Concepts of Thermodynamics
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Lecture – 58
Thermodynamic Relationships (Contd.)

So, we were discussing about Thermodynamic Relationships and today we will continue with very interesting thermodynamic relationships concerning internal energy enthalpy and specific heats at constant pressure and volume.

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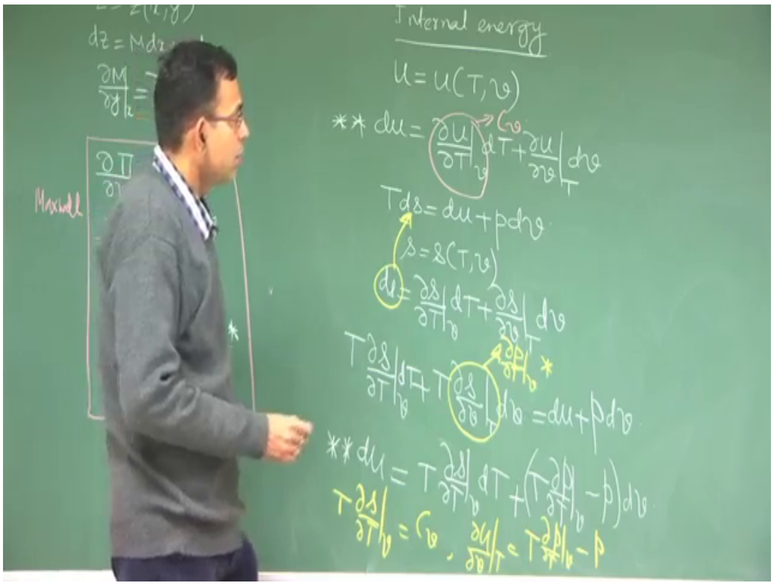

So, we will start with the Internal energy, so you can write the internal energy as a function of 2 independent intensive thermodynamics properties u as a function of T and v. So, du is this one so this is the rule of partial total derivative is the sum of the partial derivatives. So, this is one expression u as a function of T and v ok.

Now, let us use the T ds relationship, why we use this T ds relationship because, this also gives you u as a function of not T and v, but u as a function of s and du as a function of ds and dv. But you can write now s as a function of T and v if you do that you can have an expression from here which can be compared with this form. So, with that motivation we will write s as a function of T and v so ds.

So, then we will substitute that ds here. So, let us write T then del s del v at constant temperature this one of the thermodynamic relationships will give you the corresponding in terms of the measurable parameters. See this third Maxwell's equation that from here we can write this is del p del T at constant v from this star which is written on this part of the board, following that we can write du so this is d T right. So, du is equal to T del s del T at constant v d T plus T del p del T at constant v minus p dv right.

So, now compare this equation with this equation they are essentially the same, before comparing this is my definition nothing but C v right. So, by comparing these 2 the first observation that you have T del s del T at constant v is C v and similarly T del p del u del T at constant sorry del u del v at constant temperature is T del p del T at constant volume minus p ok. So, to summarize you can write du is equal to from this equation C v d T plus dv not dp.

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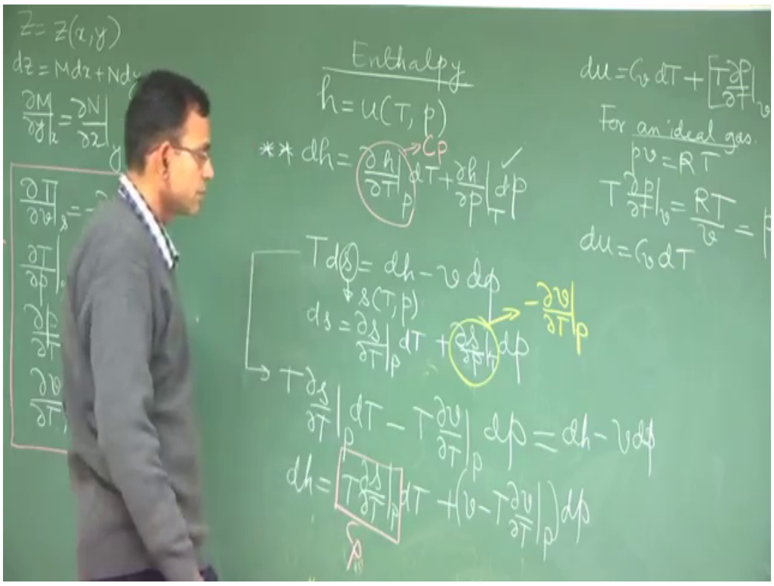

So, this is an expression now for an Ideal gas you have pv is equal to RT. So, del p del T at constant volume is equal to R by v right. So, T del p del T at constant volume is RT by T that v that is p, so this part becomes 0 p minus p. So, then du is C v d T for an ideal gas this we prove by this derivation which we assumed earlier that du equal to C v d T for an ideal gas this we now prove here, now does it so this is for an ideal gas.

Now is it sufficient to tell that u for an ideal gas is the function of temperature only not really sufficient because, u also at to establish that C v is a function of temperature only for an ideal gas, so that we will see as another step. But before that we will consider enthalpy instead of internal energy and do a similar exercise I will just follow exactly the similar steps, so just so that you can follow it nicely.

So, enthalpy; so enthalpy we will write h as the function of T and p ok. So, dh will del h del T at constant pressure, why we use it as why we write enthalpy is a function of T and p because we will use the T ds equal to dh minus T dp that is why this p dependence, we are we could also write it as a function of T an v. But will not solve the mathematical manipulation purpose fundamental it will not be wrong, but it will not solve the mathematical derivation purpose, so this is not C v anymore. Next we will write T ds is equal to dh minus v dp and this s as a function of T and p so ds.

So, then we will use one of the Maxwell's relations here del s del p lp at constant temperature let us find out it is the last Maxwell's equation del s del p at constant temperature is minus del v del T at constant pressure. So, T into del s del T at constant pressure, so we substitute we make it here with substitution into d T plus or so minus T del v del T at constant pressure into this is T dp this is dp is equal to dh minus v dp.

So, dh is equal to T del h del T at constant pressure d T plus v minus T del v del T at constant pressure into dp, this by definition is cp. So, if you compare this two this is C p, so your left with d h is equal to C p d T plus v minus.

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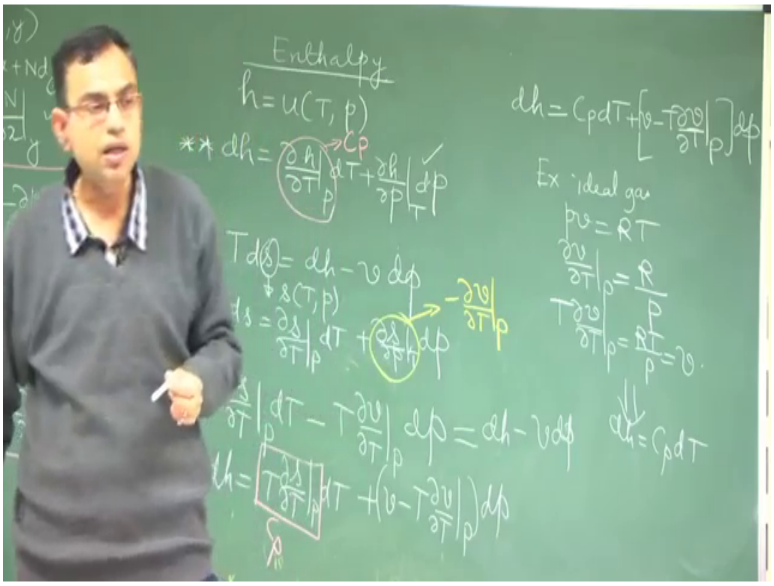

So, this is the pressure dependence of enthalpy this is the temperature dependence of enthalpy very similar to the internal energy expression, this kind of expressions are very useful because if you know the equation of state pressure volume temperature relationship you can easily calculate this partial derivatives and get an expression for h by integrating this right. So, again we consider an example ideal gas, so ideal gas pv is equal to RT so del v del T at constant pressure is equal to R by p.

So, T del v del T at constant pressure is equal to RT by p that is v. So, v minus that becomes 0 so that means dh is equal to C p dT, so for ideal gas dh equal to C p d T and du equal to C v d T this 2 things we have derived. But we have more general expressions even if it is not ideal gas, but you give an equation of state you can find out the change in enthalpy and change in internal energy.

These 2 are very important things why out of all the things we have done all this because, to calculate the heat transfer what done etcetera using the 1st law of thermodynamics for a closed system you require change in internal energy and for a flow process you require change in enthalpy. So, that is why the dh and du these expressions are very important which can be used fundamentally in conjunction with the 1st law of thermodynamics. So, we have considered internal energy and enthalpy now will consider the expression for C p and C v. In particular it is the expressions for C p minus C v that is important, because C p C v we have the expressions as they are.

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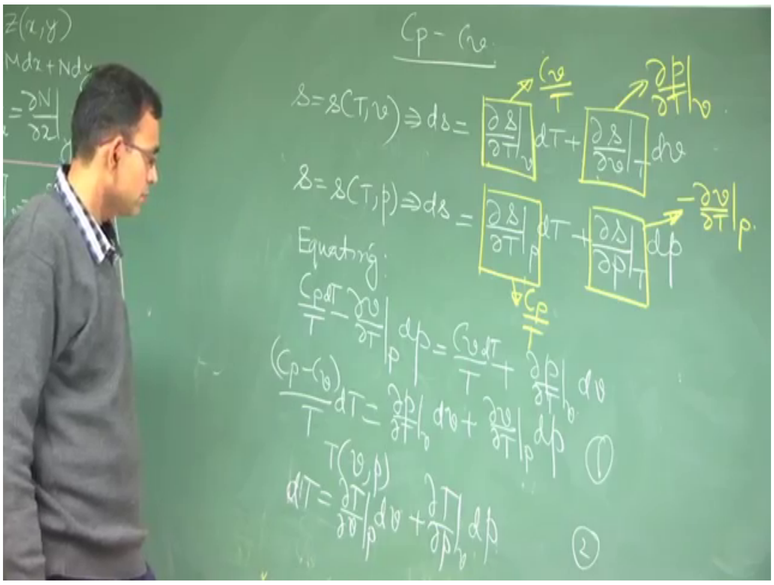

So, our objective now is to find out C p minus C v ok, so to do that because the entropy derivative can be written in terms of C p and C v if s is expressed as a function of temperature pressure volume etcetera. So, we will start with s as the function of T and v. So, ds right so just now we have done a derivation which tells that this is equal to C v by T, because T ds T del s del T at constant volume is C v for the internal energy derivation just now we have done it and this one from one of the Maxwell's relationships this star mart Maxwell relationship this is del p del T at constant volume.

So, we are expressing the non measureable in terms of measurable, this T ds relationship is very important sorry this Maxwell relationship is very important in fact, all these are important because right hand side there are non measurable parameters left hand side you have pressure volume temperature which are measurable parameters. So, then we have s as the function of T and p, so ds this just now we have derived is C p by T and this one. From one of the Maxwell relationships del s del p at the last one at constant temperature is minus del v del T at constant pressure.

Now, this is ds this also ds so they can be equated. So, if you equate this two you have C p by T minus del v del T at constant pressure dp is equal to Cv by T minus sorry this is C p by T dt C p dt by C p by T dt C p by T dt minus del v del p at constant pressure dp is equal to C v by T dt plus del p del T at constant volume v.

So, C p minus C v by T dT is equal to del p del T at constant volume dv plus del v del T at constant pressure dp ok. Now, see this has a form of T as a function of v and p right d T expressed in terms of dv and dp. So, if you write T as a function of v and p then d T right. So now, you can compare this 1 and 2 if you compare 1 and 2 then you have C v C p minus C v by T ok.

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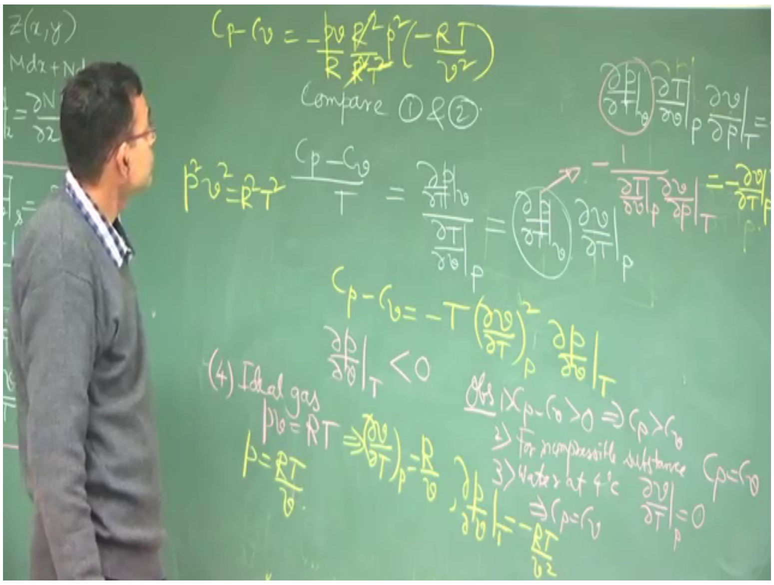

So, the ratio of these 2 coefficients is same as ratio of these 2 coefficients right then. So, this is nothing but del p del T at constant volume into del v del T at constant pressure right, because 1 by del T del v is del v del T. Now we can, so, this is an expression for C p minus C v, but we want to get a little bit more simplification, so we can use this chain rule del p del T at constant v into del T del v at constant p into del v del p at constant T is equal to minus 1 right. So, if I do that then del p del T at constant v this one is equal to minus 1 divided by del T del v at constant pressure into del v del p at constant temperature and this is nothing but minus del v del T at constant pressure into del p del v at constant temperature right just inverse.

So, C p minus C v the final expression is minus T del v del T whole square right at constant pressure into del p del v at constant temperature ok. So, with this equation so this is a very important equation because, this does not depend on which fluid I mean what is the constitutive what is the equation of state.

Now, one thing we can conclude that irrespective of the equation of state this will be negative right, if you increase the pressure the volume should decrease right. So, del p del v at constant temperature is negative T is absolute temperature which is positive and this is a square term so this is positive. So, minus minus plus makes the entire thing positive, so that means the first observation is that C p minus C v is greater than 0 that is C p is greater than C v this is first observation.

Second observation is that for incompressible substance there is no change in volume that means the right hand side is 0. So, C p is identically equal to C v not approximately identically equal to C v there is another case when C p is identically equal to C v, but the substance is not perfectly incompressible can you give an example. So, I am repeating my question one case perfectly incompressible you can understand that perhaps no fluid is perfectly incompressible typically if it is in liquid or gas state solid almost perfectly incompressible, but liquid and gas state will have some compressibility liquid less gas more but still some compressibility.

So, can you tell can you give an example when C p is perfectly equal to C v although it is not a perfectly incompressible scenario. Consider water at 4 degree centigrade, so water at 4 degree centigrade will have maximum density right. So, because it has maximum density it is specific volume versus temperature derivative this is a representative of density 1 by density. So, this will be 0 for water at 4 degree centigrade that means C p is equal to C v exactly right.

This is a very interesting situation where incompressibility is not exact but C p minus C v equal to 0 is exact and the final observation that we considered is ideal gas ideal gas you have pv equal to RT, so that means you have and del p del v at constant temperature is so p is equal to RT by v square RT by v. So, del p del v at constant temperature is minus RT by v square right.

So, this is so C p minus C v is equal to minus T into the square of this that is R square by v square into minus RT by v square right. So now, you use the equation of state so p square v square is equal to R square T square right, so v square is equal to R square T square by p square so this R square and this R square cancels, so then you can also use T is equal to pv by R. So, if we change everything to so you can cancel this one hopefully all this yes.

Student: I think del v del T at a constant pressure is (Refer Time: 29:11).

So, del v del T at constant.

Student: (Refer Time: 29:16).

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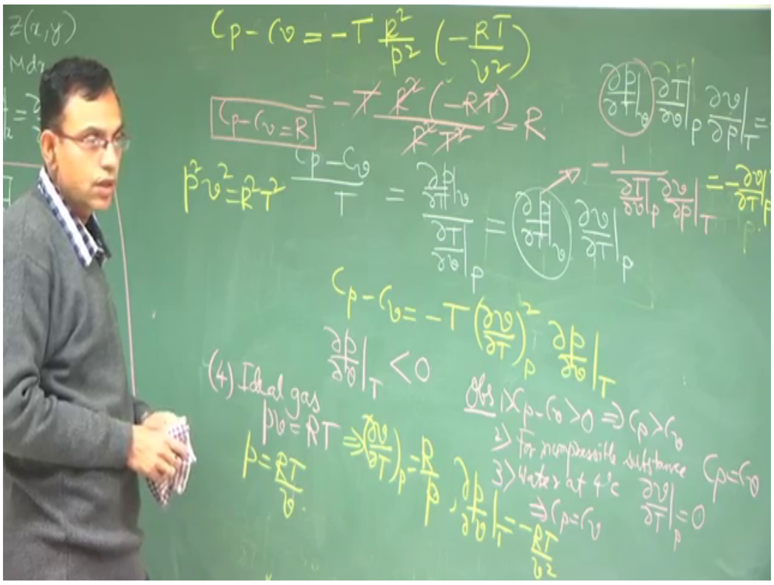

Pressure is R by p sorry that is why this is so I will re do it there was algebraic thing, so C p minus C v so this is R by p not R by v right del v del T at constant pressure is R by p right. So, C p minus C v will be minus T into del v del T at constant pressure square R square by p square not v square last time we wrote v square into this 1 minus R T by v square ok. Now p square v square is R square T square right, so you can write this as minus T R square into minus RT p square v square is R square T square. So, you get R square cancelled T square gets cancelled with this T square so this becomes R.

So, this proves that C p minus C v is equal to R for an ideal gas this does not assume constant C p and C v ok. So, we can derive from these thermodynamics relationships certain very useful expressions for internal energy enthalpy and differences in the specific heats. We can derive many more relations it is just mathematical manipulation of partial derivatives, but these relationships are very useful for conceptually deriving some unknown properties or derivatives of unknown properties in terms of derivatives of measurable or non properties. With this we conclude this lecture and we will start with a different topic in the next lecture.

Thank you very much.