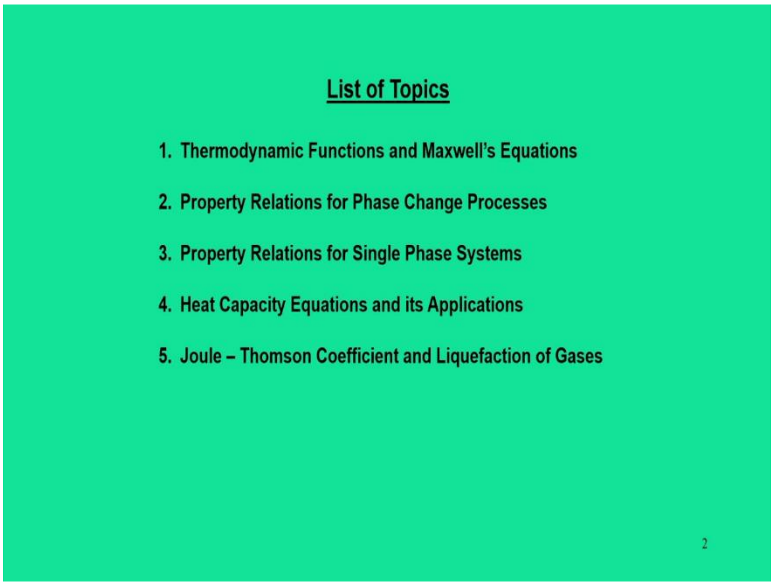
Advanced Thermodynamics and Combustion
Prof. Niranjan Sahoo
Department of Mechanical Engineering
Indian Institute of Technology, Guwahati

Module - 03
Thermodynamic Property Relations
Lecture - 12
Property Relations for single-phase Systems

Dear learners, greetings from IIT, Guwahati. We are in the course Advanced Thermodynamics and Combustions, module 3: Thermodynamic Property Relations.

(Refer Slide Time: 00:39)

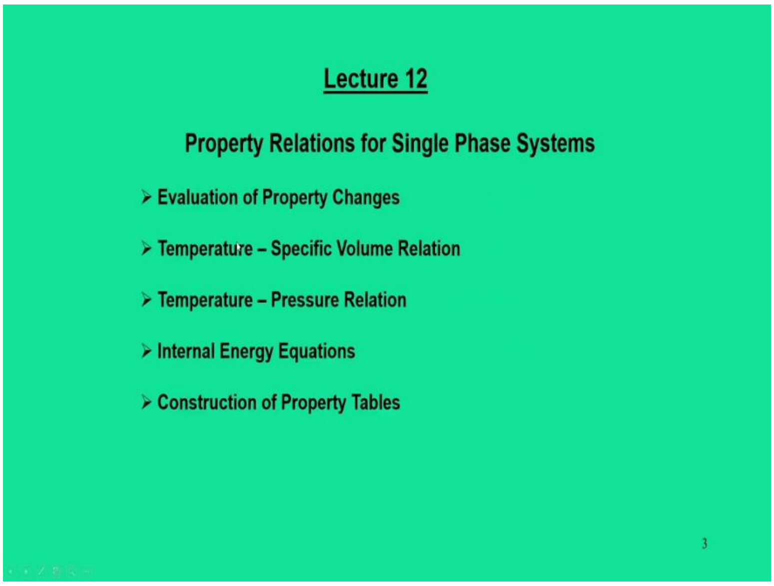


List of Topics

1. Thermodynamic Functions and Maxwell's Equations
2. Property Relations for Phase Change Processes
3. Property Relations for Single Phase Systems
4. Heat Capacity Equations and its Applications
5. Joule – Thomson Coefficient and Liquefaction of Gases

So, till this point of time, we have covered 2 lectures on this module. First one was thermodynamic functions and Maxwell equations. Second one was property relations that were derived for a phase change process. In today's class we will discuss about the Property Relations that are used for Single-Phase Systems.

(Refer Slide Time: 01:04)



Lecture 12

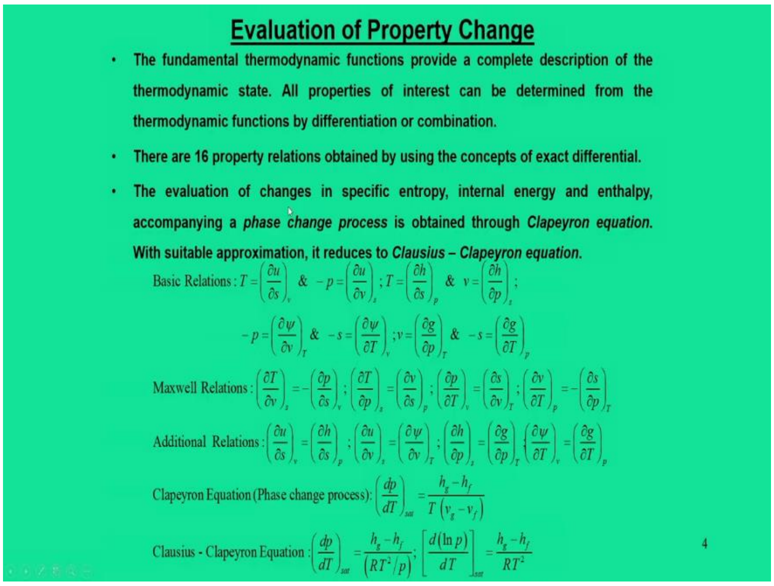
Property Relations for Single Phase Systems

- Evaluation of Property Changes
- Temperature – Specific Volume Relation
- Temperature – Pressure Relation
- Internal Energy Equations
- Construction of Property Tables

Now, on this lecture we are going to discuss the following segments, will give the brief introductions what we have covered till now that is evaluation of property changes, mathematical relations. Then, after that we will move to derivations related to property relations for single-phase systems. So, there are two approaches. One is temperature - specific volume relations, other is temperature pressure relations.

Then, in addition to this we will also explore the concepts of internal energy equations in the mathematical form. And, towards the end we will try to see that whatever you have discussed so far as the mathematical expressions how those concepts can be used for construction of property tables. By construction of property tables I mean it is for pure substance and we can see that the entire concepts mathematical relations derived in this model will be useful for construction of property tables.

(Refer Slide Time: 02:14)



Evaluation of Property Change

- The fundamental thermodynamic functions provide a complete description of the thermodynamic state. All properties of interest can be determined from the thermodynamic functions by differentiation or combination.
- There are 16 property relations obtained by using the concepts of exact differential.
- The evaluation of changes in specific entropy, internal energy and enthalpy, accompanying a *phase change process* is obtained through *Clapeyron equation.* With suitable approximation, it reduces to *Clausius – Clapeyron equation.*

Basic Relations: $T=\left(\frac{\partial u}{\partial s}\right)_v$ & $-p=\left(\frac{\partial u}{\partial v}\right)_s$; $T=\left(\frac{\partial h}{\partial s}\right)_p$ & $v=\left(\frac{\partial h}{\partial p}\right)_s$;

$$-p=\left(\frac{\partial \psi}{\partial v}\right)_T \;\&\; -s=\left(\frac{\partial \psi}{\partial T}\right)_v ;v=\left(\frac{\partial g}{\partial p}\right)_T \;\&\; -s=\left(\frac{\partial g}{\partial T}\right)_p$$

Maxwell Relations: $\left(\frac{\partial T}{\partial v}\right)_s=-\left(\frac{\partial p}{\partial s}\right)_v$; $\left(\frac{\partial T}{\partial p}\right)_s=\left(\frac{\partial v}{\partial s}\right)_p$; $\left(\frac{\partial p}{\partial T}\right)_v=\left(\frac{\partial s}{\partial v}\right)_T$; $\left(\frac{\partial v}{\partial T}\right)_p=-\left(\frac{\partial s}{\partial p}\right)_T$

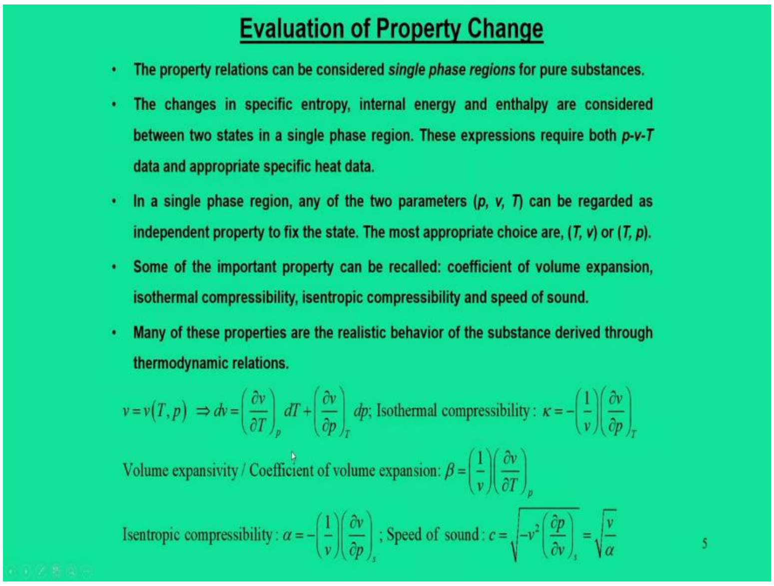
Additional Relations: $\left(\frac{\partial u}{\partial s}\right)_v=\left(\frac{\partial h}{\partial s}\right)_p$; $\left(\frac{\partial u}{\partial v}\right)_s=\left(\frac{\partial \psi}{\partial v}\right)_T$; $\left(\frac{\partial h}{\partial p}\right)_s=\left(\frac{\partial g}{\partial p}\right)_T$; $\left(\frac{\partial \psi}{\partial T}\right)_v=\left(\frac{\partial g}{\partial T}\right)_p$

Clapeyron Equation (Phase change process): $\left(\frac{dp}{dT}\right)_{sat}=\frac{h_g-h_f}{T\left(v_g-v_f\right)}$

Clausius - Clapeyron Equation: $\left(\frac{dp}{dT}\right)_{sat}=\frac{h_g-h_f}{\left(RT^2/p\right)}$; $\left[\frac{d(\ln p)}{dT}\right]_{sat}=\frac{h_g-h_f}{RT^2}$

Now, let us recall that we have covered the mathematical representations, in total there are 16 property relations that were derived from the concept of exact differentials. Then, that 16 property relations includes some of the basic relations, Maxwell equations and additional relations among the properties. Now, with respect to phase change process, we derived Clapeyron equations and also Clausius-Clapeyron equations.

(Refer Slide Time: 02:47)



Evaluation of Property Change

- The property relations can be considered *single phase regions* for pure substances.
- The changes in specific entropy, internal energy and enthalpy are considered between two states in a single phase region. These expressions require both *p-v-T* data and appropriate specific heat data.
- In a single phase region, any of the two parameters (*p, v, T*) can be regarded as independent property to fix the state. The most appropriate choice are, (*T, v*) or (*T, p*).
- Some of the important property can be recalled: coefficient of volume expansion, isothermal compressibility, isentropic compressibility and speed of sound.
- Many of these properties are the realistic behavior of the substance derived through thermodynamic relations.

$v=v(T,p) \Rightarrow dv=\left(\frac{\partial v}{\partial T}\right)_p dT+\left(\frac{\partial v}{\partial p}\right)_T dp$; Isothermal compressibility: $\kappa=-\left(\frac{1}{v}\right)\left(\frac{\partial v}{\partial p}\right)_T$

Volume expansivity / Coefficient of volume expansion: $\beta=\left(\frac{1}{v}\right)\left(\frac{\partial v}{\partial T}\right)_p$

Isentropic compressibility: $\alpha=-\left(\frac{1}{v}\right)\left(\frac{\partial v}{\partial p}\right)_s$; Speed of sound: $c=\sqrt{-v^2\left(\frac{\partial p}{\partial v}\right)_s}=\sqrt{\frac{v}{\alpha}}$

Now, we are going to discuss the concepts of those 16 property relations and how we can use those relations for considering or deriving the expressions for single-phase regions for pure substance. So, by single-phase region I mean for a pure substance essentially there are three phases: solid, liquid and gas. Now, considering a single-phase region either we are in solid region or liquid region or gas phase region.

Now, thermodynamically in a single-phase region there are two parameters that are required to fix the state. Now, out of these two, parameters has to be considered from the measured data. Measured data I mean it is pressure, specific volume or density and temperatures. And, in this case. the most appropriate choice would be temperature, because it caters the heat transfer. Other is either you can take volume or pressure.

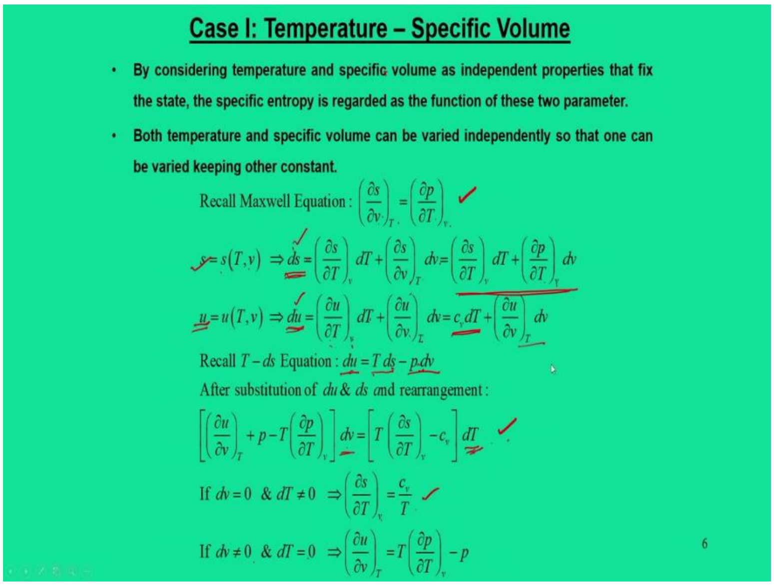
So, this concept also you have been studied, the temperature volume diagram and temperature pressure diagram or pressure volume diagrams that were used for pure substances. Now, we will see how these equations will help us in finding the coordinates in those diagrams. Now, we are going to recall some additional properties which are very important as per as our ongoing discussions. And, those properties are coefficient of volume expansion, isothermal compressibility and isentropic compressibility and speed of sound.

So, if you take one particular situations, volume is a function of pressure and temperatures. We can write $dv = \left(\frac{\partial v}{\partial T}\right)_p dT + \left(\frac{\partial v}{\partial p}\right)_T dp$. So, now, here we say the isothermal compressibility $\kappa = -\left(\frac{1}{v}\right)\left(\frac{\partial v}{\partial p}\right)_T$.

So, here negative sign means since it is a compressed phenomena. Other parameter of interest, that we can have a volume expansivity and or coefficient of volume expansion that is $\beta = \left(\frac{1}{v}\right)\left(\frac{\partial v}{\partial T}\right)_p$. In fact, here the volume change is associated with the change in the temperature, but at constant pressures.

Apart from this there is another parameter which you call as isentropic compressibility $\alpha = -\left(\frac{1}{v}\right)\left(\frac{\partial v}{\partial p}\right)_s$. Then, from that also we have another property called as speed of sound $c = \sqrt{-v^2\left(\frac{\partial p}{\partial v}\right)_s} = \sqrt{\frac{v}{\alpha}}$. So, anyway what I am trying to emphasize is that the exact differentials also help us in defining many thermodynamic properties of interest.

(Refer Slide Time: 06:33)



Case I: Temperature – Specific Volume

- By considering temperature and specific volume as independent properties that fix the state, the specific entropy is regarded as the function of these two parameter.
- Both temperature and specific volume can be varied independently so that one can be varied keeping other constant.

Recall Maxwell Equation : $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$

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

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

Recall $T-ds$ Equation : $du = T\,ds - p\,dv$

After substitution of du & ds and rearrangement :

$$\left[\left(\frac{\partial u}{\partial v}\right)_T + p - T\left(\frac{\partial p}{\partial T}\right)_v\right] dv = \left[T\left(\frac{\partial s}{\partial T}\right)_v - c_v\right] dT$$

If $dv = 0$ & $dT \neq 0 \Rightarrow \left(\frac{\partial s}{\partial T}\right)_v = \frac{c_v}{T}$

If $dv \neq 0$ & $dT = 0 \Rightarrow \left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p$

Now, let us focus our attention for considering the property relations for single-phase region. First one we say case I, where we consider the temperature and volume as independent properties to fix the state. So, if you say so, then other parameters like entropy can be regarded as the function of these two parameters. Another point I need to emphasize, that when I say temperature and specific volume are independent properties, in a situations both the parameters can vary simultaneously or because these two are independent in nature; so, you can keep temperature constant, vary specific volume and vice versa. Keep specific volume constant, vary temperatures. So, this is the basic concept that we are going to follow in deriving this relation. So, first thing that we say is that we have to recall our basic governing equations from that is Maxwell equations, that is in terms of one of the relations Maxwell equation is $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$.

Now, as I mentioned that we say temperature and specific volume are independent properties. So, we write s is equal to as a function of temperature and volume. So, from this we can find its exact differential $s = s(T,v) \Rightarrow ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$. Then, we can use this Maxwell relations and we can write $\left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial p}{\partial T}\right)_v dv$.

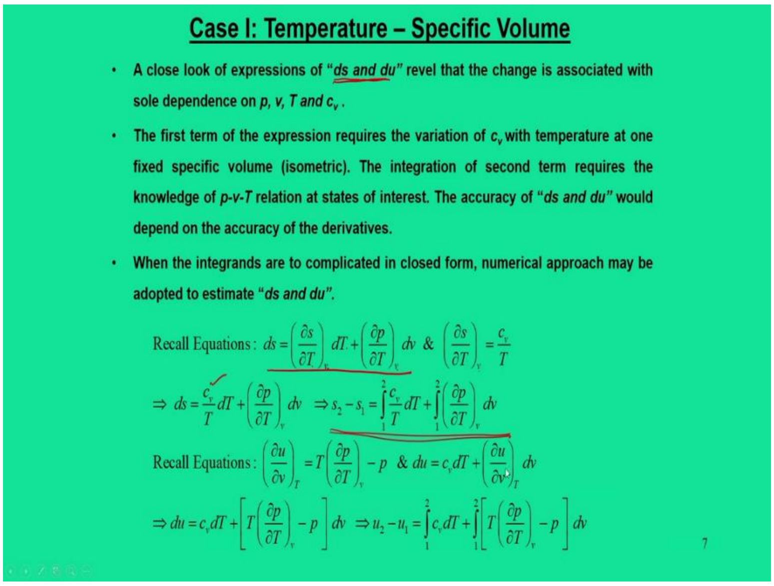
Now, another way of representing is that we can say internal energies and other parameters, u is a function of temperature and volume. So, we can write the exact differential $u = u(T,v) \Rightarrow du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$.

So, you know that internal energy is a function of temperature at constant volume, we say $du = c_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$. So, we have 2 equations ds and du. Now, one of the Tds equation is $du = Tds - pdv$. Now, what we do now is that we have expressions for ds, we have expressions for du. Now, ds and du is placed in this T ds equations.

And, when I do some kind of arrangements and simplify it, then we have this expression $\left[\left(\frac{\partial u}{\partial v}\right)_T + p - T\left(\frac{\partial p}{\partial T}\right)_v\right] dv = \left[T\left(\frac{\partial s}{\partial T}\right)_v - c_v\right] dT$. In one side of the expressions, variation is dv and the other side is variation of dT. So, which means that these two are the independent properties. Now, let us see what is the significance of these equations. First thing is that we can say that when both the parameters are varying, then we can use this equations as it is.

But, in a situation that when dv is equal to 0; that means, in some situation the changes are happening at constant volume that is change in the specific volume is 0, but temperature is not non-zero. So, in that case the left hand side of the equation becomes 0. So, we get a simplified relations $\left(\frac{\partial s}{\partial T}\right)_v = \frac{c_v}{T}$. And, in the second situations when $dv \neq 0 \& dT = 0 \Rightarrow \left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p$. So, this is the two important lesson you get.

(Refer Slide Time: 10:39)



Case I: Temperature – Specific Volume

- A close look of expressions of "*ds and du*" revel that the change is associated with sole dependence on *p, v, T and* c_v .
- The first term of the expression requires the variation of c_v with temperature at one fixed specific volume (isometric). The integration of second term requires the knowledge of *p-v-T* relation at states of interest. The accuracy of "*ds and du*" would depend on the accuracy of the derivatives.
- When the integrands are to complicated in closed form, numerical approach may be adopted to estimate "*ds and du*".

$$\text{Recall Equations: } ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial p}{\partial T}\right)_v dv \;\&\; \left(\frac{\partial s}{\partial T}\right)_v = \frac{c_v}{T}$$

$$\Rightarrow ds = \frac{c_v}{T} dT + \left(\frac{\partial p}{\partial T}\right)_v dv \;\Rightarrow s_2 - s_1 = \int_1^2 \frac{c_v}{T} dT + \int_1^2 \left(\frac{\partial p}{\partial T}\right)_v dv$$

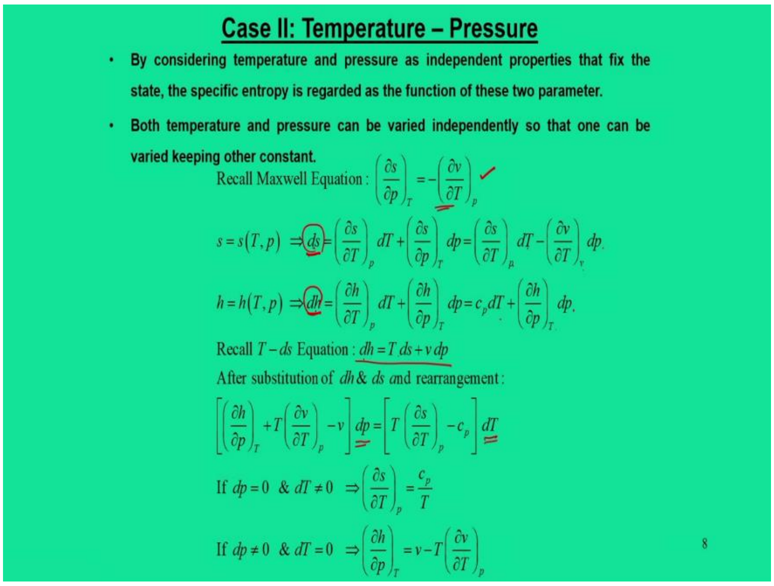
$$\text{Recall Equations: } \left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p \;\&\; du = c_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

$$\Rightarrow du = c_v dT + \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] dv \;\Rightarrow u_2 - u_1 = \int_1^2 c_v dT + \int_1^2 \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] dv$$

Now, again we look into closely about these equations again. There are other expressions that are also can be possible. To find out what is ds and du. And that is the essential need of our requirement, change in the entropy and change in the internal energy. So, in our previous slides, we have derived these two expressions. $ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial p}{\partial T}\right)_v dv$ & $\left(\frac{\partial s}{\partial T}\right)_v = \frac{c_v}{T} \Rightarrow ds = \frac{c_v}{T} dT + \left(\frac{\partial p}{\partial T}\right)_v dv \Rightarrow s_2 - s_1 = \int_1^2 \frac{c_v}{T} dT + \int_1^2 \left(\frac{\partial p}{\partial T}\right)_v dv.$

And, also from this previous slides, we have other expressions like $\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p \& du = c_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv \Rightarrow du = c_v dT + \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] dv \Rightarrow u_2 - u_1 = \int_1^2 c_v dT + \int_1^2 \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] dv.$ So, very basic bottom line is that we from temperature, specific volume we have this relation.

(Refer Slide Time: 12:48)



Case II: Temperature – Pressure

- By considering temperature and pressure as independent properties that fix the state, the specific entropy is regarded as the function of these two parameter.
- Both temperature and pressure can be varied independently so that one can be varied keeping other constant.

Recall Maxwell Equation : $\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$ ✓

$$s = s(T,p) \Rightarrow ds = \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T dp = \left(\frac{\partial s}{\partial T}\right)_p dT - \left(\frac{\partial v}{\partial T}\right)_v dp.$$

$$h = h(T,p) \Rightarrow dh = \left(\frac{\partial h}{\partial T}\right)_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp = c_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp.$$

Recall $T-ds$ Equation : $dh = T\,ds + v\,dp$

After substitution of dh & ds and rearrangement :

$$\left[\left(\frac{\partial h}{\partial p}\right)_T + T\left(\frac{\partial v}{\partial T}\right)_p - v\right] dp = \left[T\left(\frac{\partial s}{\partial T}\right)_p - c_p\right] dT$$

If $dp = 0$ & $dT \neq 0 \Rightarrow \left(\frac{\partial s}{\partial T}\right)_p = \frac{c_p}{T}$

If $dp \neq 0$ & $dT = 0 \Rightarrow \left(\frac{\partial h}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p$

Now, in the second case situations, we consider temperature and instead of volume we consider pressure as the independent properties. And, if you do that how our mathematics becomes simplified and that gives the other fundamental expressions. So, here also similar logic also applies where both temperature and pressure can be varied either independently or both can vary simultaneously or we can vary them independently keeping other constants.

So, here we have to recall another equations from the Maxwell lessons that involves p. So, $\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$. Then, we have to start with two parameters again with entropy $s =$

$s(T, p)$. Another parameter of interest should be enthalpy. There it was internal energy, here it was enthalpy $h = h(T, p)$.

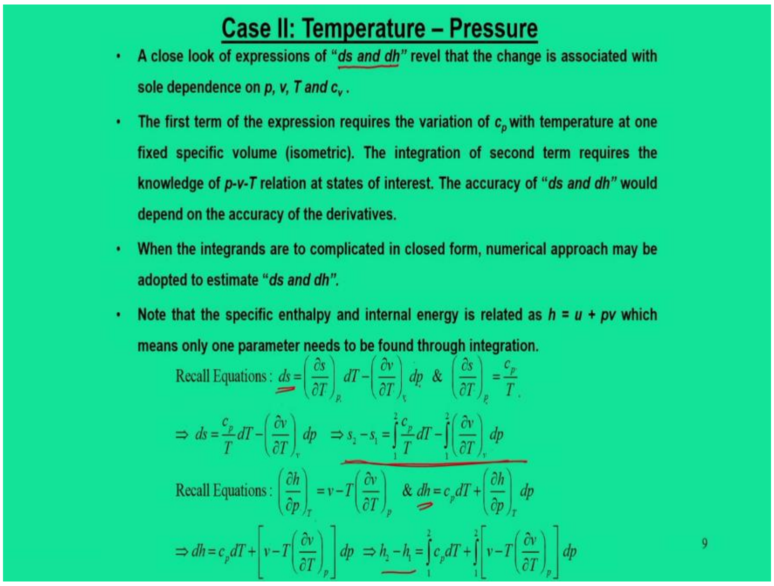
Now, from these equations we can find the exact differential ds and also exact differential of dh. So, by expanding this equations and using this Maxwell equations, we find two expressions. One is $ds = \left(\frac{\partial s}{\partial T}\right)_p dT - \left(\frac{\partial v}{\partial T}\right)_p dp$. Other expression is $dh = c_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp$.

Then, we have to recall the Tds equations involving dh and ds. So, $dh = Tds + vdp$. Now, substituting ds and dh in this T ds equations, we arrive at the following expressions which involves left hand side is change in the pressure, right hand side is the change in the temperatures. So, mathematically this equation is correct, but practically or thermodynamically how we are going to find its significance.

$$\left[\left(\frac{\partial h}{\partial p}\right)_T + T\left(\frac{\partial v}{\partial T}\right)_p - v\right] dp = \left[T\left(\frac{\partial s}{\partial T}\right)_p - c_p\right] dT$$

Now, in one situation we say the change $dp = 0 \& dT \neq 0 \Rightarrow \left(\frac{\partial s}{\partial T}\right)_p = \frac{c_p}{T}$. Now, if $dp \neq 0 \& dT = 0 \Rightarrow \left(\frac{\partial h}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p$.

(Refer Slide Time: 15:44)



Case II: Temperature – Pressure

- A close look of expressions of "*ds and dh*" revel that the change is associated with sole dependence on *p, v, T and* c_v .
- The first term of the expression requires the variation of c_p with temperature at one fixed specific volume (isometric). The integration of second term requires the knowledge of *p-v-T* relation at states of interest. The accuracy of "*ds and dh*" would depend on the accuracy of the derivatives.
- When the integrands are to complicated in closed form, numerical approach may be adopted to estimate "*ds and dh*".
- Note that the specific enthalpy and internal energy is related as $h = u + pv$ which means only one parameter needs to be found through integration.

Recall Equations : $ds = \left(\frac{\partial s}{\partial T}\right)_p dT - \left(\frac{\partial v}{\partial T}\right)_v dp \;\&\; \left(\frac{\partial s}{\partial T}\right)_p = \frac{c_p}{T}$.

$$\Rightarrow ds = \frac{c_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_v dp \;\Rightarrow\; s_2 - s_1 = \int_1^2 \frac{c_p}{T} dT - \int_1^2 \left(\frac{\partial v}{\partial T}\right)_v dp$$

Recall Equations : $\left(\frac{\partial h}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p \;\&\; dh = c_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp$

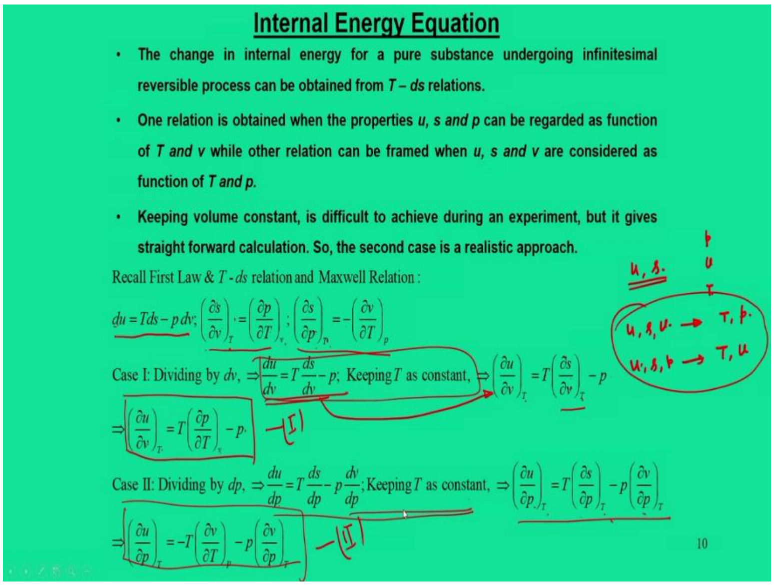
$$\Rightarrow dh = c_p dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp \;\Rightarrow\; h_2 - h_1 = \int_1^2 c_p dT + \int_1^2 \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp$$

So, from these equations we are now try to find its consequence. What are these important relations that we are going to derive for which our intention was? So, our intention was to find change in the entropy and change in the enthalpy, ds and dh. So, for that we recall again those equations and try to derive the mathematical relationships.

So, from the previous slides we recall this equations, one equation is $ds = \left(\frac{\partial s}{\partial T}\right)_p dT - \left(\frac{\partial v}{\partial T}\right)_v dp$. Second equation is $\left(\frac{\partial s}{\partial T}\right)_p = \frac{c_p}{T}$. Now, putting these equations here we find the expression of change in the entropy, that is between two thermodynamic states $s_2 - s_1 = \int_1^2 \frac{c_p}{T} dT - \int_1^2 \left(\frac{\partial v}{\partial T}\right)_v dp$.

And, similar way we recall another equations involving enthalpy and pressure at constant temperatures and of course, we also have the exact differential dh. And, from these equations we are able to find the change in the enthalpy between two states that $h_2 - h_1 = \int_1^2 c_p dT + \int_1^2 \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp$. So, this is all about the property evaluation for single-phase systems.

(Refer Slide Time: 17:22)



Internal Energy Equation

- The change in internal energy for a pure substance undergoing infinitesimal reversible process can be obtained from $T - ds$ relations.
- One relation is obtained when the properties *u, s and p* can be regarded as function of *T and v* while other relation can be framed when *u, s and v* are considered as function of *T and p*.
- Keeping volume constant, is difficult to achieve during an experiment, but it gives straight forward calculation. So, the second case is a realistic approach.

Recall First Law & T - ds relation and Maxwell Relation :

$du = Tds - p\,dv;\ \left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v;\ \left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$

Case I: Dividing by dv, $\Rightarrow \frac{du}{dv} = T\frac{ds}{dv} - p$; Keeping T as constant, $\Rightarrow \left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - p$

$\Rightarrow \left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p$ —(I)

Case II: Dividing by dp, $\Rightarrow \frac{du}{dp} = T\frac{ds}{dp} - p\frac{dv}{dp}$; Keeping T as constant, $\Rightarrow \left(\frac{\partial u}{\partial p}\right)_T = T\left(\frac{\partial s}{\partial p}\right)_T - p\left(\frac{\partial v}{\partial p}\right)_T$

$\Rightarrow \left(\frac{\partial u}{\partial p}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_p - p\left(\frac{\partial v}{\partial p}\right)_T$ —(II)

Now, we will go deep further to find out the internal energy equations that are frequently used. And, again why we require this internal energy equations? Because, we know that when the properties u, s and p that is internal energy, entropy and pressure; they regarded as the function of temperature and volume. Then, one relation we can frame because here the pressure is considered as an independent parameter. Other way of looking at is internal energy, entropy and specific volume; instead of pressure we are using specific volume is considered.

Basically, we have u, s; these are the important properties that need to be evaluated and parameters like pressure, volume and temperatures. So, in one case we say u, s, v they are regarded as functions of temperature and pressure. In other situations, when u, s and p are considered as properties, function of temperature and specific volume then we have another relations.

So, framing the internal energy equations, we have to use this particular philosophy. Now, let us see how you are going to use it. So, for that we have to recall the again the T ds equations, First Law and Maxwell's relations. So, we know this from the First Law and T ds equations, we have $du = Tds - pdv$. And, we have this Maxwell relations, two Maxwell relation we are considering. $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v ; \left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$

Now, in one case we are dividing this equations, this change in the internal energy with respect to dv means with respect to change in the specific volume.

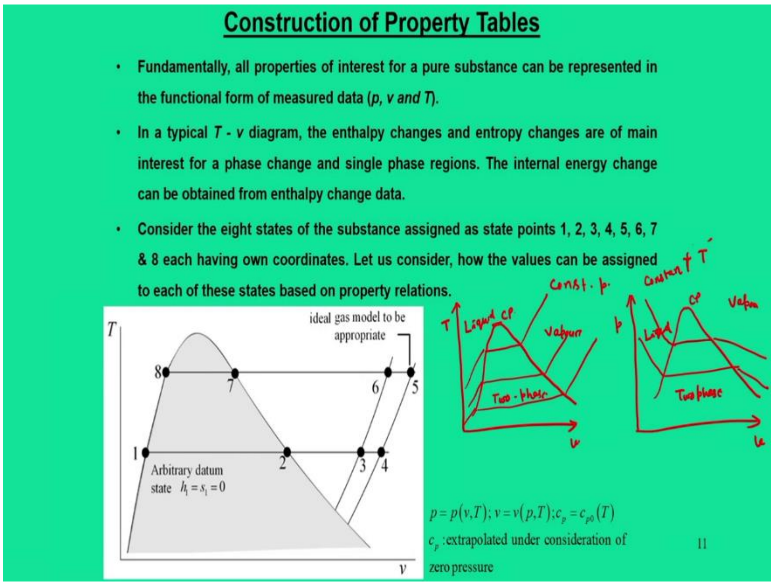
So, we write $\frac{du}{dv} = T\frac{ds}{dv} - p;$ Keeping T as constant. Now, when T is equal to constant, this ordinary differential equations reduces to partial differential equations like this. So, instead of writing the entire expressions, we are simply writing $\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - p.$

So, this is the first internal energy equations we can get. Now, again we can recall our Maxwell relations $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$. Now, when you put this first Maxwell equations here, then we get the first internal energy equations $\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p$. And in other scenario we say, that if we divide this T ds equations by dp, we will get $\frac{du}{dp} = T\frac{ds}{dp} - p\frac{dv}{dp}\ keeping\ T\ constant.$

Now, instead of writing this entire expressions and ordinary differential equations, it is represented in the partial differential form that is $\left(\frac{\partial u}{\partial p}\right)_T = T\left(\frac{\partial s}{\partial p}\right)_T - p\left(\frac{\partial v}{\partial p}\right)_T$. Now, again here also you can recall the Maxwell's relations $\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$.

Now, when you put this equations in this case II, we get the second internal energy equations $\left(\frac{\partial u}{\partial p}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_p - p\left(\frac{\partial v}{\partial p}\right)_T$. Now, we will see that what are those significance.

(Refer Slide Time: 22:17)



Construction of Property Tables

- Fundamentally, all properties of interest for a pure substance can be represented in the functional form of measured data (*p, v and T*).
- In a typical *T - v* diagram, the enthalpy changes and entropy changes are of main interest for a phase change and single phase regions. The internal energy change can be obtained from enthalpy change data.
- Consider the eight states of the substance assigned as state points 1, 2, 3, 4, 5, 6, 7 & 8 each having own coordinates. Let us consider, how the values can be assigned to each of these states based on property relations.

$p = p(v,T);\ v = v(p,T); c_p = c_{p0}(T)$

c_p :extrapolated under consideration of zero pressure

Till this point of time, we have covered many mathematical relations, equations, two phase regions, single-phase regions. Now, let us take the stock of it. Let us consolidate what are their practical significance. Now, here I will try to bring your attentions to basic UG level when you deal with the properties of pure substance, we deal with the property diagrams. Normally, they are called p v diagram, T v, temperature specific volume diagram, pressure volume diagram and temperature pressure diagram or phase diagrams.

So, if you recall those diagrams, normally we have the dome like if I say temperature volume diagram, we have a dome and we consider this point as critical point. This dome separates liquid and vapour regions. So, we say this is liquid and this is vapour region and this is two phase region within the dome. Now, on this diagram we draw constant pressure lines. So, these are actually constant pressure lines drawn in T v diagram.

Now, here the question arises how did you get this data for a given situations? And in fact, the property relations that we have derived in this module are useful to get all these things. So, this is one such case, other such case we can draw as a pressure volume diagram. In the same dome we can also draw constant temperature lines. So, it is a pressure volume diagram, we can draw constant temperature lines. So, these are constant T.

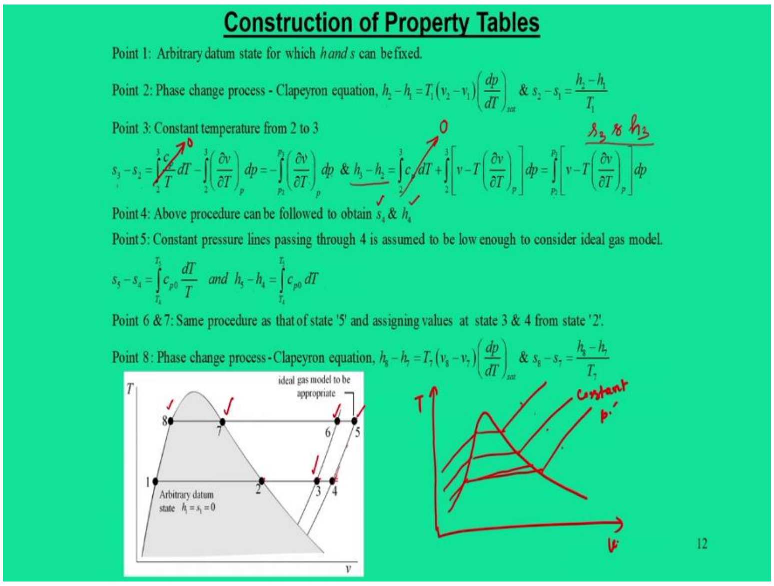
We have CP here, this is liquid, this is vapour and this is two phase. Till this point of time, we are self-sufficient that we have covered the expressions, how you are going to apply the thermodynamic relations for single-phase region and two phase regions. So, these concepts can be useful in drawing these diagrams. Now, I am going to demonstrates that whatever relations we derived so far, how they are useful for considering the construction of the property diagrams.

In a sense that what is the physical significance of generating the data using this equations. So, we consider for a typical case, let us say it is water. So, in a temperature volume diagrams we have just kept some arbitrary points like 1, 2, 3, 4, 5, 6, 7, 8. In fact, these are the points which are placed or thermodynamic coordinates on a temperature volume diagrams and that are drawn for different pressures.

Now, on these diagrams if I want to find out what is the entropy or at any state point if I want to find out the what is the change in the entropy, what is the change in the enthalpy, what is the change in the internal energy, how I am going to achieve it? So, this is the main objectives of our discussions. So, for that we consider eight states as shown in these diagrams point 1 to 8. And, we will see that how the values can be assigned at each of the states based on the property relations.

So, very basic things that we have we when you start with point 1. So, this is we can say saturated liquid point. So, we give some arbitrary reference value, either it can be given as a 0. Because, when you see the changes the arbitrary has basically no role if you are referring to changes happening between two states point, arbitrary datum has no role. But, hypothetically we can say at least that we assign value either it will be 0 or some realistic number.

(Refer Slide Time: 27:14)



Construction of Property Tables

Point 1: Arbitrary datum state for which *h and s* can be fixed.

Point 2: Phase change process - Clapeyron equation, $h_2 - h_1 = T_1(v_2 - v_1)\left(\frac{dp}{dT}\right)_{sat}$ & $s_2 - s_1 = \frac{h_2 - h_1}{T_1}$

Point 3: Constant temperature from 2 to 3

s_3 & h_3

$$s_3 - s_2 = \cancelto{0}{\int_2^3 \frac{c_p}{T} dT} - \int_2^3 \left(\frac{\partial v}{\partial T}\right)_p dp = -\int_{p_2}^{p_3} \left(\frac{\partial v}{\partial T}\right)_p dp \ \& \ \underline{h_3 - h_2} = \cancelto{0}{\int_2^3 c_p dT} + \int_2^3 \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp = \int_{p_2}^{p_3} \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp$$

Point 4: Above procedure can be followed to obtain s_4 & h_4

Point 5: Constant pressure lines passing through 4 is assumed to be low enough to consider ideal gas model.

$$s_5 - s_4 = \int_{T_4}^{T_5} c_{p0} \frac{dT}{T} \quad and \quad h_5 - h_4 = \int_{T_4}^{T_5} c_{p0}\, dT$$

Point 6 & 7: Same procedure as that of state '5' and assigning values at state 3 & 4 from state '2'.

Point 8: Phase change process - Clapeyron equation, $h_8 - h_7 = T_7(v_8 - v_7)\left(\frac{dp}{dT}\right)_{sat}$ & $s_8 - s_7 = \frac{h_8 - h_7}{T_7}$

Now, let us see that how the properties are going to be evaluated. So, you start with point 1. So, it is a arbitrary datum states in which enthalpy and entropy are either are fixed or they can be assigned value is 0. Now, when you go to point 2; obviously, it is a straight line horizontally in which there is a phase change that takes place. So when the state goes from 1 to 2, it is a change of phase from liquid to vapour.

Since, it is a change of phase and of course, there is a change in the specific volume because the state becomes saturated liquid to saturated vapour. So, we can recall Clapeyron equations for a phase change process. And, this Clapeyron's equation will give you the enthalpy change. Again, from this Clapeyron equation also we can also get the entropy change. So, basically when you see this data in the steam table, in the background Clapeyron equation was used to find the data points.

So, this is when you reach point 2. Then, from 2 to 3 we want to move. So, from 2 to 3 again it is a constant temperature line, but it is in a single-phase regions. So, you have to recall this equations that involves entropy change $s_3 - s_2$, which we derived in this class itself as $s_3 - s_2 = \int_2^3 \frac{c_p}{T} dT - \int_2^3 \left(\frac{\partial v}{\partial T}\right)_v dp$.

And, here since 2 to 3 process is a constant temperature process this goes to 0. So, we will end up having $s_3 - s_2 = -\int_{p_2}^{p_3} \left(\frac{\partial v}{\partial T}\right)_v dp$. And, for enthalpy expressions, similarly here, since there is no change in the temperatures this expression goes to 0. So, enthalpy change is from $h_3 - h_2 = \int_{p_2}^{p_3} \left[v - T\left(\frac{\partial v}{\partial T}\right)_p \right] dp$.

So, basically we know point 2. Then, from this equations we can find out s_3 and h_3. Now, when we know s_3 and h_3; so, we locate this point, then we start moving to point 4. So, point 3 to 4 is same as the process from 2 to 3. But, only difference is that here the point 2 was in the saturated vapour region, but here it is in the separated vapour region.

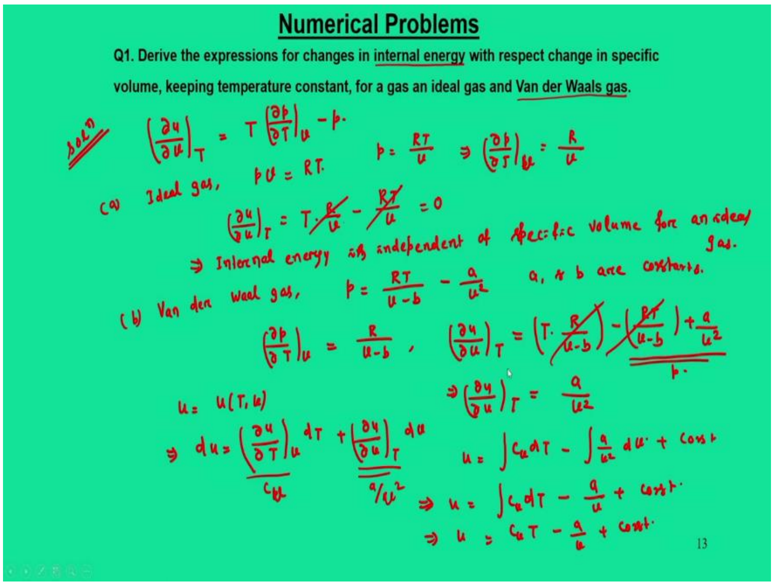
So, same procedure can be followed. So, we can locate the point 4 with the coordinates s_4 and h_4. Now, from 4 to 5, you can say it is a constant pressure line. So, when you say constant pressure line. So, we can find out the T ds equations. So, $s_5 - s_4 = \int_{T_4}^{T_5} C_p \left(\frac{dT}{T}\right)$. So, point 5 is located, similarly for enthalpy also you can find $\int_{T_4}^{T_5} C_p dT$. So, Cp value that is from datum side is known to us. So, we can find you can locate the point 5. So, all the properties at point 5 can be located.

Now, for 6 and 7, we can follow the similar procedure that is when you go from 3 to 4 similar process will be followed in a reverse manner from 5 to 6. Now, when you go to 6 to 7, the similar procedure in a reverse manner needs to be followed for what we did for 2 to 3. So, with same procedures we can locate point 6 and point 7. Now, when you reach the point 7, then we have to go to point 8. So, it is again a phase change process. We have to recall the Clapeyron equations to locate the point 8.

So, basically speaking that when you draw different values in a temperature volume diagram, we have seen that these are the constant pressure lines. And, for all these cases of p lines, all these coordinates they can be found out judiciously by using these equations. Maybe one kind of code can be written that involves the property value change which can locate the properties for which we can represent the temperature volume diagrams with the data points calculated through this mathematical relations.

So, this is all about the significance of thermodynamic property relations for constructing property tables like pressure volume diagram, temperature volume diagram, pressure temperature diagrams.

(Refer Slide Time: 32:30)



Numerical Problems

Q1. Derive the expressions for changes in internal energy with respect change in specific volume, keeping temperature constant, for a gas an ideal gas and Van der Waals gas.

Soln

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

(a) Ideal gas, $pv = RT.$ $p = \frac{RT}{v} \Rightarrow \left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v}$

$$\left(\frac{\partial u}{\partial v}\right)_T = T\cdot\cancel{\frac{R}{v}} - \cancel{\frac{RT}{v}} = 0$$

⇒ Internal energy is independent of specific volume for an ideal gas.

(b) Van der Waal gas, $p = \frac{RT}{v-b} - \frac{a}{v^2}$ a, & b are constants.

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-b}, \quad \left(\frac{\partial u}{\partial v}\right)_T = \cancel{\left(T\cdot\frac{R}{v-b}\right)} - \underbrace{\cancel{\left(\frac{RT}{v-b}\right)} + \frac{a}{v^2}}_{p.}$$

$$\Rightarrow \left(\frac{\partial u}{\partial v}\right)_T = \frac{a}{v^2}$$

$u = u(T, v)$

$$\Rightarrow du = \underbrace{\left(\frac{\partial u}{\partial T}\right)_v}_{c_v} dT + \underbrace{\left(\frac{\partial u}{\partial v}\right)_T}_{a/v^2} dv$$

$$u = \int c_v dT - \int \frac{a}{v^2} dv + \text{const}$$

$$\Rightarrow u = \int c_v dT - \frac{a}{v} + \text{const.}$$

$$\Rightarrow u = c_v T - \frac{a}{v} + \text{const.}$$

Now, let us see that whatever we have discussed so far how we are going to apply. So, we will study some of the simple numerical problems which is mainly dealt for a single-phase situations. First problem is about deriving an expressions for changes in the internal energy with respect to specific volume at constant temperatures. There are two cases. One is for ideal gas, other is for Van der Waal gas.

So, before you proceed further first of all let us see that which thermodynamic equation we are going to use. So, we require the internal energy equations. So, you have to recall

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

So, first case we say if it is an ideal gas. So, if in an ideal gas, we can recall the equation of state $pv = RT$, from this we can find $p = \frac{RT}{v}$. So, this will give you $\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v}$. Then, when you put this equation here. So, we can write $\left(\frac{\partial u}{\partial v}\right)_T = \frac{RT}{v} - \frac{RT}{v} = 0$.

So, this means internal energy is independent of specific volume for an ideal gas. Now, second case we will see that what is a Van der Waal gas. So, for a Van der Waal gas, we all know this equation of state which is $p = \frac{RT}{v-b} - \frac{a}{v^2}$, where a and b are constants. Now, again we have to use the same concept here. We need to find out what is $\left(\frac{\partial p}{\partial T}\right)_v$,so, $\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-b}$.

Then, we can find out $\left(\frac{\partial u}{\partial v}\right)_T = \frac{RT}{v-b} - \frac{RT}{v-b} + \frac{a}{v^2} = \frac{a}{v^2}$, but still that does not give our answer. We want the internal energy.

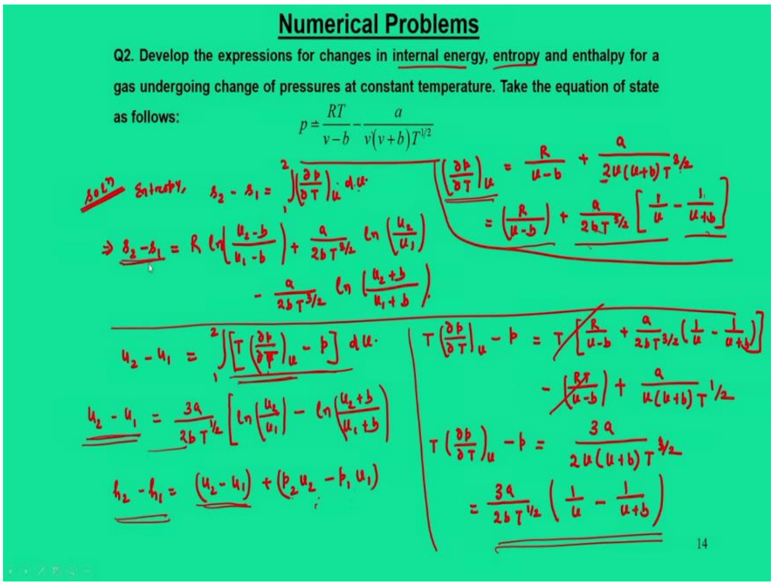
Since property changes are taking simultaneously,

$$u = u(T, v) \Rightarrow du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv = c_v dT + \frac{a}{v^2} dv$$

$$u = \int c_v dT + \int \frac{a}{v^2} dv + Const = \int c_v dT - \frac{a}{v} + Const = c_v T - \frac{a}{v} + Const$$

So, this is how we are going to find out the expressions for internal change with respect to specific volume for an ideal gas and for a Van der Waal gas.

(Refer Slide Time: 38:50)



Numerical Problems

Q2. Develop the expressions for changes in internal energy, entropy and enthalpy for a gas undergoing change of pressures at constant temperature. Take the equation of state as follows:

$$p = \frac{RT}{v-b} - \frac{a}{v(v+b)T^{1/2}}$$

Sol^n Entropy, $s_2 - s_1 = \int_1^2 \left(\frac{\partial p}{\partial T}\right)_v dv$.

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-b} + \frac{a}{2v(v+b)T^{3/2}}$$

$$= \left(\frac{R}{v-b}\right) + \frac{a}{2bT^{3/2}}\left[\frac{1}{v} - \frac{1}{v+b}\right]$$

$$\Rightarrow s_2 - s_1 = R\ln\left(\frac{v_2-b}{v_1-b}\right) + \frac{a}{2bT^{3/2}}\ln\left(\frac{v_2}{v_1}\right) - \frac{a}{2bT^{3/2}}\ln\left(\frac{v_2+b}{v_1+b}\right).$$

$$u_2 - u_1 = \int_1^2 \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] dv.$$

$$T\left(\frac{\partial p}{\partial T}\right)_v - p = \cancel{T}\left[\frac{R}{v-b} + \frac{a}{2bT^{3/2}}\left(\frac{1}{v} - \frac{1}{v+b}\right)\right] - \cancel{\left(\frac{RT}{v-b}\right)} + \frac{a}{v(v+b)T^{1/2}}$$

$$T\left(\frac{\partial p}{\partial T}\right)_v - p = \frac{3a}{2v(v+b)T^{3/2}}$$

$$= \frac{3a}{2bT^{1/2}}\left(\frac{1}{v} - \frac{1}{v+b}\right)$$

$$u_2 - u_1 = \frac{3a}{2bT^{1/2}}\left[\ln\left(\frac{v_2}{v_1}\right) - \ln\left(\frac{v_2+b}{v_1+b}\right)\right]$$

$$h_2 - h_1 = (u_2 - u_1) + (p_2 v_2 - p_1 v_1)$$

Now, second equation, it is mathematical nature. We are going to find the expressions for the changes in the internal energy, entropy and enthalpy for a gas that undergoes change of pressure at constant temperature. So, we consider this equation of state $p = \frac{RT}{v-b} - \frac{a}{v(v+b)T^{\frac{1}{2}}}$. So, you need to have two things, one is entropy, internal energy.

So, let us start with entropy. We recall the entropy expressions $s_2 - s_1 = \int_1^2 \left(\frac{\partial p}{\partial T}\right)_v dv$.

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-b} + \frac{a}{2v(v+b)T^{\frac{3}{2}}} = \frac{R}{v-b} + \frac{a}{2bT^{\frac{3}{2}}}\left[\frac{1}{v} - \frac{1}{(v+b)}\right]$$

Now, when you put this expression here, then we arrive at

$$s_2 - s_1 = Rln\left(\frac{v_2+b}{v_1+b}\right) + \frac{a}{2bT^{\frac{3}{2}}}\ln\left(\frac{v_2}{v_1}\right) - \frac{a}{2bT^{\frac{3}{2}}}ln\left(\frac{v_2+b}{v_1+b}\right)$$

So, this is the expression for entropy change. Now, we will say internal energy change.

$$u_2 - u_1 = \int_1^2 \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right]dv$$

$$T\left(\frac{\partial p}{\partial T}\right)_v - p = T\left\{\frac{R}{v-b} + \frac{a}{2bT^{\frac{3}{2}}}\left[\frac{1}{v} - \frac{1}{(v+b)}\right]\right\} - \frac{RT}{v-b} + \frac{a}{v(v+b)T^{\frac{1}{2}}}$$

$$T\left(\frac{\partial p}{\partial T}\right)_v - p = \frac{3a}{2v(v+b)T^{\frac{1}{2}}} = \frac{3a}{2bT^{\frac{1}{2}}}\left[\frac{1}{v} - \frac{1}{(v+b)}\right]$$

So, now we know this integrand. From this when can put it, we can find out

$$u_2 - u_1 = \frac{3a}{2bT^{\frac{1}{2}}}\left[\ln\left(\frac{v_2}{v_1}\right) - ln\left(\frac{v_2+b}{v_1+b}\right)\right]$$

Now, another work rework we can do; enthalpy change $h_2 - h_1 = (u_2 - u_1) + (p_2v_2 - p_1v_1)$. So, already we have the values $u_2 - u_1$ from this above expression. We know p_2, v_2, equation of state is given. We can find out p_1 , v_1 from this equation of state. So, enthalpy change can be calculated.

So, the very basic bottom line is that for any given equation of state, the mathematical relations are very useful in deriving the different properties values. And in fact, this is the significance of this particular module which is thermodynamic property relations. And with this mathematical relation, it is possible for us that we do not have to do many experiments. And, most of the times we can do some limited experiments, take the data, pressure, specific volume and temperatures and use them to measure or calculate other thermodynamic properties. With this I conclude.

Thank you for your attention.