

Applied Thermodynamics for Engineers
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Lecture – 07
Joule-Thomson Coefficient and Clapeyron Equation

Good morning everyone welcome to the third lecture of our week number two, where we are looking to finish of our module on the thermodynamic property relations. So, over the last two lectures we have developed the fundamental or generalized relations for changes in several thermodynamic properties or the thermodynamic properties which are of most importance to us. Basically, the specific internal energy, specific enthalpy, specific entropy and also two kinds of specific heats.

Along with them we have also discussed about several important topics like different kinds of thermodynamic potentials, the concepts of Helmholtz free energy and Gibbs free energy were introduced. We have developed auxiliary relationships such as the merely relation which allows us to calculate the difference between the two specific heats for a given substance and we have seen that depending upon the pressure and temperature level, there may not be any difference between the two specific heats so there may be significant difference. But as a rule, the specific heat corresponding to constant pressure that the C_p is always greater than C_v or in the limiting case of absolute zero temperature or purely incompressible fluid that can be equal to C_v , but can never be less than C_v . We have also defined two new properties which you probably have not heard before that particular lecture.

The isothermal compressibility and has which is a somewhat a way of representing the effect of pressure on specific volume. And also, we have defined volume expansivity which is a way of representing the effect of temperature on specific volume. So, both these isothermal compressibility and volume expansivity in a way is related to the PvT characteristic of a system that is they relates between these three fundamental parameters pressure volume, specific volume and temperature of a substance or a system.

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A little recap

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

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

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

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

1) P-v-T relationship

↳ Equation of state

$$2) c_v \approx c_v(T) \quad / \quad c_p \approx c_p(T)$$

$$Pv = RT$$

$$\rightarrow \left(\frac{\partial^2 v}{\partial T^2} \right)_P \approx 0$$

$$\approx (c_p - c_v)_T$$

$$\begin{aligned} f_{12} &= f_2 - f_1 = (u_2 - T_2 s_2) - (u_1 - T_1 s_1) \\ g_{12} &= g_2 - g_1 = (h_2 - T_2 s_2) - (h_1 - T_1 s_1) \end{aligned}$$

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

$$\rightarrow df = ?$$

$$dg = ?$$

$$P(v-\alpha) \approx RT \quad \alpha = 0.01$$

Just to have a quick recap, these are the relations that we have developed for changes in specific internal energy and specific enthalpy and as is clearly seen from the relations and also.

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

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

We have done a one or two sample numerical problems using them. Here we just need to have two kinds of information. One is the PvT relationship for a given substance, which is actually known as the equation of state.

So, the first thing that you need to know is the equation of state for the substance which relates these three quantities pressure, specific volume and temperature. And second information that we need to know is C_v as a function of temperature or C_p as a function of temperature. So, once we know that dependence of either of the specific heats on temperature, we can use any one of the relations.

And also, as we have seen your example problems it is not generally required in a particular problem to make use of both the relations, we can always use the relationship between specific internal energy and specific enthalpy to calculate one from the other. Like a for a certain problem if a suppose C_v is known to us and we have the PvT relationship then you can use that to calculate the changes in internal energy.

And then once we have this u_2-u_1 known to us then we can easily calculate h_2-h_1 from there, invoking the relationship between u and h . i.e.,

$$h_2 = u_2 + P_2 v_2$$

$$h_1 = u_1 + P_1 v_1$$

it becomes

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

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

that is ' Pv ' are the corresponding flow works for both state 1 and 2. Or vice versa in a certain problem if suppose we are calculating this one because we have C_p known to us then we can easily use that to calculate u .

And also, which one if we have information have related to both C_p and C_v , then which one to use that depends upon exactly what we are trying to identify and also sometimes depending upon what kind of process that we are dealing with. Like if suppose we are dealing with a constant volume process and isochoric process then for an isochoric process the dv term goes to 0. Therefore

$$du = C_v dT$$

Or it is much easier to operate with the relation for specific internal energy whereas if you are dealing with the constant pressure process for that this dp goes to 0. So the entire bracketed term does not need any consideration so

$$dh = C_p dT$$

and we can easily calculate the changes in enthalpy and from there you can calculate the changes in internal energy. Similarly, we can calculate the changes in specific entropy following a relation like this:

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

where again we need the PvT relationship and also C_v as a function of temperature or alternately you can have a different relation where we need to make use of the C_p relation as a function of temperature.

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

So, we can use either of them in a given scenario. And if we want to know how C_p and C_v varies with temperature then this is an example of relation of C_p with temperature.

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

So, from the knowledge of again just the PvT relationship we can easily calculate C_p as a function of temperature. And say if we want to perform one simple analysis say for an ideal gas to calculate the expression for C_v . We have already done in our previous module I guess but still, suppose our relation is:

$$PV = RT$$

So, from the known equation step we can easily calculate this differential:

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

is equal to whatever we get.

And from there we can easily calculate $c_p - c_{p0}$ corresponding to whatever temperature we are looking to identify. And finally, the Mayer relation which gives us the relationship between C_p and C_v .

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

So, these are the generalized relation that we have developed, here these are applicable for any kind of thermodynamic system, any kind of process that they are undergoing we can apply this particular relation.

Also, to other thermodynamic potentials that we have defined earlier the Helmholtz free energy and Gibbs free energy. Now here we have defined or developed relation for changes in two of the thermodynamic potentials: the specific internal energy and specific enthalpy because these two are the most common ones. But there may be certain situations where you are being asked to calculate the changes in specific Helmholtz energy.

Then how you can go for this? Of course, you can again that being quite similar to enthalpy being a combination property you can simply use this definition. Suppose you are looking to calculate $f_2 - f_1$ that is the changes in specific Helmholtz free energy during a particular process. Sometimes this is written as f_{12} which represents the change in value of f from 1 to 2. So, the expression will be:

$$f_{12} = f_2 - f_1 = (u_2 - T_2 s_2) - (u_1 - T_1 s_1)$$

Similarly, if you are looking to calculate the changes in specific Gibbs free energy. Then g_{12} will be:

$$g_{12} = g_2 - g_1 = (h_2 - T_2 s_2) - (h_1 - T_1 s_1)$$

Of course, we can still develop relationship something like

$$df = \text{whatever}$$

or

$$dg = \text{whatever}$$

but using the Maxwell relation but there is no need for this because we can still just use the definition and use the changes in these properties as well.

So, I am leaving one exercise for you, please try to solve that exercise using the information that I am providing you. Say, for example we are dealing with a system where helium is being used as the working substance so you are having helium as the working substance which is following the equation of state in the form of:

$$P(v-a) = RT$$

where this $a = 0.01 \text{ m}^3/\text{kg}$.

So, this is the PvT relationship that is given to you and it is said that the system is undergoing a change of state from 100 kPa, 20 °C to 600 kPa, 300 °C. So, state 1 corresponds to a 100 kPa, 20 °C and so i.e.,

$$P_1 \text{ is } 100 \text{ kPa}$$

$$T_1 \text{ is } 20 \text{ }^\circ\text{C or } 293 \text{ K}$$

Similarly

$$P_2 \text{ is } 600 \text{ kPa}$$

this particular relation or how can we prove this particular relation? Let us go one by one, let us take the left-hand side.

So,

$$LHS = \left(\frac{\partial P}{\partial T} \right)_S$$

Now can you get this particular one from Maxwell relation, P and T are there in the same horizontal line like this. However, the diagonal of P is V and not S that means we definitely call and do not have any Maxwell's relation which is directly applicable for this. Then how can you proceed with this? Look carefully P and S are not diagonal to each other but T and S they are at the diagonal, so we actually making use of something called reciprocity i.e., we are taking the inverse of this or we are writing this as:

$$LHS = \left(\frac{\partial P}{\partial T} \right)_S = \left[\left(\frac{\partial T}{\partial P} \right)_S \right]^{-1}$$

Now $(\partial T / \partial P)_S$, is it there in the Maxwell's equations? It is there definitely, because T and S are opposite to each other and P as neighbour to T . So, see the Maxwell's square so what the above expression will be:

$$= \left[\left(\frac{\partial T}{\partial P} \right)_S \right]^{-1} = \left[\left(\frac{\partial v}{\partial S} \right)_P \right]^{-1} = \left(\frac{\partial S}{\partial v} \right)_P$$

So, we have converted this to some other form. Now let us work on the right-hand side it is a much more calculation involved in this. So, we have:

$$RHS = \frac{k}{k-1} \left(\frac{\partial P}{\partial T} \right)_v$$

$(\partial P / \partial T)_v$ can be replaced using the Maxwell's solution, so what can we do for this? P and T again are neighbour and v is reciprocal to P . So, this will become:

$$= \frac{k}{k-1} \left(\frac{\partial S}{\partial v} \right)_T$$

But before that we have to know what is this ' K ' parameter? I hope you know the definition of K that's why I have directly gone for this, but K actually this as per the standard thermodynamic notation, K is:

$$K = \frac{C_p}{C_v}$$

So,

$$\frac{K}{K-1} = \frac{C_p/C_v}{C_p/C_v - 1} = \frac{C_p}{C_p - C_v}$$

And $C_p - C_v$, we have developed in the previous lecture can be written as:

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

So, we have to make use of this here and therefore though we could have used the Maxwell's relation directly that we are not doing here. What we are doing is we are putting this substitution for K . So, the RHS becomes:

$$RHS = \frac{k}{k-1} \left(\frac{\partial P}{\partial T} \right)_v = \frac{C_p}{C_p - C_v} \left(\frac{\partial P}{\partial T} \right)_v$$

Replacing $C_p - C_v$, now using on the relation we have to have C_p/T remaining in the numerator multiplied by $(\partial T/\partial P)_v$, using the reciprocity multiplying with $(\partial T/\partial v)_p$ and $(\partial P/\partial T)_v$ we can write it as:

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

So what substitution we can do now? Here we have used the reciprocity for the relationship $C_p - C_v$. Now $(\partial T/\partial P)_v$ and $(\partial P/\partial T)_v$ can cancel out leaving us with:

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

Now what kind of substitutions we can do here so that the right-hand side becomes equal to the left-hand side? $(\partial T/\partial P)_v$, Is that available on the Maxwell's square? That is definitely available because, you can see the Maxwell's square T and v are neighbour to each other and P is opposite to this or P actually is a neighbour to this. So, we cannot get this from the equation. But again here we can make use of the reciprocity, i.e., $(\partial T/\partial v)_p$ can be written as:

$$\left(\frac{\partial T}{\partial v}\right)_p = \left[\left(\frac{\partial v}{\partial T}\right)_p\right]^{-1}$$

This can be written using Maxwell equation as:

$$= \left[-\left(\frac{\partial S}{\partial P}\right)_T\right]^{-1}$$

So accordingly, the RHS becomes:

$$= \frac{C_p}{T} \left[-\left(\frac{\partial P}{\partial S}\right)_T\right]$$

So, what is the next substitutions that we have to do?

Now what is the C_p/T ? If you can invoke one of the earlier equations that we have used while deriving the relation for changes in entropy was:

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

So again, for these substitutions, there are several ways we can substitute the relations. But some of the substitutions that are not required, here we are directly going to substitute what we have developed here the relation for C_p/T .

So the RHS is now:

$$= \left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial T}{\partial v}\right)_p$$

So, if we combine them, we have:

$$= \left(\frac{\partial S}{\partial v}\right)_p$$

So, now your LHS and RHS are equal to each other which proves our relation. So, see the way I have developed this particular one. There are several ways we can substitute something make use of the Maxwell's relations, but at least twice we actually use some substitutions and when you are in the opposite direction like this is some substitution which was not required. And another substitution we have used here by directly putting a Maxwell's equation that was also not required rather we have to make use of the $C_p - C_v$ relation and you have to make use of this relation to prove whatever we are supposed to do. This way using the Maxwell's equation and

also using the generalized equations that we have developed there are several other relations which can be proved and they again have several applications in practice.

Let us have another small problem here we have to prove something involving β and α :

Prove that,

$$\beta = \alpha \left(\frac{\partial P}{\partial T} \right)_v$$

So, let us try. What is your expression for α ? Alpha is the isothermal compressibility, i.e.,

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

So here we have

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

So what should be the substitution we can use here? Anything click in your mind that is cyclic relation. What is the cyclic relation between P , v and T , that will be:

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

something we have used.

So if we put it in the RHS of the equation in question, it will be:

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

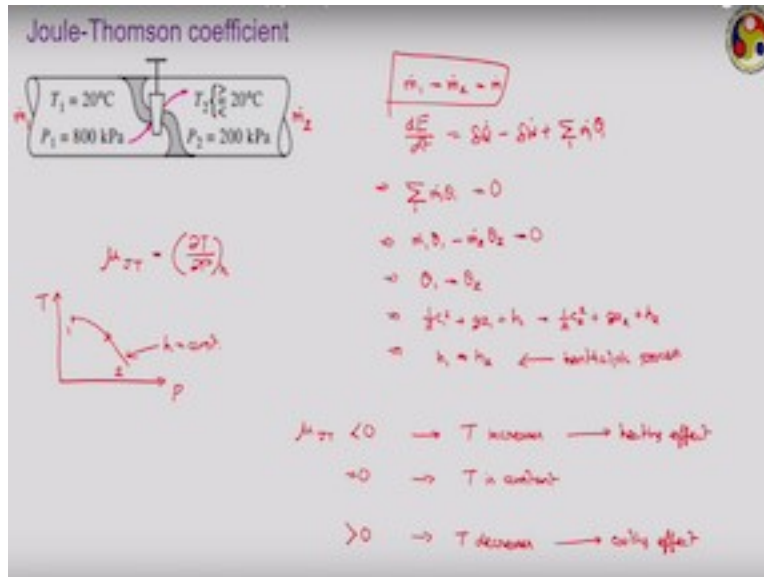
So, it is a very simple proof that is

$$\beta = \alpha \left(\frac{\partial P}{\partial T} \right)_v$$

and these are numerous relations can be proved just using the definitions, this using some fundamental equations of partial differentials and of course the Maxwell's relations. These are the couple of good exercise to have which I have shown here. Like the second one is quite straightforward but on the first one we have seen how we can or we may go in alternate direction, just trying to substitute something without understanding exactly where you are trying to go.

I hope I am able to convey the we can approach such kind of problems. Always try to make use of the substitutions judiciously because there are several ways you can substitute the same variable. But there maybe situations where only one may give you the correct result.

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Let us now move to the discussion of couple of other concepts which are unrelated but again very important and gives rise to very important thermodynamic applications. And the first one of them is the Joule-Thomson coefficient. The Joule-Thomson coefficient characterizes a throttling process. Now what do you mean by throttling? When a fluid a liquid or gaseous is allowed to pass through a very small restriction like a flow across the valve or flow through a very small dimension tube like a capillary tube, then that kind of process is generally known as throttling. During the throttling process there is no heat and work interaction involved, there is hardly any changes in kinetic and potential energies. However, there is significant change in the pressure the outlet pressure commonly is much lower than the inlet pressure.

Like the situation shown here, if fluid is passing through a valve it is coming at 800 kPa pressure and 20°C and outlet pressure on the downstream of the valve is just 200 kPa, so there is a significant reduction in the pressure. However, its temperature maybe $> 20^\circ\text{C}$, maybe $< 20^\circ\text{C}$ or may remain equal to 20°C , that will depend upon the nature of the process and which can be characterized by this Joule-Thomson coefficient. Before defining the Joule-Thomson coefficient, let us try to understand the thermodynamic nature of this particular process, and for that we have

to apply the first law of thermodynamics on this particular process. So, let us assume it is a steady flow process where mass is coming with \dot{m}_1 , outlet mass is \dot{m}_2 . Now under steady state applying principle of mass conservation we know that:

$$\dot{m}_1 = \dot{m}_2 = \dot{m}$$

Now we apply the first law of thermodynamics on this, so the general expression the change in their total energy content for the system or the time rate of change of total energy content of a system will be equal to:

$$\frac{\partial E}{\partial t} = \delta \dot{Q} - \delta \dot{W} + \sum_i \dot{m}_i \theta_i$$

where

$\delta \dot{Q}$ is the amount of heat added to the system

$\delta \dot{W}$ is the amount of work done by the system

$\dot{m}\theta$ is the amount of energy coming into the system in form of a mass transfer coming in or going out.

Now in this particular case there is no heat transfer, there is no work transfer, and also we are talking about the steady flow system, i.e., energy content of the system is not changing with time. Therefore we have:

$$\sum_i \dot{m}_i \theta_i = 0$$

Now there is only one inlet and one outlet for the system. So we have:

$$\dot{m}_1 \theta_1 - \dot{m}_2 \theta_2 = 0$$

Here \dot{m}_1 is positive because it is coming to the system and \dot{m}_2 is going out of the system, so that is negative. \dot{m}_1 and \dot{m}_2 are equal to each other as per the mass conservation principle. So, we have:

$$\theta_1 = \theta_2$$

Now if we expand this θ_1 and θ_2 in terms of their components, then what will it be?

$$\theta_1 = h_1 + \frac{1}{2} c_1^2 + g z_1$$

Similarly,

$$\theta_2 = h_2 + \frac{1}{2} c_2^2 + g z_2$$

That means:

$$h_1 + \frac{1}{2}c_1^2 + gz_1 = h_2 + \frac{1}{2}c_2^2 + gz_2$$

Now changes in kinetic and potential energies can virtually be neglected in this particular case.

Therefore, what we are getting ultimately is:

$$h_1 \approx h_2$$

i.e., we are talking about the process during which the enthalpy remains constant or we conventionally call that as isenthalpic process. So, the throttling process is an isenthalpic process during which the enthalpy of the fluid remains constant throughout the system or during the process.

Now we are therefore talking about an isenthalpic process there is a reduction in pressure but temperature may increase or may decrease and that is being expressed by this Joule-Thomson coefficient. Joule-Thomson coefficient is expressed by the symbol μ . Sometimes a subscript JT is added to signify that this is Joule-Thomson coefficient because some properties like viscosity etc also given in terms of μ . So, this subscript JT is often put into indicate that it is Joule-Thomson coefficient only, and the definition of Joule-Thomson coefficient is:

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

i.e., the change in temperature with pressure for a constant enthalpy process.

In a way you can say that it represents the slope of isenthalpic on that TP plane, i.e., if we plot the process on a temperature pressure graph T here and P here then and if this is the line during which enthalpy remains constant i.e., along this line where starting point 1, and this is ending point 2 during which enthalpy remains constant and the arrow indicates from start to end. Then the slope of this particular line is the Joule-Thomson coefficient.

Now during the throttling process pressure is always decreasing that is your ∂P is negative. That means if we are talking about Joule-Thomson coefficient to be lesser than 0. What does that mean? We know that during the process pressure is decreasing, then for process this coefficient

to be negative temperature has to increase, so a negative value of Joule-Thomson coefficient during the throttling process indicates an increase in temperature.

$$\mu_{JT} < 0 \rightarrow T \text{ increases}$$

If this is equal to 0, that means temperature remains constant or there is no change in temperature during the process.

$$\mu_{JT} = 0 \rightarrow T \text{ is constant}$$

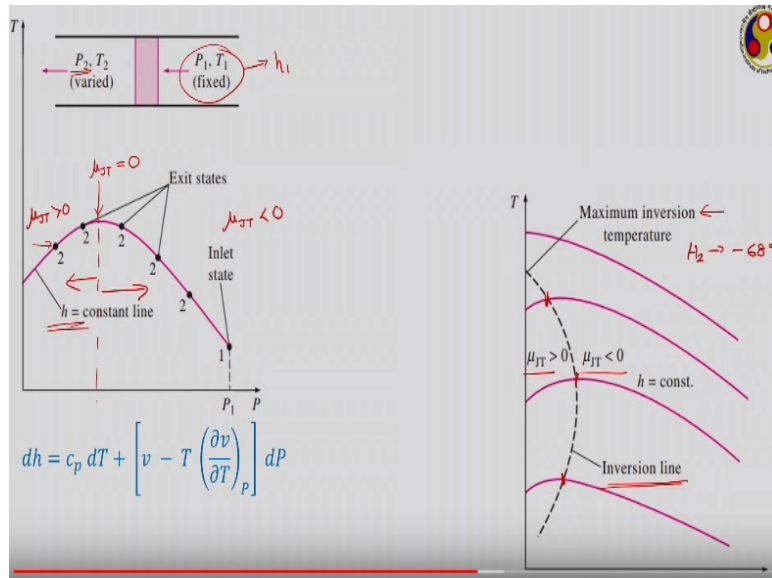
Whereas when the Joule-Thomson coefficient was positive, what does that indicate? ∂P is negative then the coefficient can be positive only when ∂T is also negative, i.e., temperature also decreases similar to pressure and this magnitude of Joule-Thomson coefficient therefore gives us an idea exactly what kind of thermal effect that we are going to get.

If your Joule-Thomson coefficient is negative, temperature at the outlet will be higher than temperature in the inlet and therefore you are going to get a heating effect. Whereas when the Joule-Thomson coefficient is positive, temperature at the outlet will be lower than the temperature at inlet and therefore we are going to get that cooling effect or an application towards the refrigeration industry.

So, when Joule-Thomson coefficient is negative its application is a heating effect or when we want some room heating kind of application, we can go for this. However, if we are looking at our target application is the refrigeration industry that you want the cooling effect then we have to ensure that the magnitude of Joule-Thomson coefficient is positive that is then only we are going to get the cooling effect.

So, the choice for choosing a refrigerate we have to ensure that under the given circumstances the value of the Joule-Thomson coefficient is a positive one. Now, this discussion is for a particular enthalpy similarly for every enthalpy or every given value of a inlet enthalpy, the nature of Joule-Thomson coefficient will show certain kinds of trend and that is what is shown here during this simple experiment.

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Here we are doing a particular experiment, where we have taken a capillary tube just like this where the inlet state is fixed, that is a fluid supplied at a pressure P_1 and T_1 and outlet pressure is controlled, this P_2 is outlet pressure which is controlled. As the fluid is flowing through this restriction it is losing some pressure for a given value of P_2 , a certain amount of pressure drop is suffering and outlet temperature will keep on varying with the choice of your outlet pressure. And therefore, this temperature T_2 can be higher than T_1 or can be lesser than T_1 .

Just look at the TP diagram that has been plotted here. This is the state from which you are starting and we are moving in this direction that is pressure is reducing during the process. If our final state is somewhere here, then the temperature is higher, i.e., what is the value of your Joule Thomson-coefficient in this particular state? Here the value of your Joule-Thomson coefficient is negative, because pressure is decreasing but temperature is increasing. If pressure is decreased further, if we reach our state points somewhere like this there is further increase in temperature Joule-Thomson coefficient remains negative.

If we continue this way, we reach this particular state where again temperature is higher but the slope of the curve has started to flatten out. So, Joule-Thomson coefficient is still negative, but maybe its magnitude is approaching 0. And there is somewhere here the curve becomes a flat one that is it reaches the maximum possible temperature we have some kind of inversion.

At this particular point of inversion, there is no change in temperature with change in pressure that is a value of the Joule-Thomson coefficient is 0, at this point of inversion. If the pressure is reduced further, so that we reach this particular point, then you can see now there is a reduction in temperature or temperature started to reduce, because now Joule-Thomson coefficient has become positive.

If we reach a sign further here there is a further reduction in temperature and therefore, we can see on this particular side the Joule-Thomson coefficient is positive there is a reduction in pressure temperature is also started to reduce. This is the constant enthalpy line, and if we divide this particular line into two zones, then you can see on this side Joule-Thomson coefficient is negative.

So, if our operation is restricted to this right-hand side you are going to get a heating effect. Whereas if we are operating on this side then you are going to get a cooling effect our operation can be extended to the refrigeration industries because the Joule-Thomson coefficient is positive. And this point of inversion or the point of maximum temperature is very important because for the given value of this inlet enthalpy, from the property of the fluid we can identify the maximum possible temperature, and accordingly can identify the location of this inversion on this constant enthalpy curve. Here now if we repeat the experiments for several such inlet states, this inlet state actually specifies your inlet enthalpy which remains constant during the process. If we modify the inlet state, the value of the enthalpy also changes and we are going to go to a different line.

This way we have got several lines by continuously increasing the enthalpy. And for all of them during the experiment we can see that the same nature is repeated. So, for the first line we are getting our inversion here for the second line we are getting inversion here for a third value of inlet in that we are getting inversion somewhere here if we join all these inversion points then the line that we get that is called the inversion line.

So, inversion line is basically the locus of all this inversion points corresponding to individual inlet enthalpy curves. And the point where this inversion line touches the vertical axes i.e., the P

= 0 situation, this line has the restriction or has the equation of $P = 0$. So, this temperature is known as the maximum inversion temperature. It is a characteristic of any fluid. When we are operating below the maximum inversion temperature, we can see that we can have both situations:

$$\mu_{JT} > 0$$

or

$$\mu_{JT} < 0$$

Also

$$\mu_{JT} < 0$$

is on the right-hand side of your inversion line and

$$\mu_{JT} > 0$$

is on the left-hand side of the inversion line. However, if your operation is on the higher side of this maximum inversion temperature, then what we can get? Then the value of μ_{JT} is always negative, you can never reach the zone where μ_{JT} greater than zero.

That means, if your operation is happening at a temperature level above the maximum inversion temperature then throttling is going to give you only the heating effect but no cooling effect. Whereas if your operation is restricted below the maximum inversion temperature you can get both higher heating and cooling effect by choosing the outlet temperature and thereby modulating the value of this μ_{JT} .

As I mentioned this maximum inversion number is the property of the substance. For example, for substances like hydrogen maximum inversion temperature is $-68\text{ }^{\circ}\text{C}$. That means if we want to apply hydrogen for some kind of cooling process or refrigeration process then first we have to reduce the temperature lower than this $-68\text{ }^{\circ}\text{C}$ and then only you can use hydrogen as a refrigerant.

But if we are operating at the normal ambient condition, then there as this temperature is higher than the maximum inversion temperature, so the Joule-Thomson coefficient for hydrogen will always be negative for any pressure level and hence it can only give you the heating effect but no

cooling effect. Whereas if you are operating at cryogenic levels at -150°C or something hydrogen can also be used as a refrigerant.

Most of the common synthetic refrigerants that we use in refrigerator industries or in air conditioning industries they generally have maximum inversion temperatures substantially higher than the ambient condition. And therefore, we generally do not need to bother about this. Finally let us try to get to some kind of mathematical criteria for the Joule-Thomson coefficient. We know that we are talking about an isentropic process.

Now these are the relations that we have developed earlier for changes in enthalpy and is as follows:

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

then during the throttling process enthalpy remains constant hence:

$$dh = 0$$

So, let us rearrange this taking dP on one side and dT on another side. That means we can write:

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


i.e.,

$$\left(\frac{\partial T}{\partial P} \right)_h = \mu_{JT} = \frac{1}{C_p} \left[T \left(\frac{\partial v}{\partial T} \right)_p - v \right]$$

So, this way we can easily calculate the value of Joule-Thomson coefficient again from the knowledge of the PvT characteristic and the value of C_p for a given situation. As a final point the magnitude of Joule Thompson coefficient, I repeat is very important in the HVAC industry particularly that is what kind of application we are going for the heating application or cooling application your outcome or the choice of refrigerant will depend upon the level of Joule Thomson coefficient corresponding to that operating conditions.

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Exercise 5



$$\begin{aligned}
 Pv &= RT & \mu_{JT} &= -\frac{1}{C_p} \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] & P_0 &\sim RT \Rightarrow v \sim \frac{RT}{P} \\
 & & & & & \Rightarrow \left(\frac{\partial v}{\partial T} \right)_p = \frac{R}{P} \\
 & & & & & \sim -\frac{1}{C_p} \left[v - \frac{RT}{P} \right] \sim -\frac{1}{C_p} [v - v] = 0
 \end{aligned}$$

$$\begin{aligned}
 \left(P + \frac{a}{v^2} \right) (v - b) &= RT & \Rightarrow v - b &\sim \frac{RT}{P + \left(\frac{a}{v^2} \right)} \Rightarrow v \sim b + \frac{RT}{P + \left(\frac{a}{v^2} \right)} \\
 \left(\frac{\partial v}{\partial T} \right)_p &= \frac{R \left[P + \frac{a}{v^2} \right] - RT \left[-2av^{-3} \right] \left(\frac{\partial v}{\partial T} \right)_p}{\left[P + \frac{a}{v^2} \right]^2} & \Rightarrow \left(P + \frac{a}{v^2} \right)^2 \left(\frac{\partial v}{\partial T} \right)_p &= R \left[P + \frac{a}{v^2} \right] + \left[\frac{2aRT}{v^3} \right] \left(\frac{\partial v}{\partial T} \right)_p \\
 & & \Rightarrow \left(\frac{\partial v}{\partial T} \right)_p &= \frac{\left(P + \frac{a}{v^2} \right) R}{\left(P + \frac{a}{v^2} \right)^2 - \frac{2aRT}{v^3}} \\
 \mu_{JT} &= \frac{1}{C_p} \left[\frac{\left(P + \frac{a}{v^2} \right) RT}{\left(P + \frac{a}{v^2} \right)^2 - \frac{2aRT}{v^3}} - v \right]
 \end{aligned}$$

Let us do again a couple of small exercises to calculate the Joule-Thomson coefficient now. And for this we are going to choose an ideal gas:

$$Pv = RT$$

Now this is the expression for Joule-Thomson coefficient:

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

So, to get this let us get this $\partial v / \partial T$ for this Joule Thompson coefficient first for this ideal gas. So, we have:

$$Pv = RT$$

i.e.,

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

i.e.,

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

So, if you put this R/T in the expression μ_{JT} :

$$\mu_{JT} = -\frac{1}{C_p} \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] = -\frac{1}{C_p} \left[v - \frac{RT}{P} \right] = -\frac{1}{C_p} [v - v] = 0$$

i.e., Joule-Thomson coefficient for an ideal gas is 0 and that is logical only because we have proved in the previous class, that for an ideal gas enthalpy is the sole function of temperature, pressure does not have any role. So, enthalpy of an ideal gas can change only when there is

change in temperature or vice versa. If the enthalpy is constant that means temperature is also constant. And during the throttling process, as we are mentioning it to be isenthalpic that is enthalpy remains constant, temperature also has to be constant and hence we are getting a 0 value of the Joule-Thomson coefficient.

Another case, here we have the more complicated Van der Waal's equation of state:

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

We have to calculate the expression for the Joule-Thomson coefficient for this. So same procedure let us write this as:

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

i.e.,

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

So, if we differentiate this with respect to temperature maintaining pressure constant, i.e.,

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R \left[P + \left(\frac{a}{v^2}\right)\right] - RT[-2av^{-3}] \left(\frac{\partial v}{\partial T}\right)_P}{\left[P + \left(\frac{a}{v^2}\right)\right]^2}$$

Or if we simplify this then we have:

$$\left[P + \left(\frac{a}{v^2}\right)\right]^2 \left(\frac{\partial v}{\partial T}\right)_P = R \left[P + \left(\frac{a}{v^2}\right)\right] + \left[\frac{2aRT}{v^3}\right] \left(\frac{\partial v}{\partial T}\right)_P$$

Or

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{\left[P + \left(\frac{a}{v^2}\right)\right] R}{\left[P + \left(\frac{a}{v^2}\right)\right] - \left[\frac{2aRT}{v^3}\right]}$$

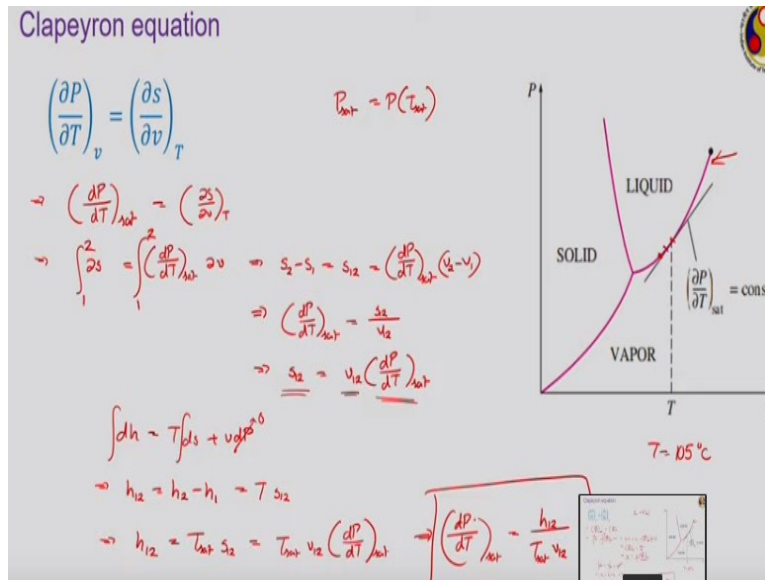
and therefore the expression for the Joule-Thomson coefficient becomes:

$$\mu_{JT} = \frac{1}{C_p} \left(\frac{\left[P + \left(\frac{a}{v^2}\right)\right] RT}{\left[P + \left(\frac{a}{v^2}\right)\right] - \left[\frac{2aRT}{v^3}\right]} - v \right)$$

This is a quite complicated expression. Now you can simplify this in whatever way you want. And once we have the given information available that is you are talking about the particular

state point, you know the expression for the pressure, temperature etc. putting this you can get with the value of the Joule-Thomson coefficient. So that is the concept of the Joule-Thomson coefficient. Let us quickly move on to discuss the final concept in this particular module which is of the Clapeyron equation.

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Clapeyron equation is the application of the Maxwell's relation during a phase change process. It can be any kind of exchange process, a liquid to vapor, a solid to liquid or a solid to vapor or vice versa. But the Clapeyron relation provides us a generalized platform of calculating that changes in entropy and changes in enthalpy during a phase change process. Now this is one of the Maxwell's relation that we have developed in the very first lecture of this module:

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

When you are talking about the phase change process, then we know that the saturation pressure is a function of temperature alone. That is, during the phase change process thus pressure is a sole function of temperature and therefore we can instead of using the partial differential notation we can write this: just $(dP/dT)_{sat}$ which actually represent the slope of the saturation called on a pressure temperature players and that is:

$$\left(\frac{dP}{dT}\right)_{sat} = \left(\frac{\partial s}{\partial v}\right)_T$$

Or if we separate them out i.e.,

$$\partial s = \left(\frac{dP}{dT} \right)_{sat} \partial v$$

Integrating this say from state point 1 to 2:

$$\int_1^2 \partial s = \int_1^2 \left(\frac{dP}{dT} \right)_{sat} \partial v$$

where state point 1 indicates that starting point of his change or starting state of the phase change where we have only the first phase available and point 2 refers to exactly the finishing point of the phase change where we have the second phase available. Like if you are talking about the liquid vapour phase change process then point 1 refers to 100% liquid which is just about to vaporize about to start the phase change and point 2 refers to a 100% vapour state where the phase change has just completed. So, we can then write this as:

$$s_2 - s_1 = s_{12} = \left(\frac{dP}{dT} \right)_{sat} (v_2 - v_1)$$

or the changes in the slope of the curve can be retained as:

$$\left(\frac{dP}{dT} \right)_{sat} = \frac{s_{12}}{v_{12}}$$

This is a typical saturation curve on PT diagram. This is actually a curve which corresponds to all the three processes. I shall be coming to this curve, reviewing this curve in as a part of the next module in the very first lecture of the next module. But here, this third curve represents your saturation curve and $(dP/dT)_{sat}$ or $(\partial P/\partial T)_{sat}$, which is actually a constant at a given temperature it represents the slope of this particular curve this is what we are referring.

Now if we are talking about or if our objective is to calculate the changes in entropy you can easily do this. How we can do this? Let me just rearrange the above expression. So it is:

$$s_{12} = v_{12} \left(\frac{dP}{dT} \right)_{sat}$$

Say, for example, we do the experiment for quite a few different temperature levels. Say, at a temperature of a 100 °C, we measure the corresponding pressure, that gives us 1 point somewhere on this curve.

Then at a temperature of 105 °C, we again allow the water to change its phase then measure corresponding pressure. Then we do the experiment at 110 °C and again measure the

corresponding pressure. Then this way we can get a few points of the curve and then combining these points we can calculate the slope of this curve. And now suppose our objective is to calculate do this calculation at $T=105^{\circ}\text{C}$.

Then at 105°C starting from phase 1 i.e., 100% liquid it is about to vaporise going to phase 2 which is 100% vapour just finish the vaporisation. We can easily calculate the change in volume thereby knowing the second term. So once we know both of them then we can easily calculate the change in entropy during this particular phase change process. And if we want to calculate the change in enthalpy, we have to make use of that TdS relation.

What will be a TdS relation? We know that:

$$dh = TdS + vdP$$

Now, when the phase change process is going on i.e., from liquid to vapour or any similar phase change process both pressure and temperature remains constant, i.e., dP goes to 0 and temperature remains constant. So, if we integrate this one, over the phase change process now then:

$$\int dh = T \int dS + v dP$$

This will be your h_{12} , i.e.,

$$h_{12} = h_2 - h_1 = Ts_{12}$$

i.e.,

$$h_{12} = T_{sat} s_{12}$$

or invoking the earlier relation

$$= T_{sat} v_{12} \left(\frac{dP}{dT} \right)_{sat}$$

or if our interest is to know the saturation curve or expression for the saturation curve then you can also write:

$$\left(\frac{dP}{dT} \right)_{sat} = \frac{h_{12}}{T_{sat} v_{12}}$$

This particular relation or its alternative version is known as the Clapeyron equation which allows us to calculate the change in enthalpy and consequently the change in entropy during a

phase change process using the knowledge of the slope of the curve, the measurement of the saturation then pressure and also the measurement of the change in specific volume during this process. It is a very important relation more application of it can be applied to any kind of phase change process we just need to know the slope of the curve properly, which of course its complicated. But more on the nature of this curve we shall be learning as a part of the next module.

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Clapeyron-Clausius equation \rightarrow Lig-vapor phase change

At low pressure, $v_2 \gg v_1 \Rightarrow v_2 = v_2 - v_1 \approx v_2 = \frac{RT_{sat}}{P_{sat}} \approx \frac{RT}{P}$

$$\left(\frac{dP}{dT}\right)_{sat} \approx \frac{h_{12}}{T_{sat} v_2} \approx \frac{P_{sat} h_{12}}{RT_{sat}^2}$$

$$\Rightarrow \int_1^2 \frac{dP_{sat}}{P_{sat}} = \int_1^2 \frac{h_{12}}{R} \frac{dT_{sat}}{T_{sat}^2}$$

$$\Rightarrow \ln\left(\frac{P_{sat,2}}{P_{sat,1}}\right) \approx \left(-\frac{h_{12}}{R} \left(\frac{1}{T_{sat,2}} - \frac{1}{T_{sat,1}}\right)\right)$$

An alternate version or an approximate version of the Clapeyron relation is sometimes used to know that saturation pressure which is called the Clapeyron-Clausius equation. If we are talking about a saturation of very low pressure, as the pressure keeps on decreasing then the pressure of the vapour phase particularly if you are talking about the liquid-vapor phase change process. This Clapeyron-Clausius equation is particularly applicable to liquid-vapor phase change.

Now when we are talking about very low pressure then this

$$v_2 \gg v_1$$

such that

$$v_{12} = v_2 - v_1 \approx v_2$$

and we can sometimes assume that this v_1 at low pressure again as an ideal gas. As the pressure keeps on approaching the absolute 0 pressure the behaviour of vapour also approaches that of an ideal gas and therefore, we can approximate this by the ideal gas equation which is:

$$= \frac{RT_{sat}}{P_{sat}}$$

or if we just drop the subscript just:

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

So, if we now invoke the Clapeyron equation where we had:

$$\left(\frac{dP}{dT}\right)_{sat} = \frac{h_{12}}{T_{sat} v_{12}}$$

Then using this approximation at low pressure this now becomes v_{12} , we are replacing so we have:

$$= \frac{P_{sat} h_{12}}{RT_{sat}^2}$$

or if we rearrange the terms now, we have:

$$\frac{dP_{sat}}{P_{sat}} = \frac{h_{12}}{R} \frac{dT_{sat}}{T_{sat}^2}$$

If we integrate this entire thing say for two different saturation point which is 1 and 2, we have:

$$\int_1^2 \frac{dP_{sat}}{P_{sat}} = \int_1^2 \frac{h_{12}}{R} \frac{dT_{sat}}{T_{sat}^2}$$

where 1 refers to one particular saturation state 2 refers to a different saturations state which correspond to a different saturation pressure and temperature, but they are reasonably close to each other so that we can make use of this low-pressure assumption. If this 1 and 2 are again reasonably close to each other than this h_{12} can be approximately taken to be a constant. Then this becomes:

$$\ln\left(\frac{P_{sat_2}}{P_{sat_1}}\right) \approx \left(\frac{h_{12}}{R}\right) \left[\frac{1}{T_{sat_1}} - \frac{1}{T_{sat_2}}\right]$$

This particular equation is known as Clapeyron-Clausius equation which allows us to calculate the changes in saturation pressure from the knowledge of the changes in saturation temperature. We just need to know that our corresponding enthalpy or change in enthalpy during the phase change and also the value of this R . We shall be finishing of by doing a small numerical example which will allow us to understand the use of the Clapeyron-Clausius equation.

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Exercise 6



Estimate the saturation pressure of R-134a at -45°C , using the data available corresponding to -40°C .

$$\begin{aligned}
 R &= 81.49 \text{ J/kg.K} \\
 h_{12} @ -40^{\circ}\text{C} &= 225.86 \text{ kJ/kg} = 225.86 \times 10^3 \text{ J/kg} \\
 P_{\text{sat}} @ -40^{\circ}\text{C} &= 51.25 \text{ kPa} \\
 T_{\text{sat}_1} &\approx -40^{\circ}\text{C} = -40 + 273.15 = 223.15 \text{ K} \\
 T_{\text{sat}_2} &\approx -45^{\circ}\text{C} = -45 + 273.15 = 228.15 \text{ K} \\
 P_{\text{sat}_1} &\approx 51.25 \text{ kPa} = 51.25 \times 10^3 \text{ Pa} \\
 \ln\left(\frac{P_{\text{sat}_2}}{P_{\text{sat}_1}}\right) &= \frac{h_{12}}{R} \left(\frac{1}{T_{\text{sat}_1}} - \frac{1}{T_{\text{sat}_2}} \right)
 \end{aligned}$$

So here is my problem, we have to assume in that saturation pressure of R-134a which is a refrigerant, at -45°C using that data available corresponding to -40°C and these are the data provided:

$$R = 81.49 \text{ J/kgK}$$

$$h_{12} @ -40^{\circ}\text{C} = 225.86 \text{ kJ/kg}$$

$$P_{\text{sat}} @ -40^{\circ}\text{C} = 51.25 \text{ kPa}$$

Therefore,

$$T_{\text{sat}_1} = -40^{\circ}\text{C} = -40 + 273.15 = 223.15 \text{ K}$$

And the second point for which we are looking to the calculation is:

$$T_{\text{sat}_2} = -45^{\circ}\text{C} = -45 + 273.15 = 228.15 \text{ K}$$

The known saturation pressure i.e.,

$$P_{\text{sat}_1} = 51.25 \text{ kPa} = 51.25 \times 10^3 \text{ Pa}$$

I will always suggest convert everything to basic SI unit so that there is less chance of making any mistake within the units.

Here R is given as:

$$R = 81.49 \text{ J/kgK}$$

so that is given in basic SI unit.

However, there is a kilo factor in h_{12} so this can be written as:

$$h_{12} @ -40^{\circ}\text{C} = 225.86 \text{ kJ/kg} = 225.86 \times 10^3 \text{ J/kg}$$

So now we have to make use of the Clausius Clapeyron equation and therefore as the one we have just developed:

$$\ln\left(\frac{P_{sat_2}}{P_{sat_1}}\right) = \left(\frac{h_{12}}{R}\right) \left[\frac{1}{T_{sat_1}} - \frac{1}{T_{sat_2}}\right]$$

$$= \left(\frac{225.86 \times 10^3}{81.49}\right) \left[\frac{1}{223.15} - \frac{1}{228.15}\right]$$

And you have to put the expression for P_{sat_1} :

$$P_{sat_2} = P_{sat} |_{-45^{\circ}C} = 39.48 \text{ kPa}$$

which is the desired result that we are looking for. So, this way using the Clapeyron equation and various approximate version in the form of Clapeyron-Clausius relation we can calculate the saturation properties of any fluid easily. And while the Clapeyron equation is applicable for any kind of phase change process, Clausius-Clapeyron relation is generally restricted to liquid-vapor phase change only.

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Highlights of Module 2

- Mathematical perspective of property
- Thermodynamic potentials
- Maxwell relations
- Generalized relations for du , dh & ds
- Generalized relations for specific heat
- Mayer relation

So that takes us to the end of our second module, where we have focused on developing generalized relations for changes in most important thermodynamic properties. So, we started with the mathematical perspective of property, we understood how to understand whether a

parameter z is property or not once you that is a function of x and y and both x and y are properties. Then we discussed about the four possible thermodynamic potentials: the specific internal energy specific enthalpy, specific Gibbs free energy and specific Helmholtz free energy. Then we derived the four Maxwell's relations, from the definition of these four thermodynamic potentials. We have also understood the Maxwell's square and which is an adhoc way of remembering this Maxwell's relations and corresponding TdS relations. Then we have developed generalized relations for three most important thermodynamic properties: du , dh and ds .

And then we went on to the generalized relations for changes in specific heat or both the specific heats: C_p and C_v , and their relation in form of Mayer relation. Then we have seen several kinds of application of each of these relations in different problems, like we can define new properties in the form of volume expansivity and isothermal compressibility, we can develop different relations between properties and different other kinds of suitable forms can be developed. And today we have discussed the concept of Joule-Thomson coefficient which is very important regarding the choice of a fluid for heating or refrigeration applications. And finally, we discussed about Clapeyron equation which has its application in the phase change processes in order to understand the changes in specific enthalpy and specific entropy during a phase change process and also sometimes to calculate the saturation pressure for a given saturation temperature using the values at some other point. So, all these are actually the application of the Maxwell's relations which allows us to perform thermodynamic analysis in a much easy and better way. So that takes us to the end of module number 2. I hope you have understood their discussion that you had because I have tried to develop all the relations here.

If you have any confusion first try to develop the relations on your own, listen to the lecture once more, may refer to your textbooks and if still, there is doubt please write to me I shall be very happy to help. So, the assignment will be online along with this video. You please try to solve the assignments and maybe some additional problems you referring to the standard textbooks so that you grasp the concept properly.

So next to we shall be again back discussing about the properties of pure substances. Till then, take care.