Applied Thermodynamics for Engineers

Prof. Dipankar N. Basu
Department of Mechanical Engineering
Indian Institute of Technology - Guwahati

Lecture – 06
Generalized relations for entropy and Specific heats

Good morning everyone, welcome to the second lecture of our week number two and we are talking about the thermodynamic property relations. So how was the previous lecture? I hope it has gone down well to you where we have tried to develop the Maxwell's relation using the $T\mathrm{d}s$ equations and from there we have got some generalized expressions for the changes in internal energy and enthalpy of any thermodynamic system.

Now if the lectures are clear to you that is excellent, if that is not, I request you to go back to the previous lecture and just listen the lecture once again. If required, go through the books there are several standard textbooks available on thermodynamics. I have told earlier also I am particularly following the book of Cengel and Boles. However, you can also refer to the book of Sonntag which is a very standard book or any other traditional book on thermodynamics.

And all these topics are always covered there. So please proceed with this lecture only when you are clear with the development of the Maxwell's equations. Now just to quickly summarize what we have done in the previous lecture, we have seen that there are four primary thermodynamic potentials namely, the internal energy, enthalpy, Helmholtz free energy and Gibbs free energy each of them having their own implications in different kinds of thermodynamic systems.

Now once we express the rate of change or change in each of those thermodynamic potentials in terms of entropy and combination of other thermodynamic parameters, then correspondingly we can get four Maxwell's relations. The Maxwell's relations are basically partial differential equations which relate the changes in temperature, pressure, specific volume and entropy.

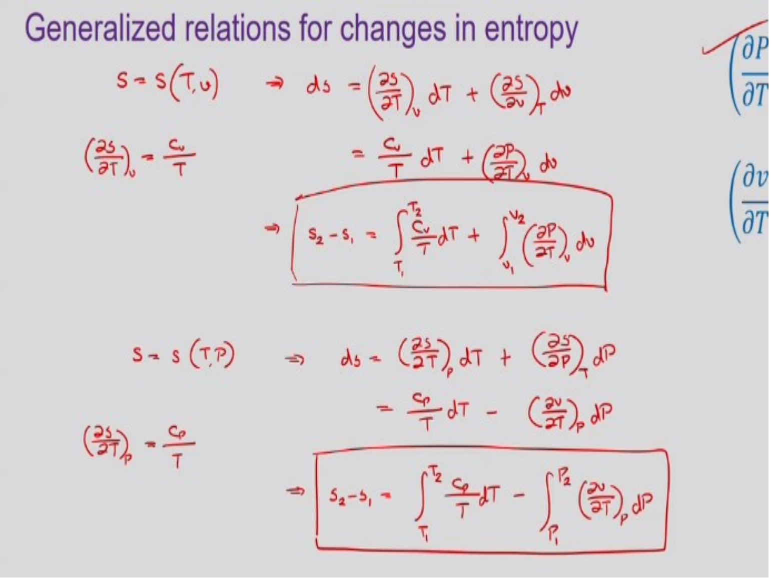
Remember that the first three properties temperature, pressure and specific volume they are directly measurable properties whereas entropy cannot be measured directly and therefore Maxwell's equation solve the basis of calculation of entropy as a function of the other three. We have also discussed about the Maxwell’s square which is one of the easier ways of remembering all the four *T*d*s* equations and the four Maxwell’s relations.

I hope the use on the Maxwell’s square you have understood, please try to develop the Maxwell’s equations and all the four *T*d*s* relations in terms of the Maxwell’s square so that you are in a better position to make use of that. And then we have developed generalized expressions for the changes in internal energy and enthalpy, quite a bit of mathematics was involved there.

I hope you have a tried to do that on your own also,tried to develop the final expressions for du and dh. If you have not done that then please pause this lecture here, just take your pen and paper and develop those relations. If you have any doubt you can refer to the previous video and also the textbooks but please proceed with this video only when you are able to develop the relations for d*u* and d*h* on your own.

Because not only in this course in several other scenarios you have to make use of those relations. And, it is very rare that you are asked to develop the equations for d*u* or d*h*. So you may be thinking that what is a need of that? but there are several situations where you have to calculate some other parameters or maybe the changes in enthalpy or changes in internal energy of a thermodynamic system, where you have to make use of those relations and therefore you need to remember those relations. Now those are quite complicated relations even I am also not in a position to remember that. But that is much easier to develop the relations by taking one or two minutes before solving any particular problem and therefore it is important that you know how to develop those relations. So today we shall be developing the similar relation for changes in entropy to start with and then we shall be seeing examples of applying those relations.

(Refer Slide Time: 04:26)



Generalized relations for changes in entropy

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

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{c_v}{T} \qquad = \frac{c_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_v dv$$

$$\Rightarrow \boxed{s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_v}{T} dT + \int_{v_1}^{v_2} \left(\frac{\partial P}{\partial T}\right)_v dv}$$

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

$$\left(\frac{\partial s}{\partial T}\right)_P = \frac{c_p}{T} \qquad = \frac{c_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_P dP$$

$$\Rightarrow \boxed{s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_p}{T} dT - \int_{P_1}^{P_2} \left(\frac{\partial v}{\partial T}\right)_P dP}$$

$$\left(\frac{\partial P}{\partial T}\right.$$

$$\left(\frac{\partial v}{\partial T}\right.$$

So, our first target is to develop a generalized relation for changes in entropy. Now while we had only a single equation for changes in internal energy and a single equation for changes in enthalpy. Changes in entropy can be expressed in two possible ways. And which one to use that depends / the available information. Once I develop the equation you will be able to see how we can use each of them in separate situations.

Now in the first phase we are assuming entropy to be a function of temperature and specific volume i.e.,

$S = S(T, v)$

So, what we can write for ds? ds can be written as:

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

Here now there are two relations that we have to make use of to substitute for each of these partial differentials, one of the relations that we have developed while developing the expression for du.

Remember that I told you to keep this quantity separate there also we encountered this quantity: $(\partial s/\partial T)_v$ what was this expression for this I asked you to remember this one to keep it separately because I have to make use of that in future. So, it was in the form:

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

whereas so $(\partial s/\partial T)_v$ can be replaced with the above in the initial expression for ds. To replace the next term $(\partial s/\partial v)_T$ in the ds equation you have to make use of one of the Maxwell's relation. So, what is that? These are ones that we are going to make use of.

So correspondingly we can say this to be:

$$ds = \frac{C_v}{T}dT + \left(\frac{\partial P}{\partial T}\right)_v dv$$

And therefore, if a system is undergoing a change of state from state 1 to state 2 then we can easily represent the corresponding changes in specific entropy as:

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{C_v}{T}dT + \int_{v_1}^{v_2} \left(\frac{\partial P}{\partial T}\right)_v dv$$

where

T_1 is the initial state temperature

T_2 is the final state temperature

v_1 is the initial specific volume

v_2 is the final specific volume

So, what are the information we need to calculate the change in specific entropy following this way? We of course need to know the *PvT* relationship again because that will helping us to calculate this particular differential $(\partial P/\partial T)_v$ and also we need to have information about C_v. So, this is one of the expressions for changes in entropy.

The other one we can develop by assuming s to be a function of temperature and pressure i.e.,

$$s = s\,(T, P)$$

So, following the similar procedure, we can write ds as:

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

Now how to replace the first differentials? I hope now you have got the idea $(\partial s/\partial T)_P$. What is this? This one while developing the expression for dh we encountered this term, it was:

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

So accordingly, we can write it as the first term of the initial expression for ds here. Now, how can we replace the second term of the equation one using any Gibbs equation or using any Maxwell's relation. Like in the previous one we used this particular Maxwell's relation what we have to make use of? $(\partial s/\partial P)_T$. I hope we are able to use the Maxwell's square now and from there we can develop, so this is the corresponding equation this will become:

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

Please try to use the Maxwell's square instead of directly taking the Maxwell's reaction to substitute these partial differentials. Now for change of state from 1 to 2, we can write:

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{C_p}{T}dT - \int_{P_1}^{P_2} \left(\frac{\partial v}{\partial T}\right)_P dP$$

So, this is the second relation so in both the cases or in the second case particularly what are the information that we need to know? Again, we need to know the *PvT* relationship to evaluate that partial differential and also you need to know C_p as a function of temperature. So, in a given situation which one you should select, as I have mentioned that depends upon the available information. Of course, you need to make use of the *PvT* relationship in both the cases. But what is the difference between the two? The first expression makes use of C_v whereas the second one makes use of C_p. And therefore, if we have information available in terms of C_p as a function of temperature which one you should go for?

If you have C_p as a function of temperature then you should go for the second expression for $s_1 - s_2$, whereas if we have C_v as a function of temperature we should go for the first expression for $s_1 - s_2$. Or let us take another scenario where we have both C_p and C_v available with us we shall shortly be deriving the expression for $C_p - C_v$ or relationship between C_p and C_v so generally if we know the expression for one of them, the other one is also directly available.

Then if we have information available about both C_p and C_v then which one you should go for? that depends upon what kind of process we are dealing with. If we are dealing with the constant pressure process suppose, then what we should do? Constant pressure process means dP = 0, then for the constant pressure process the second term will automatically go to 0 and then your relation will involve only as a simple term i.e., for a constant pressure process you will be having:

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{C_p}{T} dT$$

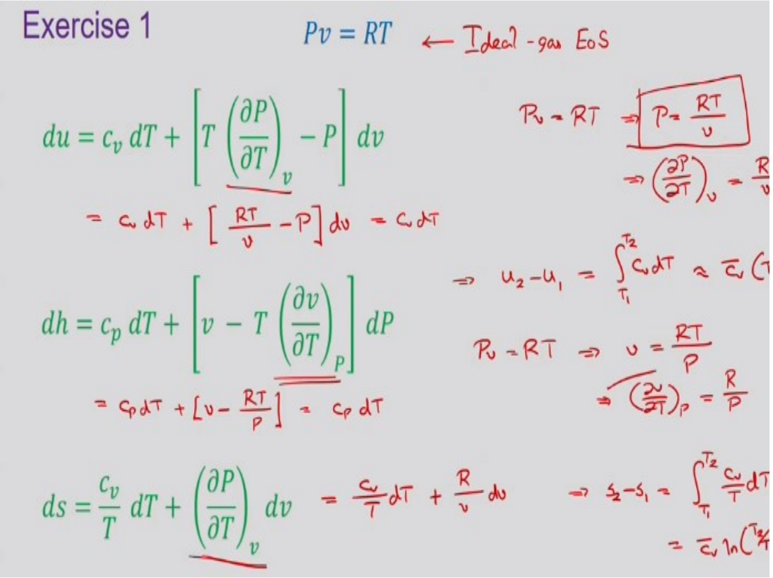
which is a very simple relationship and we should go for this.

Similarly, if we are going for a constant volume process then what we should do? Constant volume process means dv = 0. So, the second is term in the first expression for $s_1 - s_2$ will go to 0 for a constant volume process. And therefore, it will be much easier to evaluate the change in entropy as:

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{C_v}{T} dT$$

Because in the second expression, we have to evaluate both the ones for a constant volume process. However, it will reduce to only a single integration following the first approach. Of course, if we are processing neither constant volume and neither constant pressure then both are equivalent, we can choose any one of them depending on our convenience or depending upon other scenario. So, these are the generalized expressions for changes in entropy. So, we have now got expressions for changes in internal energy, changes in enthalpy and changes in entropy or specific for all of this quantities, specific internal energy, specific enthalpy and specific entropy.

(Refer Slide Time: 12:12)



Exercise 1

$$Pv = RT \leftarrow \text{Ideal-gas EoS}$$

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

$$= c_v\,dT + \left[\frac{RT}{v} - P\right]dv = c_v\,dT$$

$$Pv = RT \Rightarrow \boxed{P = \frac{RT}{v}}$$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v}$$

$$\Rightarrow u_2 - u_1 = \int_{T_1}^{T_2} c_v\,dT \approx \bar{c}_v(T$$

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

$$= c_p\,dT + \left[v - \frac{RT}{P}\right] = c_p\,dT$$

$$Pv = RT \Rightarrow v = \frac{RT}{P}$$

$$\Rightarrow \left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P}$$

$$ds = \frac{c_v}{T}\,dT + \underline{\left(\frac{\partial P}{\partial T}\right)_v}\,dv = \frac{c_v}{T}dT + \frac{R}{v}dv$$

$$\Rightarrow s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_v}{T}dT$$

$$= \bar{c}_v \ln(T_2/$$

Let us try to make use of those expressions for a known *PvT* relationship, so the first expression one handicap that we have here actually is we do not know too many *PvT* relationship because that is something that we are going to covered in the next week where shall be talking about the properties of pure substances. But one *PvT* relationship that you definitely know is the ideal gas equation of state which is:

$$Pv = RT$$

Let us try to make use of this expression to evaluate the expressions for changes in specific internal energy, specific enthalpy and specific entropy for ideal gases. So, this is ideal gas equation of state EoS in general is an acronym is often used for equation of state which is the *PvT* relationship for an ideal gas. Here *R* is the gas constant so that is a constant but *PvT* all of them can be variable.

Then first is changes in internal energy, this is the expression that we have developed in the last lecture:

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

So, to use this expression we have to evaluate this differential first, then go back to the ideal gas equation of state, we have:

$$Pv = RT$$

or

$$P = \frac{RT}{v}$$

therefore $(\partial P/\partial T)_v$ that is the one that we are trying to evaluate. So, what it will be here? Here v and R is constant. So differentiating with respect to temperature will reduce to:

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v}$$

So now what do we have? Here we have the expression for internal energy as:

$$du = C_v dT + \left[\frac{RT}{v} - P\right] dv$$

Now what is RT/v? i.e., P only. So it is:

$$du = C_v dT + [P - P]dv = C_v dT$$

And therefore, the changes in internal energy or specific internal energy during a particular process will be:

$$u_2 - u_1 = \int_{T_1}^{T_2} C_v dT$$

And in a special case if C_v is constant or if we can use some average value of C_v over this given temperature range. Then this one will become:

$$u_2 - u_1 = \int_{T_1}^{T_2} \overline{C_v}(T_2 - T_1)$$

where

C_v bar is average C_v.

It can be shown that the specific heat generally is a function of at least for ideal gases is a function of only temperature and therefore we can see here that the specific internal energy is also as sole function of temperature. This is something that we have actually used in the previous one:

$$\mathrm{d}u = C_v \, \mathrm{d}T$$

for an ideal gas. But may not be true for real gas where the equation of state is something else.

Now changes in enthalpy, for changes in enthalpy what we have? We have the expression for enthalpy as:

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

Here we have to evaluate this particular differential $(\partial v/\partial T)_P$.
So

$$Pv = RT$$

now

$$v = \frac{RT}{P}$$

which gives

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P}$$

So, putting in the expression of d*h*, it becomes:

$$dh = C_p dT + \left[v - \frac{RT}{P}\right]$$

As, $RT/P = v$, i.e., it becomes only $C_p dT$. So, we can clearly see that for an ideal gas enthalpy is a sole function of temperature.

What about changes in entropy? Here we can calculate changes in entropy following two of the approaches, these are the two expressions which we have just derived in the previous slide. So, which one we should use now? Let us try both of them, because here we are not restricting ourselves to any constant volume or constant pressure process.

If you are trying to follow the first approach then we need to evaluate this particular differential which we have already done. We have the expression of entropy for constant volume process as:

$$ds = \frac{C_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_v dv$$

Putting $(\partial P/\partial T)_v$ that was $(R/v)dv$, remember this was the expression that we have actually developed as a part of first module to calculate the changes in entropy. Therefore, following this is:

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{C_v}{T} dT + R\int_{v_1}^{v_2} \frac{dv}{v}$$

Or we can write this as if C_v is a constant:

$$= \overline{C_v}\, ln\left(\frac{T_2}{T_1}\right) + R\, ln\left(\frac{v_2}{v_1}\right)$$

where C_v is average C_v.

Similarly, if we use the second expression, we have the expression of entropy for constant pressure process as:

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

Putting $(\partial v/\partial T)_P$ that was $(R/P)dP$, then we have to develop these differential so this becomes:

$$= \frac{C_p}{T}dT - \frac{R}{P}dP$$

Accordingly, we have is:

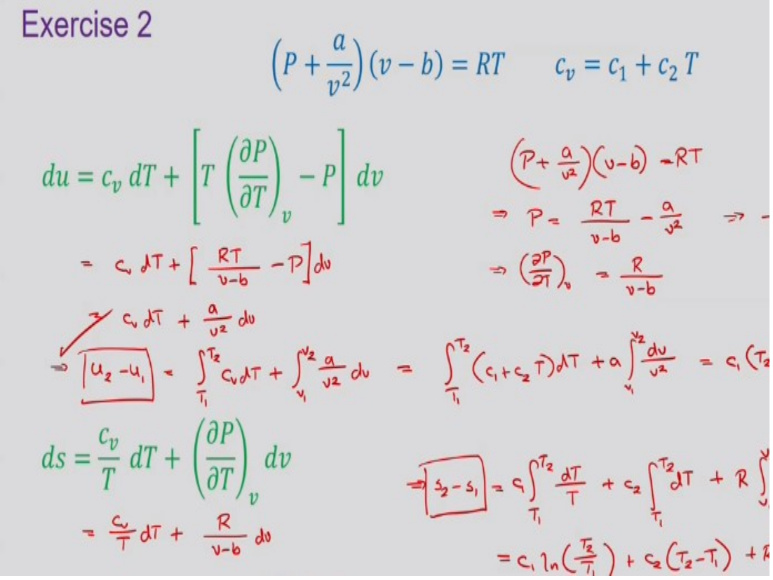
$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{C_p}{T}dT - R\int_{P_1}^{P_2} \frac{dP}{P}$$

$$= \overline{C_p}\, ln\left(\frac{T_2}{T_1}\right) + R\, ln\left(\frac{P_2}{P_1}\right)$$

where C_p is average C_p.

These are the expressions that we actually have developed in the previous module itself for an ideal gas using the *T*d*s* relationship directly. Now this is another way of proving the same relationship. But remember the expression that we have got here they are applicable only for ideal gases and generally we are assuming a constant specific heat constant values of C_p and C_v or some average value of C_p and C_v are applicable for this. Similarly, if we know the *PvT* relationship we can do it for any other kind of substances as well.

(Refer Slide Time: 18:54)



Exercise 2

$$\left(P+\frac{a}{v^2}\right)(v-b)=RT \qquad c_v=c_1+c_2T$$

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

$$= c_v\,dT + \left[\frac{RT}{v-b} - P\right]dv$$

$$\Rightarrow c_v\,dT + \frac{a}{v^2}\,dv$$

$$\Rightarrow \boxed{u_2-u_1} = \int_{T_1}^{T_2} c_v\,dT + \int_{v_1}^{v_2}\frac{a}{v^2}\,dv = \int_{T_1}^{T_2}(c_1+c_2T)\,dT + a\int_{v_1}^{v_2}\frac{dv}{v^2} = c_1(T$$

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

$$\Rightarrow P = \frac{RT}{v-b} - \frac{a}{v^2} \quad \Rightarrow -$$

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

$$ds = \frac{c_v}{T}\,dT + \left(\frac{\partial P}{\partial T}\right)_v dv$$

$$= \frac{c_v}{T}\,dT + \frac{R}{v-b}\,dv$$

$$\Rightarrow \boxed{s_2-s_1} = c_1\int_{T_1}^{T_2}\frac{dT}{T} + c_2\int_{T_1}^{T_2} dT + R\int$$

$$= c_1 \ln\left(\frac{T_2}{T_1}\right) + c_2(T_2-T_1) +$$

Let us try another example. Here we are having another *PvT* relationship of this form:

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

This is a very famous Van der Waals equation of state, the development of this one will be part of the next module. Here we are just taking it for granted. And it is also given for this particular problem c_v is a function of temperature is a linear function of temperature given as:

$$c_v = c_1 + c_2T$$

So, we have to calculate the expressions or evaluate the expressions for changes in internal energy and changes in entropy or specific internal energy and specific entropy using this equation of state and this particular expression for c_v as a function of temperature. So, this the expression for d*u* that we had:

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

Let us try to develop the expressions for d*u* for this particular scenario. So, using the equation of state first, we have:

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

by the way here *R, a* and *b* are constants. So, we can write:

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

So, what is your $(\partial P/\partial T)_v$,? As we are differentiating this respect to temperature, *v* also becomes a constant so it becomes (*R/v-b*) all constant and the second term becomes 0 because *v* is a constant.

So, if we put it in the initial expression for d*u*, we have:

$$du = C_v dT + \left[\frac{RT}{v-b} - P\right] dv$$

To evaluate the term inside the square bracket, let us look back into the expression for the equation of state or maybe here, so from here if we rearrange the terms we can also write:

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

So we can reduce the second term and write the expression for d*u* as:

$$du = C_v dT + \frac{a}{v^2} dv$$

Therefore, for a change of state from 1 to 2 changes in specific internal energy will be:

$$s_2 - s_1 = \int_{T_1}^{T_2} C_v dT - \int_{v_1}^{v_2} \frac{a}{v^2} dv$$

Now if we put the expression for c_v here, then we have:

$$= \int_{T_1}^{T_2} (c_1 + c_2 T) dT - a \int_{v_1}^{v_2} \frac{dv}{v^2} = c_1(T_2 - T_1) + \frac{c_2}{2}\left(T_2{}^2 - T_1{}^2\right) - a\left(\frac{1}{v_2} - \frac{1}{v_1}\right)$$

So, this is the final expression for the changes in specific internal energy that we are going to get in this particular scenario.

Similarly, if we want to calculate the changes in specific entropy, this is the expression for specific entropy:

$$ds = \frac{C_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_v dv$$

So there also we have to make use of this $(\partial P/\partial T)_v$. So, what we have? We are putting it here in the above expression and we have:

$$= \frac{C_v}{T} dT + \frac{R}{v-b} dv$$

Putting the expression for c_v now:

$$= \frac{c_1}{T} dT + c_2 dT + \frac{R}{v-b} dv$$

Therefore,

$$s_2 - s_1 = c_1 \int_{T_1}^{T_2} \frac{dT}{T} - c_2 \int_{T_1}^{T_2} dT + R \int_{v_1}^{v_2} \frac{dv}{v-b}$$

Now, performing the integration and putting the limit, so we are going to have:

$$= c_1 \, ln\left(\frac{T_2}{T_1}\right) + c_2(T_2 - T_1) + R \, ln\left(\frac{v_2 - b}{v_1 - b}\right)$$

So, here again we are able to calculate from the knowledge of the PvT relationship and c_v as a function of temperature we are able to calculate the expressions for changes in internal energy and changes in entropy. If we want to calculate the changes in enthalpy, we need to know the expressions of c_p or relationship of c_p with temperature if we can assume c_p to be a constant or if somehow you can evaluate relationship between cp and c_v. Then we shall also be able to evaluate the changes in enthalpy.

But truly speaking in a given scenario we hardly have to go for changes in both internal energy and changes in enthalpy. Because even without any knowledge of c_p you can calculate the changes in enthalpy in this particular case. How can you do that? I am repeating my question, here now we have already developed one relation for changes in specific internal energy that is u_2-u_1 and expression for changes in a specific entropy s_2-s_1. Now I am trying to say that we do not need to do any further differentiation or we do not need to have any information about c_p. But still we can calculate h_2-h_1, how can you do that? Just try to remember the relationship between u and h. What is h_2?

$$h_2 = u_2 + P_2 v_2$$

Similarly,

$$h_1 = u_1 + P_1 v_1$$

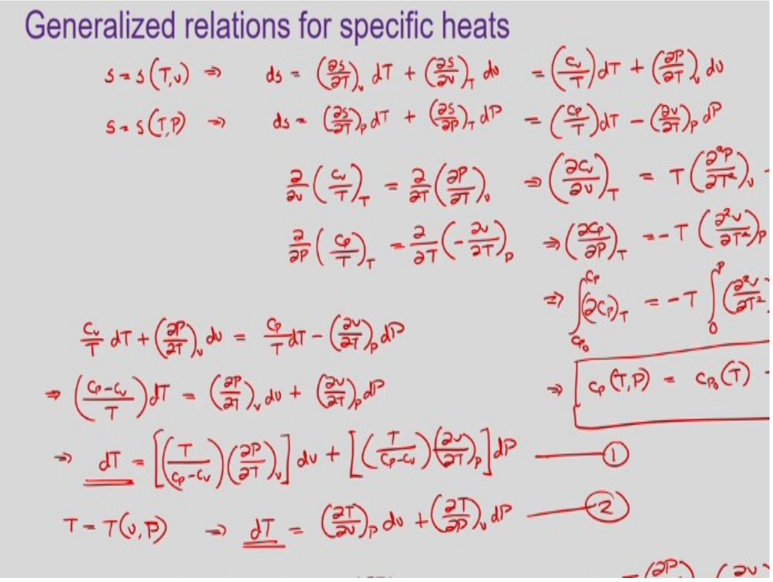
so, we can write this as:

$$h_2 - h_1 = (u_2 + P_2 v_2) - (u_1 + P_1 v_1)$$

$$= u_2 - u_1 + (P_2 v_2 - P_1 v_1)$$

u_2-u_1, you already have evaluated right here and now you know the PvT relationship, you know state 1 and state 2. So both P_2v_2 and P_1v_1, these two products are known to you. So you can easily calculate this h_2-h_1. Therefore, in a given problem we generally never have to calculate both the changes in specific enthalpy and specific internal energy. One alone is sufficient because from one we can get the knowledge about the other one. And therefore, we hardly need to have information both about c_p and c_v, knowledge about one is sufficient. Like for ideal gases, we have developed the relation we generally know that $C_p - C_v = R$ but that is true only for ideal gases, but for real gases for non-ideal gases this is not true so. There is some generalized relationship that is available between c_p and c_v and that is the next one that we are looking to perform.

(Refer Slide Time: 27:06)



Generalized relations for specific heats

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

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

$$\frac{\partial}{\partial v}\left(\frac{c_v}{T}\right)_T = \frac{\partial}{\partial T}\left(\frac{\partial P}{\partial T}\right)_v \Rightarrow \left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_v$$

$$\frac{\partial}{\partial P}\left(\frac{c_p}{T}\right)_T = \frac{\partial}{\partial T}\left(-\frac{\partial v}{\partial T}\right)_P \Rightarrow \left(\frac{\partial c_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_P$$

$$\Rightarrow \int_{c_{p0}}^{c_p} (\partial c_p)_T = -T\int_0^P \left(\frac{\partial^2 v}{\partial T^2}\right.$$

$$\Rightarrow c_p(T,P) = c_{p0}(T)$$

$$\frac{c_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_v dv = \frac{c_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_P dP$$

$$\Rightarrow \left(\frac{c_p - c_v}{T}\right) dT = \left(\frac{\partial P}{\partial T}\right)_v dv + \left(\frac{\partial v}{\partial T}\right)_P dP$$

$$\Rightarrow \underline{dT} = \left[\left(\frac{T}{c_p - c_v}\right)\left(\frac{\partial P}{\partial T}\right)_v\right] dv + \left[\left(\frac{T}{c_p - c_v}\right)\left(\frac{\partial v}{\partial T}\right)_P\right] dP \quad ①$$

$$T = T(v,P) \Rightarrow \underline{dT} = \left(\frac{\partial T}{\partial v}\right)_P dv + \left(\frac{\partial T}{\partial P}\right)_v dP \quad ②$$

So, changes in specific heat is very important to know, because specific heat gives you an idea about the amount of heat required to cause one degree change in temperature for unit mass of a substance and therefore in any heat transfer application or sensible heat transfer application specific heat or knowledge about specific heat is very important. Now specific heat for ideal gases, it is more or less constant but general it is a strong function of temperature.

Even for ideal gases also at high temperature specific heat can vary a lot with temperature and for non-ideal gases even pressure also can have some role on the magnitude of specific heats and therefore along with enthalpy, entropy and internal energy it is also important to know how specific heat is varying with temperature and pressure and that is our next job.

So, to start with we shall be making use of the relationship that we have already developed earlier for the changes in entropy. We had two relations:
First one, instead of trying to remember this let us develop them again from scratch. So, we are assuming entropy to be a function of *T* and *v* from where we can write:

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

Similarly, if we assume entropy to be a function of *T* and *P*. Then we get:

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

We are not going to put any expression for C_p or C_v here. Let us use the Maxwell relations now, to get the final expressions for d*s* that we had that will actually help our analysis or make it much shorter. So we can write for the first ds expression:

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

Similarly, for the second one we know we can write as:

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

So these are the 2 relations for changes in entropy we have developed earlier and we also used in the previous slides. Now we know that entropy is a property similarly temperature and specific volume is also a property, here we are talking about the first one.

Now temperature and specific volume both are properties. So, if entropy is a property then we can use the definition of property in terms of differentials and therefore we can write that:

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

Now temperature being constant we can take it out. So, we can write:

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

So, this is an expression for changes in specific volume at constant volume i.e., C_v with volume itself at constant temperature.

Similarly, if we use a second definition, again knowing that temperature and pressure have properties so for entropy to be a property it should satisfy the condition i.e.,

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

So, this way we can express C_v as a function of volume or C_p as a function of pressure. And using this expression integrating them along an isotherm between two given state points you can easily calculate expressions for C_p and C_v. Say for example if we take of the second expression and integrate this from a given state point 1 to another state point 2.

Then we can integrate this, for say:

$$\int_{C_{p0}}^{C_p} \partial C_{p_T} = -T\int_0^P \left(\frac{\partial^2 v}{\partial T^2}\right)_P dP$$

And if we put the integration limits say from absolute zero pressure to a certain pressure P, then C_{p0} we generally they call the absolute pressure absolute zero specific heat or ideal gas specific heat. So,

$$C_P(T,P) = C_{P0}(T) - T\int_0^P \left(\frac{\partial^2 v}{\partial T^2}\right)_P dP$$

So, this is one expression which represents the C_p as a function of temperature and pressure. $C_{p0}$the ideal gas specific heat or absolute 0 specific heat is a function of temperature alone because they are talking about the absolute 0 pressure no effect of pressure on the magnitude of this but for different temperature this C_{p0} can have different values even for ideal gases also.

And second integral can be evaluated only if we know that PvT relationship because then we can express this and differentials and then we can perform this. A similar expression can also be obtained for C_v using this particular expression. But generally, the separate expression for C_p and C_v both are not required like we have seen for ideal gases C_p and C_v are separated by the gas constant only similar relationship exist for even for real gases as well and let us try to evaluate that relation.

So, what we are going to do now look at the two expressions for d*s*, from the two expressions for d*s* let us equate both of them so from that first expression, we have:

$$\frac{C_v}{T}dT + \left(\frac{\partial P}{\partial T}\right)_v dv$$

and from the second one we have:

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

both of them giving the expressions for changes in specific entropy and therefore they can be equated to each other.

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

And let us now separate out dT from this so to do this we are writing:

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

keeping dT on one side, we can get the following expression:

$$dT = \left[\left(\frac{T}{C_p - C_v}\right)\left(\frac{\partial P}{\partial T}\right)_v\right]dv + \left[\left(\frac{T}{C_p - C_v}\right)\left(\frac{\partial v}{\partial T}\right)_P\right]dP$$

We are doing quite long expressions is it getting boring? If you feel bored you can pause the video just turn go back take a break and come back after five minutes. But still I am doing each of the steps in detail.

So that you are able to understand exactly what I am trying to do. I repeat, here I have just equated the two expressions for d*s* and then from there we have separated out this dT quantity. Now as per the PvT relationship we can always write that temperature is a function of v and p so from there we can also write:

$$dT = \left(\frac{\partial T}{\partial v}\right)_P dv + \left(\frac{\partial T}{\partial P}\right)_v dP$$

This is the simple relationship about changes in temperature. Now we have two expressions for dT here, say, first one, equation number (1) and second one equation number (2). On the right-hand side of both the equations we have dv and dP. So, we can equate the coefficients for them we can take any one of them let us speak up the coefficients for dv we could have done with dP also that should lead to the same result.

But here we are picking up the coefficients for dv so we have:

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

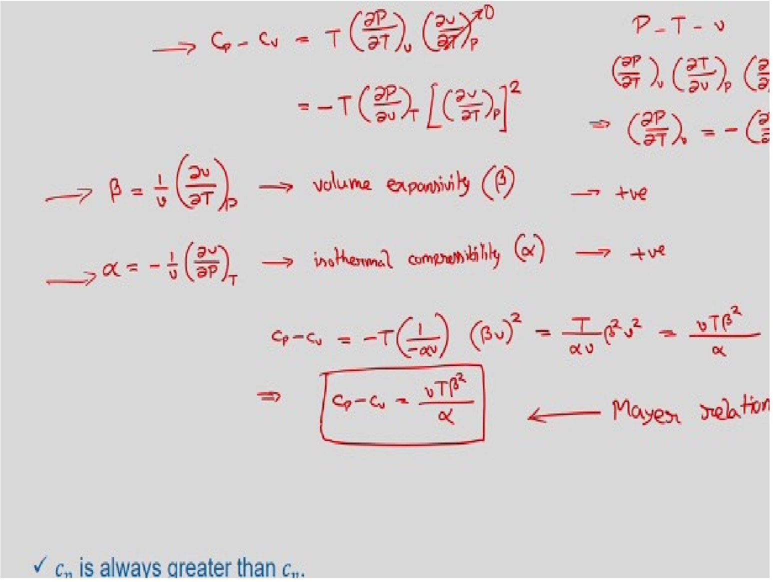
Or just taking $C_p - C_v$ out, we have here:

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

So, this is the expression for $C_p - C_v$ we are getting. And it is a quite simple expression again if we know the PvT relationship.

We can evaluate both the differentials it involves both the two differentials, this one which gives a change in pressure with temperature along a constant volume line and one which represent the changes in specific volume with temperature along a constant pressure line. We also have absolute temperature here, from here we can calculate the $C_p - C_v$. But instead of directly evaluating these two differentials there are easier ways of expressing the same.

(Refer Slide Time: 38:36)



$\rightarrow C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_P^{\neq 0}$

$= -T\left(\frac{\partial P}{\partial v}\right)_T \left[\left(\frac{\partial v}{\partial T}\right)_P\right]^2$

$P - T - v$

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

$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_v = -$

$\rightarrow \beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P \rightarrow$ volume expansivity (β) $\rightarrow$ +ve

$\rightarrow \alpha = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \rightarrow$ isothermal compressibility (α) $\rightarrow$ +ve

$C_p - C_v = -T\left(\frac{1}{-\alpha v}\right)(\beta v)^2 = \frac{T}{\alpha v}\beta^2 v^2 = \frac{vT\beta^2}{\alpha}$

$\Rightarrow \boxed{C_p - C_v = \frac{vT\beta^2}{\alpha}}$ $\leftarrow$ Mayer relation

✓ c_p is always greater than c_v.

To do that let us write this once more, we have:

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

Here we are going to make use of something known as the cyclic rule of partial differentials. If we are given with three partial differentials say *P, T* and *V,* then the cyclic rule can be represented as:

$$\left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_P \left(\frac{\partial v}{\partial P}\right)_T = -1$$

This is a cyclic rule look we are considering all the three partial differentials as possible among these three variables and will be equal to very standard rule in partial differential this is equal to -1. Now look at the present expression that we have, let us separate out the first term, so we will have:

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

So, we are putting it back in the expression for $C_p - C_v$ and can be written as follows:

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

Now what are these two partial differentials representing? One is $(\partial P/\partial v)_T$, and the other one is $(\partial v/\partial T)_P$. First let me write $(\partial v/\partial T)_P$ what is this one representing? This one is giving you the change in specific volume with temperature with pressure remaining constant. Therefore this quantity or just slightly modified version of this quantity where we divide this by specific volume say,

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

Now what we have is the change in specific volume per unit volume with temperature with pressure constant or along an isobar. What is this quantity called? Can you guess? This, you had in school level physics itself, change in volume with temperature per unit volume. So, this is called somewhat similar to the thermal expansion coefficient in thermodynamics we commonly call it volume expansivity. We call it volume expansivity with just the thermal expansion of gas or whatever medium that we are dealing with per unit volume and this commonly represented by the symbol β.

$$\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P \rightarrow volume\ expansivity\ (\beta)$$

And what is the other quantity? We take the inverse of that:

$$\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$$

Now what this particular quantity is giving? It is giving you the effect of pressure on specific volume per unit volume along an isotherm at constant temperature. So, if temperature is maintained constant this quantity is going to give you how volume is going to change with change in pressure and this particular quantity in thermodynamics is define as isothermal compressibility commonly represented by α.

$$\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \rightarrow \text{isothermal compressibility } (\alpha)$$

Actually, to make it positive we always know for any substance as a pressure increases as volume decreases. So, v and T goes in the opposite direction and therefore this differential is a negative one to make it positive we only put a − sign in front of this i.e.,

$$-\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \rightarrow \text{isothermal compressibility } (\alpha)$$

So,

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

whereas

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

So, take this back to our expression for $C_p - C_v$. Putting these in the expression for $C_p - C_v$, we get:

$$C_p - C_v = -T\left(\frac{1}{-\alpha v}\right)(\beta v)^2$$

So, simplifying it, we get as

$$= \frac{T}{\alpha v}(\beta v)^2 = \frac{vT\beta^2}{\alpha}$$

Or if we write formally then,

$$C_p - C_v = \frac{vT\beta^2}{\alpha}$$

This particular relation is known as Mayer relation. It is a very important relationship in thermodynamics because it allows us to relate that two specific heats: specific heat at constant volume and specific heat at constant pressure, in terms of four properties: specific volume, temperature and these two newly defined properties volume expansivity and isothermal compressibility which are denoted by β and α respectively. To calculate the difference between C_p and C_v for any particular gas we need to know the *PvT* relationship, because using *PvT* relationship we can always calculate the expressions for this β and α, and then putting that for at a particular state point we can calculate the difference between C_p and C_v. But there are several direct consequences that we can obtain from this relation. What are those? First, consider the at the expression for α,

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

Is it positive or negative? We know that for any substance as the pressure increases the volume will decrease or vice versa i.e., volume and pressure go in opposite direction. Therefore, $(\partial v/\partial P)_T$ is always negative. Now to define α, we are putting a − sign before that and therefore this αis always a positive quantity. What other expressions we have in $C_p - C_v$? We have specific volume, volume has to be a positive, T is the absolute temperature so that also has to be positive α is also positive now that leaves us with β. Now β is positive or negative β is volume expansivity which gives the change in volume with temperature. Now generally for substances, as the temperature increases volume also increases and therefore *v* and *T* goes in the same direction so β is also a positive one.

So, we can write β is also a positive one. But is it true always? It is not true always for most of the general situation volume keeps on increasing with temperature. Just think about the anomalous expansion of water. Water as the temperature keeps on decreasing its density keeps on increasing but till that 4 ^{0}C, below 4 ^{0}C it goes in the opposite direction.

Like, if we plot specific volume with temperature, for most of the common substances with temperature specific volume keeps on increasing. But that does not happen for water, for water as the temperature decreases specific volume keeps on decreasing till 4 ^{0}C. At 4 ^{0}C it reaches a minima or density reaches a maxima and if the temperature is reduced further the volume keeps on increasing till the 0 ^{0}C or till the freezing point as a constant at that corresponding pressure. That is why ice is having lesser density compared to water and ice is able to float in water. Because the volume of ice is higher, specific volume of ice higher than liquid water or density of ice is lower than liquid water. Now if we divide this region of the plot into two parts, towards the right of the graph temperature and specific volume both are going in same direction. Therefore, β is positive. But what about the left-hand side? Here as the temperature is decreasing volume is increasing so β is negative such anomalous expansion though very rare but can be found in a few other substances as well and therefore β can be positive or can be negative. But all this discussion does not matter in this context of the $C_p - C_v$ expression because here we are having a β^2. So β^2 is always a positive quantity and therefore the $C_p - C_v$ given by the Mayer relation is always a positive quantity. Or we can write $C_p - C_v$ is always greater than 0 or maybe greater equal to the in some limiting case. Therefore, C_p is always greater equal to C_v, i.e., specific heat at constant pressure is always greater than the specific heat at constant volume for any substance. Now how much greater it will be that will depend upon the PvT relationship but it can never be less than C_v, at the limiting case it can be equal to C_v.

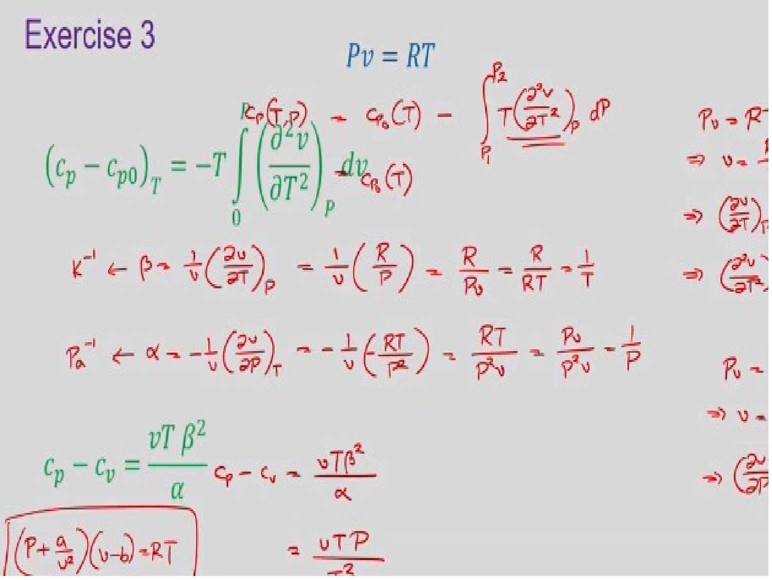
Second important conclusion as the temperature keeps on decreasing $C_p - C_v$ difference also keeps on decreasing or magnitude of $C_p - C_v$. When absolute temperature becomes 0 then $C_p = C_v$ that is the limiting case that we are mentioning, the C_p and C_v will be equal to each other when that we reach that absolute 0 temperature. But in general, as the temperature keeps on reducing, the difference between both specific heats also starts to diminish.

And in the third conclusion when you are talking about a truly incompressible substance, truly incompressible substance means whose specific volume does not change. Then what will be the expression for $C_p - C_v$? It is difficult to obtain from Mayer relation but just look at this. Here when we are talking about a truly incompressible substance.

This particular differential is equal to 0 because specific volume is not changing. And therefore $C_p - C_v$ is also equal to 0 that means for a truly incompressible substance both the specific heats are identical to each other. And that is why when you are talking about an incompressible substance generally for solids or liquids, we do not need to bother about two specific heats, we can just equate a single specific heat generally given by *c*.

However, when we are talking about gases, they have much higher level of compressibility. And therefore, for gases we need to consider C_p and C_v separately. So, with the Mayer relation now we know how to calculate the difference between the two specific heats for any given situation.

(Refer Slide Time: 50:53)



Exercise 3

$Pv = RT$

$C_p(T,P) = C_{p0}(T) - \int_{P_1}^{P_2} T\left(\frac{\partial^2 v}{\partial T^2}\right)_P dP$

$(c_p - c_{p0})_T = -T\int_0 \left(\frac{\partial^2 v}{\partial T^2}\right)_P dv$

$K^{-1} \leftarrow \beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = \frac{1}{v}\left(\frac{R}{P}\right) = \frac{R}{Pv} = \frac{R}{RT} = \frac{1}{T}$

$Pa^{-1} \leftarrow \alpha = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T = -\frac{1}{v}\left(-\frac{RT}{P^2}\right) = \frac{RT}{P^2 v} = \frac{Pv}{P^2 v} = \frac{1}{P}$

$c_p - c_v = \frac{vT\beta^2}{\alpha}$ $c_p - c_v = \frac{vT\beta^2}{\alpha}$

$= \frac{vTP}{T^2}$

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

I would like to close up on this particular lecture by discussing another example. Again, we have the ideal gas equation of state but here we shall be talking about the expressions for specific heat C_p and C_v. There are two expressions we have developed; one is a Mayer relation but before that we developed another relation for C_p as a function of temperature and pressure as:

$$C_P(T,P) = C_{P0}(T) - \int_{P_1}^{P_2} T\left(\frac{\partial^2 v}{\partial T^2}\right)_P dP$$

So, this was the relation that we already had we have developed for C_p. Now let us try to apply this for an ideal gas situation. For ideal gas:

$$Pv = RT$$

or

$$v = \frac{RT}{P}$$

So, if we differentiate this specific volume with respect to temperature maintaining pressure constant then what it will be? It will be equal to:

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P}$$

If you differentiate it once more to get the differential this particular differential we shall be having:

$$\left(\frac{\partial^2 v}{\partial T^2}\right)_P = \frac{\partial}{\partial T}\left(\frac{R}{P}\right)_P = 0$$

So, for this scenario what we have in the expression for C_p as a function of temperature and pressure?

$$C_P(T, P) = C_{P0}(T)$$

i.e., for ideal gases pressure has no role on the magnitude of specific heat we can get it only from the information of temperature. Whatever absolute zero pressure ideal gas in specific heat it has, the same will continue for any pressure level. Therefore, when we are talking about an ideal gas or specific heat for an ideal gas, we do not need any information about pressure, temperature alone is sufficient so here we get C_p. Now let us try to evaluate the relationship between C_p and C_v, i.e., Mayer equation. For this first we evaluate β. So,

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = \frac{1}{v}\left(\frac{R}{P}\right) = \frac{R}{Pv}$$

and if we put the expression again $Pv = RT$,

$$= \frac{R}{RT} = \frac{1}{T}$$

i.e., for an ideal gas the volume expansivity is inversely proportional to temperature and that also gives you the dimension of this β. What it will be? It is a reciprocal to temperature. S,o its dimension is inverse of temperature or in SI unit it will be K^{-1}.

Now look at α,

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

$$Pv = RT$$

or

$$v = \frac{RT}{P} = (RT)P^{-1}$$

So,

$$\left(\frac{\partial v}{\partial P}\right)_T = -\frac{RT}{P^2}$$

So, if we put it back in the expression for α*,* we have:

$$\alpha = -\frac{1}{v}\left(-\frac{RT}{P^2}\right) = \frac{RT}{P^2 v} = \frac{Pv}{P^2 v} = \frac{1}{P}$$

So, what is the unit of this isothermal compressibility? That is the reciprocal of pressure. The SI unit of it can be Pa^{-1} or kPa^{-1} or MPa^{-1} whatever we would like to represent. So, for an ideal gas isothermal compressibility is just that the reciprocal of pressure and volumetric expansivity is a reciprocal of temperature.

Now, we use the Mayer equation where we have:

$$C_p - C_v = \frac{vT\beta^2}{\alpha}$$

So, we are putting the expressions for α and β in terms of *P* and *T*, here we have:

$$= \frac{vTP}{T^2}$$

So, we have:

$$= \frac{Pv}{T}$$

Using

$$\frac{Pv}{T} = \frac{RT}{T} = R$$

i.e., for an ideal gas the difference between C_p and C_v is a constant which is given as the gas constant itself. It is expressed as follows:

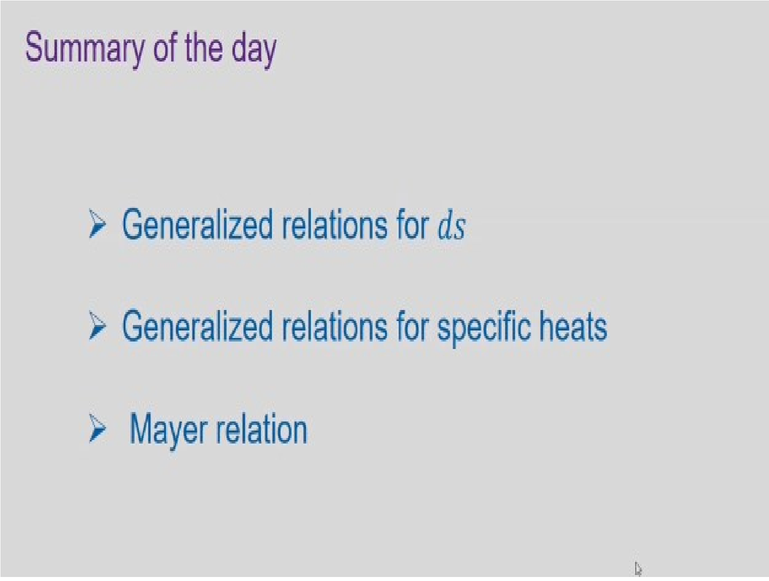
$$C_p - C_v = R$$

I just wrote this equation just a few slides back is the proof for this. For an ideal gas, we can calculate the difference between C_p and C_v using Mayer equation to get the gas constant itself. For any real gas, we need to use the corresponding equation of state, I would like to request you to perform the same exercise for the Van der Waals equation of state i.e., when you have:

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

as your equation of state or the PvT relationship. Then calculate the expression for C_p and also the difference between C_p and C_v for this Van Der Waals equation of state that will be your exercise for this particular lecture. So, I would like to complete here for today's work.

(Refer Slide Time: 57:31)



Summary of the day

- Generalized relations for ds
- Generalized relations for specific heats
- Mayer relation

So today we have talked developed the generalized relationship for ds, then we have done several exercises about how to use the generalized expressions for du, dh and ds, then we have developed the generalized relations for specific heats and finally the Mayer relation which gives the difference between C_p and C_v. So that's it for today, in the next lecture we shall be discussing about two unrelated topics which are the Joule-Thomson coefficient and also, the enthalpy calculation for phase change processes. Till then you review this particular lecture and as I have asked you to develop the relationship between C_p and C_v for a Van der Waals equation of state. Please try that, so that once you start the next lecture you will be in a better position to handle any other kind of problems. So, thanks for your attention. Take care.