

Indian Institute of Technology Kanpur

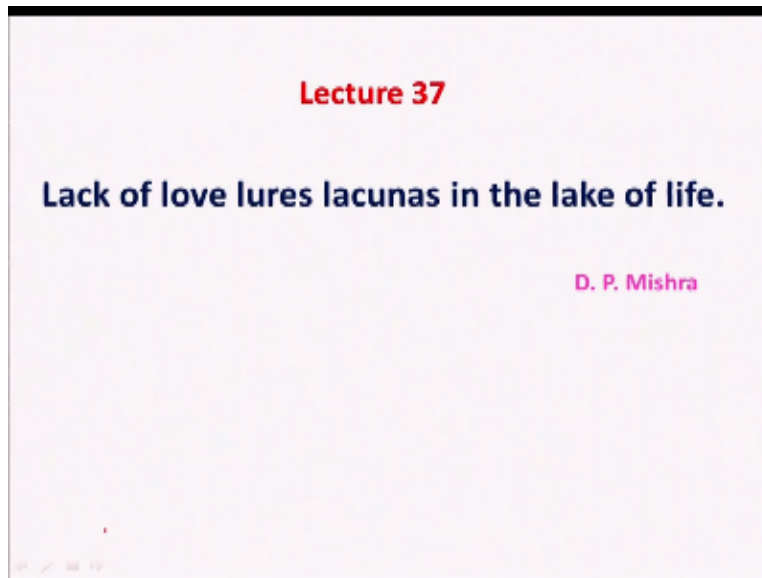
National Programme on Technology Enhanced Learning (NPTEL)

**Course Title
Engineering Thermodynamics**

**Lecture – 37
Thermodynamic Property Relations 1**

**By
Prof. D. P. Mishra
Department of Aerospace Engineering**

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Let us start this lecture with the thought purpose that lack of love lures lacunas in the lake of light whatever lacunas we find in ourselves is because of we do not have a power to love others and also our self. So that is like let us now get into the thermodynamics in the last lecture we discuss about basically what you call the psychometry kind of things and there we looked at the properties how to handle the weight mixtures, and it can be useful for the air conditioning and we have seen various applications how you can use the relationship and also psychometric charts.

Psychometric chart is very useful to do the calculation very quickly and have a visualization of the process very easily.

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Thermodynamic Relations

And today we will be looking at basically the thermodynamic relations and if you look at why do we want to look at thermodynamic relations we have looked at you know various what you call relationship till now, but why we will be looking at this because there are several relationship we have learnt I mean pertaining to the first law of thermodynamics, second law of thermodynamics and if you look at Gibbs relationship all those things we have looked at several of them.

But now we will devote we will be devoting around two lectures on this, but question arises why remember that when we discuss about the thermodynamic properties right we looked at several properties and then also use those properties for evaluating the various thermodynamic terms for evaluating the work done, or the change in enthalpy, change in entropy and other things right. And all these properties are very important for analyzing the problem and arriving at some quantitative data to appreciate what is happening.

But however most of these properties if you look at are not really measurable right there are several properties which are, which cannot be measured for example and work and all internal energy you know like.

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Thermodynamic Relations (TDR)

How many properties are used for a single phase pure substance?

8 properties : P, v, T, s, u, h, g and a. **Measurable properties**: P, v, T

The non-measurable properties can be expressed in terms of measurable properties.

What are ways of relating measurable and non-measurable properties?

Let us consider a function, $P = P(x, y) \Rightarrow dP = \left(\frac{\partial P}{\partial x}\right)_y dx + \left(\frac{\partial P}{\partial y}\right)_x dy$ --- (1)

Dividing Eq (1) by dx keeping $z = \text{const}$, $\frac{dP}{dx} = \left(\frac{\partial P}{\partial x}\right)_y + \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{dy}{dx}\right)_z$

$$\left(\frac{\partial P}{\partial x}\right)_z = \left(\frac{\partial P}{\partial x}\right)_y + \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

$$\text{No of PD} = {}^8P_3 = \frac{8!}{5!} = 336$$

Total no of possible TD relations = ${}^{336}P_1 = 336$

It is quite difficult to remember these many derivatives.

Hence, we will develop systematic method by which one can handle these derivatives.

➤ Partial Derivative Method

➤ Jacobian Method

So if you look at those things we do use and if you look at we take a very simple like a single phase pure substance that there will be several properties you may question how many properties are used for describing or analyzing a single phase for your substance. So there are several of them if you look at eight properties that have been can be used like let us say pressure, volume, temperature so if you look at these are all measurable properties one can measure we can you know use also entropy, internal energy, enthalpy and the Gibbs function and A is basically the Helmers function right.

This if you look at the three properties are measurable and rest are non measurable properties if it is a complex system there will be several more properties will be coming into pictures right. And now we need to express these non measurable properties in terms of the measurable properties then only we can relate these things and find out the properties data, and then that can be utilized. So as I told this measurable properties is it only the pressure, volume, temperature or some other measurable properties are there any idea?

You know if you look at specific heat right isothermal compressibility, coefficient of volume expansion these are all can be measured it can be considered as a measurable property, because you can measure them right. But we are considering it is three of them here and these however what you call something five properties I have just mentioned for a single phase pure substance and that has to be expressed in terms of three properties which are measurable right.

So question arises what are the ways of relating the measurable properties and non measurable property that is the basis for which will be studying the thermodynamic relations right. So if you look at let us consider inner pressure, pressure is quantities, pressure is a function of X and Y right let us say. And I can write on that as change in pressure is equal to $\partial P/\partial S$ when y constant into dx + $\partial P/\partial Y$ X constant into dy this you know very well you know from the calculus.

So if I divide this equation by dx right and keeping the Z constant right if I divide this by dx here right and keeping the Z constant I will get $\partial P/\partial X$ Z because this will be one right and $\partial P/\partial X$ and Z remain constant is equal to $\partial P/\partial X$ when Y remaining constant + $\partial P/\partial Y$ and X remaining constant into $\partial Y/\partial X$ when Z is remaining constant. So if you look at these are kind of things what we will be using to have a relationship.

Now we will go back to the properties, you know like the measurable properties are basically three for a single phase pure substance, and the non measurable properties is five total is eight if I look at the permutation of this A between eight and three that means number of partial derivative one can do is basically 336 it is a big number that many relationship one can think of right. And if I look at this relationship here then there are total basically out of 336 relationship if we can express here it is a total four and if I take a permutation of that total number of possible thermodynamic relation will be around 5.2×10^8 it is a big number you know it is very difficult for a human being to remember are you getting.

This many relationship one can think of just taking eight properties start with, but if it is more then it will be much more the are you getting my point. That is basically it is very difficult to handle so many relationship which can come up of course some all of them you may not use it for your analysis, but however it can. So therefore we should know how to handle those things and we will be learning about that and we will be using two methods one is what you call partial differentiation or partial derivative method, other is Jacobian methods.

I guess all of you know these methods only thing what we'll do we will have to recapitulate the salient features of this and use it to deriving various thermodynamic relationship right.

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Partial Derivative Method (PDM)

What are the rules for PDM ?

Let us consider a relationship between 3 variables (x, y, z)
 $f(x, y, z) = 0 \Rightarrow z = z(x, y) \Rightarrow dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$

1. Reciprocal Relation (RR): $\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$

2. Cyclic Relation (CYR): $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$

Suppose, $z = z(p, y)$; $p = p(x)$; and $y = y$;

3. Chain Rule (CR): $\left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial z}{\partial p}\right)_y \left(\frac{\partial p}{\partial x}\right)_y$

So let us look at first the partial derivative method and if you recall there are basically three rules are there right of partial derivative methods. So what are those can anyone tell me, because you know this thing you have does not have courses right let me give you a clue like chain rule, cyclic rule, right reciprocal rule all those things you know right. So let us recapitulate what it can be let us consider relations between three variable X, Y, Z kind of things right.

And we can say that function which is like a X, Y, Z and then I can write on Z is basically function of XY then I can write down from this the change in Z is equal to $\partial Z / \partial X$ when Y remaining constant into $dx + \partial Z / \partial Y$ X remaining constant into dy . And similarly I can take a X is a function of Z and Y I can write down similarly change in the X right whatever it is and do that. And I can have any function and write down in the similar form.

Now if you look at is the reciprocal relation will be basically $\partial X / \partial Y$ Z remaining constant is equal to $\partial Y / \partial X$ Z remaining constant this I think you know you just recapitulate and keep it mind right I am not going to derive these things right. And the cyclic relationship if you look at it is basically $\partial X / \partial Y$ Z remaining constant into $\partial Y / \partial Z$ X remaining constant into $\partial Z / \partial X$ Y remaining constant is equal to - 1 right. And if I say that that Z is a function of P and Y where P is a function of X.

Then I can write down cyclic relationship and considering that Y remaining constant is not changing right. So by that I can write down the chain rule as $\partial Z / \partial X$ Y remaining constant is equal to $\partial Z / \partial P$ and Y remaining constant for all the case into $\partial P / \partial X$ this is basically chain rule

you know like kind of thing. So we will be using these three relationship for deriving or simplifying the various relations thermodynamic relationship. And let us take an example how we can use that and what is the usefulness.

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Example : An ideal gas in piston-cylinder at 300 K and 0.9 m³/kg undergoes a process by which its temperature and specific volume are changed by 2 K and 0.04 m³/kg respectively. Determine change in the pressure of this gas.

Given: $dT = 2\text{K}$, $dv = 0.04\text{ m}^3/\text{kg}$, $v = 0.9\text{ m}^3/\text{kg}$, $T = 300\text{ K}$.

To find: dp

Solution: Ideal gas law; $Pv = RT$
 $P = P(T, v)$; $dp = \left(\frac{\partial P}{\partial T}\right)_v dT + \left(\frac{\partial P}{\partial v}\right)_T dv$
 $= \frac{R}{v} dT + \left(-\frac{RT}{v^2}\right) dv = R \left[\frac{dT}{v} - \frac{T dv}{v^2} \right]$
 $= 0.287 \left[\frac{2}{0.9} - \frac{300 \times 0.04}{(0.9)^2} \right] = -3.19\text{ kPa}$

So if you look at an ideal gas in a piston cylinder at 300 Kelvin and 0.9m³/kg undergoes a process by which its temperature and specific volume are changed by 2 Kelvin and 0.04m³/kg respectively right. And determine the change in the pressure of these gas so how we are going to do that so if you look at that what are the given so dT is given that is 2 Kelvin and specific volume is a change in specific volume is given 0.04m³ per kg and of course ideal gas is given so you can use the ideal gas law for this and in this and the volume specific volume is given as 0.9m³ per kg and the temperature is also given right 300 Kelvin so to find basically change in pressure right.

So if you look at ideal gas law is given so therefore I can use ideal gas law PV is equal to RT right and if you look at P is basically function of what P is function of T and V so I can write down from this d_p is equal to $\partial P / \partial T$ into v into dT + $\partial P / \partial V$ into dV right so if I know this relationship what it will be then this will be basically $\partial P / \partial T$ so this will be our by V into d_T yes or no $\partial P / \partial T$ when volume remaining constant so that will be R/V + ∂P by ∂V when temperature is remaining constant it will be minus right.

Now and that will be basically $\partial P / \partial V$ so therefore it will be $V^2 - 1 / V^2$ into $RT d_v$ right if I take this a hover outside I can say this d_T why $V - RT R_1$ be there T into V^2 so I will substitute these values that will be R , R is what is the R value we can take 0.28 seven into d_T is to Kelvin right and V is 0.9 - T is T will be 300 Kelvin right and d_v is basically 0.04 into V^2 is 0.9 whole square right you will get something around 3.19 kilo Pascal right.

So if you look at I mean that way you can find out change in the pressure right kind of things so we will now see how we can basically derive this what you call.

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Jacobian Method in Thermodynamics

PD can be easily manipulated by Jacobian Method.

If $x = x(p, r)$ and $y = y(p, r)$, then the Jacobian of x, y w.r.t. p, r is defined as

$$J \begin{matrix} [x, y] \\ [p, r] \end{matrix} = \begin{matrix} \frac{\partial x}{\partial p} & \frac{\partial x}{\partial r} \\ \frac{\partial y}{\partial p} & \frac{\partial y}{\partial r} \end{matrix} = \begin{pmatrix} \frac{\partial x}{\partial p} \frac{\partial y}{\partial r} - \frac{\partial y}{\partial p} \frac{\partial x}{\partial r} \end{pmatrix} \begin{matrix} [p, r] \\ [r, p] \end{matrix}$$

Jacobian obeys the following properties

1. $\begin{matrix} [x, y] \\ [p, r] \end{matrix} \begin{matrix} [p, r] \\ [s, t] \end{matrix} = \begin{matrix} [x, y] \\ [s, t] \end{matrix}$
2. $\begin{pmatrix} \frac{\partial x}{\partial y} \end{pmatrix}_z = \begin{matrix} [x, z] \\ [y, z] \end{matrix}$
3. $[x, y] = -[y, x]$
4. $[x, x] = 0$

If $z = z(x, y)$ is a thermodynamic property, its differential is exact.

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy \Rightarrow dz = \frac{[z, y]}{[x, y]} dx + \frac{[z, x]}{[y, x]} dy \text{ -----(1)}$$

Eq (1) can be written as $dz = Mdx + Ndy$

where, $M = \frac{[z, y]}{[x, y]}$; $N = \frac{[z, x]}{[y, x]}$

Thermodynamic relationship but before that we will see the Jacobian methods right how it can be applied in thermodynamics so the parcel vertical derivative can be easily manipulated by the Jacobian methods so if I say that x is a function of pr and y is a function of pr then the Jacobian of xy with respect to pr can be defined as you know like is equal to basically $\partial x / \partial p$ and $\partial x / \partial r$

and $\partial y / \partial p$ and $\partial y / \partial r$ so it is a matrix format in that is the and you can do this cross multiplication for example that will be $\partial x / \partial p \times \partial y / \partial r$ this term right minus $\partial y / \partial p$ into $\partial x / \partial r$.

So if you look at that you can express in this form the Jacobian switch is quite you know looks to be little complex but however it will be very useful like when we handle that and Jacobian's obeys the following property the way we have looked at you know the properties for partial derivatives similar way we can also have properties for the Jacobian obeys so that is one is Jacobian xy the respect to pr into the Jacobian pr with respect to st is nothing but Jacobian xy with respect to st and ∂x by ∂y when z is remaining constant can be written as the Jacobian xz respect to yz .

Right and so you can get from here very easily from this for example like if I say this is a you know like xz like kind of thing so I can write down from here what it would be xz if I say this is $xz = x yz$ right so that will be ∂x by ∂y into $\partial z / \partial z$ - if you look at this is $\partial z / \partial y$ into $\partial x / \partial z$ so if you look at this is basically 0 right so and this is one so you will get basically x Jacobian xz with respect to yz is nothing but your ∂x by ∂y when z is remaining constant so you can very easily get this one you know this is the term which will be remaining.

So very easily you can get similarly if you look at Jacobian xy with respect to any arbitrary will be equal to the Jacobian yx that means just opposite you know like kind of thing fancy another property you can do also you can say the Jacobian xy with respect to pr is equal to - Jacobian yx with respect to pr that is the meaning and the another interesting the Jacobian xy with respect to pr can be equal to 0 I mean you can put this here in this expression and do that yourself right.

For example if you want to this thing I can show you that this Jacobian xx Jacobian xx with respect to pr will be equal to $\partial x / \partial p$ into $\partial x / \partial x$ - $\partial x / \partial p$ into $\partial x / \partial x$ so if you look at this is 1 this is 1 so therefore this is equal to 0 right you can get very easily these are the things you can verify by using that relationship so if I say that you know z is a function of xy and z is the thermodynamic property and it can be you know it can be a property thermodynamic only when it is exact that we have you know learned in the very beginning and from.

Then I can write down dZ is equal to $\partial z / \partial x$ when y the remaining constant into dx + $\partial a / \partial y$ x remaining constant into dy so I can write on this thing in terms of Jacobian obeys like this is a differential form right and this is a Jacobian form I can write down those eight by $\partial x /$ using this

second relationship like by using this relationship I can write down very easily here right $\partial z / \partial x$ is nothing but Jacobian z_y with respect to xy and similarly $\partial z / \partial y$ when x remaining constant.

We can write down the Jacobian z_x with respect to yx is a very easy to convert that you know partial derivative to the Jacobian obeys and equation 1 this you can write down as a dz is equal to $Mdx + Ndy$ because we want to you know consider see that whether it is a property or not and for that it should be exact so therefore what we will have to do we will have to basically put these conditions you know like kind of things that is basically to $M / \partial y$ when x is constant equal to $\partial n / \partial z$ when x is constant that we have seen so keep in mind that M is basically Jacobian z_y with respect to xy and whereas N is Jacobian z_x with respect to yx .

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$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$
 Dividing the above Eq. by da , keeping b constant, we get

$$\left(\frac{\partial z}{\partial a}\right)_b = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial a}\right)_b + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial a}\right)_b$$

$$\frac{(z,y)}{[a,b]} = \frac{-(z,y)}{[x,b]} \frac{(x,y)}{[a,b]} + \frac{(z,x)}{[y,b]} \frac{(y,x)}{[a,b]} \quad \text{--- (2)}$$

$$\Rightarrow [x,y][z,b] + [y,z][x,b] + [z,x][y,b] = 0$$
 Eq. (2) can be rewritten as $\frac{[z,b]}{[a,b]} = M \frac{[x,b]}{[a,b]} + N \frac{[y,b]}{[a,b]}$
 where, $M = \frac{[z,y]}{[x,y]}$, $N = \frac{[z,x]}{[y,x]}$. Then, $[z,b] = M[x,b] + N[y,b]$
 Applying the above property of Jacobian to Gibbs Relationships

$$du = Tds - Pdv; \quad [u,x] = T[s,x] - P[v,x]$$

$$dh = Tds + vdP; \quad [h,x] = T[s,x] + v[P,x]$$

So and if we will divide this equation by da right so I can write down that $\partial z / \partial a$ when b is constant we are keeping the b constant is equal to $\partial a / \partial x$ and y remaining constant into $\partial x / \partial a$ when y remaining constant + $\partial a / \partial y$ when x is remaining constant into $\partial y / \partial a$ when x remaining constant so this you can write down in the Jacobian form right which are very easily which we have seen that by using the Jacobian rule you can write down the Jacobian form so in that what you can do you can write down in a very simple expression how because what you will do you can multiplied here.

What you call let us say I will multiply it by here that xy Jacobian right and if I multiply by this then if you look at all our remaining constant but now what we will do we will have to see that

xy heavy and here also if I want to then I can say this as a minus I can say this is x this is dead and here it is minus and similarly I can also put it here minus and write down in place of this y in place of z, so I can take all these things to the from the right hand side to the left hand side I can write down very easily this expression right.

Because this is same as that you know it will go to left hand side it became positive so you can write down which is a very simple expression kind of things in a Jacobean form. So if you look at this can be written as that you know this equation 2 can be written as the informs of M I have introduced where M is the Jacobian z,y with respect to xy and N is Jacobian z,x with respect to yx then we can write down this basically the Jacobian $z,b=M$ Jacobian $x,b+N[y,b]$ right.

And if you look at we know this gives equation that is $du=Tds-Pdv$ right, if you observe this equation basically it is the change in internal is it dependent on the entropy and also the specific volume I can write on u is a function of s and v right, so if you look at if I want this to be a property right we can do that but similarly we have seen also the give second equation $dh=Tds+vdP$ this we have already derived earlier right and applying this you know above property of the Jacobian to gives relationship we can write down as $u [u,x]=T [s,x]-PX - P[v,x]$ right.

We can take x is the arbitrary we are taking variables and similar way we can write down also for enthalpy right.

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Thermodynamic Potentials

What are the thermodynamic potentials that can have capability to do work ?

- Internal Energy, u
- Enthalpy, h
- Helmholtz potential, a
- Gibbs potential, g

These are the potential (properties) of the system which cannot be measured directly.

Only 3 properties such as P , v , T can be measured directly.

For a pure substance in single phase, a thermodynamic potential can be expressed as function of 2 other properties.

So if you look at by this we can we will be using basically how to handle the Jacobian how you will convert the partial derivative into Jacobians and now we will be looking at you know thermodynamic potentials, so question arises what do mean by potential? Potential always you know basically to ability to do work you know is basically tell you that what is the potential to work and what are the properties we can think of that as an ability to do the work any idea.

So if you recall that first law of thermodynamics we looked at it right, what it is doing if you look at even the objective of the classical thermodynamics is to convert the microscopic form of energy into macroscopic form. So when you talk about this macroscopic form of energy we use basically internal energy right, and internal energy is having ability to do work and that is the first law of thermodynamics derived from there right, okay.

Rather the internal energy is defined in the first law of thermodynamics right is a property of the system so if you as a matter of fact the most natural you know like thermodynamic potential is the internal energy which is the rest of the things are derived from that and the thermodynamic properties are internal energy enthalpy, Helmholtz potential and gives potential of course there is a grand potential which will not be discussing about it right.

But will be discussing about these four potentials only that is that will be basically tell us the ability to do the work. So these potentials of the system which cannot be measured directly because these are the properties i have already told earlier that you cannot measure directly you can measure pressure, volume, temperature or specific heat you know isothermal compressibility


and others but you cannot measure and whereas for simple compressible substance you know like we need these kind of things potentials to be utilized.

And we are having three properties pressure volume temperature that can be measured directly that means we need to express this thing in terms of what we call the properties that is measurable. And as I told that for a pure substance in a single phase a thermodynamic potential has to be expressed you know in terms of two other properties we have already seen that right.

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Thermodynamic Potentials

Internal Energy:
 Suppose, a system undergoes a change of state during an adiabatic process. in $dq = 0$



Applying First Law of TD, $du = -dw$

As a decrease in u represents potential to do work, u is called **Thermodynamic Potential.**

As per First Law of TD We know: $du = dq - dw$ --- (1)

As per the 2nd Law of TD, we know, $\frac{dq}{T} = ds \Rightarrow dq = Tds$ --- (2)

Hence, by combining Eqs. 1 and 2 for a reversible process, we can have;

$du = Tds - Pdv$ --- (3)

$dw = PdV$

So as I told the internal energy is basically a one of the thermodynamic potential and let us consider a system undergoes a change during an adiabatic process you can think of our simple piston cylinder arrangement you know like kind of things let us say it is having some gas right and this is our system so it is you know at a very high pressure let us say $P_1 T_1$ and ambient pressure is P_0 kind of thing and P_1 is greater than P_0 so then when it will release this piston then piston will move right there will be expansion so there is some work being done right.

And of course if we are saying adiabatic then what will happen to the change in internal energy right will be basically the work done right, so we can apply the first law of thermodynamics that is equal to $du = -dw$ because as is adiabatic process $dq = 0$ so therefore that clearly says you know that the internal energy is a thermodynamic potential because the change in internal energy is reflected in the change in work so work is done due to the change in internal energy and vice versa. So therefore that thermodynamic u is known as the thermodynamic potential.

And from the first law of course we know that $du=dq-dw$ and from second law we know that $dq/T=ds$ so therefore I can write down as $dq=Tds$ and if I can use this here you know Tds here I will get a relationship right that is $du=Tds-Pdv$ right, and this is we are saying Pdv work what can be other thing but we are saying this is Pdv work right dw is basically Pdv right, so this is the Gibbs first equation what we have earlier derived and this week and arrived again I am like and that clearly says indicates that the internal energy is basically a thermodynamic potential.

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Thermodynamic Potential :Enthalpy

Let us consider a turbine.

By applying 1st law of TD for CV of turbine :, we can have

$$\frac{dE}{dt} + \dot{m}_e \left(h_e + \frac{V_e^2}{2} + gz_e \right) - \dot{m}_i \left(h_i + \frac{V_i^2}{2} + gz_i \right) = \dot{Q} - \dot{W}_{sh}$$

$\Rightarrow W_{sh} = -(h_e - h_i)$

we know, enthalpy $h = u + Pv$

$$\Rightarrow dh = du + Pdv + vdP \quad ; \quad Tds = du + Pdv + vdP$$

$$du = Tds - Pdv \quad \text{-----(3)}$$

$$\Rightarrow dh = Tds + vdP \quad \text{-----(4)}$$

And let us look at enthalpy like let us consider a turbine right which is a flow work one can think of and we can apply the first law of thermodynamic for control volume of a turbine right, and we can apply basically the first law of thermodynamic for a control volume system of course this is the whole equation and we can assume it is a steady flow process so therefore this will be 0 and change in kinetic energy you know is 0 and change in potential energy also 0 we are considering for the simplicity and from the mass conservation I can write down $\dot{m}_i = \dot{m}_e = \dot{m}$ for a steady flow process.

So therefore the equation you know can be written as shaft work is equal to minus $h_e - h_i$ and keep in mind that we are considering this as a adiabatic process also right this is a 0 adiabatic process. So therefore we are considering change in you know enthalpy is nothing but your shaft work right, that indicates that enthalpy is basically thermodynamic potential and of course we know

that $h=u+Pv$ and therefore we can differentiate it that $dh=du+Pdv+vdP$ and already we know the Gibbs first equation that is equal to $du=Tds-Pdv$.

So therefore I can write down this as $Tds-Pdv+Pdv+vdP$ and this cancel it out so that comes to be basically $dh=Tds+vdP$ and this is your Gibbs second equation which we will be using this you know gives first equation, second equation and very you know very much and we will be looking at that.

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Helmholtz Free energy:

Let us consider a system interacting with the surrounding.

As per 1st law of TD, the work done by the system during a given process; $dw = dq - du$ — (1)

Let the surrounding be maintained at constant temperature, T_0

By 2nd law of TD, we know, $ds + ds_0 \geq 0$

But $ds_0 = -\frac{dq}{T_0} \Rightarrow ds - \frac{dq}{T_0} \geq 0 \Rightarrow dq \leq T_0 ds$ — (2)

Then the work done by the system is given by


$dw = dq - du; \quad dq \leq T_0 ds - du \Rightarrow w \leq (u_1 - u_2) - T_0(s_1 - s_2)$

For $(T_1 = T_2 = T_0)$, we can have, $w \leq (u_1 - T_0 s_1) - (u_2 - T_0 s_2) \leq a_1 - a_2$

where $a =$ Helmholtz Potential/ Function $= u - Ts$

$da = du - Tds - sdT \Rightarrow da = -sdT - Pdv$

But $du = Tds - Pdv$



And let us look at Helmholtz free energy of course what we will be doing generally people use Helmholtz potential as it must be energy but we will be discussing about that and what are the differences for that let us consider system interacting with the surrounding right, and we can apply the first law of thermodynamics to find out was done by a system during a given process right.

And that is equal to $dw = dq - du$ right, and let the surrounding we maintained at a constant temperature T_0 right ambient temperature and which is not affected by you no interaction with that. So because it is a very thermal reservoir you can say and if you we can apply the second law of thermodynamics that is changing you know entropy this is for the system right.

If you look at this is corresponding to the system right plus the change in entropy corresponding to the surrounding that is plus $b s_0$ is will be greater than equal to 0 right and what will be the change in vertical entropy because let us say there is a you know system like for example we can take this piston and cylinder arrangement kind of thing same thing whatever you have seen just now right there is my system and this is gas at p_1 and p_1 and the surrounding is T_0 right and it will be expanded I am like you know it can go when it will be release piston can move up and it can be expanded.

So then what will happen like there will be some heat can enter into here you know from the surrounding if you allow, so that is nothing but DQ so if you look at the heat is entering into the system right and that means it is coming from the surrounding to the system so therefore the sign will be negative in this case. So $de s$ not change in entropy for the surrounding will be minus dq divided by T_0 T_0 is the ambient temperature or the surrounding temperature then if I put this thing here you know in this equation that is $d s - B^3 / T_0 \geq 0$ right.

And therefore we can write on this as basically $DQ \leq T_0 d s$ and what we will do we will use this thing in the equation this equation one I can say and this is equation 2 right I can use this expressions ion for DQ from equation 2 to the equation 1 and when you do that I will get the work done you know as basically less than equal to $t TS - d$ right this we will know and that I can write down as because you know like work done will be less than $U_1 - U_2$ let us say from state 1 to state 2 - $T_0 s_1 - s$ to write one can think of writing one to basically right.

And then I can say that if it is $t_1 = t_2$ is T_0 we can write on that very easily as the work done between the what you call state 1 to 2 is basically $U_1 - t_1 s_1 - U_2 - t_2 s_2$ and this term is nothing but your A_1 that is Elmer's function this is known as L must function right this term was basically function or potential you can write right and similarly this portion also right that is a two and these change in Elmer's potential or the function is known as the L must free energy. So


if you look at the total this portion is known as free energy of course in there some book people who use interchangeably right.

But whenever we talk about free energy is a change in the Elmer's potential right so and the Elmer's potential as I told you-PS that is the Elmer's potential at all so therefore I can write down this as da is equal to d u - TDS - SDT I am just differentiate this you know and I can do that and but whereas the D u = TDS - PDV. So if I can write down here TDS - TDS right -PDV - SD t so this will cancel out right this will cancel it out.

So therefore I will be getting the DA = -s DT - PDV right so this is again the similar to what we have derived for the internal energy and enthalpy and this is of course the gives sorry this is of course the Elmer's free energy and in the similar manner we are going to also derived the what you call the Gibb's free energy that is a change in Gibbs function or the potential.

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Gibbs Free Energy:

Let us consider a system which is operating under steady state flow through a control volume. 

Assumptions: $\Delta KE = 0, \Delta PE = 0, \frac{dE}{dt} = 0; m_1 = \dot{m}_e = \dot{m}$

$$\frac{dE}{dt} + \dot{m}_e \left(h_e + \frac{V_e^2}{2} + g z_e \right) - \dot{m}_1 \left(h_1 + \frac{V_1^2}{2} + g z_1 \right) = \dot{Q} - \dot{W}_{20}$$

$\Rightarrow w_{sh} = q - (h_e - h_1)$ ----- (1)

If the CV receives heat energy from surrounding at T_0 Then, $\Delta s_0 = -\frac{q}{T_0}$

By 2nd Law of TD, $\Delta s + \Delta s_0 \geq 0 \rightarrow \Delta s - \frac{q}{T_0} \geq 0 \Rightarrow q \leq T_0(s_e - s_1)$ ----- (2)

Combining Eqs. (1) & (2), we will get

$$w_{sh} \leq T_0(s_e - s_1) - (h_e - h_1)$$
 ----- (3)

For $(T_i = T_e = T_0)$, $w_{sh} \leq (h_1 - T_0 s_1) - (h_e - T_0 s_e) \leq (g_1 - g_e)$

where $g =$ Gibbs Potential = Gibbs Function = $h - T s$

$$dg = dh - T ds - s dT \Rightarrow dg = v dP - s dT$$
 ----- (4)

$\Rightarrow dh = T ds + v dP$

Gibbs free energy
 $g = g(P, T)$

So let us consider a system which is operating under steady state flow and three control volume you can talk think of about a turbine kind of things you know like you can think of it turbine right which is you know flow is coming Chloe's going out of course this is having a shaft you know kind of things the turbine. So we can apply the first law of thermodynamics for a steady flow process.

So therefore this will be equal to 0 and change in kinetic energy will be 0 and change in potential energy 0 kind of things and of course we know this mass flow rate you know like a steady flow process therefore $\dot{m} \cdot I = \dot{m} \cdot e = \dot{m} \cdot w$ and you can divide this equation by this mass flow rate and you will get an expression as what you call w_{shaft} is equal to $Q - H_E - H_I$, so this is from the first law of thermodynamics and this work done is per unit mass also the change in enthalpy too so also the heat interaction per unit mass all are per unit mass.

So if the you know control volume receives heat energy from the surrounding T_{naught} then we can write down change in entropy is equal to $-q / T_0$ right that we have already seen for the control auto cal mass system and we know from the second law of demand change in entropy of further system plus the change in entropy for the surrounding its surrounding greater than equal to 0.

So we can write down then $\delta s - Q / T_0 \geq 0$ so therefore $Q < T_0 \times \delta s$ in this case basically $AC - s$ I write this we have already derived similar you know expression for so when you combine this equation one and equation two then we can you know right on the shaft work is basically less than T_0 into change in entropy between the exit and inlet minus the change in enthalpy between the exit and the inlet right.

So therefore you know we can also make this thing that $TI = PE = T_0$ we can say that the shaft work will be less than $H_I - P_I S_I$ - of course there is another the same thing like change in you know like a enthalpy and then $T_0 \times SC$ and this we call it as a Gibbs function or the potential right and that is G is basically $h - T_s$ keep in mind that this Gibbs function is being very much used for the chemical systems kind of things and this change in the gifts or to call gives function this portion we can call it as it basically Gibbs free energy right.

And G is a Gibbs potential that is the only difference and because it says that you know the potential having to do the work and we can derive you know we can differentiate this gives a function and $DG = D H - TDS - SDT$ and we know this give second equation $DH = tds + VDP$ and we can write down that as equal to $TD s + VDP - TDS - SDT$ so this will be cancelled it out so I can get expression as DG is equal to VDP minus SDT .

So if you look at this for expression like this we have derived you know one is for internal energy change other is for the enthalpy change and we have also derived for the hell mass

function and or the potential and Gibbs function rate and all are if you look at you know some of them are function of you know entropy and specific volume and some of them also function of pressure and temperature like the Gibbs free energy change.

So I can write down here also G is a function of basically P and T , so we will be using this expression for relating this what you call major rural properties with the un measurable or non measurable properties like that we will be doing in the next class and for that we will be deriving some relationship right and we will be using that, so thank you very much for your kind attention.

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Prof. Satyaki Roy

Co-ordinator, NPTEL IIT Kanpur

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