Applied Thermodynamics for Engineers
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Lecture - 05
Thermodynamic Potentials and Maxwell Relations

Good morning friends. Welcome to the second module of our course where we are going to discuss about the thermodynamic property relations. In previous week, we have basically reviewed the fundamentals of thermodynamics over four lectures where starting from the basic definition of a thermodynamic system we went on to discuss the concepts of entropy and exergy.

And there you have learned that for a proper thermodynamic analysis of any system, open or closed, we need to apply both first and second law of thermodynamics because first law provides an energy balance thereby relating the change in the stored energy of a system to the corresponding energy interactions between the system and surrounding. However, first law fails to provide any direction to the process.

And therefore, only reliance solely upon the first law may lead to the situation like a PMM-II. Therefore we also have to apply the second law of thermodynamics to understand the realistic direction of any particular process and also to understand the theoretical limit of operation of any thermodynamic device, a heat engine or reversed heat engine or any other similar kind of thermodynamic device for which using the concept of second law of thermodynamics or maybe the exergy we can define a second law efficiency. Thereby, we shall be able to understand the performance or able to compare the performance of any device in terms of the maximum possible performance instead of some ideal performance. And there in course of those thermodynamic analysis, the application of energy concepts or exergy balance, we had to make use of several kind of properties.

And this particular module, we are going to discuss about the options of identifying some of the most crucial properties that we have to make repeated use of in course of thermodynamics.

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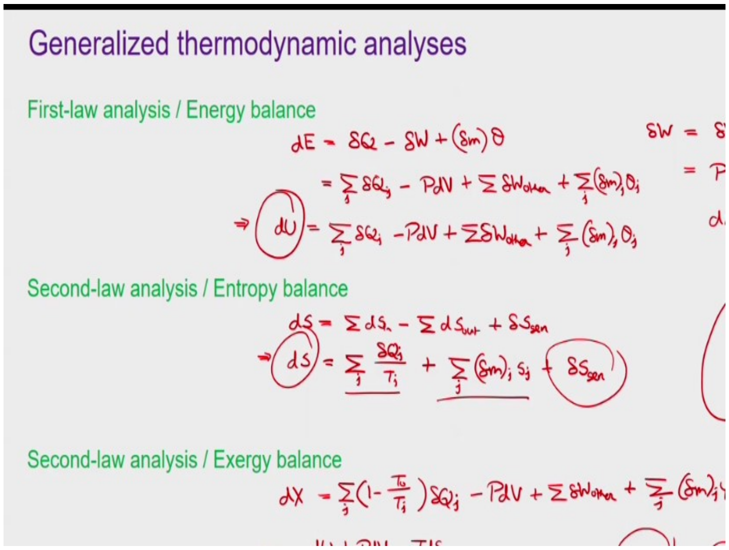

Generalized thermodynamic analyses

First-law analysis / Energy balance

$$dE = \delta Q - \delta W + (\delta m)\theta$$

$$= \sum_j \delta Q_j - PdV + \sum \delta W_{other} + \sum_j (\delta m)_j \theta_j$$

$$\Rightarrow \boxed{dU} = \sum_j \delta Q_j - PdV + \sum \delta W_{other} + \sum_j (\delta m)_j \theta_j$$

Second-law analysis / Entropy balance

$$dS = \sum dS_{in} - \sum dS_{out} + \delta S_{gen}$$

$$\Rightarrow \boxed{dS} = \underline{\sum_j \frac{\delta Q_j}{T_j}} + \underline{\sum_j (\delta m)_j s_j} + \boxed{\delta S_{gen}}$$

Second-law analysis / Exergy balance

$$dX = \sum_j \left(1 - \frac{T_0}{T_j}\right)\delta Q_j - PdV + \sum \delta W_{other} + \sum_j (\delta m)_j$$

Now, the previous lecture or I should say the previous week, the fourth lecture of module 1, I finished by mentioning about the balance equations of thermodynamics where for the application of first law we have to apply the conservation of energy principle whereas for performing a second law analysis, we can write either entropy balance or exergy balance. I did not spend too much time on this. Because I want to spend just a couple of minutes more on that now and therefore, I just decided to go through very quickly there.

Let us just start from that particular point onwards. So, we know that for any generalized thermodynamic system if we want to perform a first law analysis, we can write an energy balance or a principle of energy conservation. And for an infinitesimal process, the principle of energy conservation can always be written as rate of change of energy of the system (dE) to be:

$$dE = \delta Q - \delta W + (\delta m)\theta$$

where

δQ is rate of heat supplied to the system

δW is the rate of work done by the system

$(\delta m)\theta$ is the amount of energy supplied with the mass

It is very much possible particularly in case of open system that the system may involve multiple type of mass interactions and similarly multiple types of heat and work interactions. And also work interactions quite often we try to divide into two convenient forms, one is the moving boundary work and other is the any other kind of work such as electrical surface tension or anything related to kinetic or potential energies, whatever may be the other form of work that we generally like to group here just keeping the moving boundary work separately.

$$\delta W = \delta W_{mb} + \delta W_{other}$$

and moving boundary work we know for an infinitesimally small process can be represented as PdV. So, the work interaction can be represented as:

$$\delta W = PdV + \delta W_{other}$$

So, if you take that form then we can often represent this equation as summation of all kinds of heat interaction that is possible:

$$dE = \Sigma_j \delta Q_j - PdV + \Sigma \delta W_{other} + \Sigma_j (\delta m)_j \theta_j$$

where

Qj indicates that particular heat interaction that we are talking about

PdV is the moving boundary work associated with that particular process

$\Sigma \delta W_{other}$ summation over all other kind of heat interaction that may be there

$(\delta m)\theta$ is all possible kinds of mass interactions

Here, the direction of mass transfer is taken to be into the system. If we are talking about mass flowing out of the system, then there will be negative sign coming in. Now, let us just go into the expression for this dE.

$$dE = d\left(\frac{1}{2}mc^2 + gmz + U\right)$$

So, we know that the rate of change of energy for a system can be represented as a combination of three parts, the kinetic and potential energies which form the macroscopic part. So, this is kinetic and potential energies, the microscopic part in the form of internal energy and if we are talking about a stationary system which is the case for most of the thermodynamic system that we practically deal with, the changes in kinetic and potential energies can be considered to be 0 and also in most of the cases you will find that the change in internal energy is so much that the corresponding change in kinetic and potential energies can often be neglected.

And in that situation, this equation can be represented as just dU where this energy has only the internal energy part now:

$$dU = \Sigma_j \delta Q_j - PdV + \Sigma \delta W_{other} + \Sigma_j (\delta m)_j \theta_j$$

and the right-hand side is written as it is the equation for dE.

where

$\Sigma \delta Q_j$ is the summation of all possible heat interaction in the direction of Q taken to be into the system

PdV is the moving boundary work

$\Sigma \delta W_{other}$ summation over all other kind of heat interaction that may be there in certain special cases

$(\delta m)_j \theta_j$ is all possible kinds of mass interactions

This is a general equation, there can be several possible simplifications of this equation like if we are talking about a closed system, then this part, $(\delta m)_j \theta_j$ will not be there. If we are talking about an adiabatic system, then this part, $\Sigma \delta Q_j$ will not be there. If we are talking about a simple compressible system, that means it can produce work only in the form of moving boundary work, then this δW_{other} will not be there.

But of course, I have strike out three does not mean that all these three parts will go off, each of the three parts can be retained or may not be. Like in certain situations, if there is no moving boundary work, then this PdV may also go off. So, while there are four terms, I am just going back to the original equation, there are four terms on the right-hand side but all four are hardly present in practical situations. And we have to choose whichever we need to talk about but the left-hand side is dU for a stationary system which is always retained.

Now, let us go to the second law analysis based upon the entropy or exergy. So, we can perform second law analysis based upon entropy generation concept or entropy balance and similarly by exergy balance. So, if we perform an entropy balance, then as we have written in the previous lecture.

So, total change in entropy of a system can be considered to be the entropy coming in i.e., dS can be expressed as:

$$dS = \Sigma dS_{in} - \Sigma dS_{out} + \delta S_{gen}$$

where

ΣdS_{in} is the summation of all the sources of entropy into the system

ΣdS_{out} is the summation of all sources of entropy moving out of the system

δS_{gen} is entropy generation

Here, we are putting the 'δ' sign in front of entropy generation because that depends on the process. If we are talking about a reversible process, the entropy generation will not be there.

Or we can write this equation, considering all possible types of entropy flowing into a system or out of the system as:

$$dS = \Sigma_j \frac{\delta Q_j}{T_j} + \Sigma_j (\delta m)_j s_j + \delta s_{gen}$$

where

($\delta Q_j/T_j$) is the entropy coming in with heat transfer. Again, there may be several possible types of heat transfer, there is no entropy transfer with work transfer, whether it is moving boundary work, any other kind of work there is no entropy transfer but there will be entropy transfer with mass.

$\delta m_j s_j$ is the specific entropy of that corresponding mass

δs_{gen} is the entropy generation part.

So, once we have knowledge about the amount of heat interaction and mass interaction, the system is subjecting, we can easily calculate these terms. Again, if we are talking about a closed system, then the mass related term will not be there. If we are talking about an adiabatic situation, the first term will not be there. Whereas if we are talking about a reversible process, then the entropy generation will not be there. But the left-hand side is dS which is the change in entropy which is always there.

Similarly, if we talk about the exergy balance, then the change in exergy for a system, as per the equation, that can be the amount of exergy coming with the heat.

$$dX = \Sigma_j \left(1 - \frac{T_0}{T_j}\right) \delta Q_j + -PdV + \Sigma \delta W_{other} + \Sigma_j (\delta m)_j \psi_j - \delta X_{des}$$

where

T_j is the temperature at which this δQ is j is supplied

$W_{othe}r$ is the other kind of work interaction

$\Sigma \delta m_j \psi_j$ is all possible kinds of mass interaction

X_{des} is the exergy destruction which is again dependent on the process.

Now, what is the expression for this ψ? Or if we just think about the expression for this X, the change in the exergy of our system, then how we can relate this? If you remember, the way we have represented the change in exergy for a stationary system, then we know that this $\mathrm{d}X$ can be represented as:

$$\mathrm{d}X = \mathrm{d}U + P\mathrm{d}V - T\mathrm{d}S$$

for a closed system
whereas for an open system, it was:

$$\mathrm{d}X = \mathrm{d}H - T\mathrm{d}S$$

So, now look at all these expressions and you will find a particular trend that in all the cases, the terms that are appearing on the right hand side of the equations that generally depends upon the interactions that we are talking about, like the heat interaction or work interaction or mass interactions which we generally can calculate by considering the system surrounding exchange that is happening.

The specific nature of the entropy generation or exergy destruction that can be calculated again by considering the nature of the process and these two are related to each other. So, if we calculate one, the other is also known. However, the terms which are appearing on the left-hand side, that which are actually properties of the system. Like on the left-hand side we are getting terms like the change in internal energy change, change in entropy.

If we are talking about the exergy, then we are getting terms like change in enthalpy, something like this. And therefore, we are mostly trying to express this equation ultimately in terms of the change in certain extensive properties like internal energy or enthalpy or entropy but the problem is there. These three properties that I have summarized here, none of them can be measured directly. Just think about a real-life situation.

If we want to identify exact physical state of our system, then you can easily calculate the pressure, temperature, volume, mass or using the value of volume and mass, you can calculate specific volume or maybe density. So, these are certain parameters which can be calculated or I should say measured very easily. However, the basic conservation equations of thermodynamics or basic balanced equation of thermodynamics we are getting not in terms of those properties rather in terms of these three properties: changes in internal energy, changes in enthalpy and changes in entropy. But none of them can be measured directly and that is where we need to develop certain kind of property relations where we can represent the change in these parameters in terms of the measurable parameters. So, in common thermodynamics, we generally can classify properties in two different manners.

Of course, one type of classification is intensive and extensive but here you are talking about the practical sense. Say, group of parameters like temperature, pressure, specific volume, mass, etc can be measured very easily, whereas parameters like internal energy, enthalpy, entropy, etc cannot be measured directly. So, the objective of this particular module that is thermodynamic property relation is to develop certain relation where we can represent this second group in terms of the first group.

Or we want to represent or develop mathematical relations where we can represent the internal energy, enthalpy and entropy or this kind of other properties in terms of the measurable quantities like temperature, pressure, specific volume, etc. And a second thing of importance here is that truly speaking we are not bothered about the absolute value of *U* or *S*.

We are trying to identify the change in this internal energy or change in this entropy or change in this enthalpy. So, what we are trying to develop now is relations not to have perfect value of these quantities rather to get the expressions of the change of them i.e., changes in internal energy or changes in enthalpy or changes in entropy and similar parameters which we are trying to develop in this particular module.

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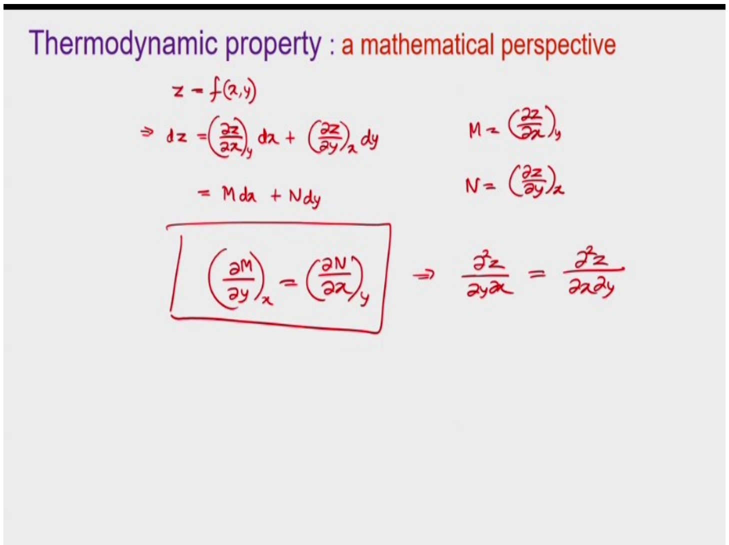

Thermodynamic property : a mathematical perspective

$$z = f(x,y)$$

$$\Rightarrow dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \qquad M = \left(\frac{\partial z}{\partial x}\right)_y$$

$$= M dx + N dy \qquad N = \left(\frac{\partial z}{\partial y}\right)_x$$

$$\boxed{\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y} \Rightarrow \frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y}$$

Before going to the derivation of that, I would like to go back to the thermodynamic property. Now, you know the definition of property which is any quantifiable characteristic of a system and so you may be thinking what else to discuss about that. You know the definition of property; you know different types of classifications; you already have idea about several kinds of properties and how to use them in relations.

We are not talking in thermodynamic point of view, rather we are trying to get a mathematical perspective of a thermodynamic property. Let us consider a parameter z which is a function of x and y.

$$z = f(x, y)$$

Now, here x and y represent two intensive, independent properties. Just remember the phase rule that we discussed in the very first lecture.

As far the phase rule, the state of our simple compressible system can be defined in terms of two independent intensive properties. That is once we specify two independent intensive properties; all other properties of the system at that particular state can be calculated. So, in this module actually we are looking to calculate those property relations or certain of those property relations.

So, here x and y represent two independent intensive properties and we are trying to develop a way of understanding whether z is a property of the system or not. So, if we differentiate on both side, we can write z to be something like:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

It is a simple partial differential form. Let us write this as:

$$= Mdx + Ndy$$

where M is the first partial differential i.e.,

$$M = \left(\frac{\partial z}{\partial x}\right)_y$$

and N is the second partial differential i.e.,

$$M = \left(\frac{\partial z}{\partial y}\right)_x$$

Now, if z is a property, then what should be the mathematical relation between M and N? If M or z is a property then it is a very standard mathematical principle that for z to be an exact function of x and y or dz to be an exact differential, then we need to have:

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

because then only we are going to have:

$$\left(\frac{\partial^2 z}{\partial y \partial x}\right) = \left(\frac{\partial^2 z}{\partial x \partial y}\right)$$

So, this is the condition for *z* to be a perfect function or exact function of *x* and *y* and that is how we can identify any unknown parameter whether that is a property or not. Once, we have specified two independent intensive properties *x* and *y* and then we have represented *z* as a function of this *x* and *y*, then using the simple principle we can understand whether there is a property or not.

Because if *z* is a property then as per the phase rule, it must be an exact function of this *x* and *y*, provided *x* and *y* are independent and intensive. Let us see some examples.

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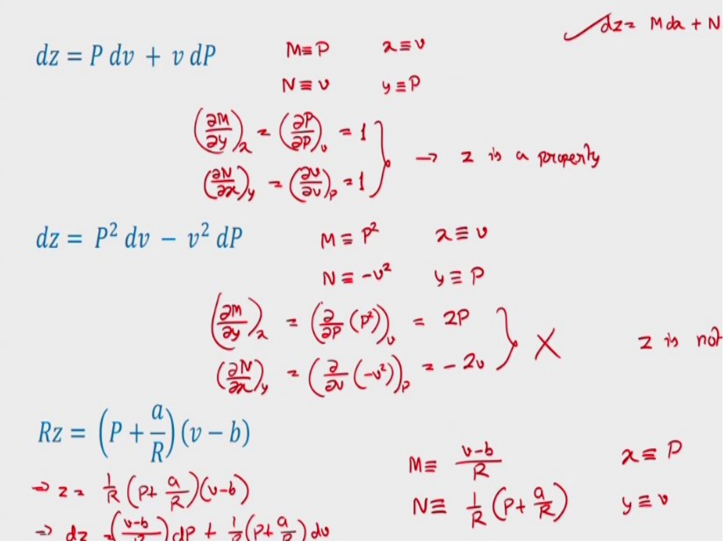

$\checkmark\ dz = M dx + N$

$dz = P\,dv + v\,dP$ $\quad M \equiv P \quad x \equiv v$

$N \equiv v \quad y \equiv P$

$$\left.\begin{aligned}\left(\frac{\partial M}{\partial y}\right)_x &= \left(\frac{\partial P}{\partial P}\right)_v = 1\\ \left(\frac{\partial N}{\partial x}\right)_y &= \left(\frac{\partial v}{\partial v}\right)_P = 1\end{aligned}\right\} \rightarrow z \text{ is a property}$$

$dz = P^2\,dv - v^2\,dP$ $\quad M \equiv P^2 \quad x \equiv v$

$N \equiv -v^2 \quad y \equiv P$

$$\left.\begin{aligned}\left(\frac{\partial M}{\partial y}\right)_x &= \left(\frac{\partial}{\partial P}(P^2)\right)_v = 2P\\ \left(\frac{\partial N}{\partial x}\right)_y &= \left(\frac{\partial}{\partial v}(-v^2)\right)_P = -2v\end{aligned}\right\} \times \qquad z \text{ is not}$$

$$Rz = \left(P + \frac{a}{R}\right)(v - b)$$

$\Rightarrow z = \frac{1}{R}\left(P + \frac{a}{R}\right)(v-b)$ $\quad M \equiv \frac{v-b}{R} \quad x \equiv P$

$\Rightarrow dz = \left(\frac{v-b}{R}\right)dP + \frac{1}{R}\left(P + \frac{a}{R}\right)dv$ $\quad N \equiv \frac{1}{R}\left(P + \frac{a}{R}\right) \quad y \equiv v$

This is our first example where we have taken

$$dz = P dv + v dP$$

and it is given that *P* and specific volume i.e., *v* are independent and intensive properties. So, we compare with this, so here:

$$M \equiv P$$

$$N \equiv v$$

Just remember the form that we had there, we had:

$$= Mdx + Ndy$$

So, we are trying to compare with that form. So, we got M and N, so:

$$x \equiv v$$

$$y \equiv P$$

Then,

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial P}{\partial P}\right)_v = 1$$

whereas now if we take by just putting the expressions for *N* and *x*, we have:

$$\left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial v}{\partial v}\right)_p = 1$$

These two are equal to each other and therefore we can say that this *z* is a property of the system. Let us take a second example.

So,

$$\mathrm{d}z = P^2\mathrm{d}v + v^2\mathrm{d}P$$

so if we compare in this one,

$$M \equiv P^2$$

$$N \equiv -v^2$$

$$x \equiv v$$

$$y \equiv P$$

So,

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial}{\partial P}(P^2)\right)_v = 2P$$

and

$$\left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial}{\partial v}(-v^2)\right)_p = -2v$$

and these two are not equal to each other.

So, z is not a property, as it is not satisfying the phase rule or it is not the exact function of this *P* and *v*.

A third example, here actually the differential form is not given rather z as a function of P and v is given.

$$Rz = \left(P + \frac{a}{R}\right) + (v - b)$$

So, first we have to convert this one into the differential form into a form like this. So, we write this as:

$$z = \frac{1}{R}\left(P + \frac{a}{R}\right) + (v - b)$$

Now, differentiate both sides, so we have:

$$dz = \left(\frac{v - b}{R}\right) dP + \frac{1}{R}\left(P + \frac{a}{R}\right) dv$$

If we compare with the exact form now or the standard form, here:

$$M \equiv \frac{(v - b)}{R}$$

$$N \equiv \frac{1}{R}\left(P + \frac{a}{R}\right)$$

$$x \equiv P$$

$$y \equiv v$$

So, if you calculate

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{1}{R}$$

then what will be that? as '*y*' is '*v*' *here*, so it will become *1/R* and similarly if you calculate, as your *x* is *P* here. So, if you differentiate *N* with respect to *P*,

$$\left(\frac{\partial N}{\partial x}\right)_y = \frac{1}{R}$$

then again you are going to get *1/R*.

So, these two are equal that means here *z* is a property. This way we can identify any parameter once we know the relation of this *z* with *x* and *y*, then we can easily identify it is a property or not. This particular formulation we are going to make use of in today's work.

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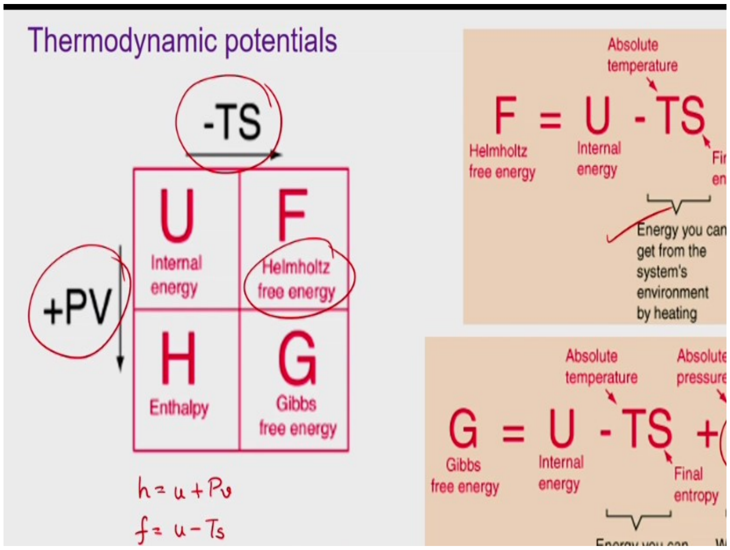

Thermodynamic potentials

-TS

+PV

U Internal energy

F Helmholtz free energy

H Enthalpy

G Gibbs free energy

$h = u + Pv$

$f = u - Ts$

Absolute temperature

F = U - TS

Helmholtz free energy

Internal energy

Fi
en

Energy you can get from the system's environment by heating

Absolute temperature

Absolute pressure

G = U - TS +

Gibbs free energy

Internal energy

Final entropy

Next, I would like to introduce you the concept of thermodynamic potential. The four symbols that I have listed here, two of them are already known to you *U* and *H* but other to *F* and *G* this put together are called the thermodynamic potentials because they represent the energy of a system under different situations. Here *U* is the internal energy and we know that this is the manifestation of the molecular activity of a system. Or you can say *U* is a representative of the energy required to create a system by virtue of the molecular activities and molecular orientation.

Then, what is enthalpy? We know to get enthalpy; we have to add this *PV* with *U* or if we write in here all symbols are shown in extensive sense. If you write in intensive sense, then we know that

$$h = u + Pv$$

where

v is specific volume

So, with internal energy we have to add this flow work and this flow work can be visualized as a work which you need to make some space for this particular system. So, enthalpy is representative of the amount of energy needed to create the system plus the amount of energy required to make some space for the system, this is enthalpy.

Then, what about this capital F? That is called the Helmholtz free energy, as shown here it is a Helmholtz free energy and it is represented as

$$F = U - TS$$

just follow these symbols. Once we subtract *'$-TS$'* then from this internal energy, we get this Helmholtz free energy or intensive sense if we write

$$f = u - Ts$$

In certain textbooks, symbol *'a'* is also used like the book that we are mostly following this course, the book of Cengel and Boles that actually uses *'a'* as a symbol.

Now, Helmholtz free energy means from the internal energy part that is the amount of energy needed to create the system you have to subtract this TS portion and this TS can be viewed as the energy that we get from the system's environment by heating. That is once the system is created because of its thermal non-equilibrium in the surrounding, some heat can flow from the surrounding to the system to get the thermal equilibrium back.

Here, s refers to the entropy of the system. So, this Helmholtz free energy is

$$U - TS$$

and you can visualize this as the amount of energy needed to create a system minus the amount of energy that the system is getting from the environment and finally G. So, what will be the expression for the G? Here, you have to subtract TS from H. So, this G in intensive sense is

$$\mathrm{g} = \mathrm{h} - \mathrm{Ts}$$

i.e.,

$$= u + pv - Ts$$

i.e., Gibbs free energy.

So, expression for your Gibbs free energy is:

$$G = U - TS + PV$$

where

U is the amount of energy needed to create the system

PV is the amount of energy needed to make space for the system

TS is the energy the system is getting from the environment.

So, these four together are called the potential of the system. Let me summarize this one,

$$h = u + Pv$$

$$f = u - Ts$$

$$g = h - Ts = u + Pv - Ts$$

and these four together are called the thermodynamic potentials of a system.

In the analysis that we are restricting ourselves, we generally have to use U and H but in certain situations particularly when talking about the chemical thermodynamics, this Helmholtz free energy and Gibbs free energy also comes into picture because there this amount of energy the system is receiving from the surrounding becomes important.

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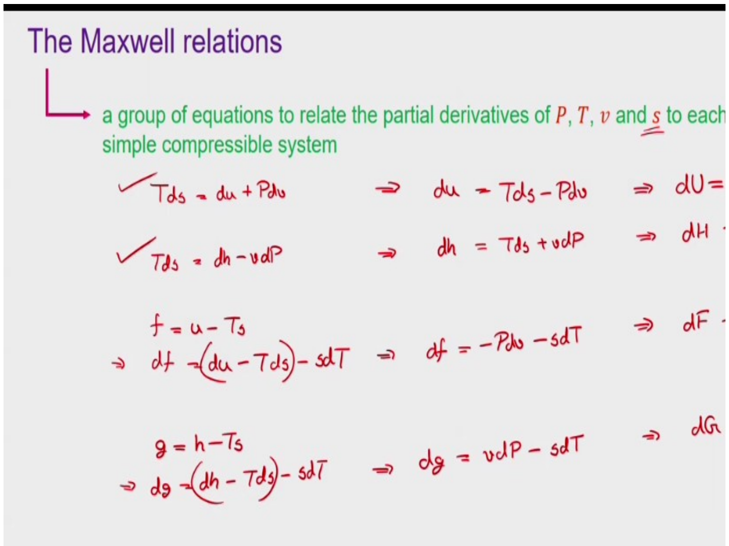

The Maxwell relations

a group of equations to relate the partial derivatives of P, T, v and $\underline{\underline{s}}$ to each

simple compressible system

✓ $Tds = du + Pdv \Rightarrow du = Tds - Pdv \Rightarrow dU =$

✓ $Tds = dh - vdP \Rightarrow dh = Tds + vdP \Rightarrow dH$

$f = u - Ts$

$\Rightarrow df = (du - Tds) - sdT \Rightarrow df = -Pdv - sdT \Rightarrow dF$

$g = h - Ts$

$\Rightarrow dg = (dh - Tds) - sdT \Rightarrow dg = vdP - sdT \Rightarrow dG$

Now, the one that we are looking to develop, the Maxwell's relation. Maxwell's relations are a group of equations to relate the partial derivatives of pressure, temperature, specific volume and entropy to each other for a simple compressible system. Look at the four properties you are talking about: pressure, temperature, specific volume and entropy. Now, out of this, the first three pressure, temperature, specific volume as I mentioned earlier can be measured very easily.

For most of the situations using simple instruments, we can measure each of the three. However, entropy is the one that we cannot measure that is only a theoretical definition. So, the Maxwell's relations actually provide an option to relate the change in entropy in terms of the changes in these three quantities by relating the partial derivatives of these four quantities.

And to develop the Maxwell's relations, there will be four equations that we are going to develop. We have to make use of the four thermodynamic potentials that I mentioned in the previous slide. Now, what was the first thermodynamic potential that was U. Now, I would like to take you back to the third lecture of this course where you develop a couple of tedious relations.

Do you remember those TdS relations or so-called Gibbs equations? I hope you remember the first equation was:

$$T\mathrm{d}s = \mathrm{d}u + P\mathrm{d}v$$

i.e.,

$$\mathrm{d}u = T\mathrm{d}s - P\mathrm{d}v$$

or if we write in terms of extensive properties:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V.$$

That was the first $T\mathrm{d}s$ relation.

What was the second $T\mathrm{d}s$ relation? It was:

$$T\mathrm{d}s = \mathrm{d}h - v\mathrm{d}P,$$

So, we can separate h out, the second potential as:

$$\mathrm{d}h = T\mathrm{d}s + v\mathrm{d}P$$

or if we write in extensive sense, it will be:

$$dH = T\mathrm{d}S + V\mathrm{d}P$$

So, we have got two equations representing the rate of change in the corresponding two potentials. Now, let me use the definition of the Helmholtz energy now. Now, what was your definition for Helmholtz energy? You had

$$a = u - Ts$$

i.e.,

$$\mathrm{d}a = \mathrm{d}u - T\mathrm{d}s - s\mathrm{d}T.$$

As I am more confident of writing this f writing in terms of a, let me stick to using f instead of '$\mathrm{d}u - T\mathrm{d}s$'

So,

$$\mathrm{d}f = \mathrm{d}u - T\mathrm{d}s - s\mathrm{d}T$$

Now we are replacing '$\mathrm{d}u - T\mathrm{d}s$' using '$-P\mathrm{d}v$' or in extensive sense

$$\mathrm{d}F = -P\mathrm{d}V - S\mathrm{d}T$$

So, we got now an equation representing the change in this Helmholtz free energy and hopefully you have understood what we are going to do next. We are going to use the expression for the Gibbs energy, Gibbs free energy, so

$$g = h - Ts$$

$$\mathrm{d}g = \mathrm{d}h - T\mathrm{d}s - s\mathrm{d}T$$

Now, replacing this '$\mathrm{d}h - T\mathrm{d}s$' we get:

$$\mathrm{d}g = v\mathrm{d}P - s\mathrm{d}T$$

That is in extensive sense, change in the Gibbs free energy

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T$$

So, here we have now four equations representing the change in each of the thermodynamic potentials.

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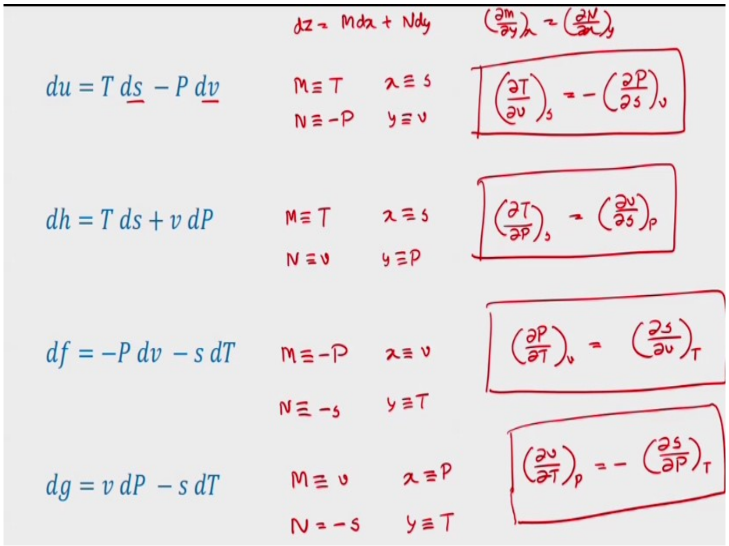

$$dz = Mdx + Ndy \qquad \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

$$du = T\,\underline{ds} - P\,\underline{dv} \qquad M \equiv T \quad x \equiv s \qquad N \equiv -P \quad y \equiv v \qquad \boxed{\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v}$$

$$dh = T\,ds + v\,dP \qquad M \equiv T \quad x \equiv s \qquad N \equiv v \quad y \equiv P \qquad \boxed{\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P}$$

$$df = -P\,dv - s\,dT \qquad M \equiv -P \quad x \equiv v \qquad N \equiv -s \quad y \equiv T \qquad \boxed{\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T}$$

$$dg = v\,dP - s\,dT \qquad M \equiv v \quad x \equiv P \qquad N \equiv -s \quad y \equiv T \qquad \boxed{\left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial s}{\partial P}\right)_T}$$

So, these are the four equations that we have now:

$$\mathrm{d}u = T\mathrm{d}s - P\mathrm{d}v$$

$$\mathrm{d}h = T\mathrm{d}s + v\mathrm{d}P$$

$$\mathrm{d}f = - P\mathrm{d}v - s\mathrm{d}T$$

$$\mathrm{d}g = v\mathrm{d}P - s\mathrm{d}T$$

Here, I have again represented each in their corresponding intensive sense.

We first consider the equation for internal energy:

$$\mathrm{d}u = T\mathrm{d}s - P\mathrm{d}v,$$

Now, as internal energy is a property, then if this s and v are independent intensive properties, they are intensive of course, they are written in intensive sense and if they are independent of each other, then we can use the previous principle.

So, I am rewriting that:

$$\mathrm{d}z = M\mathrm{d}x + N\mathrm{d}y$$

and if z has to be a property, we know that the principle is:

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

So, here what we have is:

$$M \equiv T$$

$$N \equiv -P$$

$$x \equiv s$$

$$y \equiv v$$

We know that internal is a property of the system, so we can directly write now using the principle that

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

that is the first Maxwell's equation.

Now, considering the second equation for enthalpy:

$$\mathrm{d}h = T\mathrm{d}s + v\mathrm{d}P$$

In the second case, we have:

$$M \equiv T$$

$$N \equiv v$$

$$x \equiv s$$

$$y \equiv P$$

So, from there what can we write? We know enthalpy is a property, so we can directly write this as:

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

Look at the third one, which is the one involving the Helmholtz free energy or change in the Helmholtz free energy:

$$\mathrm{d}f = -P\mathrm{d}v - s\mathrm{d}T$$

So, here what we have is:

$$M \equiv -P$$

$$N \equiv -s$$

$$x \equiv v$$

$$y \equiv T$$

So, from there what we can write:

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

The minus sign we can omit from here, so:

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

So, this is a third Maxwell's equation. Now, we have got three Maxwell's equations now. The first one from the internal energy expression, second one from the enthalpy expression, third one from the Helmholtz free energy expression.

And the last one from the Gibbs free energy expression:

$$\mathrm{d}g = v\mathrm{d}P - s\mathrm{d}T$$

where we have:

$$M \equiv v$$

$$N \equiv -s$$

$$x \equiv P$$

$$y \equiv T$$

So, if we write there, we have here:

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

So, this is the fourth Maxwell's equation.

These are the four Maxwell's equations, where we are relating the partial derivatives of these four quantities: temperature, pressure, specific volume and entropy.

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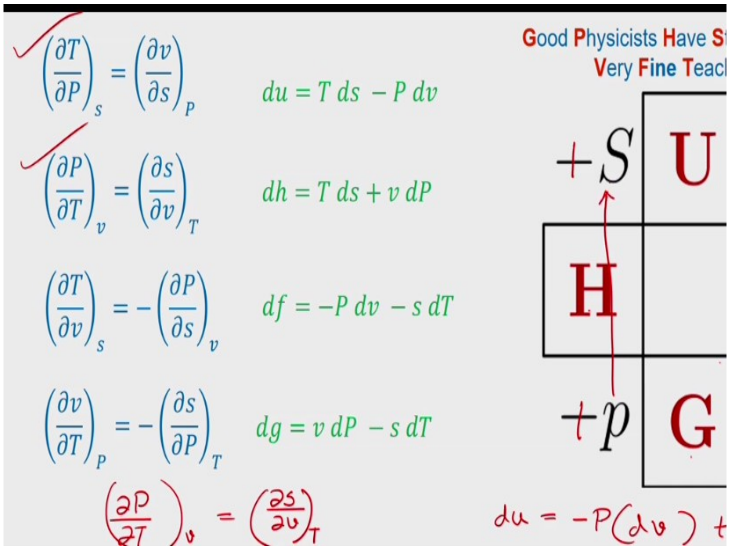

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P \qquad du = T\,ds - P\,dv$$

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \qquad dh = T\,ds + v\,dP$$

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v \qquad df = -P\,dv - s\,dT$$

$$\left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial s}{\partial P}\right)_T \qquad dg = v\,dP - s\,dT$$

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

$$du = -P(dv) +$$

This is a summarized view; I have just organized the equations in a different pattern. So, we have:

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

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

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

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

Seems complicated, right? Because you have to remember these equations. Of course, you now know how to derive them.

You can easily derive them, but there is actually a way of remembering these equations. I am just writing all the corresponding four Gibbs equations that are so called the Gibbs-Duhem equation for the four thermodynamic potentials that we have. So, I have the four expressions, actually it is not that these two are corresponding to each other because here we have changed the order of the Gibbs equations and also the Maxwell's equations.

We are just writing the equations as for our convenience. So, to get an idea about how to remember these equations, we make use of something that is known as the Maxwell’s square or thermodynamics square or mnemonic. Just see how we have written them in a square form. We have basically made a 9 ×9 grid inside square and the middle one is empty or the central one and other eight have been occupied by the eight terms that we are talking about.

Here, the middle ones are the four potentials and the corner ones are the four properties that we are using in these Maxwell's equations. Here, everything is written in extensive sense but commonly we use the intensive notation that is what I shall be doing. Before I am going to tell you how to use this, it is important to present the numbers in the particular order that is shown because otherwise there is no point remembering this.

You have to represent the symbols exactly the way that is presented there. And there are several kinds of mnemonics by which you can remember them, this is one of the sample.

Good physicists have studied under very fine teachers. So, good the G is there and then we go in the clockwise direction. So, we have *G P H*, we have *G P H S U V F* and *T* to finish.

So, just repeating it once, good physicists have studied under very fine teachers. There is nothing in between. So, this we will represent by going in the clockwise direction and making use of this particular mnemonic. This diagram I have taken from Wikipedia but similar kind of diagrams you can get from several other sources also and sometimes even in textbooks also. Now how to make use of this?

Let us first try to develop the Gibbs equation that is equations for the thermodynamic potentials using this. Let us take the example of this internal energy *U*. So, this is your internal energy. To write the expression for the change in internal energy, we have to see the two corners opposite to that, I mean there are two variables on either side of the *u*, do not look at that, look at that other two corners.

That is this one and this one, these two will be the coefficients of the expression. That is your expression will be of the form:

$$\mathrm{d}u = -P \times \mathrm{d}(\textit{of something}) + T \times \mathrm{d}(\textit{of something})$$

So, – *P* and *T* that is the terms which are appearing in the opposite corners will be the two coefficients. The terms which appear on the left-hand side like the *P* and *S* or left-hand side corners, they are generally will have this minus sign. Now, what will be going into the differentials? Into the differentials, we shall be using the terms which are adjacent to the *U*. So, for *P* we have to, when the coefficient *P* we already have like here, this particular part to get this we have to go to the diagonal, the one opposite to *P* which is *v*. So, write *v* here. Similarly, for getting *T* we have to go to the opposite of this which is *s*. We generally do not consider the negative sign while writing the differentials. So, it is :

$$\mathrm{d}u = T\mathrm{d}S - P\mathrm{d}v$$

is this equation.

Let us take another sample. Let us consider the *f*. So, if we want to consider or write this expression of d*f* then what will be our coefficients, to check the coefficients go to the two corners which are opposite to this. So, this is one of the corners and this is the other corner.

So, you know that these two will be the coefficients. So, one of the coefficients will be:

$$\mathrm{d}f = -S \times \mathrm{d}(\textit{of something}) + -P \times \mathrm{d}(\textit{of something})$$

To identify what goes inside this, then for S, you have to go to the opposite corner that is it will be dT, for P you have to go to the opposite corner that will be equal to dv. So it is:

$$\mathrm{d}f = -S\mathrm{d}T + -P\mathrm{d}v$$

Look at this is the expression:

$$\mathrm{d}f = -P\mathrm{d}v - S\mathrm{d}T$$

Can you work out anything else following the same pattern?

So, if we want to write say for dg what it will be? For g, you have to identify both the opposite corners. So, opposite corners are V and S or $-S$. So, we will be having:

$$\mathrm{dg} = \mathrm{v} \times \mathrm{d}(\mathit{of\ something}) + s \times \mathrm{d}(\mathit{of\ something})$$

for v what will be there, opposite to v is $-P$. Now, I will write in differential, so you do not consider the minus sign. So, it will be:

$$\mathrm{d}g = v\mathrm{d}P - s\mathrm{d}T$$

which is this expression.

So, this is how we can make use of this square to develop the expressions for all these four Gibbs-Duhem equations. Now, what about the Maxwell's relations? The first four that are more complicated to remember. To develop these relations, let us just drop the minus sign for the moment. So, let us consider for these two, $+s$ and $+v$. So, the rule of developing these relations is we have to go either in the horizontal direction or in the vertical direction.

And let us speak up, say, P and we move in the horizontal direction from P. Then, we shall be writing:

$(\partial P/\partial T)$ it is something that is constant that will be equal to go to the other arm so parallel to P is s so we shall be going here also in this direction, it will be equal to $(\partial s/\partial \mathrm{v})$ i.e.,

$$\left(\frac{\partial P}{\partial T}\right)_{somet\ hing} = \left(\frac{\partial s}{\partial v}\right)_{somet\ hing}$$

And what will be the constants or subscripts? For P, the first one that we have written, we have started with P so we have to check the diagonal to that. So, subscript will be v. Similarly, for s you have to go to the diagonal which is T. Have you seen this relation? This is the one that we are talking about. Similarly, for developing the second one, we can again go in the horizontal direction but now starting from the right moving to the left. So, for the bottom row, we have $(\partial T/\partial P)$ with what will be the constant, the one in the diagonal of T, so that is s.

That will be equal to what? Can you guess? We are moving along the horizontal line from the right to the left, so we have started with *T* and moved to *P*. So, go to the parallel row which is (∂*v*/∂*s*) and the subscript will be the one opposite to *v* or the diagonal opposite to *v* which is *P* which is the first relation. So, this way we can develop or recover two of the relations.

Now, how to get the other two? To get the other two, we have to make use of the verticals. Let us move from this, from *P* to *s*, similarly from *T* to *v*.

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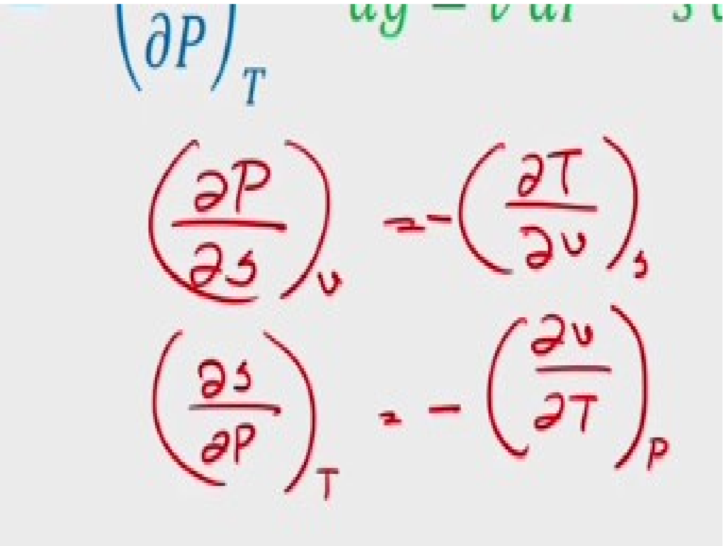

$$\left(\frac{\partial P}{\partial s}\right)_v = -\left(\frac{\partial T}{\partial v}\right)_s$$

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

So, we shall be writing (∂*P*/∂*s*), now you know what to put in a corner, so we are starting with *P*, so diagonal opposite is *v* that will be equal to (∂*T*/∂*v*) and diagonal opposite to *T* is *s* but one exception. When you go in the vertical direction, you put a minus sign before that. So, what do you have here? Have you got this relation? This is the relation that we are talking about:

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

Similarly, now if we come from top to bottom that is starting from *s* moving to *T*, similarly from *v* moving to *T*. So, we have:

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

and this is the fourth relation that we have developed.

So, if you make judicial use of this square, you can easily recover each of the four Gibbs equations and the four Maxwell's equations and subsequently can make use of that. Try to remember this equation.

I have provided you enough options of remembering this like this is one of the mnemonics that we generally follow and using this, only thing that you have to remember or only two things, one is this mnemonic and then moving in the clockwise direction. Once you go in the clockwise direction starting with *G* at the bottom you can easily get this.

So, these are the Gibbs equations and subsequent Maxwell's relations where we are finding an option of relating the derivatives of entropy with temperature, volume, specific volume and pressure. But we started with the objective of developing relations of d*u*, d*h* and d*s*. Of course, Gibbs equations are there but that like if you see here the equation for d*u* also incorporates d*s*, similarly, d*h* incorporates d*s*. So now we have to make use of this Maxwell's relation to update this Gibbs equation so that we can replace this d*s* and write this only in terms of *T, P* and *v*.

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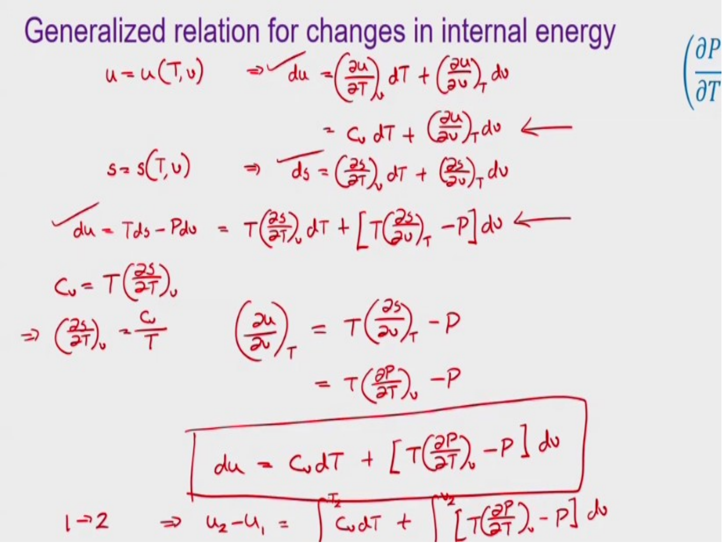

Generalized relation for changes in internal energy

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

$$= C_v\, dT + \left(\frac{\partial u}{\partial v}\right)_T dv \leftarrow$$

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

$$du = Tds - Pdv = T\left(\frac{\partial s}{\partial T}\right)_v dT + \left[T\left(\frac{\partial s}{\partial v}\right)_T - P\right] dv \leftarrow$$

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

$$\Rightarrow \left(\frac{\partial s}{\partial T}\right)_v = \frac{C_v}{T} \qquad \left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - P$$

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

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

$$1 \rightarrow 2 \Rightarrow u_2 - u_1 = \int^{T_2} C_v dT + \int^{v_2} \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] dv$$

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

So, let us try to develop some generalized relations for changes in internal energy. For that, let us assume

$$u = f(T, v)$$

i.e., temperature and specific volume are the two independent intensive properties that we are choosing. So, we can write:

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

Now, what is your ($\partial u/\partial T$)? If we apply the first law of thermodynamics for a closed system, closed stationary system we know that:

$$\mathrm{d}u = \delta q - \delta w$$

We have written everything in per unit mass sense, and if we are talking about a simple compressible stationary system,

$$\delta w = P\mathrm{d}v.$$

If you separate out δq from there, what will be δq?

$$\delta q = \mathrm{d}u + P\mathrm{d}v$$

And if we are talking about a constant volume process now, then there is no moving boundary work which means

$$P\mathrm{d}v = 0$$

which gives

$$\delta q = \mathrm{d}u$$

During a constant volume process δq can be represented as

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

that means

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

where C_v is the coefficient or specific heat at constant volume.

Putting this in the initial expression for du i.e.,

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

We get,

$$du = C_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

Now, we take entropy as a function of the same two intensive properties T and v *i.e.,*

$$S = f(T, v)$$

So, we can write:

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

Now, we know that Tds equation is:

$$\mathrm{d}u = T\mathrm{d}S - P\mathrm{d}v$$

So, if we put this expression for ds there, so we have du as:

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

I am doing several calculations here. My suggestion is you keep on doing parallel to me, so that you can immediately grasp what I am doing. Of course, you do not have the option of asking me to repeat anything directly, but you can pause the video and go back wherever you have some confusion. Now, you have one expression for du here (initial equation), another expression for du here (last equation) and you can see on the right-hand side here your coefficients or terms are dT and dv, similarly, in the second case also you have dT and dv.

So, if you compare the coefficients of dT then you can write:

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

or

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

This one, we shall be using in the next lecture when we develop generalized relations for entropy. Let us take the second part. So, we have:

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

Now, we make use of this particular Maxwell's relation and accordingly we can substitute this:

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

i.e.,

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

So, combining this with the original expression, we now have:

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

So, what do we have now? Look at the left-hand side, here we are talking about the changes in internal energy or specific internal energy whereas what we have on the right-hand side, we have specific volume or specific heat at constant volume, C_v on one side and we only have temperature, pressure and specific volume. So, if we know the PVT relationship of any particular substance, like an equation of ideal gas equation of state etc you can easily calculate the changes in internal energy using that knowledge and also the knowledge of this C_v.

If we integrate this, we are talking about a process moving from 1 to 2 then you can easily calculate the change in internal energy

$$u_2 - u_1 = \int_{T_1}^{T_2} C_v dT + \int_{v_1}^{v_2} \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] dv$$

where

T_1 is the initial temperature

T_2 is the final temperature

We shall be doing some exercise about how to use these relations in the next class but before that you try to repeat these calculations on your own just to develop this particular relation for these changes in internal energy.

Let us just follow the same procedure to quickly develop the relation for the changes in enthalpy.

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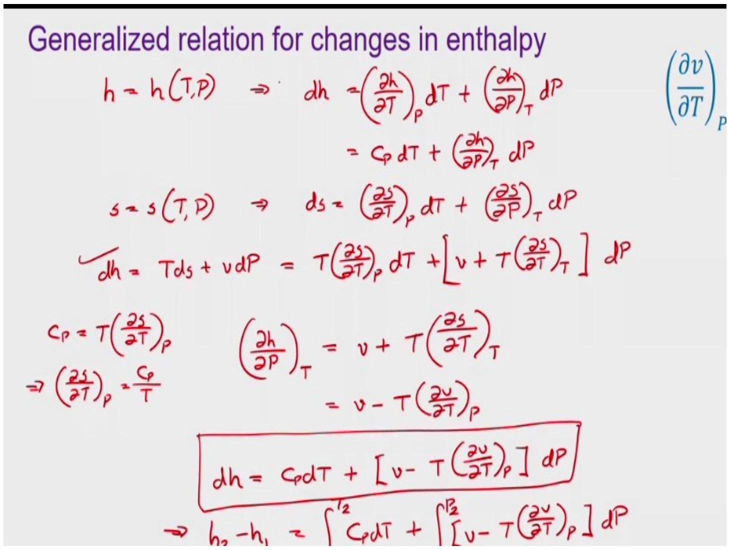

Generalized relation for changes in enthalpy

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

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

$$= C_p dT + \left(\frac{\partial h}{\partial P}\right)_T dP$$

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

$$dh = Tds + vdP = T\left(\frac{\partial s}{\partial T}\right)_p dT + \left[v + T\left(\frac{\partial s}{\partial T}\right)_T\right] dP$$

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

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

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

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

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

$$\Rightarrow h_2 - h_1 = \int^{T_2} C_p dT + \int^{P_2} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dP$$

Here, we shall be considering h to be a function of T and P, i.e.,

$$h = f(T, P)$$

We are following similar procedure, so I am trying to do a bit quickly. So,

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

and again, we can make use of the first law of thermodynamics for a simple compressible closed system where we can write:

$$\delta q = \mathrm{d}u + \delta w$$

$$= \mathrm{d}u + Pdv$$

when pressure is constant, we can write this one as:

$$= \mathrm{d}\,(u + Pv)$$

$$= \mathrm{d}h$$

So, for a constant pressure process, δq can be represented as:

$$C_p \mathrm{d}T = \mathrm{d}h$$

That means,

$$\left(\frac{\partial h}{\partial T}\right)_P = C_P$$

So, we substitute it in the initial expression for dh:

$$dh = C_p dT + \left(\frac{\partial h}{\partial P}\right)_T dP$$

So, what you should do next, like we have done in the previous case. If you are not sure, just go to the previous slide to check. We are going to consider entropy s as the function of T and P, i.e.,

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

so that you can make use of the Maxwell's relation.

So, we have,

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

Now, we make use of the second Gibbs equation where we have ,

$$\mathrm{d}h = T\mathrm{d}s + v\mathrm{d}P$$

$$= T\left(\frac{\partial s}{\partial T}\right)_P dT + \left[v + T\left(\frac{\partial s}{\partial T}\right)_T\right] dP$$

So, if you compare the two expressions for dh mentioned above,we get,

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

or

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

Again, make a note of this one, this one we shall be using in the very first slide of the next lecture.

But our interest is the second term that is a term which is the coefficient of d*P* where we have,

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

So, finally we get,

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

or during a particular process, the change in specific enthalpy can be represented as:

$$h_2 - h_1 = \int_{T_1}^{T_2} C_p dT + \int_{P_1}^{P_2} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dP$$

So, again by knowing the *PVT* relationship of a substance and from knowledge of how specific heat at constant pressure that is C_p varies with temperature, you can easily calculate the changes in enthalpy. So, this is the second relation. Again, my suggestion is, try to develop this particular relation on your own by repeating this particular exercise.

It would have been logical to develop the expression for changes in entropy where we shall be making use of this relation and the one, we developed in the previous slide or kept aside in the previous slide. But that I shall be doing in the next class so that I can allow you sufficient time to develop these two relations. So, please develop these relations for d*u* and d*h* and also the Maxwell's equations on your own.

And also try to remember or try to find a way about remembering that Maxwell square, so that you can make use of that in any subsequent discussion. So, I would like to stop here today.

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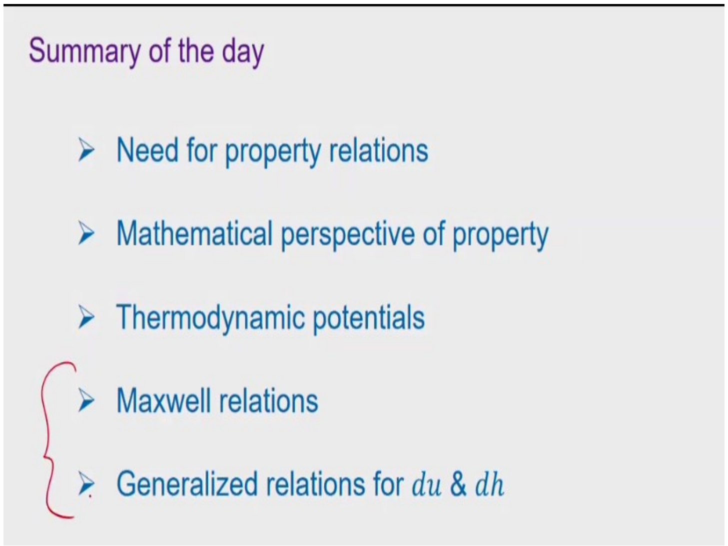

Summary of the day

- Need for property relations
- Mathematical perspective of property
- Thermodynamic potentials
- Maxwell relations
- Generalized relations for du & dh

Just to quickly summarize what we have done today, we have discussed about the need of developing property relations particularly the relations of changes in internal energy, enthalpy and entropy in terms of the measurable quantities like pressure, temperature and specific volume. Then, we have provided a mathematical perspective property, defined the four thermodynamic potentials like internal energy, enthalpy, Gibbs free energy and Helmholtz free energy.

Then, we developed four Maxwell's relations and generalized relations for du and dh and I repeat you try to develop this on your own because we have done a bit of method is quite simple mathematics following standard procedure but if you are not doing that on your own, you will not be able to remember that. So, try to do it on your own before moving to the next lecture.

So, that is it for the day, I would like to stop here and in the next lecture, we shall be discussing about developing the generalized relations for entropy to start with. Then, we shall be seeing how to use this for certain kind of substances and then we shall be talking about the specific heat, so thank you.