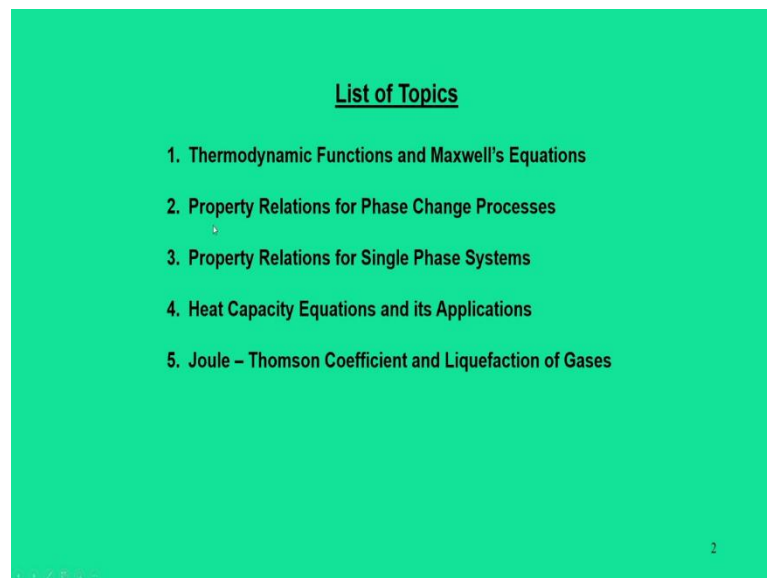


Advanced Thermodynamics and Combustion
Prof. Niranjan Sahoo
Department of Mechanical Engineering
Indian Institute of Technology, Guwahati

Module - 03
Thermodynamic Property Relations
Lecture - 10
Thermodynamic Functions and Maxwell's Equations

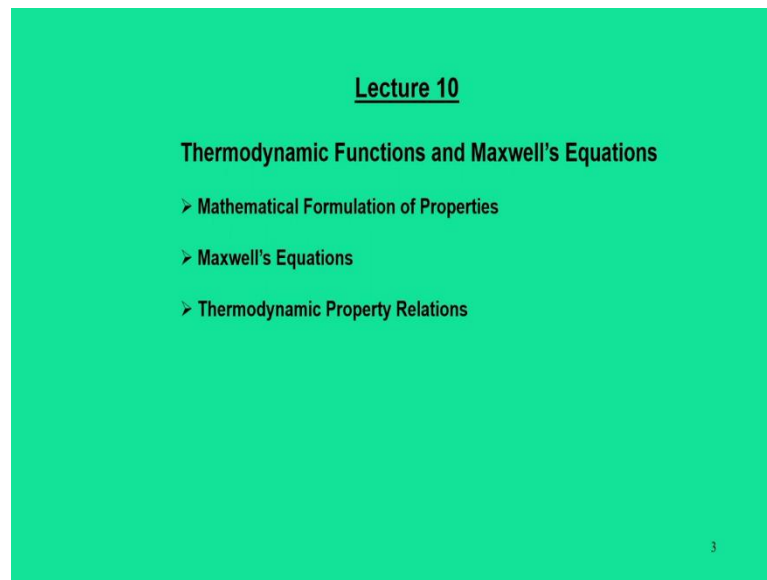
Dear learners, greetings from IIT Guwahati. We are in the course Advanced Thermodynamics and Combustions. Today we are going to start the next module that is module 3. The name of this module is Thermodynamic Property Relations.

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In this module, we will cover 5 lectures. The first one would be the thermodynamic functions and Maxwell equations. Second one is property relations for phase change process, third lecture would be property relations for single phase systems. Then, we have heat capacity equations and applications. Then, in the last lecture we will discuss about Joules-Thomson coefficient and how this parameter is very vital while consideration of liquefaction of gases.

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So, in this lecture number 10, in this series and lecture number 1 for this module; we are going to start the lecture Thermodynamic Functions and Maxwell's Equations. So, basically this module deals with the fundamental concepts of mathematics and how you are going to make use of those mathematical concepts into thermodynamic property evaluations.

So, in this lecture we are going to discuss some important concept of mathematics. And, these mathematics concepts is going to be utilized to derive various thermodynamic parameters. And, those parameters we call as thermodynamic functions and many property relations they can be closely related to each others.

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Mathematical Formulation of Properties

- The applications of thermodynamic principles to engineering systems require the property data especially for specific internal energy, enthalpy and entropy.
- The learning objectives include the mathematical expressions to allow the above specific properties to be evaluated from measured experimental data (pressure, temperature, specific volume and mass) for a simple compressible system.
- Ideally, two independent intensive property values are required to fix the state of a simple compressible system having specified mass and composition. All other intensive properties can be expressed as a functions of two independent properties.
- Most of the intensive properties can be expressed as a "characteristics functions" of two independent properties. Any other equations can be rearranged to produce another function.
- There are two important characteristics functions that represent thermodynamic potentials for a given system, namely, "Helmholtz function and Gibbs function".
- By representing the functions in appropriate form, all thermodynamic properties of a system can be calculated by differentiation only.

$p = p(T, v); u = u(T, v); h = h(T, p); s = s(T, p); \quad \psi = \psi(v, T) \text{ \& } g = g(p, T)$

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So, before we start first thing that we are going to discuss is that mathematical formulation of properties. The main significance is that why do we require the formulation of mathematical properties? Please recall that during UG courses, you must be aware of properties of pure substance where we discussed the different states of matter; solid, liquid, gas. And, those states of matter are represented in a PVT surface; Pressure, Volume and Temperature surface.

Now, on any of the surface either it is pressure volume or temperature volume or pressure temperatures. So, one way to represent the state of the system is graphical representations by drawing either constant pressure line, constant volume line, constant entropy line all these things. But the very basic fact that remains is that how did we arrive at these lines?

So, there are some mathematical treatment to it and we will try to recall some fundamental concepts of partial differential equations. And, we will try to use those equations in this thermodynamic analysis; so, that we can build a foundation with respect to mathematical formulation of thermodynamic properties.

So, with this background let me start that the application of thermodynamic principle engineering systems require the property data. And in fact, we have introduced specific internal energy, enthalpy, entropy, but these are actually derived properties. But our measured parameters that are mainly pressure, temperature, specific volume or density. So, the main intention or main learning objectives for this lecture would be to form some

mathematical expressions that will allow the specific properties to be evaluated from the experimental data.

By experimental data, we mean the property that we are going to measure during the experiments and they are mainly pressure, temperature, specific volume and mass. And, these are for simple compressible systems. In fact, just to remind you we normally do not measure internal energy, but we calculate internal energy from measured data. So, this is the basic fundamentals behind this derived properties.

So, now in order to define or fix the state of the systems in thermodynamic coordinates for a simple compressible systems, we need two independent intensive properties. And, they can be expressed by any other independent properties. So, if you say that we have pressure, temperature, specific volume. So, our choice would be pressure can be expressed at a function of volume and temperatures and volume can be expressed as a pressure and temperature and like this.

So, this is one way we look at the properties. Other way to look at this, in addition to this we can also express some characteristics functions. In fact, these characteristics functions we are going to introduce in this module and two important functions are mainly Helmholtz function and Gibbs function.

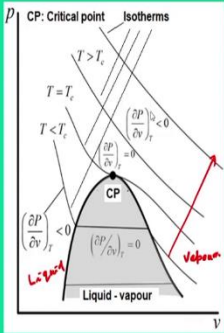
So, we will discuss the significance of these functions towards the latter part of this course. But however, this function when I define, we typically say that they are similar to other thermodynamic functions like pressure, temperature or we can correlate with the thermodynamic properties. So, in all the main summary is that first thing we talked about the parameters pressure, temperature, specific volume; they can be related. And, one can write any thermodynamic properties as a function of other two.

So, for example, pressure can be function of temperature volume, internal energy can be function of temperature volume, enthalpy also can be function of temperature and pressure, entropy can be represented as a temperature or pressure. Even many other things derived properties can be written in this fashion. Apart from this two important characteristics functions we introduce; one is Helmholtz function ψ , other is Gibbs function g . Typically, $\psi = \psi(v, T)$ and $g = g(p, T)$.

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Mathematical Formulation of Properties

- The need for mathematical formulation is the graphical representation on p - v - T surface for a pure substance.
- On a p - v plane with single phase region, the slope is negative at every point on the isotherm and it is zero at critical point.
- On a p - v plane with two phase region, the slope is zero and pressure is independent on specific volume and function of temperature alone.



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So, having said this, I will just explain the need of thermodynamic properties; why we require mathematical formulations. So, if you just revisit particular diagram like representing the properties of pure substance in a pressure volume diagrams, we can say that this is the dome we are talking about. And, within this dome we can say some region which are liquid, other is vapour region.

And, when you are going along this the pressure increases and these are constant temperature lines on a pressure volume diagrams. So, why we say that these are constant temperature lines, because with change in the volume pressure also changes, but at constant temperatures. Now, if you look the dome, within the dome we have liquid vapour phase, where pressure as well as temperature always remains constants; that means, saturated pressure is a function of temperature only and vice versa.

So, main significance of this is that the way of representing the parameters in mathematical form, we say either $\partial p/\partial v$ can be less than 0 or it can be greater than 0 or it can be equal to 0. So, in this way it is possible to represent these lines. But these lines are nothing but the derivation of mathematical formulations. So, our main target is that how we derive this kind of relations mathematically.

Another significant fact is that when you talk about the critical point, the slope is $\left(\frac{\partial p}{\partial v}\right)_T = 0$. And, beyond this line, it is always less than 0, because we are in the single phase zone and at the same time we can say these are the isotherm lines that are drawn here.

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Mathematical Formulation of Properties

- On a p - T plane (phase diagram), the isometric lines represent the change of pressure or temperature under the conditions of constant volume. Several such lines can be represented with respect to critical volume.
- On the p - T plane and in a single phase region, the isometrics are nearly straight and slightly curved with positive slope at each state along the curve.
- The slopes of isometrics passing through two-phase states corresponding to specified temperature are all equal. So, the slope at that point is represented as ordinary differential.

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Now, again another significance would be if you recall the pressure temperature plane or we call this as a phase diagram. Similar points can be represented. On a pressure temperature plane, we can represent a triple point and the critical point. And, one can draw that line and this line is not exactly a straight line, but what you can say it is a constant specific volume line on a pressure temperature diagram.

And, this constant specific volume line is nothing, but your $v = v_c$; that is critical volume. And, also we can have the isometric lines which is nothing, but the change of pressure or temperature under the conditions of constant volumes. So, this also can be represented.

Now, while deriving them in a partial differential form, other way of looking at them is in some situations like for example, when you join this line this triple point to this critical point, because this is a phase change process. And, during the phase change process, this partial differential equations becomes ordinary differential equation. So, this is nothing, but the locus of all saturation states. So, this is the way or background why we require the mathematical formulation of thermodynamic properties.

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Maxwell Relations

- The fundamental thermodynamic functions are important for simple compressible systems of fixed chemical composition using the concept of exact differential.

Recall mathematical expression: $z = z(x, y) \Rightarrow dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy = M dx + N dy$

For exactness of the function, $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$ should be satisfied.

\mathcal{P} -ds Equations: $du = T ds - p dv$; $dh = T ds + v dp$

Specific Helmholtz function: $\psi = u - Ts \Rightarrow d\psi = du - T ds - s dT = -p dv - s dT$

Specific Gibbs function: $g = h - Ts \Rightarrow dg = dh - T ds - s dT = v dp - s dT$

Maxwell Relations:

- $du = T ds - p dv$; $M = T$, $N = -p$, $x = s$, $y = v \Rightarrow \left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v$
- $dh = T ds + v dp$; $M = T$, $N = v$, $x = s$, $y = p \Rightarrow \left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p$
- $d\psi = -p dv - s dT$; $M = -p$, $N = -s$, $x = v$, $y = T \Rightarrow \left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$
- $dg = v dp - s dT$; $M = v$, $N = -s$, $x = p$, $y = T \Rightarrow \left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T$

Now, we will go back one by one. So, first important relations that we are going to derive is the Maxwell relations or simply we call this as a Maxwell equations. So, the very basic fundamental things that we need to understand while considering the Maxwell equation is that we must recall the fundamentals of exact differential.

For example, if you say that any parameter z is a function of x and y , where x and y are independent in nature. So, $z = z(x, y) \Rightarrow dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy = M dx + N dy$

So, typically if you put this parameter as M and this parameter as N and now it has been proved that for this mathematical function, the function will be exact. Means, the exactness of a function will be justified when $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$.

So, with this very basic background, let us recall that what equations we have studied. So, the first one we have studied is Tds equations and these Tds equations are derived from the combined equations of first law and second law. $du = T ds - p dv$; $dh = T ds + v dp$. Now, apart from this we will now introduce another function what we call as specific Helmholtz functions and specific Gibbs functions.

We will discuss the significance of these functions towards the latter part of the course, but however, for the sake of mathematical importance; if you can just rewrite this equation

that $\psi = u - Ts$. Another function Gibbs function we define is as $g = h - Ts$. Then, from this we can write $d\psi = du - Tds - sdT$.

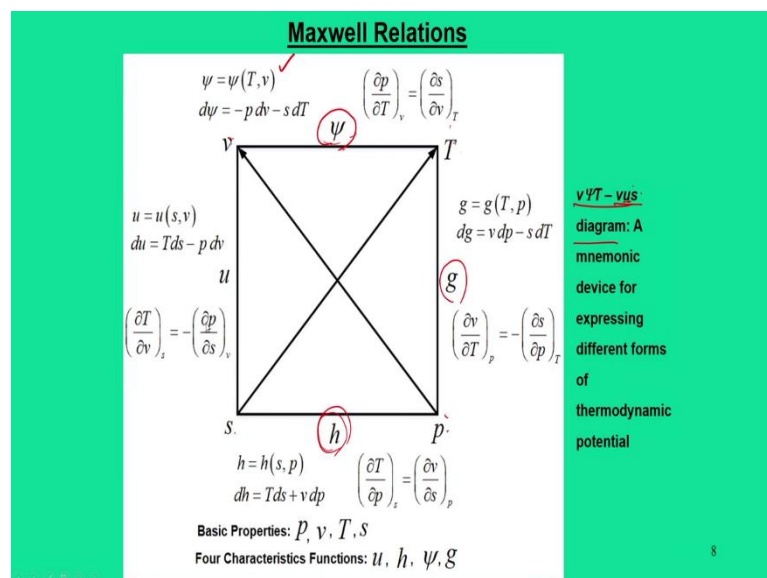
Now, from this Tds equations, the first Tds equations can be utilized here. So, this function now can be expressed as $d\psi = -pdv - sdT$ and similar way for Gibbs functions, $g = h - Ts \Rightarrow dg = dh - Tds - sdT$. Then, we get the dh from second Tds equations, put it here. Then we get $dg = vdp - sdT$.

So, we have now basically 4 equations, 2 Tds equations, 1 Helmholtz function, other is Gibbs functions. So, if you summarize that equations; so, you can write the first expression $du = Tds - pdv$. Now, here if you recall this particular equations $Mdx + Ndy$ and our mathematical expression this, we can find out $M = T, N = -p, x = s, y = v$.

Now, if this exact condition is to be satisfied, we can find out the relations $\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v$. Again, from the second Tds equations $dh = Tds + vdp$, similar analogy can be followed. So, we can find out $\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p$.

Third equation from $d\psi = -pdv - sdT$, similar analogy is followed. We can write $\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$. Then, if you have the last one which is $dg = vdp - sdT$, then we can get $\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T$.

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Now, these 4 relations we call this as a Maxwell equations; or Maxwell relations. Now, question remains that how to remember this Maxwell equations? So, to do that first thing that we have to remember is what is called as $v\psi T - vus$ diagram. So, we know that v is specific volume, ψ is Helmholtz function and u is internal energy and s is this.

Now, what does this means? First thing we have to draw a square, we start with v first, then ψ , then T . So, one line you can represent as $v\psi T$ and which means that ψ is a function of v and T and other one is vus . So, when I put this $v T$ line first, then also I can put p and s here and this is related with function u . And, when I have this triangle, the rest of the parameters will be opposite, from v will have p , opposite from T will have s and this p and s will have relation and function that can be formed is enthalpy. And, from T and p function can be formed that is g .

So, basically by drawing this diagram, I can name this square as $v T p s$ diagram. And, the lines or length of the lines I can put in this way as ψ , g , h and u . So, which one will be ψ , which one will be g that is decided by when you remember $v \psi T$ and vus .

So, when I say ψ is a function of T and v . So, we can write the first equations and of course, since the T and v are in the bracket so, corresponding differential will be dv and dT and when I write this. So, if I say they must come from v , so that means, one you can see this arrow is entering into v . So, when it is entering, there is a negative sign here.

So, we will have $-p$ and this arrow is entering into T so, it is $-s$. So, in both the cases it is entering into v and T so, it is minus. Let us say another situations or in the opposite side of this ψ , we have h here where both the arrows are coming out and here we start this enthalpy which is a function of s and p . So, when I write this. So, differential will be ds and dp and here both the arrows is coming out of p and s . So, accordingly both v and T will be positive.

In other situation one positive, other negative. Let us see in this line that is $v s$ line, the function is u . So, u is a function of v and s . So, you can write $du = Tds - pdv$. So, here we will have ds , we will have dv . Now, from s we are going out of this towards T ; so, it will be T . So, this is positive because it is going out and in this case, if you say v , the arrow that goes is entering into v ; so, it is $-p$.

And, once we know this we can derive this corresponding functions. So, basically by remembering this diagram, we can promptly write the equations. So, in summary what we have is we have basic properties pressure, volume, temperature and entropy. And these are nothing but the cardinal points of the square. And, the characteristics functions are internal energy, enthalpy, Helmholtz functions and Gibbs functions.

They are represented as the lines and this is nothing but a mnemonic device for expressing differential form of thermodynamic potential. And, this is the easy way that how one can write these Maxwell relations. Here all the partial differential relations are known as the Maxwell equations.

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Thermodynamic Property Relations

- The concept of exact differential can be extended to obtain mathematical expressions for thermodynamic properties.

Basic Relations:

- $u = u(s, v); \quad du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv$
 T - ds Equation: $du = Tds - pdv \Rightarrow T = \left(\frac{\partial u}{\partial s}\right)_v$ & $-p = \left(\frac{\partial u}{\partial v}\right)_s$
- $h = h(s, p); \quad dh = \left(\frac{\partial h}{\partial s}\right)_p ds + \left(\frac{\partial h}{\partial p}\right)_s dp$
 T - ds Equation: $dh = Tds + vdp \Rightarrow T = \left(\frac{\partial h}{\partial s}\right)_p$ & $v = \left(\frac{\partial h}{\partial p}\right)_s$
- $\psi = \psi(T, v); \quad d\psi = \left(\frac{\partial \psi}{\partial v}\right)_T dv + \left(\frac{\partial \psi}{\partial T}\right)_v dT$
Helmholtz function: $d\psi = -pdv - sdT \Rightarrow -p = \left(\frac{\partial \psi}{\partial v}\right)_T$ & $-s = \left(\frac{\partial \psi}{\partial T}\right)_v$
- $g = g(T, p); \quad dg = \left(\frac{\partial g}{\partial p}\right)_T dp + \left(\frac{\partial g}{\partial T}\right)_p dT$
Gibbs function: $dg = vdp - sdT \Rightarrow v = \left(\frac{\partial g}{\partial p}\right)_T$ & $-s = \left(\frac{\partial g}{\partial T}\right)_p$

Now, let us revisit or go little bit further; where we are going to discuss the exact differential which can be extended to obtain certain other mathematical expressions. So, if you recall one of the basic relations while deriving the Maxwell equation is $u = u(s, v)$. We can write this as an exact differential $du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv$ and we can compare with the first Tds equation $du = Tds - pdv$.

So, from these equations we can find one expressions that is $T = \left(\frac{\partial u}{\partial s}\right)_v$ & $-p = \left(\frac{\partial u}{\partial v}\right)_s$. Another relation is the where enthalpy is a function of entropy and pressures $h = h(s, p)$, we can find exact differential for enthalpy $dh = \left(\frac{\partial h}{\partial s}\right)_p ds + \left(\frac{\partial h}{\partial p}\right)_s dp$.

We can recall the Tds equations $dh = Tds + vdp$ and from this two equations by comparing, we can say $T = \left(\frac{\partial h}{\partial s}\right)_p$ & $v = \left(\frac{\partial h}{\partial p}\right)_s$. The next equation will be Helmholtz function $\psi = \psi(T, v)$. So, we can find exact differential $d\psi = \left(\frac{\partial \psi}{\partial v}\right)_T dv + \left(\frac{\partial \psi}{\partial T}\right)_v dT$ and by definition also we can write $d\psi = -pdv - sdT$.

So, from these two equations, we can say the $-p = \left(\frac{\partial \psi}{\partial v}\right)_T$ & $-s = \left(\frac{\partial \psi}{\partial T}\right)_v$. And, the last one is from Gibbs functions which is $g = g(T, p)$. We can find out this as $dg = \left(\frac{\partial g}{\partial p}\right)_T dp + \left(\frac{\partial g}{\partial T}\right)_p dT$ and then Gibbs function by definition we can write $dg = vdp - sdT$. And, then from this we can get another relations $v = \left(\frac{\partial g}{\partial p}\right)_T$ & $-s = \left(\frac{\partial g}{\partial T}\right)_p$. So, we have Maxwell equations. Next we have basic relations.

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Thermodynamic Property Relations

- 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 Maxwell relation allows the derivatives to be determined by evaluating the partial derivatives from p-v-T surface of a pure substance.

Additional Relations:

1. $T = \left(\frac{\partial u}{\partial s}\right)_v$; $T = \left(\frac{\partial h}{\partial s}\right)_p \Rightarrow \left(\frac{\partial u}{\partial s}\right)_v = \left(\frac{\partial h}{\partial s}\right)_p$
2. $-p = \left(\frac{\partial u}{\partial v}\right)_s$; $-p = \left(\frac{\partial \psi}{\partial v}\right)_T \Rightarrow \left(\frac{\partial u}{\partial v}\right)_s = \left(\frac{\partial \psi}{\partial v}\right)_T$
3. $v = \left(\frac{\partial h}{\partial p}\right)_s$; $v = \left(\frac{\partial g}{\partial p}\right)_T \Rightarrow \left(\frac{\partial h}{\partial p}\right)_s = \left(\frac{\partial g}{\partial p}\right)_T$
4. $-s = \left(\frac{\partial \psi}{\partial T}\right)_v$; $-s = \left(\frac{\partial g}{\partial T}\right)_p \Rightarrow \left(\frac{\partial \psi}{\partial T}\right)_v = \left(\frac{\partial g}{\partial T}\right)_p$

Now, we will go little bit further from this last previous analysis, we have 4 Maxwell equations. And, we have 8 basic relations and from those we find out temperature expressions that is $T = \left(\frac{\partial u}{\partial s}\right)_v$; $T = \left(\frac{\partial h}{\partial s}\right)_p$. So, from this we can find out another relation

$$\left(\frac{\partial u}{\partial s}\right)_v = \left(\frac{\partial h}{\partial s}\right)_p$$

Other relations are $\left(\frac{\partial u}{\partial v}\right)_s = \left(\frac{\partial \psi}{\partial v}\right)_T$; $\left(\frac{\partial h}{\partial p}\right)_s = \left(\frac{\partial g}{\partial p}\right)_T$; $\left(\frac{\partial \psi}{\partial T}\right)_v = \left(\frac{\partial g}{\partial T}\right)_p$. So, all the 4 equations can be remembered from this simple diagram. So, in total we have 16 property relations that are obtained from the concept of exact differentials.

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Numerical Problems

Q1. Consider the following equation of state: (a) Determine the expression for exact differential of pressure; (b) Show that the mixed second partial derivatives are equal; (c) Find the expression for change in specific volume with temperature at constant pressure.

$p = \frac{RT}{v-b} - \frac{a}{v^2}$; a and b are constants.

Handwritten solution:

(a) $dp = \left(\frac{\partial p}{\partial T}\right)_u dT + \left(\frac{\partial p}{\partial v}\right)_T dv$; $M = \left(\frac{\partial p}{\partial T}\right)_u = \frac{R}{v-b}$
 $N = \left(\frac{\partial p}{\partial v}\right)_T = RT \left[\frac{\partial}{\partial v} (v-b)^{-1} \right] - \frac{\partial}{\partial v} (v^{-2})$
 $\Rightarrow N = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3}$

(b) $\left(\frac{\partial M}{\partial v}\right)_T = -\frac{R}{(v-b)^2}$; $\left(\frac{\partial N}{\partial T}\right)_v = -\frac{R}{(v-b)^2}$; $\left(\frac{\partial M}{\partial v}\right)_T = \left(\frac{\partial N}{\partial T}\right)_v$

(c) $\left(\frac{\partial u}{\partial T}\right)_p \left(\frac{\partial v}{\partial u}\right)_T \left(\frac{\partial T}{\partial p}\right)_u = -1$; $\left(\frac{\partial u}{\partial T}\right)_p = \frac{-1}{\left(\frac{\partial v}{\partial u}\right)_T \left(\frac{\partial T}{\partial p}\right)_u}$
 $\Rightarrow \left(\frac{\partial u}{\partial T}\right)_p = \frac{-1}{\left[-\frac{RT}{(v-b)^2} + \frac{2a}{v^3}\right]}$

So, this is all about the thermodynamic differential equations which we have derived. Now, let us try to attempt some of the important problems which we learnt in this lecture. So, basically the typical nature of the problem in this model will be more towards the partial differential equations, where we must take a complete strength of the differential equations. The first problem that we are going to solve is that we are going to consider a equation of state that is $p = \frac{RT}{v-b} - \frac{a}{v^2}$. This is nothing but van der Waals equation.

Now, we will see that how this van der Waals equations is always not the same as equation of state. There are real gases, they follow different nature of equation or state equations. So, let us see that how we can use this concept of exact differential for these situations which we are going to discuss, we need to find out the expression for exact differential of pressures. So, by exact differential of pressure we mean we are required to find out dp .

And then we need to find out mixed second partial derivatives, which means that you have to recall M and N and second partial derivative needs to be obtained with respect to M and N. Now, let us see that what is this dp and what is this M and N. We have to make the

correlation first. So, let me start, first if I write $p = p(T, v)$. And so, $dp = \left(\frac{\partial p}{\partial v}\right)_T dv + \left(\frac{\partial p}{\partial T}\right)_v dT$.

So, here we can say $M = \left(\frac{\partial p}{\partial T}\right)_v$; $N = \left(\frac{\partial p}{\partial v}\right)_T$. Now, let us compare what is our functional relations. So, if you start this particular equation and differentiate pressure with respect to temperature at constant volume; so, we can get $M = \left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-b}$

Similarly, we can write $N = \left(\frac{\partial p}{\partial v}\right)_T = RT \left(\frac{\partial}{\partial(v-b)}(v-b)^{-1} \cdot \frac{\partial(v-b)}{\partial v}\right) - a \left(\frac{\partial}{\partial v}(v^{-2})\right)$

Now, if you do this differentiation, $N = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3}$. So, we can write the first answer that is $dp = \left(-\frac{RT}{(v-b)^2} + \frac{2a}{v^3}\right) dv + \frac{R}{v-b} dT$. Next thing is that mixed second partial derivative. So, here we need to find out mixed partial derivative, means we have to find out $\left(\frac{\partial M}{\partial v}\right)_T, \left(\frac{\partial N}{\partial T}\right)_v$.

$$\left(\frac{\partial M}{\partial v}\right)_T = -\frac{R}{(v-b)^2}; \left(\frac{\partial N}{\partial T}\right)_v = -\frac{R}{(v-b)^2} \Rightarrow \left(\frac{\partial M}{\partial v}\right)_T = \left(\frac{\partial N}{\partial T}\right)_v$$

So; that means, this proves that mixed second partial derivatives are equal. Third one we need to find out find the expression of change of specific volume at constant temperatures.

Now, we recall $\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial T}{\partial p}\right)_v = -1$. So, what question this is asked is we need to

find out $\left(\frac{\partial v}{\partial T}\right)_p = -\frac{1}{\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial T}{\partial p}\right)_v} = -\frac{\frac{R}{v-b}}{\left(-\frac{RT}{(v-b)^2} + \frac{2a}{v^3}\right)}$. So, this is how we gave the demonstration,

how the partial derivatives can be obtained from this simple concept of exact differential.

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Numerical Problems

Q2. The thermodynamic state of water vapour is fixed at 240°C with specific volume of 0.4646 m^3/kg . Evaluate change in entropy change with respect to specific volume at constant temperature for the following equation of state.

$$p = \frac{\bar{R}T}{\bar{v}-b} - \frac{a}{\bar{v}(\bar{v}+b)T^{0.5}}; a = 142.6 \text{ bar}(\text{m}^3/\text{kmol})^2 (\text{K})^{0.5}; b = 0.0211 (\text{m}^3/\text{kmol}); \bar{R} = 8314 \left(\frac{\text{J}}{\text{kmol}\cdot\text{K}}\right)$$

Maxwell eqn. $\left(\frac{\partial s}{\partial \bar{v}}\right)_T = \left(\frac{\partial p}{\partial T}\right)_{\bar{v}}$

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

$\Rightarrow \left(\frac{\partial p}{\partial T}\right)_{\bar{v}} = \frac{8314}{(8.372 - 0.0211)} + \frac{142.6}{2(8.372)(8.372 + 0.0211)(513)^{1.5}}$

$\Rightarrow \left(\frac{\partial p}{\partial T}\right)_{\bar{v}} = 1.003 \text{ kg}/\text{m}^3 \cdot \text{K}$

$\left(\frac{\partial s}{\partial \bar{v}}\right)_T = 1.003 \text{ kg}/\text{m}^3 \cdot \text{K}$

Handwritten notes:
 $\bar{v} = 0.4646 \times 18$
 $\Rightarrow \bar{v} = 8.372 \text{ m}^3/\text{kmol}$
 $a = 142.6$
 $b = 0.0211$
 $\bar{R} = 8314$
 $T = 240^\circ\text{C} = 513 \text{ K}$

Now, next problem which is similar where it is given that we need to find out the thermodynamic state of water vapour. And, the vapour exist at a state 240 C and specific volume of 0.4646 m^3/kg .

We need to find out what is the change in the entropy with respect to specific volume at constant temperatures. For example, if I keep temperature constant and change the specific volume, what happens to entropy? So, this is very difficult to find out experimentally. But, you can see what is the importance of this mathematical analysis, how we can find the change in the entropy with respect to specific volume at constant temperature.

So, this change in entropy with respect to specific volume at constant temperature for which we have to recall one of the Maxwell equation. And, that Maxwell equation states $\left(\frac{\partial p}{\partial T}\right)_{\bar{v}} = \left(\frac{\partial s}{\partial \bar{v}}\right)_T$. So, you see that entropy change is related to property data, that is pressure and temperatures.

And we have these equations $p = \frac{\bar{R}T}{\bar{v}-b} - \frac{a}{\bar{v}(\bar{v}+b)T^{0.5}}$. So, we can find the first expression.

$\left(\frac{\partial p}{\partial T}\right)_{\bar{v}} = \frac{\bar{R}}{\bar{v}-b} - \frac{a}{2\bar{v}(\bar{v}+b)T^{3/2}}$. And, remember here the data a and b are constant and are expressed in the form of mole. But whereas, the specific volume data is given in m^3/kg .

So, that is what this \bar{v} needs to be changed. So, I can say that \bar{v} would be specific volume that is 0.4646 multiplied by the molar mass of water vapour. So, $\bar{v} = 0.4646 \times 18 =$

$8.372 \text{ m}^3/\text{kMol}$. So that means, from the specific volume we can get the molar specific volume.

We all know $a = 142.6 \text{ bar} \left(\frac{\text{m}^3}{\text{kmol}}\right)^2 (\text{K})^{\frac{1}{2}}$; $b = 0.0211 \left(\frac{\text{m}^3}{\text{kmol}}\right) \bar{R} = 8314 \left(\frac{\text{J}}{\text{kmol.K}}\right)$. So, all the data is given. So, by putting this number, we can write $\left(\frac{\partial p}{\partial T}\right)_v = \frac{8314}{8.372 - 0.0211} - \frac{142.6}{2(8.372)(8.372 + 0.0211)(513)^{\frac{3}{2}}} = 1.003 \text{ kg/m}^3 - \text{K}$.

So, $\left(\frac{\partial p}{\partial T}\right)_v$ is $1.003 \text{ kg/m}^3 - \text{K}$. This can be equal to change in the specific entropy with respect to change in the specific volume at constant temperature.

So, this talks about the how the equation of state will be useful to find the state of the systems. This equation of state is required, because these are the major data. And, from this major data by solving this problem, we see the that how entropy change with respect to specific volume at can be addressed through Maxwell equations. With this I close the lecture for today.

Thank you for your attention.