Engineering Thermodynamics
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Module 8
Lecture No 54
Thermodynamic property relations: Joule-Thomson coefficient, cyclic relations

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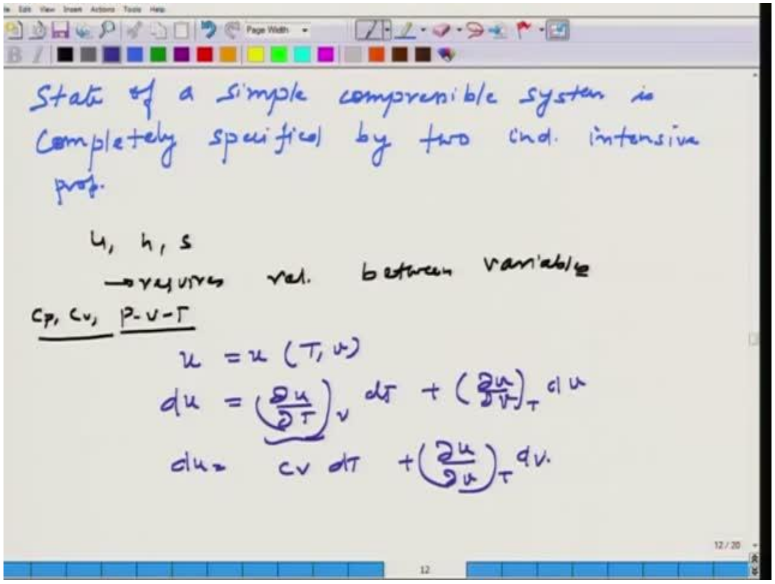

State of a simple compressible system is completely specified by two ind. intensive prop.

u, h, s

→ requires rel. between variable

Cp, Cv, P-v-T

$$u = u(T, v)$$

$$du = \underbrace{\left(\frac{\partial u}{\partial T}\right)_v} dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

$$du = c_v\, dT + \left(\frac{\partial u}{\partial v}\right)_T dv.$$

Ok welcome back uh, so in this lecture we are going to look at the law of specific us ways to find out the properties which are not directly calculated or directly measurable in experiments. Now in principle for simple compressible systems two particular intensive variable can define the properties. So theoretically we should be able to calculate all properties such as entropy by just providing this two intensive variable ok?

We can try to develop this relation in order to reflect the changes in the variable such as U or such as your entropy in some measurable variable, such as changes in the pressure with respect temperature or volume with respect to temperature or in other word using the PVT relation which we can develop or measure in experiments ok. So our interest is to calculate the changes in let us say U, H, S which requires ok relation between variables ok.

Now remember these are not directly measureable ok, so what we can do measure is nothing but CP, CP, CV and other relations related to so all related to this we can calculate. Now let us try to develop general relations which evolves specific heat ok? So let me try with internal energy, ok so internal energy that we say we are interested in variables TV, so we can write in differential form DU as del U by del TV DT plus and thus I can write this as CV which we know and this is your del U by del VTDV ok.

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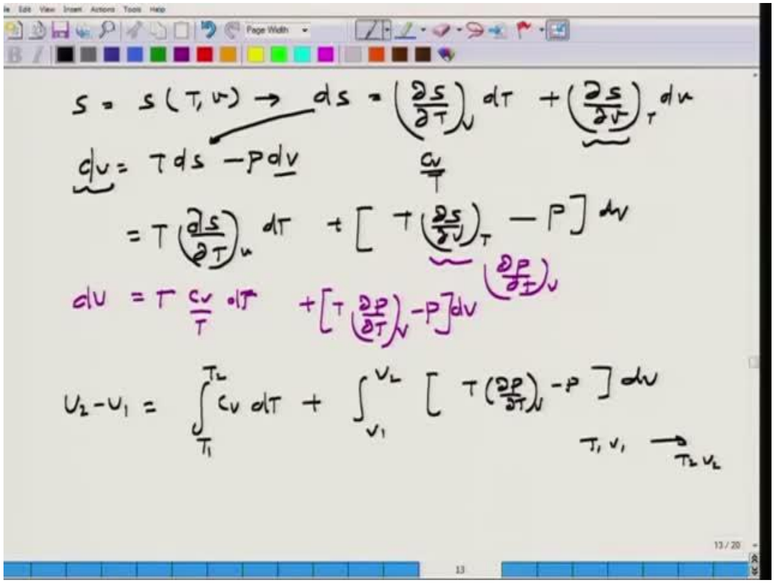

$$s = s(T,v) \rightarrow ds = \underset{\frac{c_v}{T}}{\left(\frac{\partial s}{\partial T}\right)_v} dT + \underbrace{\left(\frac{\partial s}{\partial v}\right)_T}_{} dv$$

$$\underbrace{du}_{} = T\,ds - P\,\underline{dv}$$

$$= T\left(\frac{\partial s}{\partial T}\right)_v dT + \left[T\underbrace{\left(\frac{\partial s}{\partial v}\right)_T}_{\left(\frac{\partial P}{\partial T}\right)_v} - P\right] dv$$

$$du = T\frac{c_v}{T}\,dT + \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] dv$$

$$U_2 - U_1 = \int_{T_1}^{T_2} c_v\,dT + \int_{v_1}^{v_2}\left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] dv$$

$T_1 v_1 \rightarrow T_2 v_2$

So similarly I can also express entropy two independent variables TV ok as follows. Now what we are interested is to represent this in a different way, of course we know del is TV which we connect to heat capacity ok which we know ok that is your nothing but your CV by T ok but what about this? ok, so here we are going to make use of Maxwell relations ok, so we also know that DU is your TDS minus PDV.

So let me make use of TDS directly here because our interest was to calculate first U change in U. So this I can make use of DS, so this becomes your TDS by DT VDT and V is common here, so we will use this T del S by del T minus PDV ok. So so this is something which I can write as CVTDT ok and here at this point I am going to make use of Maxwell relation which tells me that del S by del V at constant T is nothing but DP by DT at constant V and thus following expression would be T del P by del T at constant V minus PDT, so this is nothing but your DU ok.

So it contains constant volume term here and this will be your constant temperature term ok, so when you integrate this to get your change in internal energy, this is going to be your CVDT which will be from T1 to T2 and this is going to be V1 to V2 T del P by del TV minus PDV. So here of course the initial state was T1 V and we went to T2 ok.

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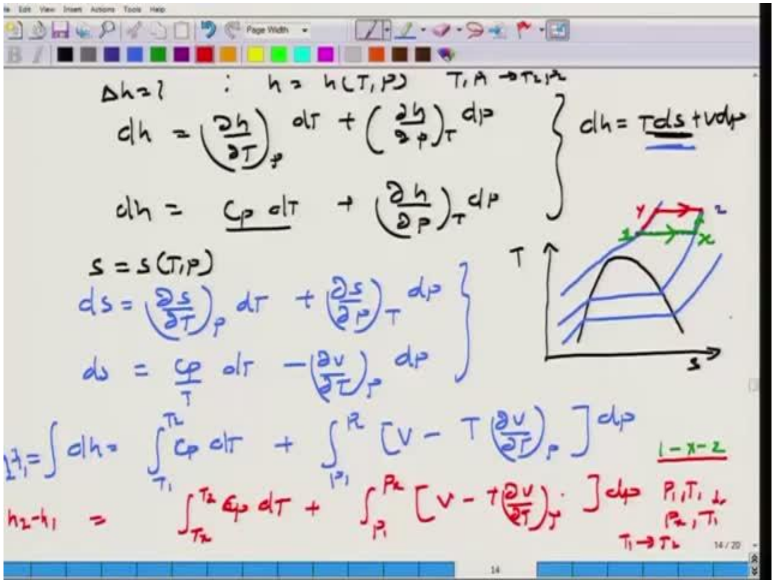

$\Delta h = ?$: $h = h(T, P)$ $T_1 P_1 \rightarrow T_2 P_2$

$$dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP$$

$$dh = \underline{C_p\, dT} + \left(\frac{\partial h}{\partial P}\right)_T dP$$

$$dh = \underline{T ds} + v dP$$

$s = s(T, P)$

$$ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP$$

$$ds = \frac{C_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_P dP$$

$$h_1 = \int dh = \int_{T_1}^{T_2} C_p\, dT + \int_{P_1}^{P_2} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dP$$

$\underline{1 - x - 2}$

$$h_2 - h_1 = \int_{T_2}^{T_2} C_p\, dT + \int_{P_1}^{P_2} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dP$$

P_1, T_1 ↓

P_2, T_1

$T_1 \rightarrow T_2$

So similarly we can also calculate the change in enthalpy, would it be change in enthalpy, so we already know HTP, so DH is going to be del H by del TP ok. This is going to be CPDT plus ok. Now here again we are going to make use of S as STP ok, we are going to make use of the differential form of entropy here ok and we also know that your DH is nothing but TDS plus VDP, so though we have written here DH as in the form of these two terms which connect CP and then the partial derivative of H, so this will be the like path corresponds to constant pressure, this would be the path correspond to constant temperature.

And by taking two paths you can change state one to state two from T1 P1 to T2 P2 ok? But we need this expression in order to get that, so let me try to first derive this. So DS is equal to STP, so we can get your DS is del S by del TP DT plus del S by del P ok, this is nothing but CP by T and this we are going to make use of Maxwell relation, this becomes del V by del TVDP ok.

So you can use DS directly in this expression ok and this DS would be your, so finally if we make use of this expression we get DH as CN integrated CP DT plus integral of V minus this would be T times del V by del TV ok and this integral would be from T1 to T2, so this will be from P1 to P2 ok and this is going to be your delta S2 minus S1. So let us try to understand a bit how to make use of such an expression.

Now let us consider this TS plot ok diagram and we are going to consider isobars ok. So let us say this is here and then you have this ok, so now what we are interested is, going from one to somewhere here let us say two ok. You can take this path one, so this is here is one and this is two and if you can take this path from one to let us say this is X at a constant temperature then you are here constant pressure. So this will be the path let us say 1X2, 1X is a constant isothermal and X to 2 is isobaric ok or you can do this exercise in a different way where you can take it to let us say Y where 1Y is isobaric followed by isothermal, there are many possibilities one can think ok.

For the case of 1X2, this expression would be because you remember this is at constant presure, this is this term is useful for constant temperature hence I can write H2 minus H1 as TX T2 CPDT plus your P1 PX and of course this rest of the term ok. So the first one would be you are taking a system from P1 ok T1 to PX whatever PX here is and you T1 and then you taking this T1 to T2 ok. Naturally the PX in this case is P2 because of the isobar ok.

Ok, so this is a way to make use of simple enthalpy change or internally change and you can come up with this kind of changes using different reversible path and this is one of the illustration which we used but now I can make use of this kind of expression to explain couple of things ok.

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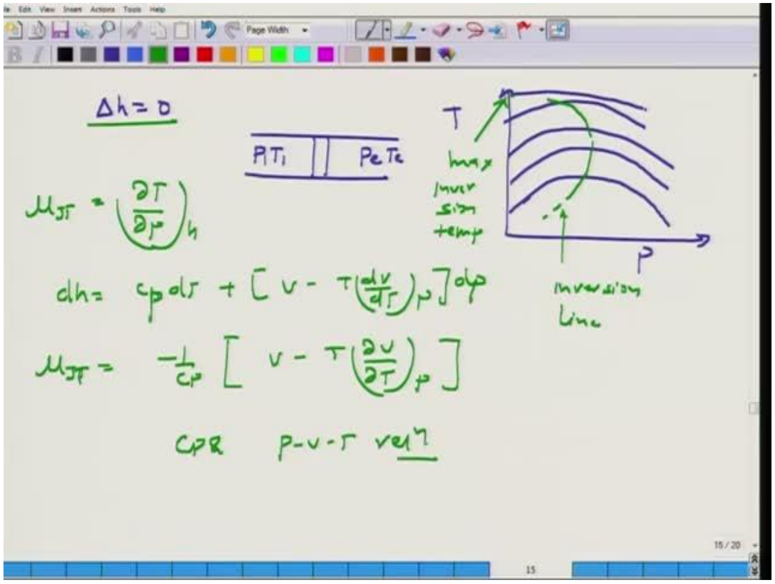

$\Delta h = 0$

$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h$

$dh = c_p\,dT + \left[v - T\left(\frac{dv}{dT}\right)_P\right]dP$

$\mu_{JT} = -\frac{1}{c_P}\left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right]$

CP & P-V-T relⁿ

For example considering that what we have developed for the case of enthalpy ok, we can directly use this expression for the case where delta H is zero and this would be the case for throttling process which we have looked at earlier where we have developed this expression that if the FT and P then for a throttling system ok with a throttle here, for given P1 and T1 you can vary the property of the throttling valve and you can change your PT and this is an example of the inversion curve which you get and this inversion curve you can have different initial condition and you will get different kind of curves and the maximum you can connect to obtain ok, something like this, so this will be your inversion line ok and this will be the temperature which at the end of this curve would be your maximum inversion temperature.

Ok, so we in the earlier discussion we have already discussed Joule Thomson coefficient we used JT which is nothing but the change in temperature with respect to pressure constant H. Now considering your delta H is going to be zero because H is constant, you can use the expression derived earlier and the following which can come up with ok, CPDT plus V ok. So considering DH is equal to zero so your new JT which is going to be del T, del T by del P is nothing but minus CP V minus T del V by TH constantly ok.

Alright so this is your simple Joule Thomson coefficient relation which can be evaluated using CP and PVT relations ok. Now we will take a look at how to calculate entropy change ok.

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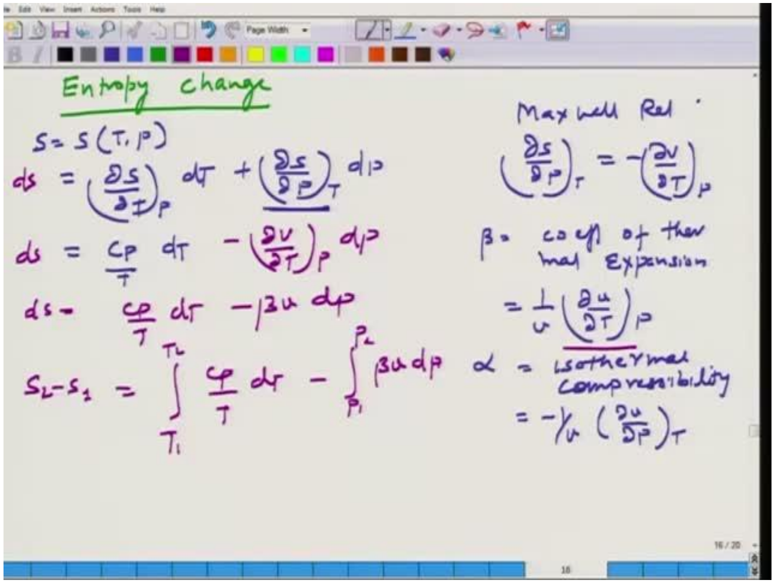

Entropy change

$S = S(T, P)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \underline{\left(\frac{\partial S}{\partial P}\right)_T} dP$$

$$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$dS = \frac{C_P}{T} dT - \beta V dP$$

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{C_P}{T} dT - \int_{P_1}^{P_2} \beta V dP$$

Maxwell Rel.

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

β = coeff of thermal Expansion

$$= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

α = isothermal compressibility

$$= -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

So let us consider S as function of T and P and this we can write as a in terms of partial derivatives del S by del PP DT plus ok and this we already know, this is nothing but your CP by TDT. Now here we have to make use of Maxwell relation, so Maxwell relation tells us that del S by del P at constant T is minus del V by del T as constant P ok. The other thing which we are going to also define here is coefficient of thermal expansion which is 1 by V del V by del T at constant pressure and alpha which is isothermal compressibility.

And this will be your minus 1 by V del V by del P at constant T, so we are going to make use of this relation, Maxwell relation and these two variables which we have defined which depends on the changes in the volume with respect to temperature or with respect to the pressure. Ok, so this term is now can be written in terms of del V by del TEDP ok and this is nothing but can be connected to the coefficient of thermal expansion here, so I can write this DS as CPT DT minus beta VD. So you can integrate now ok. So this is a way of calculating the entropy which we define as intensive variable T and P.

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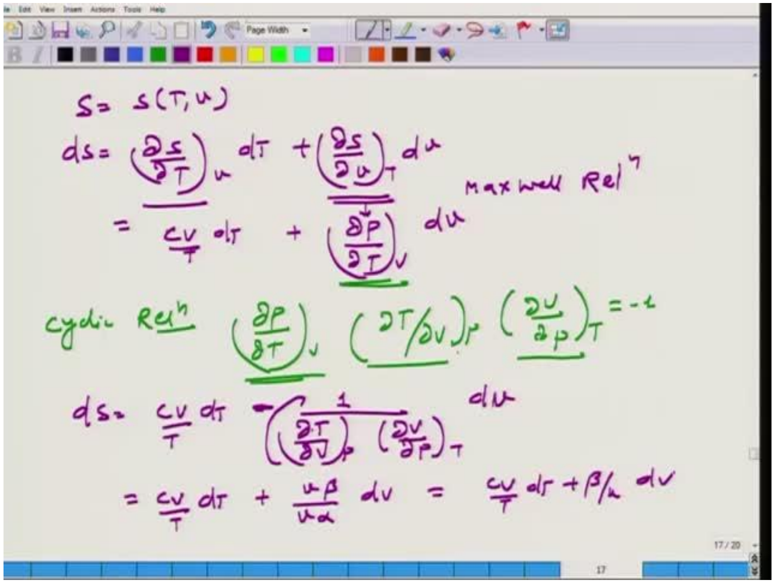

$S = S(T, v)$

$$ds = \underline{\left(\frac{\partial s}{\partial T}\right)_v} dT + \underline{\left(\frac{\partial s}{\partial v}\right)_T} dv \quad \text{Maxwell Rel}^n$$

$$= \frac{C_V}{T} dT + \underline{\left(\frac{\partial P}{\partial T}\right)_V} dv$$

$$\text{cyclic Rel}^n \quad \underline{\left(\frac{\partial P}{\partial T}\right)_V} \underline{\left(\partial T / \partial V\right)_P} \underline{\left(\frac{\partial V}{\partial P}\right)_T} = -1$$

$$ds = \frac{C_V}{T} dT - \frac{1}{\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T} dv$$

$$= \frac{C_V}{T} dT + \frac{v\beta}{v\alpha} dv = \frac{C_V}{T} dT + \beta/\alpha \, dv$$

Similarly I can also derive an expression where S is function of T and V ok, so your DS is in terms of partial derivatives, this is nothing but your CV by TDT and what about this? and based on the natural relation this is nothing but your DP by DT at constant volume, this is from Maxwell relation. So what we are interested is to connect this expression here in terms of either CP or isothermal compressibility or your coefficient of thermal expansion.

So we are going to make use of cyclic relation here. A cyclic relation can be written in this way for PTV variables ok. So I can get this in terms of these terms and note that this connects the change in the volume with respect to temperature and this connects change in volume with respect to pressure and thus we can connect these two variables to isothermal compressibility or the beta expansion, coefficient thermal expansion.

So I can write this DS as CVTDT minus 1 by del T by del VPT, I can take this here in a numerator ok and this can be written as further as following. If I take it in numerator I can represent this in terms of your beta V ok and the denominator would be in terms of alpha ok, so this becomes nothing but V plus V beta V alpha PV or CVTDT plus beta ok.

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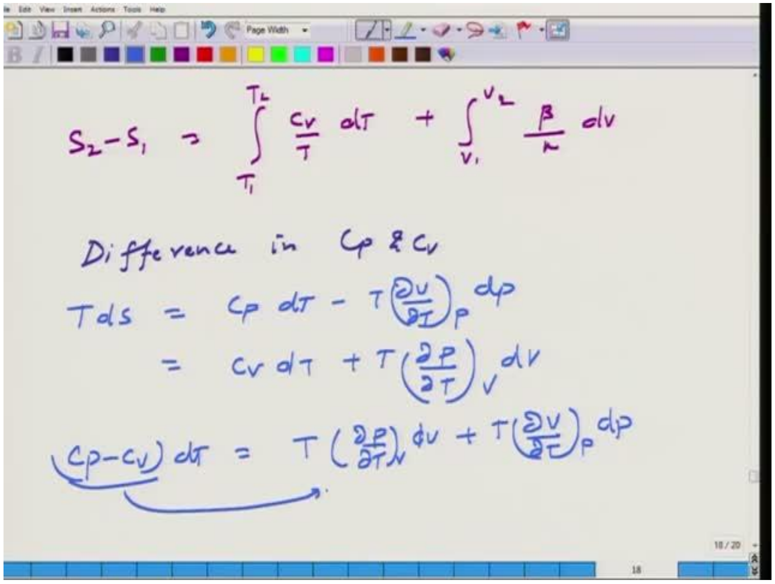

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{C_v}{T}\, dT + \int_{V_1}^{V_2} \frac{\beta}{\kappa}\, dV$$

Difference in C_p & C_v

$$T ds = C_p\, dT - T\left(\frac{\partial v}{\partial T}\right)_p dp$$

$$= C_v\, dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

$$(C_p - C_v)\, dT = T\left(\frac{\partial P}{\partial T}\right)_V dV + T\left(\frac{\partial V}{\partial T}\right)_P dP$$

Thus you can get your S2 minus S1 as T1 T2 CVT ok. So this was an exercise of getting the entropy changed by two different paths by using two different combination of intensive variable. So let me just try to do more of exercise making use of Maxwell relation and here what we are going to do is we are going to calculate the difference in the heat capacities that is CP minus CV ok.

So let me start with here, this is to evaluate difference in CP and CV, ok so let me start with this expression of TDS which we know that it can be written as CPDT minus T del V by del TPDP and this is CPDT plus T ok, DP DT constant volume multiplied by DV. So of course I can take the difference between these two and if y9ou take the difference this will become because the left hand side is zero so this becomes CP minus CVDT and this I can take it to the right hand side, this becomes TDPDTVDV plus TPDP ok.

Now I can divide this term here, I can get the following expression ok.

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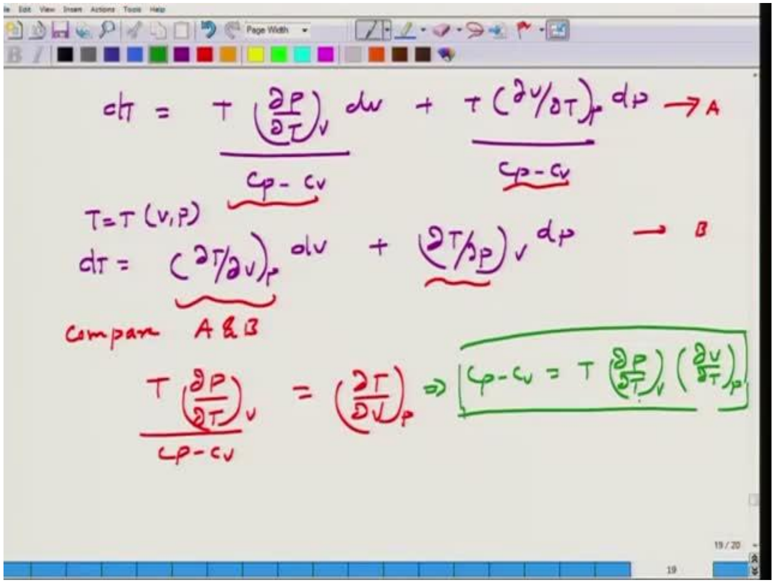

$$dT = \frac{T\left(\frac{\partial P}{\partial T}\right)_V}{\underbrace{C_P - C_V}} dV + \frac{T\left(\partial V/\partial T\right)_P}{\underbrace{C_P - C_V}} dP \rightarrow A$$

$T = T(V, P)$

$$dT = \underbrace{\left(\partial T/\partial V\right)_P} dV + \underbrace{\left(\partial T/\partial P\right)_V} dP \rightarrow B$$

Compare A & B

$$\frac{T\left(\frac{\partial P}{\partial T}\right)_V}{C_P - C_V} = \left(\frac{\partial T}{\partial V}\right)_P \Rightarrow \boxed{C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P}$$

So we have an expression of T as a function of V and P ok. So in other word I can now represent this T as a function of V and P, so I can take a differential of T. Now this the reason which I am doing is to relate this partial derivative with this term ok and this essentially means that this term is nothing but equal to this term and similarly this term is nothing but equal to this term.

So by comparing these two expression, by comparing this expression with this one, so let us say, so compare A and B and both this expression will give us the same final expression of T, so let me just take one of them T del P by del TVCP minus CV is nothing but ok and this tells you that CPCV is nothing but T del P by del T and using reciprocative relation I can get del V by del TP ok.

So this is one expression which I got, now here in order for me to make use of our coefficient of thermal expansion and isothermal compressibility I would have to use cyclic relation ok, so let me make use of cyclic relation now.

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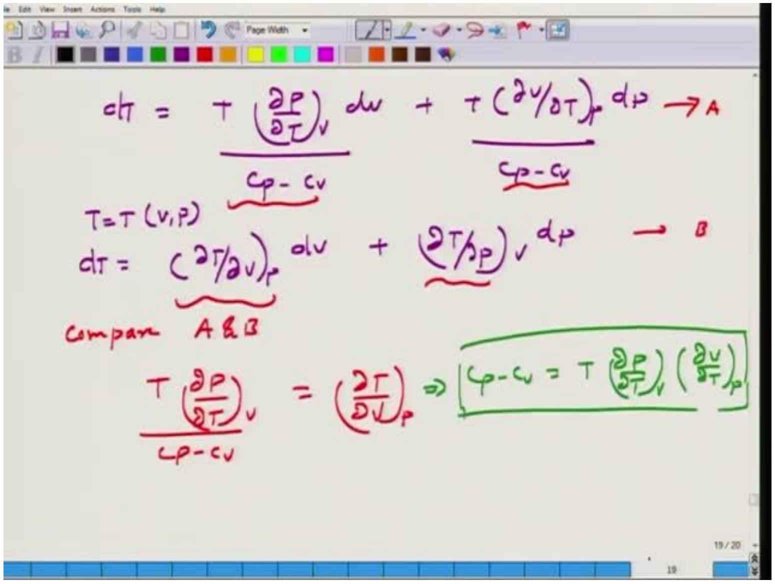
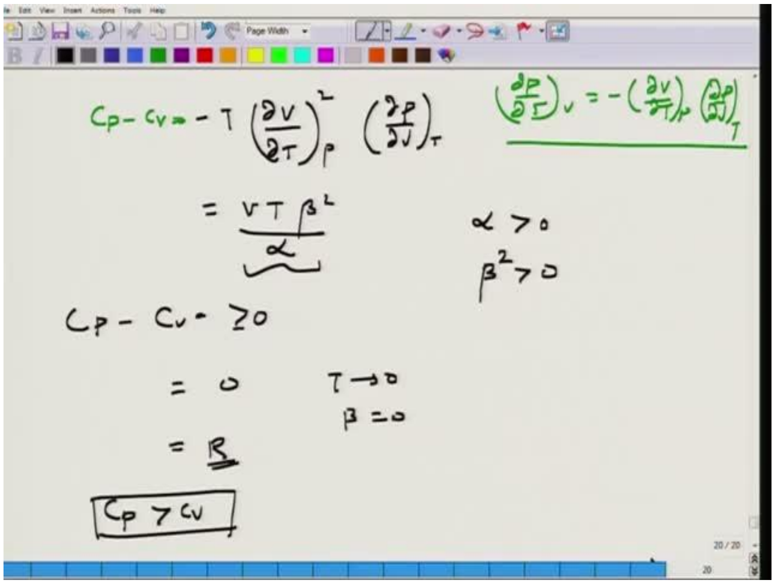

$$dT = \frac{T\left(\frac{\partial P}{\partial T}\right)_v}{\underbrace{C_p - C_v}} dv + \frac{T\left(\partial v/\partial T\right)_P}{\underbrace{C_p - C_v}} dP \rightarrow A$$

$T = T(v, P)$

$$dT = \underbrace{\left(\partial T/\partial v\right)_P} dv + \underbrace{\left(\partial T/\partial P\right)_v} dP \rightarrow B$$

compare A & B

$$\frac{T\left(\frac{\partial P}{\partial T}\right)_v}{C_p - C_v} = \left(\frac{\partial T}{\partial v}\right)_P \Rightarrow \boxed{C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_P}$$


$$C_p - C_v = -T\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial V}\right)_T$$

$$\left(\frac{\partial P}{\partial T}\right)_v = -\left(\frac{\partial v}{\partial T}\right)_P\left(\frac{\partial P}{\partial v}\right)_T$$

$$= \frac{VT\beta^2}{\underbrace{\alpha}}$$

$\alpha > 0$

$\beta^2 > 0$

$C_p - C_v \geq 0$

$= 0$ $T \rightarrow 0$

$\beta = 0$

$= R$

$\boxed{C_p > C_v}$

CP minus CV with cyclic relation of del P by del T at VS minus of del P by del VT, so this is based on cyclic relation and using these expression I can plug in back here ok and what I can get is the following minus T del V by del T square at P and del T by del V at T ok and this you can show that this is nothing but VT beta square by alpha. Ok beta we have already defined, now alpha is compressibility, your del V by del P is always negative and alpha is defined as minus 1 by V, so alpha is than zero.

But beta usually is positive but can be negative, for example for water beta is maximum at 4 degree Celsius but it is negative below 4 degree Celsius but beta square is going to be greater than zero. So with this, this particular term is going to be greater than or equal to zero. For the case where your beta is zero, this term is going to be zero ok, this can be zero when temperature reaches zero or beta is zero ok otherwise for the case of ideal gas, this is nothing but R ok.

So with this of course we showed that CP is of course greater than CV with a formal expression ok and I think what we went through this particular set of lectures is to find out the changes in the variables which are of interest but they are not directly calculated or measurable from the experiment but what we can do is, we can make use of CP, CV and PVT relations and the set of derivations which we did and making use of cyclic relation and Maxwell relation we can calculate the changes in the desired thermodynamic properties, so with that I am going to end this particular lecture and as well as this topic. We will start a new topic like in the next lecture.