefficient and the specific volume can be measured at a given temperature, we can always compute the C p minus C v difference. So, that is where we stop for this lecture.

In the next lecture we will be discussing quantity called free energy. I mean it is not one quantity but a group of functions which are called the free energy function, till then goodbye.