Engineering Thermodynamics
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Module 8
Lecture No 52
Thermodynamic property relations: Gibbs equation, Mnemonic diagrams and reciprocity relations

Ok welcome back uh, we are going to start a new topic, it is on thermodynamic property relation and essentially what we are going to do is, we are going to relate the changes in the partial derivatives of various different properties, we will try to connect these properties together.

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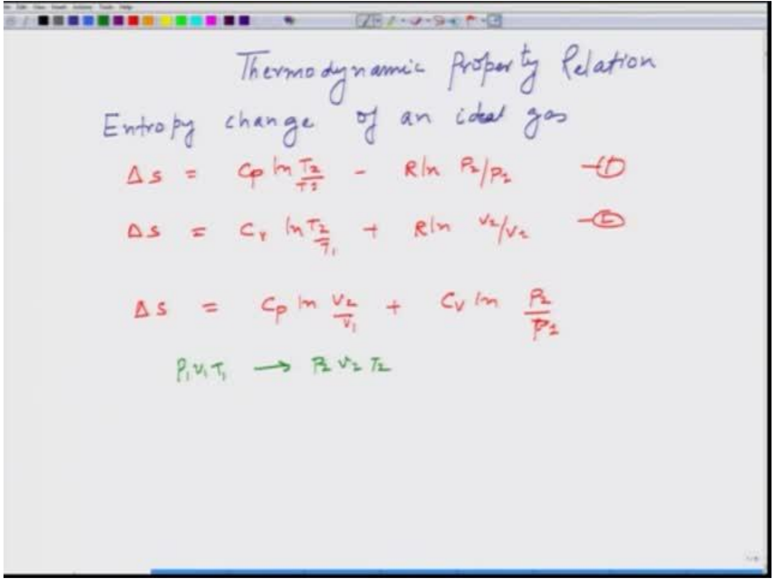

Thermodynamic Property Relation

Entropy change of an ideal gas

$$\Delta s = C_p \ln \frac{T_2}{T_1} - R \ln P_2/P_2 \quad -①$$

$$\Delta s = C_v \ln \frac{T_2}{T_1} + R \ln V_2/V_2 \quad -②$$

$$\Delta s = C_p \ln \frac{V_2}{V_1} + C_v \ln \frac{P_2}{P_2}$$

$$P_1 V_1 T_1 \longrightarrow P_2 V_2 T_2$$

So let me just first start with basic changes in the thermodynamic property which is of interest to us and we have already discussed earlier that in thermodynamics we are not essentially interested in absolute value of the properties, we are interested in the changes in the properties. So we can start with the dropet relation which we have written earlier for an ideal gas. So we have got this one relation which we derived earlier and there is another relation based on CV.

So this was one equation and this is one another equation for the for obtaining the changes in their entropy for an ideal gas. Now we can also derive another relation for finding out the changes in entropy for an ideal gas without deriving I am going to write this expression. Ok and this changes in the entropy relation can be derived based on the path which you undertake from

P1 V1 T1 to P2 V2 T2 ok, so our interested is to obtain similar kind of changes for other property such as changes in internal energies, enthalpy sense or both ok.

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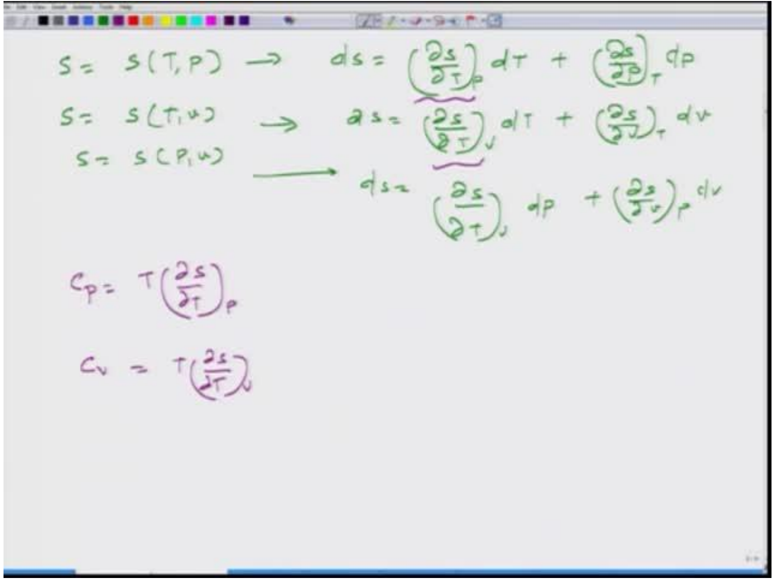

$$s = s(T,P) \rightarrow ds = \underline{\left(\frac{\partial s}{\partial T}\right)_P} dT + \left(\frac{\partial s}{\partial P}\right)_T dP$$

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

$$s = s(P,v) \longrightarrow ds = \left(\frac{\partial s}{\partial T}\right)_v dP + \left(\frac{\partial s}{\partial v}\right)_P dv$$

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

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

As we know that for a simple compressible system we need two intensive variable for the pure system ok, so one can write entropy for example as the function of TP or as a function of TV or as a function of PV. Now based on this, the intensive variable, the changes in the entropy expressions will be different ok. One can write the differential form of S in the following way ok. And similarly for second expression. So these are the three expression which we can clearly write in differential form based on the partial derivative ok.

And the previous values of delta S apparently, one can show that this is clearly derivable from this differential form of S. Now if you recall there are this expression has been already developed or has been defined in terms of heat capacity. So we know that CP is nothing but T and similarly for CV. Now these two partial derivatives can be clearly written in terms of CP and CV which are experimentally calculatable, which essentially means that you can calculate CP and CV from experiment.

Hence this partial derivatives are measureable in this two particular partial derivatives but what about this four derivatives which are still left? So in order to develop this four remaining partial derivative we will start with first law of thermodynamics and from there we will try to derive certain expression which we are going to say thermodynamic potential, ok which relate different intensive variables ok. So let me just start in this exercise in order to understand how to connect this partial derivatives or evaluate this remaining partial derivatives ok.

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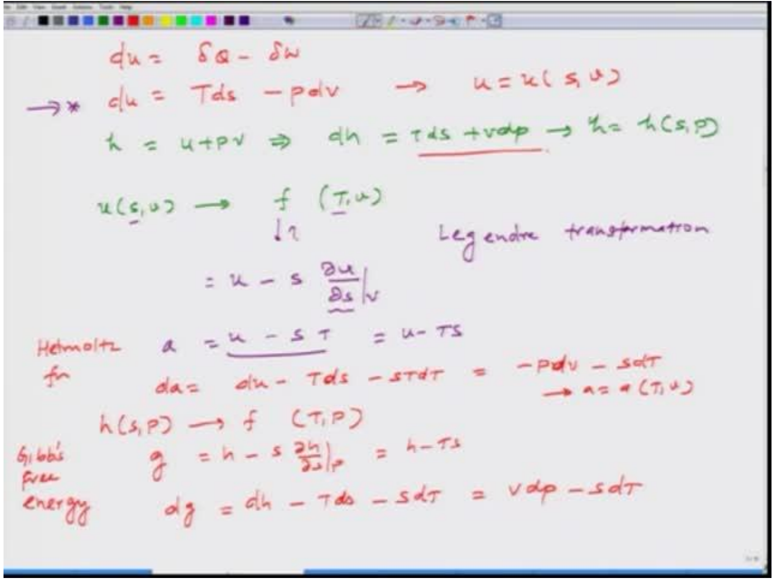

$du = \delta Q - \delta w$

$\rightarrow * \quad du = Tds - pdv \rightarrow u = u(s, v)$

$h = u + pv \Rightarrow dh = \underline{Tds + vdp} \rightarrow h = h(s, P)$

$u(\underline{s}, v) \longrightarrow f\ (\underline{T}, v)$

$\downarrow$

Legendre transformation

$= u - s \left.\frac{\partial u}{\partial s}\right|_v$

Helmoltz fn $\quad a = \underline{u - sT} = u - TS$

$da = du - Tds - sdT = -pdv - sdT$

$\rightarrow a = a(T, v)$

$h(s, P) \longrightarrow f\ (T, P)$

Gibb's free energy $\quad g = h - s \left.\frac{\partial h}{\partial s}\right|_P = h - Ts$

$dg = dh - Tds - sdT = vdp - sdT$

So let me start with the first law, ok. We can write this del Q by in TDS form for reversible case and this is PDV, now this tells you that this is U is as a function of S and V, similarly you can also write H which is H plus which is U plus PV is can be written in terms of differential form, DH is TDS plus VDP which tells you that H is a function of SNP ok. Now what we are interested is first is that if you are doing an experiment and you would like to evaluate your you know changes in internal (ena) energy, it would be difficult for to control directly the entropy.

And thus this is relevant to change this variable to something which is measurable in the experiment such as temperature, volume and pressure and this is the reason that we would like to change this U to some function which we can measure. Now what we can do to obtain F? That we can make use of something called legendary transformation ok. So without giving a formal proof if you want to change this variable from S to T, this can be done by taking this function U minus the variable which you would like to change and take the derivative of U, partial derivative of U with respect to the variable which you would like to change at constant V.

Now this from this expression if you take the partial derivative of del U with respect to S, this is nothing but T ok, so this way the transformation allows you to change this variable from S to T by using simple way of, by using particular equation or expression ok and this particular expression we are going to call as A, A is nothing but U minus TS. Now we are going to define this A as halmos function ok. So you can take a differential equation, you can write this expression in differential form which is nothing but PDV minus SDT which tells you that A is nothing but function of TNV that is what we wanted to obtain.

Similarly we can change SH to another function which depends on T and P as a variable using the same legendary transformation that will be H minus S del H by del S at P which is nothing but H minus TS using this function ok. And this H minus TS is defined as G which is we are going to call Gibbs free energy ok, you can write the differential form of G as DG is TH minus TDS SDT which is nothing but VDP minus SD ok. So based on this we have now four different differential form of kind of energies ok.

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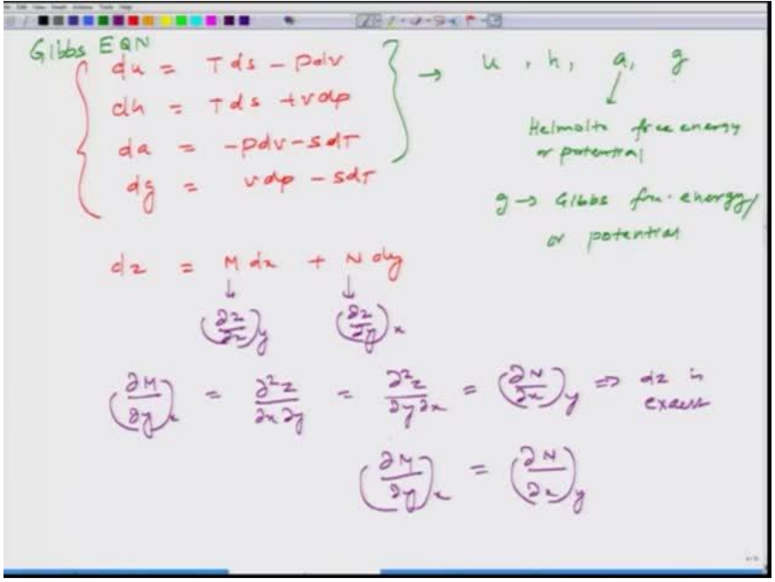

Gibbs EQN

$$\left\{\begin{aligned} du &= Tds - pdv \\ dh &= Tds + vdp \\ da &= -pdv - sdT \\ dg &= vdp - sdT \end{aligned}\right\} \rightarrow u,\ h,\ a,\ g$$

a → Helmoltz free energy or potential

g → Gibbs fre. energy/ or potential

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

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

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

We can summarise this, so we from the first law we obtain TDS minus PDV ok and the definition of enthalpy from there we obtain TS plus VDP, then we change this U from SV to TV and obtain this function called hamas function and we can write as DA in differential form. Similarly we can write for DG ok. Now this four set of equation is also called sometimes Gibbs equation ok and this is nothing but this four equations is nothing but differential form of four thermodynamic function U, H, A and G,.

U is internal energy, H is enthalpy, A is halmost function ok or sometimes we call it halmos free energy or potential. Similarly G is Gibbs free energy or potential. So that is free energy or Gibbs free energy or Gibbs potential, the potential is basically is related to the maximum work which we can obtain from the system and this can be related to the, to the minimum value of the free energy or the halmos free energy or Gibbs free energy depending on the intensive variable. Thus this can be shown that the amount of maximum work is related to the free energies and that is why they call it free energy or energy available for doing some work ok.

Now what our interest is to find out the remaining four partial derivative which we mentioned earlier here ok? So we need to connect this partial derivative to something which we can measure. So what we are going to do is first we are going to define something called exactness of the differential equation and this is something which are going to use this four equation later to connect this partial derivative which we would like to find the relations with something measurable.

So let us first define differential equation ok, where M is and N is your del Z A by del X ok. Now we can take a partial derivative of M with respect to Y keeping X constant, this is going to be del square Z, del X del Y, this you can rearrange, del Y del X ok and this should be equal to del N del XY ok. Now this becomes the statement of exactness of Z differential form of Z. So that means if DZ is exact that means exact differential then this condition must hold.

This means this DZ is exact ok. Now making use of this expression, we can use this equality which would connect the partial derivative of UM with respect to Y and that to the your partial derivative with N with respect to your X and this is something which we can now use this four equations to come up with the set of relations based on this exactness expression on.

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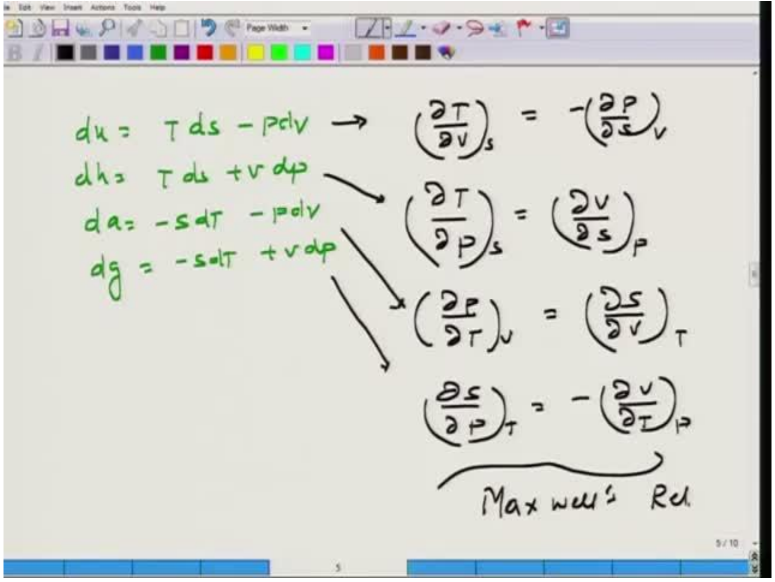

$$\begin{aligned} du &= T\,ds - p\,dv \\ dh &= T\,ds + v\,dp \\ da &= -s\,dT - p\,dv \\ dg &= -s\,dT + v\,dp \end{aligned} \quad \underbrace{\begin{aligned} \rightarrow \left(\frac{\partial T}{\partial v}\right)_s &= -\left(\frac{\partial p}{\partial s}\right)_v \\ \rightarrow \left(\frac{\partial T}{\partial p}\right)_s &= \left(\frac{\partial v}{\partial s}\right)_p \\ \rightarrow \left(\frac{\partial p}{\partial T}\right)_v &= \left(\frac{\partial s}{\partial v}\right)_T \\ \rightarrow \left(\frac{\partial s}{\partial p}\right)_T &= -\left(\frac{\partial v}{\partial T}\right)_p \end{aligned}}_{\text{Max well's Rel}}$$

In order to make use of this exact ness expression for on this four equations I will try to reproduce first this equation, thermodynamic potential equations. Ok so here we are just swapping so that we can have in one column SOT. So now making use of exactuhness expression, here we can get del T by del VS minus of del P by del S, next expression is del T by del PS is del V by del SP. So this becomes this, so fourth expression is del P by del TV ok. So this becomes from here and the last del S by del P at constant T minus del V by del T at constant, constant P ok.

Now this four equation or expression which we got or relation which we got is also called Maxwell relation ok. Now sometimes it becomes very difficult to remember this, so there are many ways which people have come in order to keep it in the memory, so one way is of course you can write this four thermodynamic potential relations and directly use exactness expression in order to get this four relation, other way is was you can come up with this mnemonic diagram.

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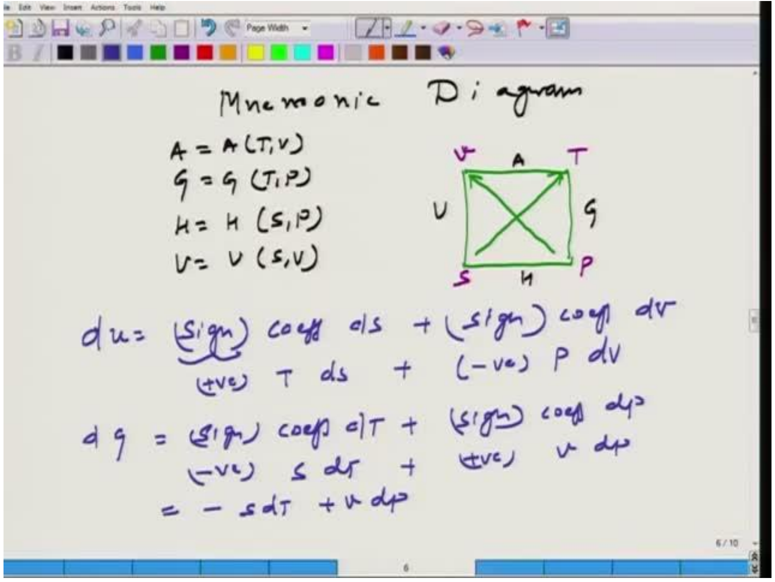

Mnemonic Diagram

$A = A(T, v)$

$G = G(T, P)$

$H = H(S, P)$

$U = U(S, V)$

$du = \underbrace{(\text{sign})}\ \text{coeff}\ ds + (\text{sign})\ \text{coeff}\ dv$

$(+ve)\ T\ ds + (-ve)\ P\ dv$

$dg = (\text{sign})\ \text{coeff}\ dT + (\text{sign})\ \text{coeff}\ dp$

$(-ve)\ s\ dT + (+ve)\ v\ dp$

$= -s\,dT + v\,dp$

Ok so instead of using specific properties specific energies, free energies potential, we will use here capital ok, so what I am doing here is, I am writing this alphabetically A, G then H is H as a function of SMP, U is a function of SMV ok and then I can draw a square ok, starting with A followed by G, H, U, now A is uh, A is connected to TV and G is connected to TP, so T is common vertex.

So T is here V is here, now here is T and of course G is the independent variables are T and A has to be P, H is P and this has to be S and of course U is VNS, so the key was to make sure that we have a connected corner between A and G, A, G, U, H was used. So the other thing which we do is that we, when we make this square we make not just square but also this kind of diagonal where we put the arrow towards the upper H and then we make use of this alphabetical order of A, G, H, U.

Ok so then you can come up with this way of getting let us say DU. So DU is the sign ok and then the coefficient and the independent variables are V and S. So we will start with let us say S plus sign coefficient and DV ok. So what is this sign for example? Sign in this case is given by this arrow. If it is pointing away from S ok then it is going to be positive and the coefficient is where it is at that is your T, so this becomes positive TDS plus this sign which we are going to take at V which is towards the cells so that is going to be a negative and the coefficient is of course P diagonally opposite to V ok.

So the where was I at the end of the line here and the coefficient is the diagonally opposite variable vertex, sign is when the arrow is away from the, the independent variable which is positive. If it is towards itself then it is negative. So that is how we can also make use of this kind of diagram ok. So with this we can also do some exercise here.

So D, let us say G ok again we can think of sign coefficient, let us say this is your T plus sign coefficient your DP. Sign for the case of T is going to be negative because it is towards itself, coefficient is S and this sign is positive and coefficient is V ok. So that is how you get minus SDT plus VDP.

Ok, so this is one way of getting this four Maxwell relation which connects different variables. Now you can clearly remember the thermodynamic relations directly by understanding the way it was derived or you can make use of this kind of diagram in order to remember that ok. So we are going to make use of this Maxwell relations in order to come up with different variables or changes in the variable which cannot be measured directly from experiment.

Hence we may we need to use such relation in order to convert to some variables which can be measured experimentally.

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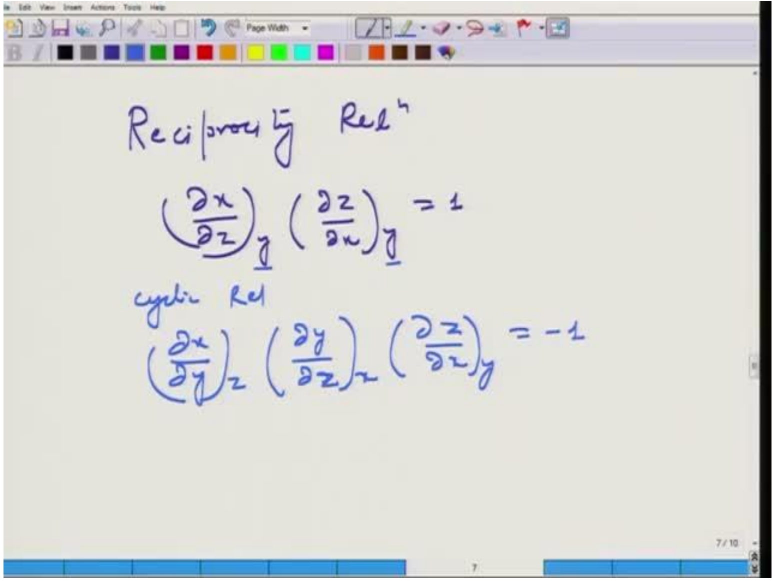

Reciprocity Rel^{n}

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

cyclic Rel

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

Ok, before I end this lecture let me also write down this two expressio which are going to also commonly used. So one is called reciprocative relation ok, so this is ok, so this is something which is well known and the other one is cyclic relation, a cyclic relation where we use three variables ok. So remember here, this is kept constant, so you just change in the swap in the variables, so this del Y by del Z keeping X constant and del Z by del X by this is minus one.

Ok, so this is a cyclic relation. S o we are going to make use of cyclic relation reciprocaticity relation and as well as the Maxwell relation in order to come up with the various relation between the variable which were of interest to us ok. So with this I will end this lecture. In the next lecture we will try to make use of this relation to solve some to come up with this interesting aspect of thermodynamics ok. So see you in the next lecture.