Thermal Physics
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Lecture - 48
The Free Energy Functions

Hello and welcome back to another lecture on this NPTEL lecture series on thermal physics. So, we have been discussing thermodynamic relations for last two classes. In lecture 46 we have derived the thermodynamic relation I mean I should not say derived we have started introducing the thermodynamic relations. And in the last lecture that is lecture 47 we have used these thermodynamic relations in order to find out useful properties in a material.

Also, you have solved some problem. Now in today's lecture we will be talking about free energy function. But before that I have realized that I have left 1 problem behind. So, from the thermodynamic relations, so, let us finish that first then we can move into free energy.

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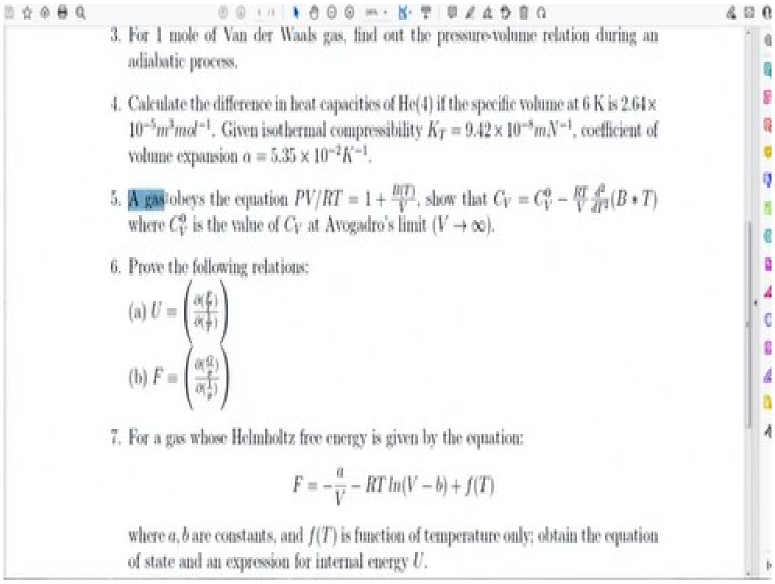

3. For 1 mole of Van der Waals gas, find out the pressure-volume relation during an adiabatic process.

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 $K_T = 9.42 \times 10^{-8} mN^{-1}$, 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 $C_V = C_V^0 - \frac{RT}{V}\frac{d^2}{dT^2}(B * T)$ where C_V^0 is the value of C_V at Avogadro's limit ($V \to \infty$).

6. Prove the following relations:

   (a) $U = \left(\frac{\partial(\frac{F}{T})}{\partial(\frac{1}{T})}\right)$

   (b) $F = \left(\frac{\partial(\frac{G}{p})}{\partial(\frac{1}{p})}\right)$

7. For a gas whose Helmholtz free energy is given by the equation:

$$F = -\frac{a}{V} - RT\,ln(V - b) + f(T)$$

where a, b are constants, and $f(T)$ is function of temperature only; obtain the equation of state and an expression for internal energy U.

So, from problem number 5 of classroom problem of week 10. A gas obeys relation PV by RT is equal to 1 plus B by T basically it is a virial coefficient as you can see B is the first virial coefficient show that C v is equal to C v 0 minus RT by V d 2 d T 2 B T where C v 0 is the value of C v in the Avogadro limit which is volume tending to infinity. That means low pressure limit actually. So, that is sometimes also called Avogadro limit.

Now what is given here? That the; virial coefficient or the coefficient B is a strictly a function of temperature only. As we see it is given in the problem that B is a function of temperature. Now in order to compute C v what we need to do is?

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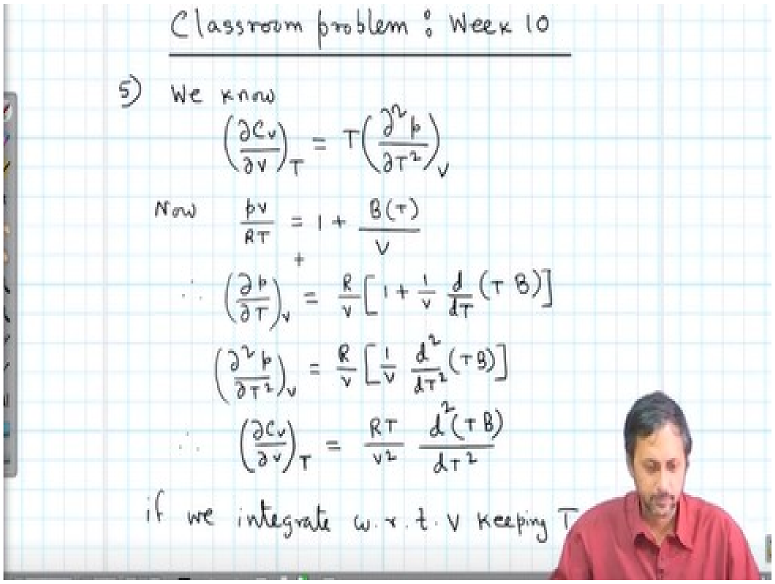

Classroom problem : Week 10

5) We know

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

Now $\frac{pv}{RT} = 1 + \frac{B(T)}{V}$

$$\therefore \left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v}\left[1 + \frac{1}{v}\frac{d}{dT}(TB)\right]$$

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_v = \frac{R}{v}\left[\frac{1}{v}\frac{d^2}{dT^2}(TB)\right]$$

$$\therefore \left(\frac{\partial C_v}{\partial v}\right)_T = \frac{RT}{v^2}\frac{d^2(TB)}{dT^2}$$

if we integrate w.r.t. v keeping T

We need to use the relation del C v del v T is equal to T del 2 p del T 2 v. So, this actually talks about the variation of C v as a function of volume. So, what is the equation of state given? It is given as PV by RT is equal to 1 plus B divided by V where V is a function of temperature only. So, if we compute del p del T v it will be simply. So, what we have to do is we have to take this R T by V on the right-hand side.

So, this equation this relation will be P is equal to RT by V 1 plus B by v which is basically the first term in the real expansion. And if we compute del P del T v it will be R by v 1 plus del p del T. So, what happens is the temperature has to go in minus del actually. So, it will be R so, it will be T, here and B T, here. Now if B is a function of temperature B T is also a function of temperature. So, the derivative will be d dT of R by v times 1 plus 1 over V, V is a constant.

Please remember d dT of TB. So, T times B is a new function which is a function of temperature. As it is a function of temperature only, we do not have to use del here. So, we can write d dT the derivative. So, del 2 p del T 2 v will be R by V 1 over V. So, once again this term will be 0 this time. This will be 1 over V the second derivative of T times B. So, if we substitute in this particular equation let us call it equation 1.

So, if I substitute 2 into 1, we get del C v del v T is equal to RT by V square d 2 dT 2 of T B. T B is a function of temperature. Now what we can do is we can integrate this relation keeping temperature intact. So, we do not have to touch this quantity here because we are not integrating over temperature we are simply integrating over volume. So, this will stay as a constant. Only the integration will affect. This 1 over V square term.

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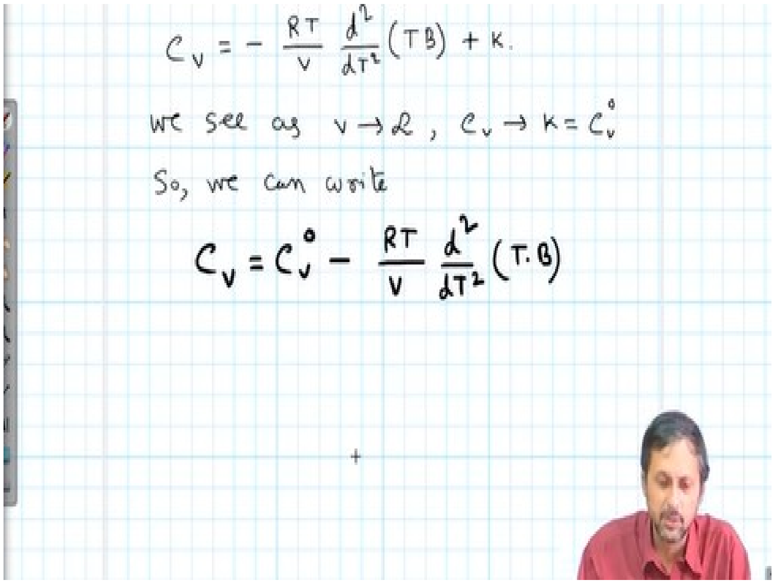

$$C_V = -\frac{RT}{V}\frac{d^2}{dT^2}(TB) + K.$$

we see as $V \to \infty$, $C_V \to K = C_V^0$

So, we can write

$$C_V = C_V^0 - \frac{RT}{V}\frac{d^2}{dT^2}(T.B)$$

So, if we perform this integration, we get C v is equal to minus RT by V d 2 dT 2 times T B plus K where K is a constant. So, at present we have not defined the value of K. We are putting this as an arbitrary constant. But what we see here is when V tends to infinity. This term goes to 0 because there is an RT by V dependence. And this term is independent of volume. So, it will not change with volume only with temperature.

So, keeping the temperature same if we increase the volume of the gas assembly, we simply have this term going to 0. So, K will be equal to C v 0 which is the value of C v at the limit v going to infinity. So, we can rearrange this and write C v is equal to C v 0 minus R T by V d 2 dT 2 of T times B and this is exactly what is given in the problem. So, with this problem we finish our discussion on thermodynamic relations for now.

And we will be using those relations very frequently as and when required till the end of this course. Because these are very really useful relation and I keep saying over and over again that these relations give us the most powerful tool. I mean it gives us the most powerful tool in thermodynamics. Because we; can compute almost any parameter from the equation of state by use of this relations.

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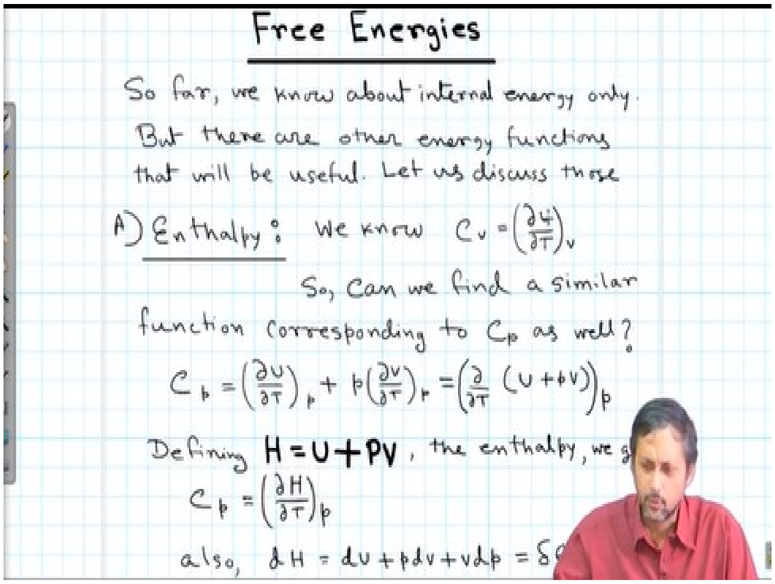

Free Energies

So far, we know about internal energy only. But there are other energy functions that will be useful. Let us discuss those

A) Enthalpy: We know $C_v = \left(\frac{\partial U}{\partial T}\right)_v$

So, can we find a similar function corresponding to C_p as well?

$$C_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial}{\partial T}(U + pV)\right)_p$$

Defining $H = U + PV$, the enthalpy, we

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

also, $dH = dU + pdV + Vdp = \delta$

Next, what we are going to define is free energy function. Now so far, we have learned about 1 function. That is the internal energy U. Now in thermodynamics there are 3 other energy functions. 2 of them are called the free energy. And there is enthalpy which is not exactly a free energy but also a very useful quantity. So, let us define those why these are important? And why do we need those? And what are the use? I mean what are the usefulness of these energy functions.

We will slowly go into that. So, we see C v is equal to del U del T v. This relation is something that we have derived in one of our previous classes. We have used it already so many times. Now the question is can we find a similar relation corresponding to C p? C p being the heat capacity at constant pressure. Now what is C p? C p is equal to del U del T p plus p del V del T p which is also a relation that is directly coming out from the first law of thermodynamics.

So, given that p is constant we can rearrange this in the form of del del T of U plus PV at constant pressure. If p is constant that means this pressure term p here will behave like a constant. So, we can rewrite this as this one. Now we define a quantity H which is U plus PV which we named the enthalpy. Then we can simply write C p is equal to del H del T p constant. Also, dH will be is equal to d U plus p dv plus v dp because of course in the case when pressure is constant, we get this particular relation.

But if pressure is not constant then in the differential of H, we will have both dp and dv present. So, we have dU + p dv + v dp. Now, what is d U + p dv? d u + p dv is nothing but dQ+ v dp. Now for an isobaric process if we have an isobaric expansion or isobaric compression V p goes to 0 and what do we have dH = dQ more precisely we can write delta H is equal to delta Q.

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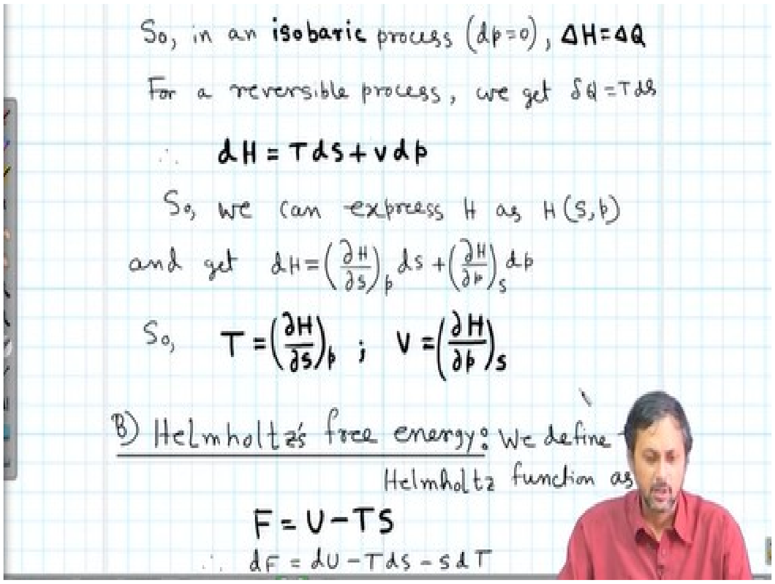

So, in an **isobaric** process ($dp=0$), $\Delta H = \Delta Q$

For a reversible process, we get $\delta Q = T\,ds$

$$\therefore\quad dH = T\,ds + v\,dp$$

So, we can express H as $H(s,p)$

and get $dH = \left(\frac{\partial H}{\partial s}\right)_p ds + \left(\frac{\partial H}{\partial p}\right)_s dp$

So, $T = \left(\frac{\partial H}{\partial s}\right)_p \;;\; V = \left(\frac{\partial H}{\partial p}\right)_s$

B) Helmholtz's free energy: We define Helmholtz function as

$$F = U - TS$$

$$\therefore\quad dF = dU - T\,ds - s\,dT$$

So, for isobaric expansion or isobaric compression the total heat that is exchanged or that goes in or out of a system is actually equal to the enthalpy change of the system. So, enthalpy actually can be measured directly from an isobaric process. If we simply calculate the energy the heat exchange in that particular process. Now for a reversible process what we can do is we can substitute this delta Q with T ds and we can write dH = T ds + v dp.

Now we have these 4 functions temperature, pressure, volume and entropy. And if we can express any other function as a function of any two of these variables, we will be happy about it. So, from this relation it actually tells you that entropy can be expressed as a state function of s and p. That means entropy and pressure. So, we can write S H as H of s and p. So, that means dH will be del H del s p ds plus del H del p s dp.

So, by comparing this relation with this relation we can equate the coefficient of ds and dp from this and we get T is equal to del H del s p V is equal to del H del ps. We will see later that this type of relations which will also be derived for the other energy functions are really useful and we will come to that. Next up is another energy function. This time it is called a free energy. Why it is called a free energy? We will see later. We define the Helmholtz function as F = U - T S. So, dF = d U – T ds - s dT.

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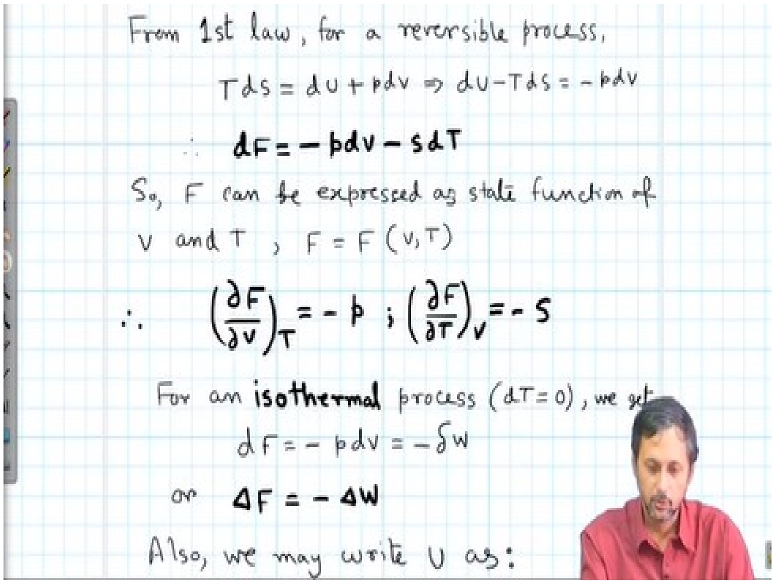

From 1st law, for a reversible process,

$$Tds = dU + pdv \Rightarrow dU - Tds = -pdv$$

$$\therefore \quad dF = -pdv - sdT$$

So, F can be expressed as state function of V and T, $F = F(V,T)$

$$\therefore \quad \left(\frac{\partial F}{\partial V}\right)_T = -p \; ; \; \left(\frac{\partial F}{\partial T}\right)_V = -S$$

For an **isothermal** process ($dT = 0$), we get

$$dF = -pdv = -\delta W$$

or $\Delta F = -\Delta W$

Also, we may write U as:

So, from the first law for any reversible process T d s = d U + p dv. So, that means d U – T d s = - p dv. So, we can simply write dF = -p dv – s d t. Once again from this particular relation we see that we can express the free energy Helmholtz free energy function as an independent state function of V and S. Please remember all the energy functions that we are talking about these are all state functions. Only a state function can be brought into a differential form like this.

So, if we write F is equal to F is equal to F of V and T then once again we can write dF is equal to del F del v T constant dv plus del F del T v constant d T. And by comparison we can write del F del v T is equal to minus p del F del T V is equal to minus S. Now if we have an isothermal process isothermal process means the temperature change is 0. So, what do we see? This term will go to 0. So, what we are left with is p dv. Now what is the p dv? For a hydroscopic system p dv is nothing but the work done.

So, delta dF is equal to minus delta W. So, we can write we can integrate both sides. So, basically what we get here that delta F the change in Helmholtz free energy function in an isothermal process is equal to the work done by the system or opposite of the work done by the system or work done on the system. So, in order to measure the Helmholtz's free energy of a particular or at least the change of Helmholtz's free energy of a particular system all we have to do is.

We need to compute the work done during an isothermal expansion or isothermal compression. So, then we can estimate the change in Helmholtz free energy of that function. Also, if we go back to this original expression from here, we can write U = F + T S.

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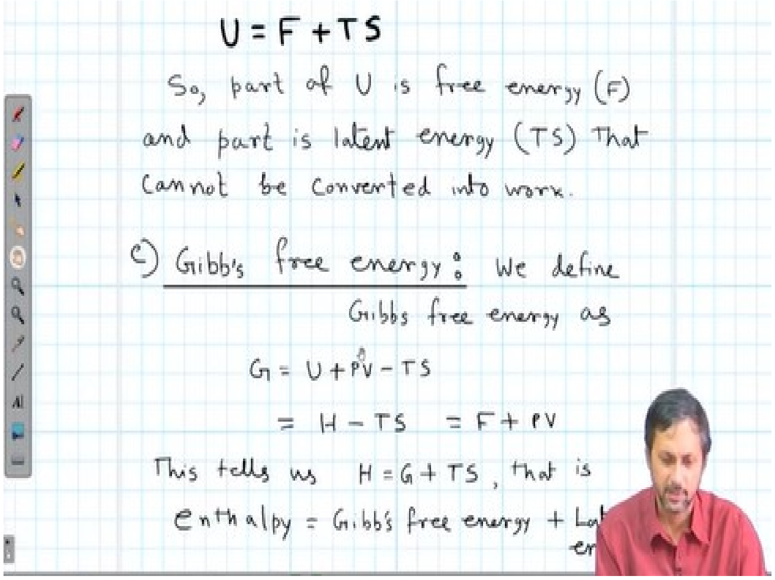

$U = F + TS$

So, part of U is free energy (F) and part is latent energy (TS) That cannot be converted into work.

c) Gibb's free energy: We define Gibbs free energy as

$$G = U + PV - TS$$
$$= H - TS \quad = F + PV$$

This tells us $H = G + TS$, that is

enthalpy = Gibb's free energy + La

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Now why it is called a free energy function? We will see later on that these are actually totally convertible into other form of energy. So, we see U the internal energy which is not a free energy has a free energy and a term which is called T S which reads T S. Now this T S over here it is the rest of the energy apart from the free energy part F. So, this T S is called the latent energy. Essentially what it means is out of the total internal energy of the system only the part which can be converted to work is the free energy.

Only that part can be converted to work and there is a latent energy T S which cannot be converted into work. So, we have defined 2 energy functions. Let us discuss the third one. It is the Gibb's free energy. We define this as U + PV – TS. Once again, we can write U + PV as H and we can write G, as equal to H - T S also U -T S = F the Helmholtz's free energy. So, we can write G = F + P V either way. So, basically, we can also manipulate this as H = G + T S.

So, that is enthalpy once again, we see there is actually, I should write this relation in bold that would be so H = G + TS very similar to what we have up here for the internal energy function. So, we see even in inside the enthalpy there is a part which is the free energy and there is one part which is the latent energy.

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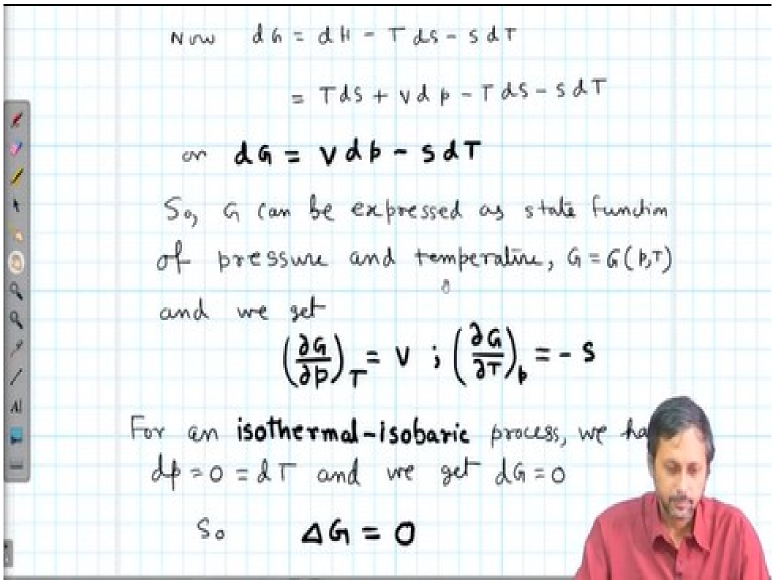

Now $dG = dH - T\,dS - S\,dT$

$= T\,dS + V\,dp - T\,dS - S\,dT$

or $dG = V\,dp - S\,dT$

So, G can be expressed as state function of pressure and temperature, $G = G(p,T)$

and we get

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

For an **isothermal-isobaric** process, we ha

$dp = 0 = dT$ and we get $dG = 0$

So $\Delta G = 0$

Now d G will be equal to dH - T d S – S d T. Now because we can use this form. G = H - T S. So, d G will be dH - T d S – S d T. Now what is dH? dH as we have already seen is equal to T d S + V dp. So, we substitute for T d S + V dp - T d S - S d T. So, T d S T d S cancels leaving us d

G = V dp - S d T. So, once again this is in a differential form of the Gibb's free energy and from there, we directly see that Gibb's energy can be written as an independent function of P and T.

So, we can write G = G of P T and take the differential, compare it and we get this relation that del G del P T is equal to V del G del T p is equal to minus S. Now for the physical significance if we look into an isothermal isobaric process, isothermal isobaric means the process that is taking place without a temperature and a pressure change. Typical example very useful example is a chemical reaction or solution let us say we have added sugar or salt inside water.

Even if we keep it under atmospheric pressure without any temperature fluctuation, if we just leave it at the room temperature, if we put it inside a glass and leave it on a table after some time salt or sugar whatever will be dissolved inside water through diffusion. So, this tells us in a diffusion process or in a chemical reaction that takes place at room temperature under normal atmospheric pressure or rather any reaction or any process that happens during in an isothermal isobaric way.

The total change in Gibb's free energy will be equal to 0 because this one will go to 0 and this one will also go to 0. So, d G will be equal to 0. So, delta G will also be equal to 0. Now this is a very important result and we will come back to that when we will be. And please remember phase change is also a process. Any form of phase transition is also a process which is isothermal and isobaric in nature.

So, this is a very useful relation result which we will be revisiting again and again over last part of the course.

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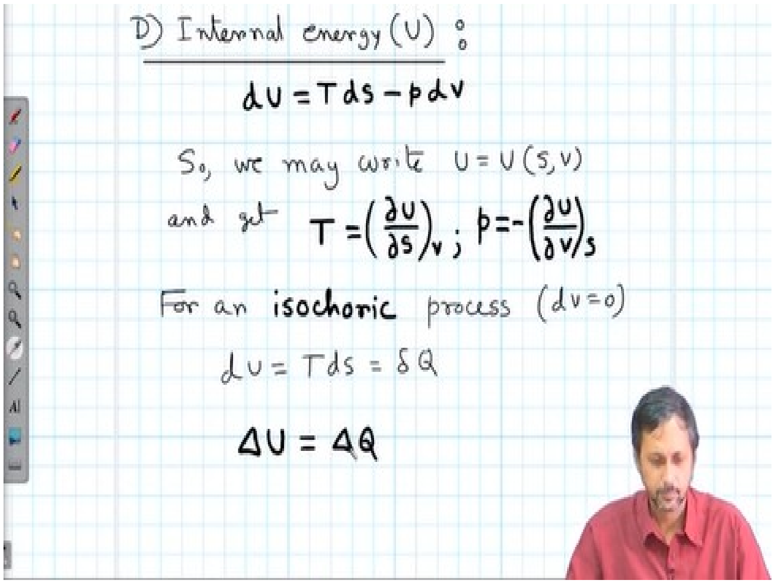

D) Internal energy (U) :

$$dU = T\,ds - p\,dv$$

So, we may write $U = U(s,v)$

and get $T = \left(\frac{\partial U}{\partial s}\right)_v$; $p = -\left(\frac{\partial U}{\partial v}\right)_s$

For an **isochoric** process $(dv = 0)$

$$dU = T\,ds = \delta Q$$

$$\Delta U = \Delta Q$$

Now internal energy which is already familiar to us. But just for completeness let us write this as well. So, we get d U = T d s – p dv. So, that means we can express U as an independent function of S and V. So, we can write U is equal to U s, v. So that T is equal to del u del S v and p is equal to del U del v S. Now for an isochoric process when we have dv is equal to 0 d U is equal to T d s that means delta U is equal to delta Q. So, if we are having a constant volume process the total heat that enters the system is actually the change in internal energy.

Either enters the system or comes out of the system does not matter; the change in heat is the change in internal energy. Now one more thing remaining that is the derivation of the Maxwell's relation.

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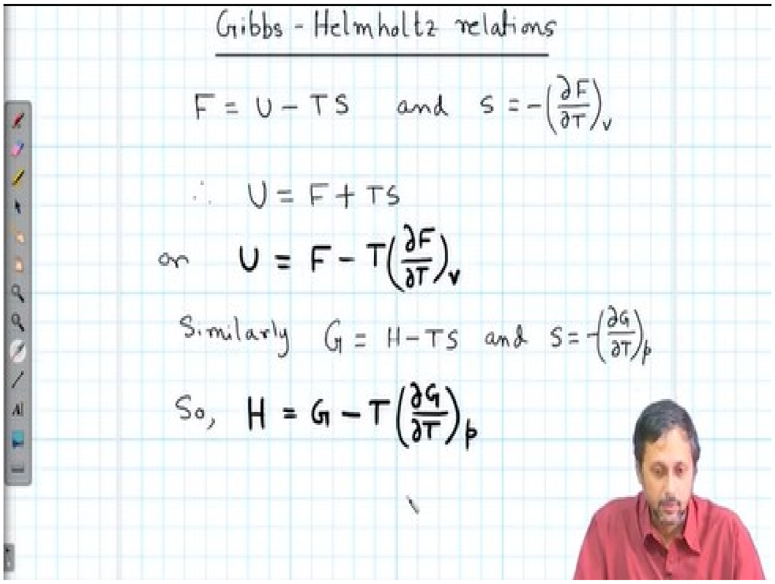

Gibbs - Helmholtz relations

$F = U - TS$ and $S = -\left(\frac{\partial F}{\partial T}\right)_v$

$\therefore \quad U = F + TS$

or $U = F - T\left(\frac{\partial F}{\partial T}\right)_v$

Similarly $G = H - TS$ and $S = -\left(\frac{\partial G}{\partial T}\right)_p$

So, $H = G - T\left(\frac{\partial G}{\partial T}\right)_p$

Before that we have one more important relation to handle. That is called the Gibbs Helmholtz relation. We have F = U - T S and S is equal to del F del T v that we have derived here if S is equal to del F del T v. So, we can combine those together and write U = F + T S which is U = F - T del F del T v. Similarly, for G the similar relation exists between G anH as H = G + T S and S is equal to del G del T P as well. So, S is either del G del T P or del F del T v with a minus sign.

So, H can be expressed as G minus T del G del T P. And these two are called the Gibbs Helmholtz relation and we will be using it as and when required. Now the last thing that we have in mind is the derivation of this Maxwell's relation. And of course, it can be derived in different ways I chose the easiest way for showing it to you. Remember during discussion of these 4 energy functions we have always written the differential of this energy function in this particular manner.

So, d U = T d s - p dv, d G = v dp - s d T so, basically, we have reduced it to the differential of two independent variables or rather it is already the functional form itself is like that. That it can be finally reduced to a differential of two independent variable. So, similarly we have d F = - p dv - s d T. dH = T d s + V dp. So, we have these 4 functions.

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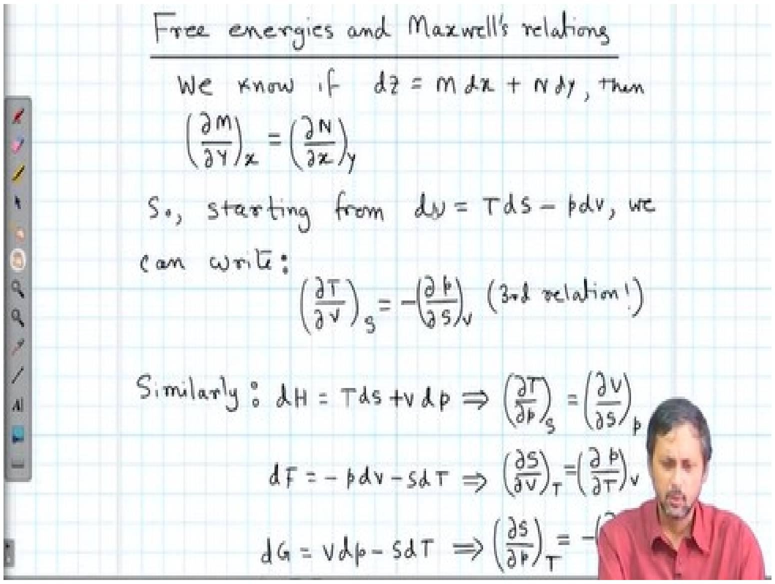

Free energies and Maxwell's relations

We know if $dz = M\,dx + N\,dy$, then

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

So, starting from $dU = T\,ds - p\,dv$, we can write:

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v \quad \text{(3rd relation!)}$$

Similarly: $dH = T\,ds + v\,dp \Rightarrow \left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p$

$dF = -p\,dv - s\,dT \Rightarrow \left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$

$dG = v\,dp - s\,dT \Rightarrow \left(\frac{\partial s}{\partial p}\right)_T = -($

Now if we have dz = M d x + N d y. If you remember we could write del M del Y x is equal to del N del x y. Because if this is the case then z is actually z of x y and dz will be equal to del z del x y dx plus del z del y x dy. Now if you remember what we did was we took the second derivative del 2 z or rather we took this term and wrote del del y of del z del x y. So, this is nothing but del 2 z del y del x is equal to del del x of del z del y x. So, from this particular form we can write M.

So, basically, we can identify M with del z del x and N with del z del y. And we can write del M del y x = del N del x y. Because both this differential will give you del 2 z del y del x. So, we have derived that. Just a quick recap. We have already discussed that. So, if we now focus on let us say the first or the simplest of the well-known most practiced energy function so far. That is d U = T d s – p dv. So, what we can do is we can use this form here.

Identify T with M and P with N and x with S and y with V. So, from there we can write del T del v S = - del p del s v which is nothing but the third Maxwell's relation. Similarly, dH = T d S + v dp will give you del T del P s is equal to del v del s p. d F = - p dv - S d T will give you del S del v T = del p del T v. And d G = v dp – S d T will give you del s del p T is equal to minus del v del T p. So, we see it is a very simple proof for these four Maxwell's relation.

Of course, for that we have to have a knowledge of the free energy functions. But apart from that this is very, very, very simple. Otherwise, also we can prove that starting from the first principle mathematics which is absolutely easy but slight I mean little more tedious. Maybe we need two pages to work it out. But that is also absolutely easy proof no complicated mathematics simple differential calculus and that is it anyway. So, now we have also proved the Maxwell's relations.

We have defined the energy functions we have not used those yet. Use will be coming slowly and slowly we will be going into the usefulness of this free energy function. But before going into that we will also take some examples today where we will have some idea of how this energy functions can be of use.

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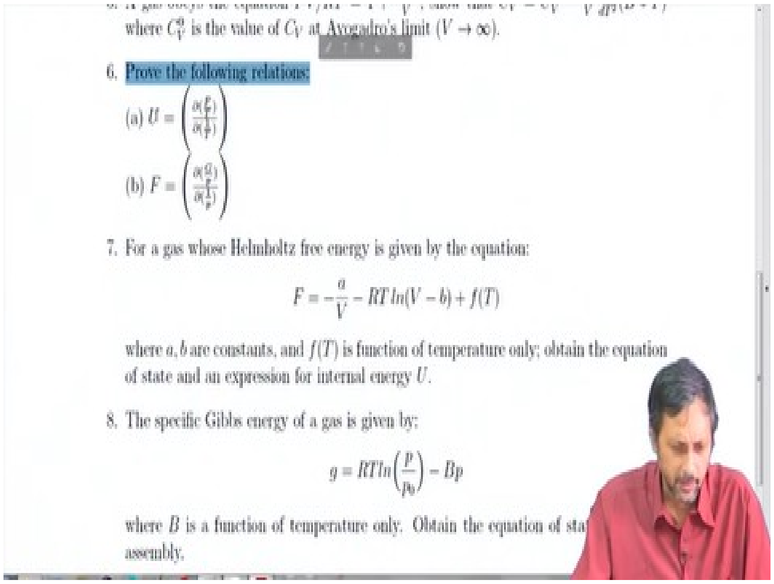

where C_V^0 is the value of C_V at Avogadro's limit ($V \to \infty$).

6. Prove the following relations:

(a) $U = \left(\frac{\partial(\frac{F}{T})}{\partial(\frac{1}{T})}\right)$

(b) $F = \left(\frac{\partial(\frac{G}{p})}{\partial(\frac{1}{p})}\right)$

7. For a gas whose Helmholtz free energy is given by the equation:

$$F = -\frac{a}{V} - RT\,ln(V-b) + f(T)$$

where a, b are constants, and $f(T)$ is function of temperature only; obtain the equation of state and an expression for internal energy U.

8. The specific Gibbs energy of a gas is given by:

$$g = RT\,ln\left(\frac{p}{p_0}\right) - Bp$$

where B is a function of temperature only. Obtain the equation of sta

assembly.

So, let us look into this example. Here we have three problems to solve for the remaining of this class. So, we have to prove the following relations U is equal to del of F by T divided by del of 1 by T. F is equal to del of G by p divided by del of 1 by p.

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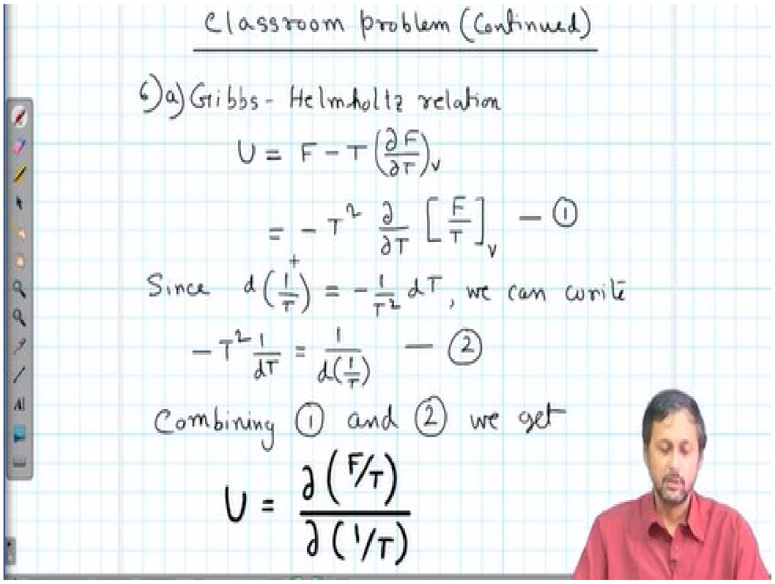

Classroom problem (Continued)

6) a) Gibbs- Helmholtz relation

$$U = F - T\left(\frac{\partial F}{\partial T}\right)_v$$

$$= -T^2 \frac{\partial}{\partial T}\left[\frac{F}{T}\right]_v \quad — ①$$

Since $d\left(\frac{1}{T}\right) = -\frac{1}{T^2}dT$, we can write

$$-T^2\frac{1}{dT} = \frac{1}{d\left(\frac{1}{T}\right)} \quad — ②$$

Combining ① and ② we get

$$U = \frac{\partial(F/T)}{\partial(1/T)}$$

So, we start from the Gibbs Helmholtz relation which is U = F - T del F del T v. What we can do is we can simply write this as minus T square del del T of F by T. So, what happens? We just focus on this term with v constant of course. So, we just focus on this term. So, it will give you del F del T v times 1 by T minus 1 by T square times F and please remember there is an overall minus T square. So, that comes in there is a minus sign there is this one so which will basically give you plus F from this one.

And minus T del F del T so, this is just another way of writing the Gibbs Helmholtz relation. So, we are using those. Now understand this d of 1 over T will be minus 1 by T square d T. So, we can write so using this relation we can write minus 1 over T square 1 by d T. So, basically this is an operator, it is not a function anymore. It is an operator 1 over d T is equal to 1 by d of 1 over T. So, this is one operator equal to another operator.

So, combining what we can do is we can take this T square del 1 by del d T operator. Substitute it with 1 by d of 1 over T operator and on the numerator, we already have del of F by T. So, we can write this U is equal to del of F by T divided by del of 1 by T. So, this is a pure mathematical form but it can be also useful this particular form. Probably we will not be using it but there are certain branches of thermodynamics where these types of relations are really useful.

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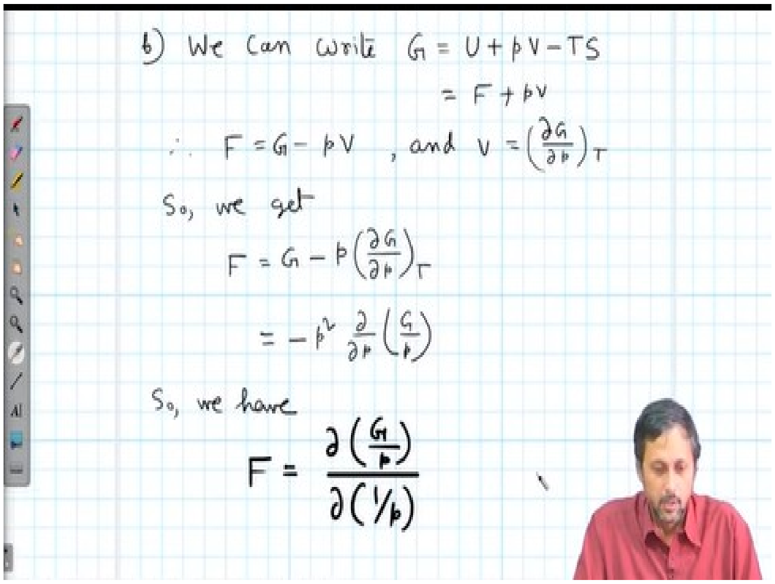

b) We can write $G = U + pV - TS$

$= F + pV$

$\therefore\ F = G - pV$, and $V = \left(\frac{\partial G}{\partial p}\right)_T$

So, we get

$$F = G - p\left(\frac{\partial G}{\partial p}\right)_T$$

$$= -p^2 \frac{\partial}{\partial p}\left(\frac{G}{p}\right)$$

So, we have

$$F = \frac{\partial\left(\frac{G}{p}\right)}{\partial\left(1/p\right)}$$

So, for the second relation we start from the Gibbs function G = F + p V. So, we can write F = G - p V and V is equal to del G del p T. So, we can write F is equal to G minus p del G del p T which is sometimes also called one of the Gibbs Helmholtz relation. And by the same logic we can convert that to minus p square del del p of G by T. So, we have F is equal to del of G by p del of 1 over p. So, similarly this minus p square 1 by dp operator is nothing but d of 1 by d of 1 over p operator.

So, that is where we get the result. Next up we have problem 7 where the Helmholtz free energy function of a gas assembly is given here which is given as F is equal to minus a by V minus RT ln V miuns b plus f of T where f is a function of temperature only and a and b these are constants. So, we have to obtain the equation of state and also an expression for the internal energy U. Now how do we do that? F is equal to minus a by V some functional form of f is given.

So, let us go back to the derivations that we have used. You see del F del v T is equal to minus p. So, if we look into this particular form of the free energy function, we have functions of temperature which will remain constant if we compute del F del V T. And we get some functional form in terms of V and T which can be equated with p pressure. And this by rearranging will simply give us the equation of state. So, let us compute this.

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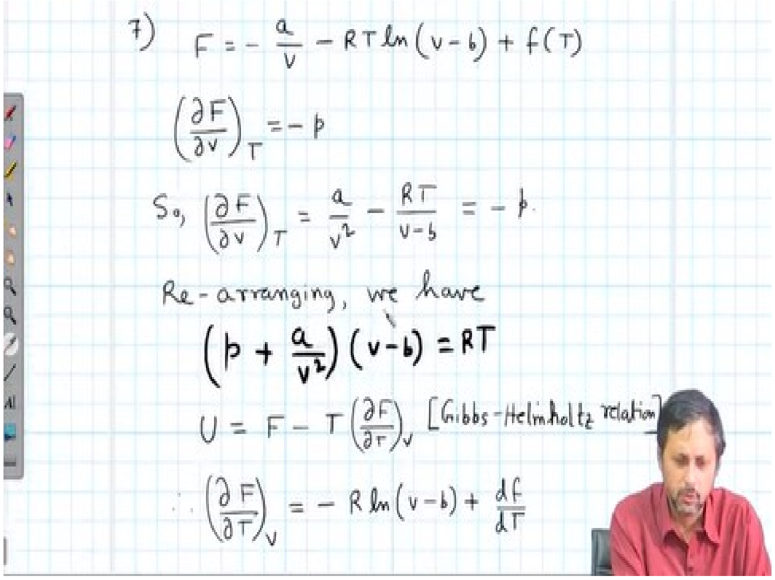

7) $F = -\frac{a}{v} - RT\ln(v-b) + f(T)$

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

So, $\left(\frac{\partial F}{\partial v}\right)_T = \frac{a}{v^2} - \frac{RT}{v-b} = -p.$

Re-arranging, we have

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

$U = F - T\left(\frac{\partial F}{\partial T}\right)_v$ [Gibbs-Helmholtz relation]

$\therefore \left(\frac{\partial F}{\partial T}\right)_v = -R\ln(v-b) + \frac{df}{dT}$

So, we have this del F del V T is nothing but minus p. So, that is what we get from the definition of Helmholtz free energy. So, del F del V T if we compute on this particular relation so there is minus a by V which will be a by V square minus RT by v minus b because there is the ln here. And this term will be equal to 0 and this will be equal to minus p from this equation. So, this is equation, let us call it equation 1, let us call it equation 2.

So, differentiating equation 1 and using equation 2 we get a by V square minus RT by v minus b is equal to minus p. And when we rearrange that we get back our familiar Van der Waals equation of state. So, basically the free energy function is corresponding to the Van der Waals gas. Now for internal energy U which is F minus T del F del T v. So, in order to get U what we have to do is we have to use the Gibbs Helmholtz relation. So, U is equal to F minus T del F del T v. So, del F del T v once again will be minus R ln v minus b plus d f d T.

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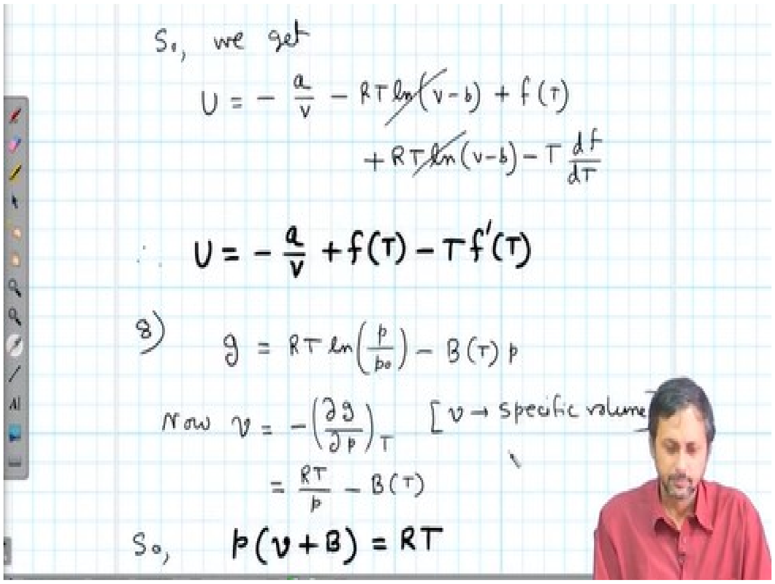

So, we get

$$U = -\frac{a}{v} - RT\cancel{\ln}(v-b) + f(T) + RT\cancel{\ln}(v-b) - T\frac{df}{dT}$$

$$\therefore U = -\frac{a}{v} + f(T) - Tf'(T)$$

8) $g = RT\ln\left(\frac{p}{p_0}\right) - B(T)\,p$

Now $v = -\left(\frac{\partial g}{\partial p}\right)_T$ [$v \rightarrow$ specific volume]

$= \frac{RT}{p} - B(T)$

So, $p(v+B) = RT$

So, if we put that here so we get U = F - T this quantity. So, now what is F? F is equal to this whole thing mins a by V minus RT ln v minus b plus f T. And then we have a minus sign here so it will be plus RT ln v minus b minus T d f d T minus T d f dT. So, these 2 cancels out leaving us with minus a by V plus f T minus T f prime T. So, we are just writing f prime for this d f T. So, this is the expression for internal energy for a Van der Waals gas.

And if you remember we have already derived another expression for internal energy in one of our earlier classes. And that is lecture 46, I guess. Let me quickly check.

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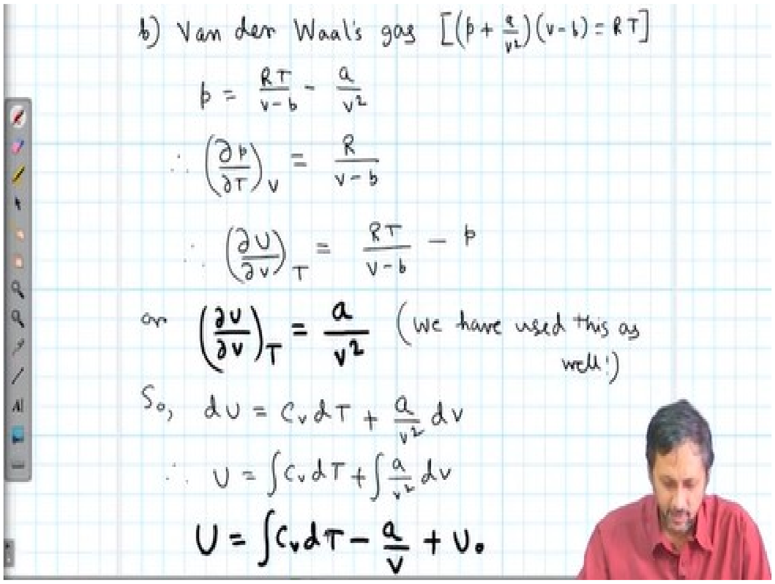

b) Van der Waal's gas $\left[\left(p+\frac{a}{v^2}\right)(v-b) = RT\right]$

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

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

$$\therefore \left(\frac{\partial U}{\partial v}\right)_T = \frac{RT}{v-b} - p$$

or $\left(\frac{\partial U}{\partial v}\right)_T = \frac{a}{v^2}$ (We have used this as well!)

So, $dU = C_v\,dT + \frac{a}{v^2}\,dv$

$$\therefore U = \int C_v\,dT + \int \frac{a}{v^2}\,dv$$

$$U = \int C_v\,dT - \frac{a}{v} + U_0$$

Yes, lecture 46. Here also we see there is an undefined constant U 0. There is a temperature dependent term and there is minus a by V term. Now let us see what have we got here. We have got minus a by V term and two temperature dependent terms. Now U 0 on that other expression was undefined. So, we can assume that this will be a temperature dependent term. So, basically, we got back the general expression that we have derived earlier.

Now for the last problem of today's lecture. So, the specific Gibbs energy of a gas is given by g is equal to RT ln p by p 0 minus B p where B is a function of temperature only. Obtain the equation of the state of the gas assembly.

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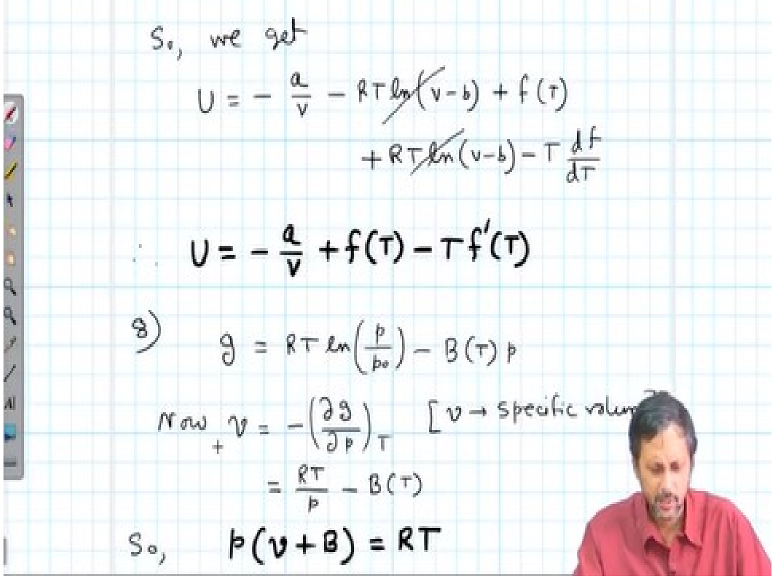

So, we get

$$U = -\frac{a}{v} - RT\cancel{\ln}(v-b) + f(T) + RT\cancel{\ln}(v-b) - T\frac{df}{dT}$$

$$\therefore U = -\frac{a}{v} + f(T) - Tf'(T)$$

8)

$$g = RT\ln\left(\frac{p}{p_0}\right) - B(T)p$$

Now, $v = -\left(\frac{\partial g}{\partial p}\right)_T$ [$v \rightarrow$ specific volum

$$= \frac{RT}{p} - B(T)$$

So, $p(v+B) = RT$

So, in a similar manner remember v is equal to minus d g dp T del g del p T. Now here we have used small g and we have used small v small g is for the specific Gibbs energy and small v is for the specific volume. Now typically when we say specific energy or specific volume, we talk about volume per unit moles or Gibbs energy per unit moles. But it could be per unit mass also it does not matter. Let us assume that this is for unit moles.

So, small g is equal to this. So, basically what we have done? v is equal to this relation is directly from the definition of Gibbs energy you see del G del p T is equal to v. So, here instead of V we have written small v and instead of G we have written small g. I think I just messed up with the minus sign here. It is a minus sign. That does not matter you understand what we are doing. So, there should not be a minus sign here.

So, del g del p T will be equal to R ln. So, there is a ln p minus ln p 0 l n p 0 is a constant which we do not get. So, it will be R T by p minus B of T. So, v is equal to RT by p minus B of T so B of T means B is a function of temperature only. So, after rearranging we get the equation as p times V plus B is equal to RT. Now this equation was first proposed by Clausius. So, it was the early I mean before Van der Waals equation came into picture this correction was proposed by Clausius himself.

And this I think we have discussed briefly. Anyway so, the outcome of today's discussion is that we have not only defined the free energy functions but also demonstrated through these few examples that free energy function can be useful in order to get to the equation of state of a system. And also, through relations like Gibbs Helmholtz equation or other internal relations between this free energy function.

If we know 1 free energy of the system it is probably possible to compute all other energy functions of the system. We will come back to those in the upcoming lectures. Now so far, we have discussed about 1 certain aspect of this free energy functions. But there are more. I mean they have greater significance actually. So, actually these free energy functions or rather all these four energy functions are significant in order to define the equilibrium of a thermodynamic system.

In the next lecture which is in the upcoming lecture actually we will be talking about this equilibrium condition. Also, we will be discussing the mnemonic diagram on how to remember this four Maxwell's relation and this differential form of this energy functions. So, till then goodbye.