Thermal Physics
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Lecture - 46
Thermodynamic Relations

Hello and welcome back to 10th week of this NPTEL lecture series on thermal physics. Now last week we have discussed about entropy and the mathematical form of second law. And of course, we have discussed about different internal combustion engine. Now this week's lecture will be more about the application of thermodynamics. Now we please understand that we cannot really measure the quantities like internal energy and entropy.

And in future we are going to encounter quantities like different free energies which are not directly measurable. But then if there something is not directly measurable how can, we really use it in the thermodynamic you know for experimental determination. Now in order to do that; for that particular purpose we have certain relations we call them the thermodynamic relations. There are you know, many different types of those thermodynamic relations.

But the most fundamental ones are the Maxwell's relation. So, let us look into those and we will try to understand how this relation really helps us to correlate some of these parameters which are not directly measurable with some measurable parameters of the system.

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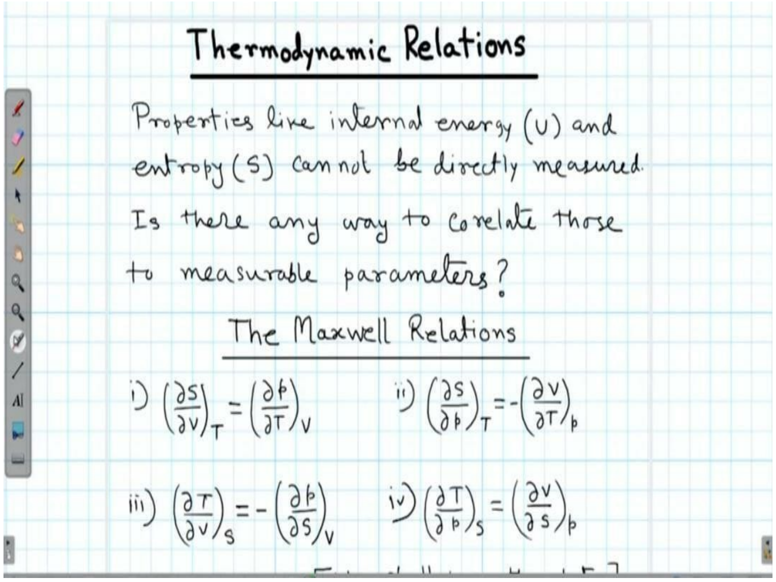

Thermodynamic Relations

Properties like internal energy (U) and entropy (S) can not be directly measured.

Is there any way to corelate those to measurable parameters?

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) $\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$

So, we will focus on the Maxwell's relation and these relations have been developed for hydroscopic system where the system volume pressure temperature these are the three primary measurable parameters. Now this Maxwell's relations actually correlate pressure volume temperature and entropy in different in four different relations. The first relation as we see here, we read it as del S del v T is equal to del P del T V.

Second relation is del S del P T is equal to minus del v del T P. The third relation is del T del v S is equal to minus del P del S V. And the fourth relation is del T del P S is equal to del v del S P. Now we will prove these relations later. I mean the proofs will be rather easy once we start from the free energy function. And we use some simple mathematical formulation that we have already established in one of the previous lectures.

At present we have to just accept these relations in their present form and we will see what are the usefulness of this relation. Now these relations as we see this in its original form it does look very you know what you call superficial in nature, we really cannot conclude anything from this. For example, for us for a hydroscopic system if we the first relation basically says that the rate of change of entropy with volume as a function of temperature with temperature constant is equal to the rate of change of pressure as a function of temperature with volume constant.

Now it is really difficult to correlate these two things because on one side we have temperature constant the other side we have volume constant and it is there for all four relations actually so it is not that intuitive so as to say.

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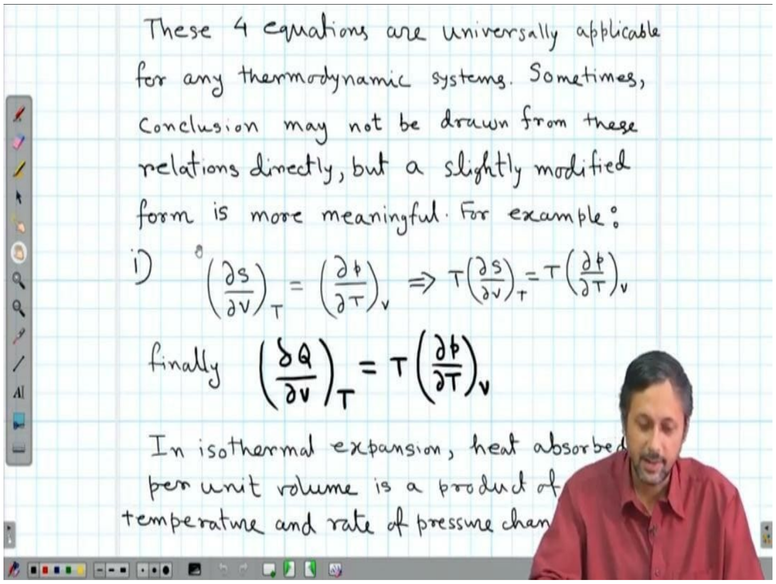

These 4 equations are universally applicable for any thermodynamic systems. Sometimes, Conclusion may not be drawn from these relations directly, but a slightly modified form is more meaningful. For example:

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

finally $\left(\frac{\delta Q}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v$

In isothermal expansion, heat absorbed per unit volume is a product of temperature and rate of pressure chan

So, but then with very slight modification of this relation we can actually make out something useful from it. So, let us take the first relation as an example the first relation that reads del S del v T is equal to del P del T V. Now we can multiply temperature from both sides and in the left-hand side temperature is a constant quantity here. So, we can take this T inside so it will be T ds in the numerator and del v in the denominator.

Now what is T ds? T ds is for any reversible process this is the infinitesimal amount of heat delta Q that has entered the system. So, the left-hand side can be modified to write del Q del v T is equal to T del P del T V. So, this means in an isothermal expansion heat absorbed per unit volume is a product of the absolute temperature and the rate of pressure change in this process. So, now of course rate of pressure change in an isochoric process.

So, this relation actually will be used later on in when we will be discussing phase transition in detail. So, for any isochoric and isothermal process so basically this two will be. I mean this equation will be correlated to the phase transition, the first order phase transition and we will get a very useful equation called the first latent heat equation from this relation itself but that will be in future.

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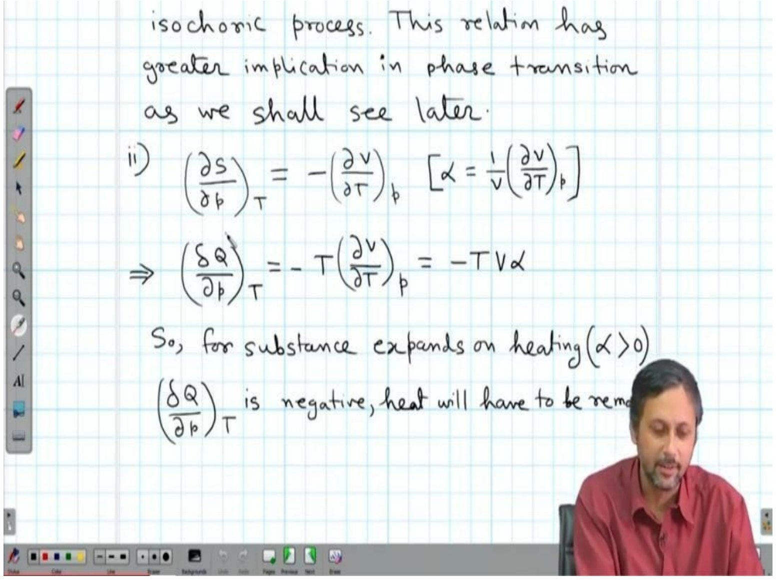

isochoric process. This relation has greater implication in phase transition as we shall see later.

ii) $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$ $\left[\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p\right]$

$\Rightarrow \left(\frac{\delta Q}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p = -TV\alpha$

So, for substance expands on heating $(\alpha > 0)$

$\left(\frac{\delta Q}{\partial p}\right)_T$ is negative, heat will have to be rem

Now for the second relation let us say del S del P T is equal to minus del v del T P. Once again, we multiply both sides with temperature and as we see the temperature is constant here just like in here the temperature was constant. So, we can take the T inside and write this as del Q so we can write this as del Q del P T is equal to minus T del v del T P. Now what is del v now if you remember we have defined this quantity alpha the bulk temperature expand the expansion coefficient alpha which we can use.

And we can write we substitute this del v del T P with V alpha. So, this relation reads del Q del T del Q del P T is equal to minus T V alpha. Now for a substance that expands on heating that means alpha is greater than 0. Now for that particular substance when so we see alpha is when it at a finite temperature when the temperature is so basically when the temperature increases the volume increases. Now during this that process what happens is del Q del P T becomes negative.

So, that means heat has to be removed from this substance. So, when for positive expansion coefficient when this is, for the positive expansion coefficient when alpha is positive then in an isothermal process when we are del Q del P basically means the variation of absorbed heat as a function of pressure. So, that means when we are you know del Q del P T is, sorry what I mean to say is as alpha is positive V is positive and T is positive always.

So, this product is a negative quantity. So, that means when the system is compressed it will release heat and when the system is expanded that means when del Q del T is negative then heat will go inside the system. So, these are the simple relations, the simple interpretation which can be understood by simple manipulation of this Maxwell's relation. Now we will come back to this type of relations and we will be discussing this you know this type of phenomena in more details in the sub subsequent classes.

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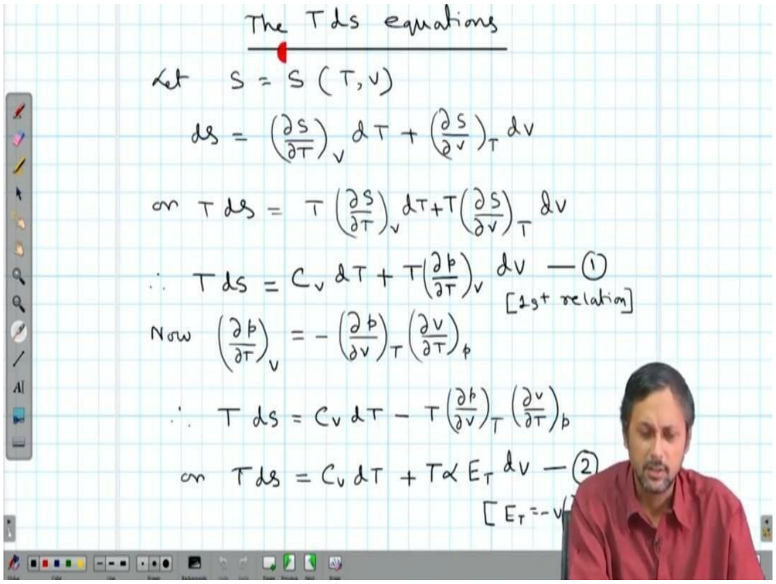

The Tds equations

Let $S = S(T, v)$

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

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

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

[1st relation]

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

$$\therefore \quad T\,ds = C_v\,dT - T\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p$$

or $$T\,ds = C_v\,dT + T\alpha E_T\,dv \quad — ②$$

$[E_T = -v$

For now, we will focus on something called the T ds equation. So, what are the T ds equation? Let us say and if you remember we have already discussed this between pressure volume and temperature we can choose any two as the independent parameter. So, if we take S as a function of temperature and volume so we can write S is equal to S of T V then, ds is equal to del S del T V dT plus del S del v T dV.

Now once again we multiply the whole thing with temperature, we can write the left-hand side as T ds then it becomes T del S del T V dT plus T del S del v T dV. Now what is this quantity? T del S del T V dT is nothing but once again we can write this as C v dT which is C v is the heat capacity at constant molar heat capacity of constant volume and this equation can be written as and using the first relation you see del S del v can be substituted by del P del T V dv.

So, the first equation reads or sorry this equation reads T ds is equal to C v dT plus T del P del T V dv. Now what is the importance of this relation? Look at this, here we have substituted so let us go back to one of these equations here. See entropy is not directly measurable so we have manipulated this in order to substitute entropy or del S the variation of entropy as the variation of total heat that is either entering or going out of the system which is directly measurable.

Similarly, here we have substituted del S del v T with del P del T V which is directly measurable given that we know the equation of state we will look at into the examples very soon. Now even further modification is possible if you remember del P del T V can be written as del P del v T times del v del T P and this is the general mathematical relation between any three independent I mean if the equation of state contains parameters like x y and z.

Then this type of relations we have already discussed that in one of the earlier classes. So, this is a general relation for any equation of state. Please remember this Maxwell's equation Maxwell's relation will have equivalent for any types of equation of states. So, if we have a magnetic system for example, we have instead of pressure volume and temperature we will have pressure sorry, we will have temperature magnetization and magnetic field.

So, this will serve as three parameters of the equation of state. So, we can always find an equivalent Maxwell's relation for any type of thermodynamic system. Although hydroscopic system is very easy to visualize easy to you know in it is more intuitive so that is why the basic relations are for hydroscopic system and we keep using this particular type of description. So, anyway after this another round of manipulation what we can write is T ds is equal to C v dT minus T del P del vT times del v delta P.

Once again, del v del T P is nothing but your alpha your that we have already discussed that is the volume expansion coefficient and this is the isothermal compressibility or rather elasticity inverse of compressibility that is E T is equal to minus V del P del v T. And this is also one of the elastic modulus that we have already discussed. So, we can write the equation as T ds is equal to C v dT plus T alpha E t dv. So, once again here it can be written in terms of equation of state.

And here even better we can write the relation T ds is equal to C v dT plus quantity which is predominantly the function of or predominantly consists of elastic modulus which are experimentally measurable for a given system. So, the equation 1 and 2 these are called the T ds, the first T ds equation any of them I mean we can use either this particular form or this particular form as our first T ds equation.

Similarly, if we assume that S is a function of temperature and pressure so in a very similar manner, we can write ds is equal to del S del T P dT plus del S del S del T P d T plus del S del P T d p and once again this quantity is nothing, we multiply it with T. So, that the left hand side becomes T ds the first term over here is nothing but your C p d T the where C p is the heat capacity at constant pressure. And the second term becomes minus T del v del T P d p.

So, once again del S del P T can be substituted with minus del v del T P from the second relation second maxwell's relation. And this can be manipulated as C T ds is equal to C p d T minus T V alpha d p. So, once again alpha is equal to 1 by V del v del P del v del T p. So, we get and relations we call it relation 3 and 4 and this relation 3 and 4 once again relation 3 is something that can correlate T ds with a term that is C p d T that is heat capacity at or for heat absorption at constant pressure.

And the second term is directly determined from the equation of state. And in the fourth relation the first term remains first term in the right-hand side remains unaltered which is the heat absorption at constant pressure. And the second term is a function of predominantly a function of the elastic modulus alpha. So, these are called the second T ds equation so these 2 1 and 2 are the first T ds equation 3 and 4 are the second T ds equation.

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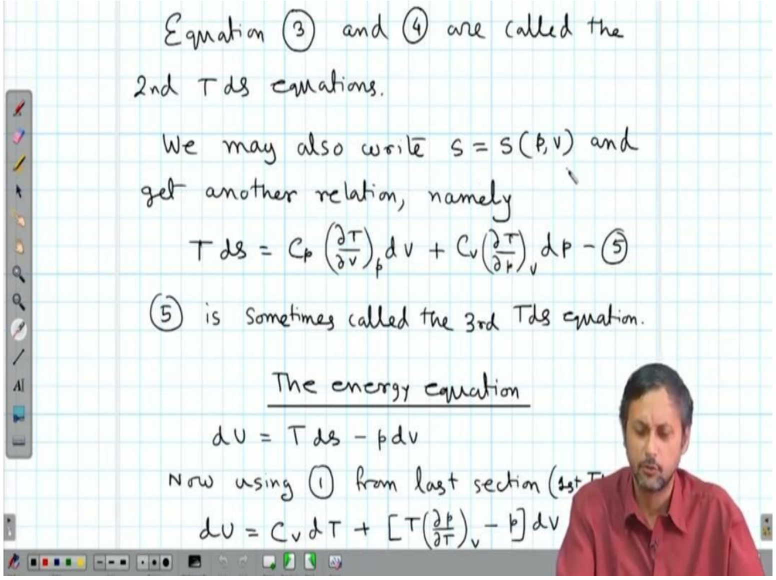

Equation ③ and ④ are called the 2nd T ds equations.

We may also write $s = s(p, v)$ and get another relation, namely

$$T\,ds = C_p \left(\frac{\partial T}{\partial v}\right)_p dv + C_v \left(\frac{\partial T}{\partial p}\right)_v dp \quad - ⑤$$

⑤ is Sometimes called the 3rd Tds equation.

The energy equation

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

Now using ① from last section (1st T

$$dU = C_v\,dT + \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] dv$$

Also, we can have a third T ds equation which is not that popular anyway so we can write S as a function of pressure and volume and we can get a relation something like T ds is equal to C p del T del v P dv plus C v del T del p v d p this is equation 5 and it is sometimes called the third T ds equation. Now let us focus on the application of this relations application of these T ds equations we will derive something called the energy equation.

And in order to get to this and then we will apply one of these T ds equations in order to see what we can get from this energy equation. So, from the first law of thermodynamics we know dU is equal to T ds minus p dv. Now what we can do is? We can use equation 1 for T ds you see there is a term T ds here so we can substitute T ds using equation 1. So, we can basically write T ds is equal to C v dT plus T del P del T v d v.

So, if we do that this becomes dU is equal to C v dT plus T del P del T v dv and there is a p dv common here. So, we can take this dv out and we can write C v dT is equal to T del P del T v minus p dv.

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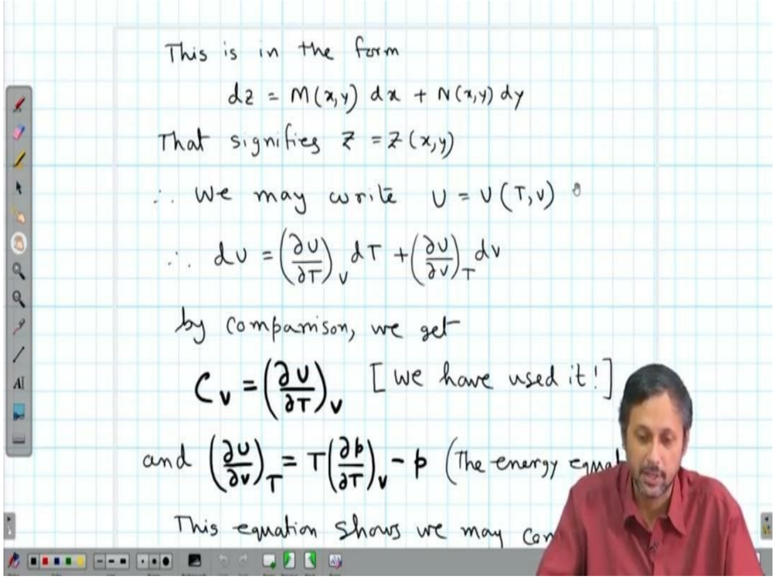

This is in the form

$$dz = M(x,y)\,dx + N(x,y)\,dy$$

That signifies $z = z(x,y)$

$\therefore$ We may write $U = U(T,V)$

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

by comparison, we get

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad \text{[We have used it!]}$$

and $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$ (The energy equa

This equation shows we may con

Now if you remember if we can write dz is equal to M x, y dx plus N x, y dy that actually signifies that z is a function of x and y. And then we can actually take it one step forward and we can write del z del x at y constant is equal to M and del z del y at x constant is equal to N. And the exactly the same thing we are going to do here we write U is a function of T U of T and V. So, that means temperature and volume see what do we have here? We have a dT here and we have a dv here.

So, exactly the same treatment so del dU is equal to del U del T V dT plus del U del v T dv. Now if we compare, we get C v is equal to del U del T v so if we compare this equation with this equation over here so, we get C v is equal to del U del T v and del U del v T is equal to T del P del T v minus P. Now look at the; first relation the first relation C v is equal to del U del T v we have used it already. If you remember during the discussion on equipartition theorem.

And also, when we were discussing the first law of thermodynamics, I said that I have not proved it yet but if you for now please accept this relation that C v is equal to del U del T v we will come back to that. So, this is exactly where we have got it from that C v is equal to del U del T v. Now the second equation which we are calling by the name the energy equation also has significance. On the left hand side, we have del U del v T which talks about the variation of internal energy as a function of volume for an isothermal process.

Now this is and on the right-hand side what do we have? On the right-hand side we have T P and del P del T v. Now once we know the equation of state of a system, we can always compute the differential on the right-hand side and we can basically we can compute this quantity. That means we can compute the variation of internal energy of a system directly from the equation of state. Now, that this tool was not available to us beforehand.

So, far, we have talked about internal energy and we said that for an ideal gas the internal energy is constant for Van der Waals gas I have said something like internal energy varies as the volume as a function of volume also I have given you an expression will come back to that in a moment and but we have never proved it. So, now it is time that and now we have a tool to see the variation of internal energy.

Or basically the functional we can by which we can calculate the internal energy directly starting from its equation of state for a system. So, let us apply this for ideal gas and for Van der Waals gas and see what do we have.

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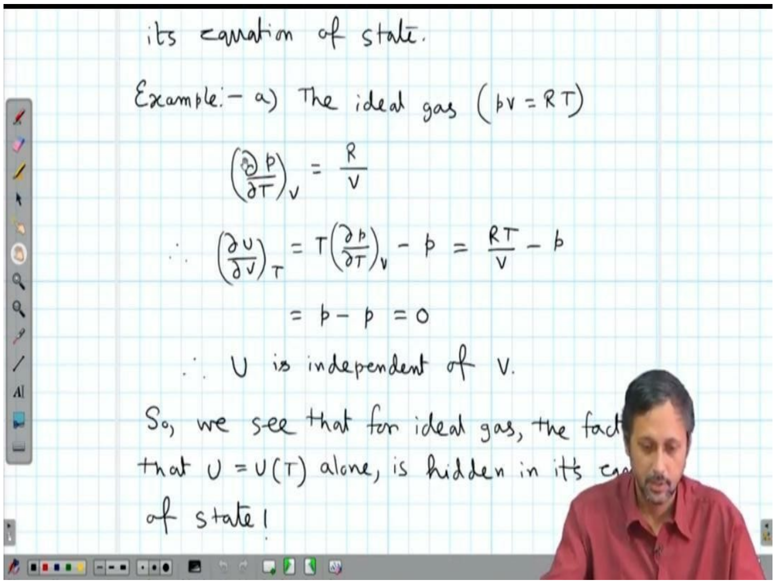

its equation of state.

Example:- a) The ideal gas $(pV = RT)$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V}$$

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

$$= p - p = 0$$

$\therefore$ U is independent of V.

So, we see that for ideal gas, the fact
that $U = U(T)$ alone, is hidden in it's
of state!

The ideal gas the equation of state is p V = R T then we are just doing it for one mole of ideal gas. So, del P del T v will be equal to R by V because V is a constant. So, del P del T at v constant this will not affect this v here. So, it will be R by v. So, del U del v T is equal to T del P del T v minus P which is once again T times R by v minus p. Now what is RT by v? RT by v is nothing but P from this equation of state again.

So, it is p minus p is equal to 0 so, what do we see U is independent of V which we have discussed many times we have said that okay for an ideal gas internal energy is a function of temperature only. So, there is no dependence on volume for an ideal gas and this is where we prove it starting from very fundamental principle. So, if we go back to this formalism over here, we have not used any special assumption with these are all very general up to this is absolutely general.

We have used the Maxwell's relation so the, where does the Maxwell’s relation comes in here. The Maxwell’s relation are used in order to compute the first T ds equation. We have used the Maxwell’s relation here from by for converting del S del v T into del P del T v. And then we wrote the mathematical form of the first law which was already established and we simply applied the first T ds equation.

So, in effect we have given the Maxwell’s relations are correct which of course they are which will prove later on. We have come to a relation in which the internal energy is related to the equation of state. And from there when we put the equation of state for an ideal gas, we see U is independent of V. So, that means that what does it essentially means that the for an ideal gas the fact that internal energy is a function of temperature only is hidden in the equation of state itself.

And that is a very powerful statement so that means once we know the equation of state of a system using and if we know the Maxwell’s relation we can compute many useful parameters like internal energy is one example which is not you know otherwise or rather we cannot measure. But we can correlate the equation of state with quantity like internal energy which is not otherwise possible. So, that is the power of Maxwell's relation.

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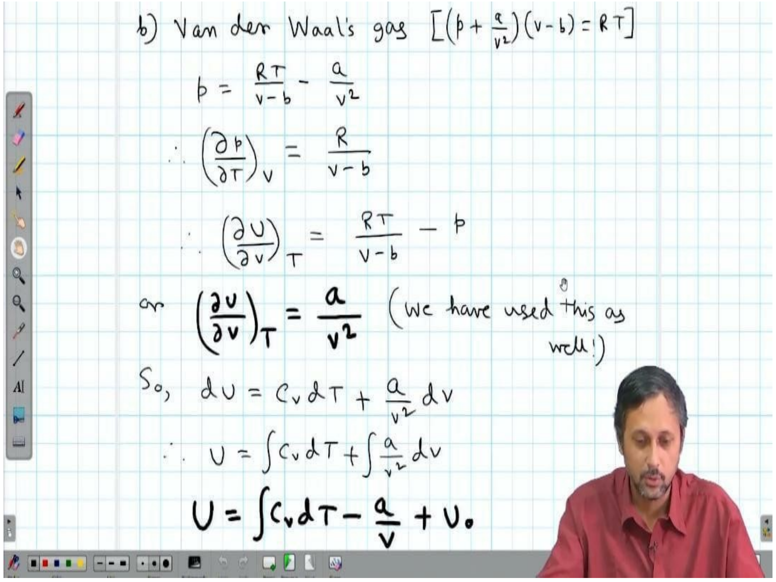

b) Van der Waal's gas $\left[\left(p+\frac{a}{v^2}\right)(v-b)=RT\right]$

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

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

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

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

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

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

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

So, now let us look into the van der Waals gas. For van der Waals gas the equation of state is p plus a by v square times v - b = RT once again we are just doing it for 1 mole of ideal gas. So, we have p is equal to RT by v minus b minus a by v square so del P del T v so that means the differential with v constant that means this term will give you 0 and this term will give you R by v minus b. So, del U del v T so applying the energy equation del U del v T will be RT divided by v minus b minus p.

Now RT by RT minus p will be nothing but a by v square so we get del U del v T is equal to a by v square. Once again, we have used this relation before when we were discussing van der Waals equation for some derivation I if you go through your notes you will find it out that for some derivation we have used this relation and I said that we will prove it later. So, that is where the proof comes that del U del T v is equal to a by v square or probably we have not done that I do not remember exactly.

But anyway, if not then we will use it. This is a very useful relation we will come back to that over and over again. So, I will just check whether we have used it or not and I will you know correct this statement accordingly. So, now it is time to compute the internal energy of a van der Waals gas or at least try to get an idea of what the internal energy function looks like for an idea for a van der Waals gas starting from this relation.

Now once we know del U del v T is equal to a by v square, what we can do is? We can go back to this original form that dU is equal to C v dT. So, basically what have we done here dU is equal to del U del T v dT plus del U del v T dT. Now this quantity is nothing but C v dT and now we have del U del v T for a van der Waals gas is equal to a by v square. So, we can write dU is equal to C v dT here and a by v square dV and that is exactly what we have done here.

So, U is equal to integration of C v dT plus integration of a by v square dT and of course internal energy like entropy cannot be quantified absolutely and we really do not want to do that. Because you know internal energy, what we are using only is the thermodynamic part and there could be many other contribution from the internal energy we have discussed it in details. So, after this and of course we are not, we do not know whether C v will be a function of temperature or not.

So, we will just keep this keep it as it is and we can write U is equal to integration C v dT minus a by v plus U 0. So, we see that using Maxwell's thermodynamic relations we can do many things we can perform many calculations that was not previously possible. Similarly, here we have I have just left an open quest. I mean I have not computed this integral. So, far what we have done is? I have taken C v out of the integral assuming that C v remains constant and just integrated this to give you T.

I am not doing it intentionally because in the next class itself we will see that C v and C p can also. I mean definitely that we know that they can vary with temperature and we will find expression where the variation of C v and C p with pressure and temperature will be computed. So, that is where we stop today. In the next lecture we will continue from here we will discuss little more about the application of thermodynamic relations.

And then we will be discussing slowly we will go into the domain of free energy and the applications of free energy and of course one more thing that we have not discussed yet and you might ask that.

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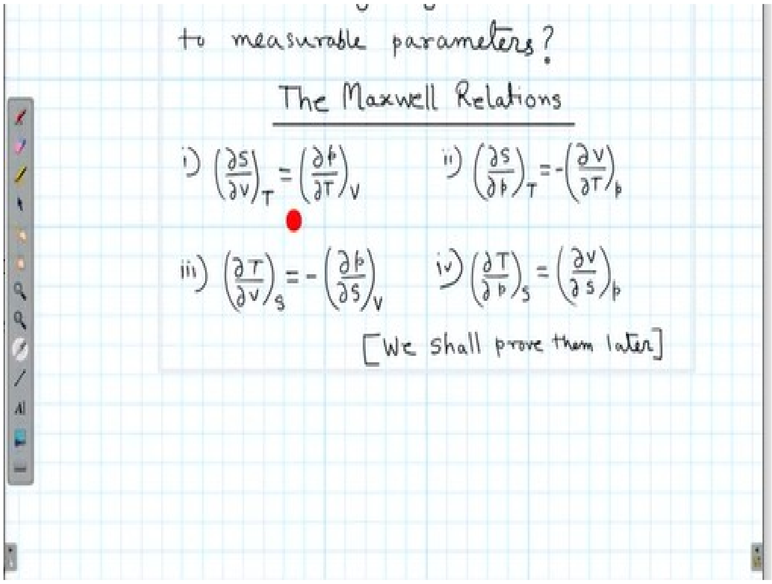

to measurable parameters?

The Maxwell Relations

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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, these relations, the thermodynamic relations we are talking about these are complicated to the Maxwell's relation. These are complicated to remember of course they are I mean they are not easy and as a student I also had tough time remembering those. But there are certain ways by which it becomes really easy to remember this relation. So, at one of the form one of the upcoming lectures we will be also discussing ah how to remember this relations in a very simple manner. So, that is all for today's lecture. See you very soon and thank you.