Chemical Engineering Thermodynamics
Professor Jayant K. Singh
Department of Chemical Engineering
Indian Institute of Technology Kanpur
Lecture 22
Maxwell's Relations and examples

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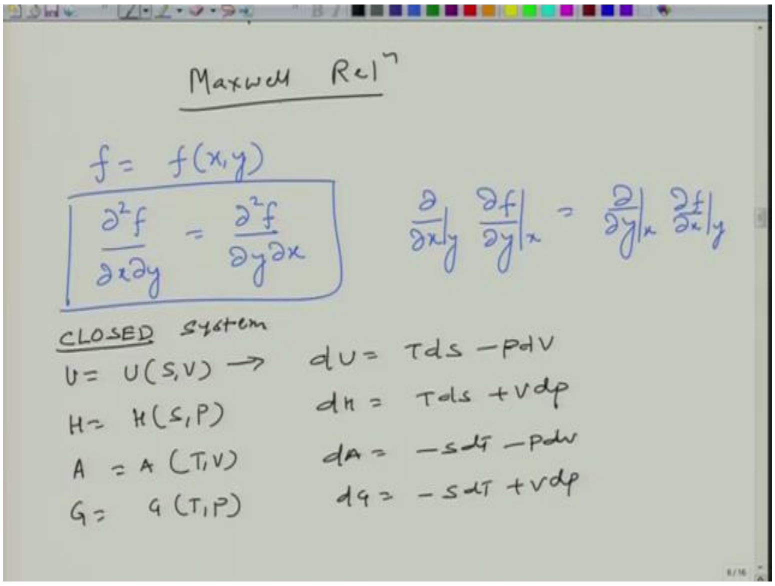

Welcome back, in today's lecture we are going to describe Maxwell's relation. So Maxwell relation is based on the fact that order of differentiation is unimportant for analytical function. so which essential means that, let us say if we consider function f is equal to f x, y and consider this to be smooth function, then it is based on the fact that the order of differentiation is unimportant and in other way we are saying the following.

$$f = f(x,y) \text{ is a smooth function.}$$

$$Then, \quad \frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$$

$$And, \qquad \frac{\partial}{\partial x}|_y \frac{\partial f}{\partial y}|_x = \frac{\partial}{\partial y}|_x \frac{\partial f}{\partial x}|_y$$

So, Maxwell relation will be developed based on this simple equality of these terms. So, it clearly tells you this that the order of differentiation is essentially does not make any difference, so this is a based on a mathematical equality of that these two expressions.

Now based on this, we are going to develop 4 important relation which are going to be extracted from our basic fundamental thermodynamic potential relations in a differential form. And I am going to now write this first so let us look at u is equal to u s v, so we are considering close system for illustration, okay, the other thermodynamic functions are H is equal to H function of S and P, A is a function of T and V, and G is the function of T and P.

Fundamental relations for closed system:

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

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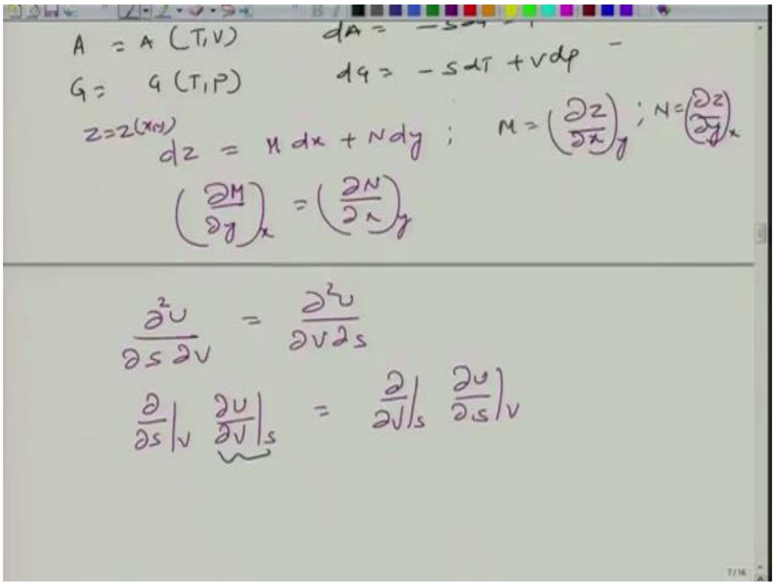

And now the way Maxwell relation is developed is based on a simple exercise.

$$z = z(x.y)$$

$$dZ = Mdx + Ndy; \quad M = \left(\frac{\partial Z}{\partial x}\right)_y ; N = \left(\frac{\partial z}{\partial y}\right)_x$$

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

Now use or apply this particular equality or this particular expression on the 4 different relations, okay thermodynamic relation. So, let us consider for the case of u.

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}$$

$$\frac{\partial}{\partial S}\Big|_V \frac{\partial U}{\partial V}\Big|_S = \frac{\partial}{\partial V}\Big|_S \frac{\partial U}{\partial S}\Big|_V$$

$$-\frac{\partial P}{\partial S}\Big|_V = \frac{\partial T}{\partial V}\Big|_S \quad \textit{For a closed system}$$

$$-\frac{\partial P}{\partial S}\Big|_{V,\{N_i\}} = \frac{\partial T}{\partial V}\Big|_{S,\{N_i\}} \quad \textit{For an open system}$$

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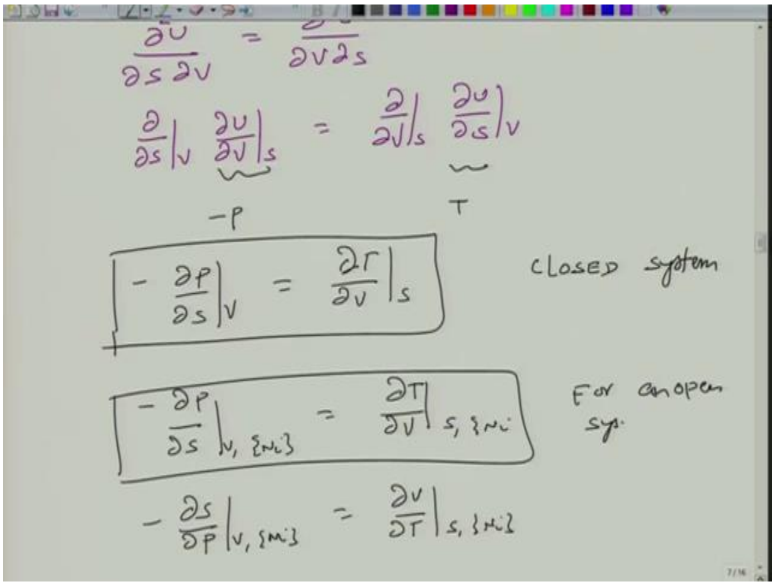

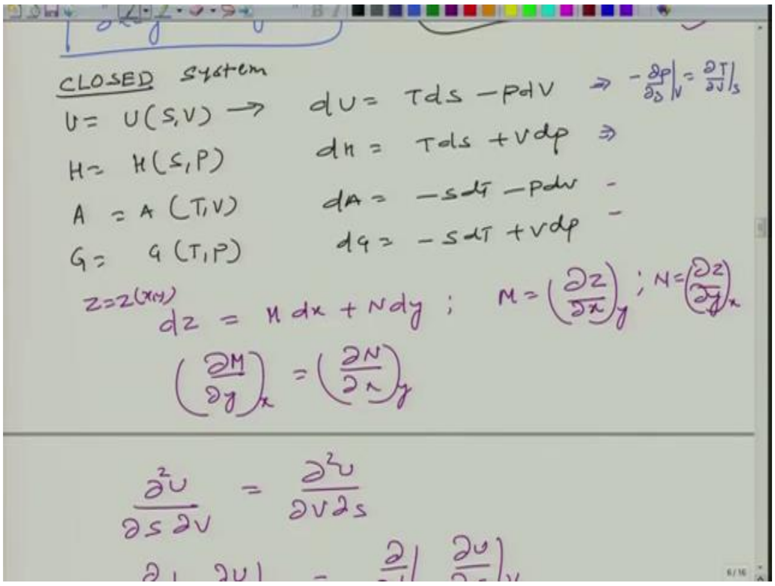

Inverse relations are also valid.

$$-\frac{\partial S}{\partial P}|_{V,\{N_i\}} = \frac{\partial V}{\partial T}|_{S,\{N_i\}}$$

So we have now first relation which comes from the internal energy expression in the differential form, now I can consider other relations and try to develop. We can do this same exercise for del h here.

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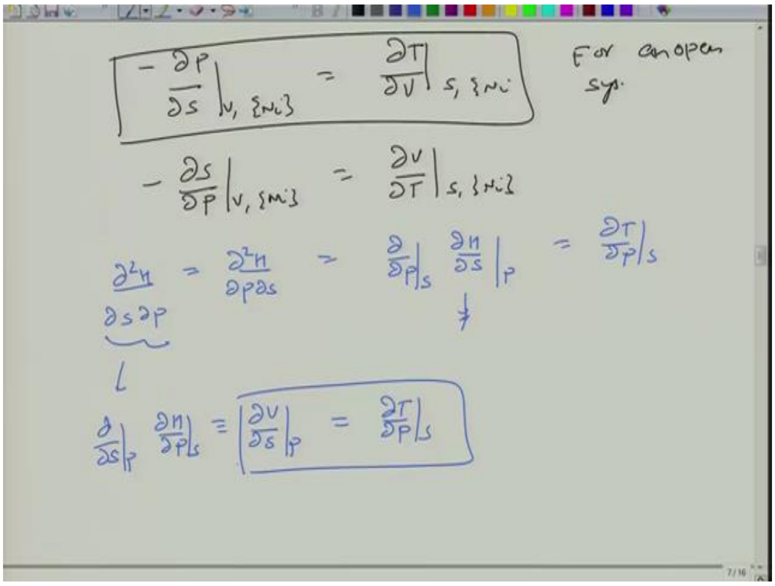

The second relation is thus obtained as:

$$\frac{\partial V}{\partial S}|_{P} = \frac{\partial T}{\partial P}|_{S}$$

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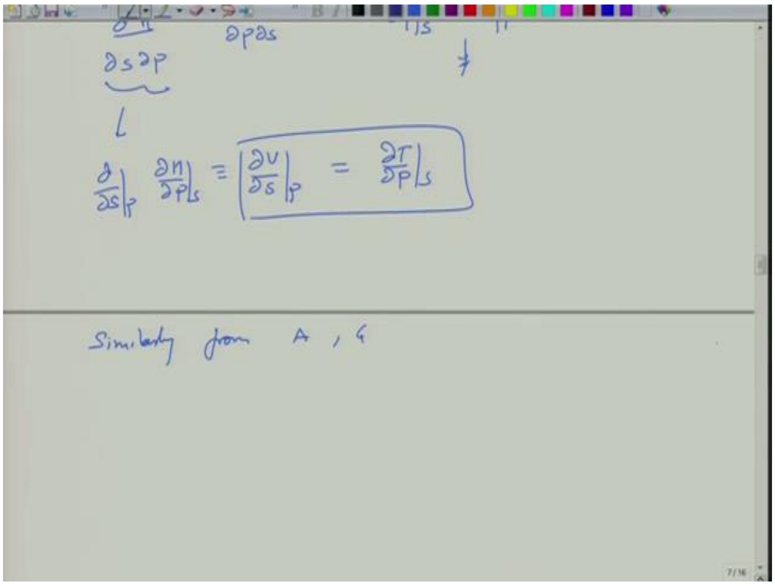

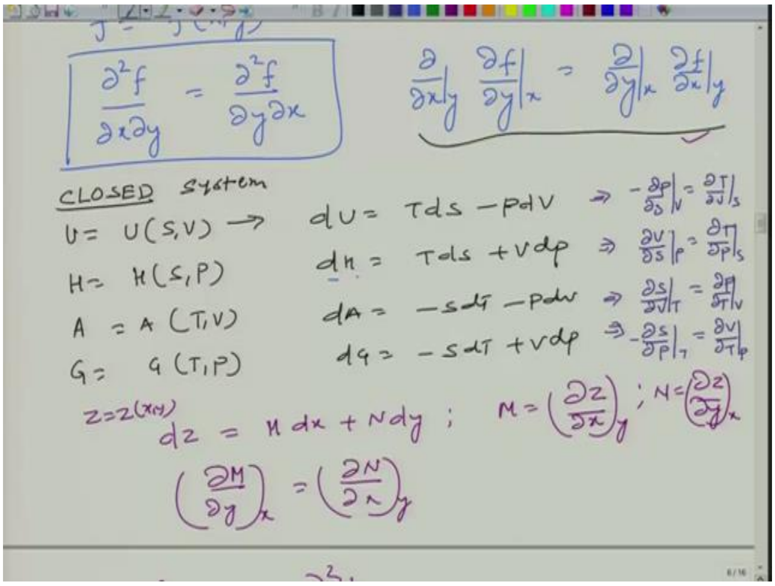

And then similarly we can get, similarly, from the expression of A and G we have the following expressions.

$$dA = -SdT - PdV \rightarrow \frac{\partial S}{\partial V}|_T = \frac{\partial P}{\partial T}|_V$$

$$dG = -SdT + VdP \rightarrow -\frac{\partial S}{\partial P}|_T = \frac{\partial V}{\partial T}|_P$$

So that is the four Maxwell relations we have obtained.

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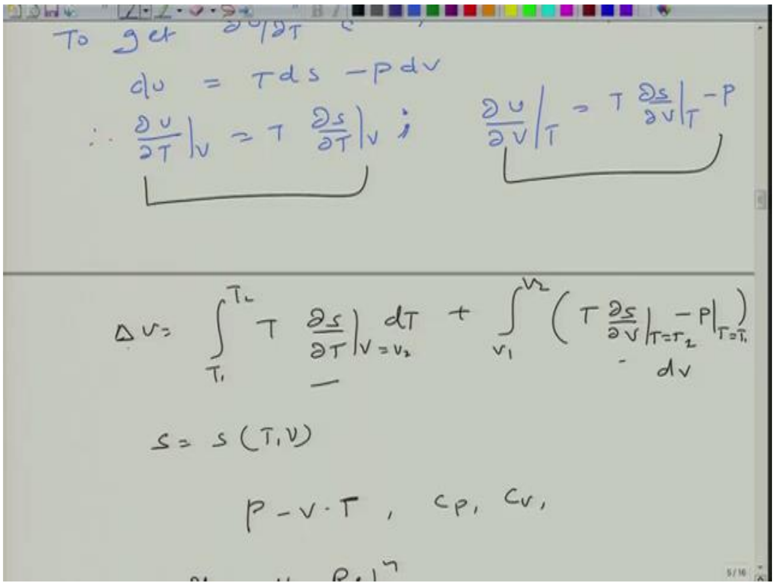

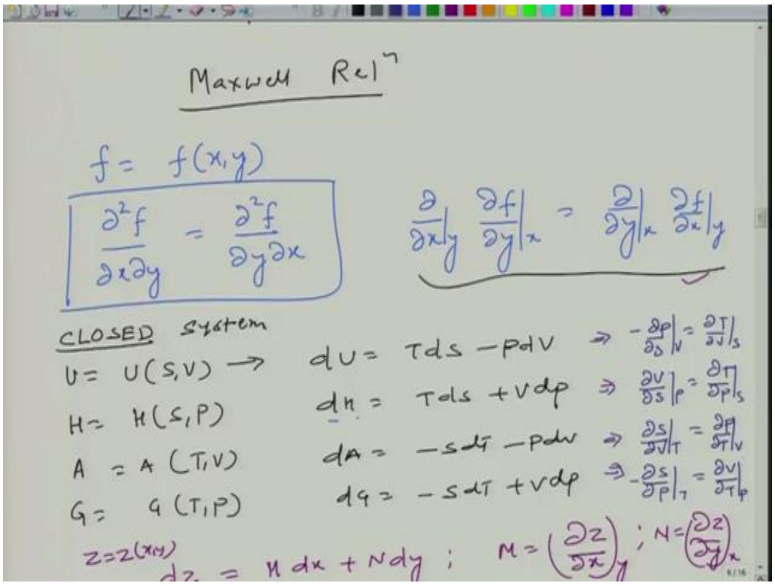

Now let us look at the problem which we have ended before the start of this lecture, we earlier wanted to have this delta u to obtained from the state point are going from t1 v1 to t2 v2, okay and we considered this s is equal to function of v so earlier we wanted to have this relational delta to u going to t1 v1 to t2 v2 and we did this exercise and we ended up with this expression were we stuck with this partial derivative of s with respect to t and partial derivative of s with respect to v, and that is why we wanted to say that we must come out with the expression where we can change this partial relation to something related to p v t and other relation properties which we can calculate from the experiments and that is where the Maxwell relations come.

So if u look at this side del s by del v, I can now make use of the Maxwell relation because del s by del v, if you look it here del s by del v here is nothing but del p by del t at a constant for v.

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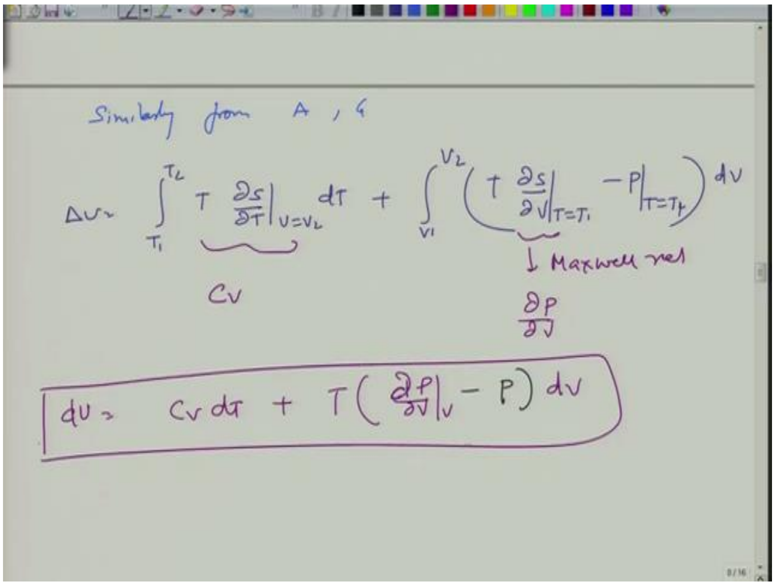

So this expression, I can write it here is delta u which was there in t1 t2 T del s by del t at v is equal to v2 dT plus v1 v2 T delta s by del v T is equal to t1 minus p T is equal to t1, and this this was the expression which we ended in the last class. Now this by definition is c v okay, okay c v is by definition is t del s by del t and this from Maxwell relation as I mentioned this is this part is nothing but del p by del v, so this is something which you can now calculate from the experiment, we can keep the temperature fix and find out the change in the pressure as we change the volume or the other way around.

And then our expression in a differential form not integral would be c v d t plus t and this term here del p del p by del v at constant, so del v by del t at t should be del p by del v del s by del v at constant t should be del p by del v at constant v. So, this must be at constant v minus p dv. So this is the differential form here.

$$dU = C_V dT + T\left(\frac{\partial P}{\partial V}|_V - P\right) dV$$

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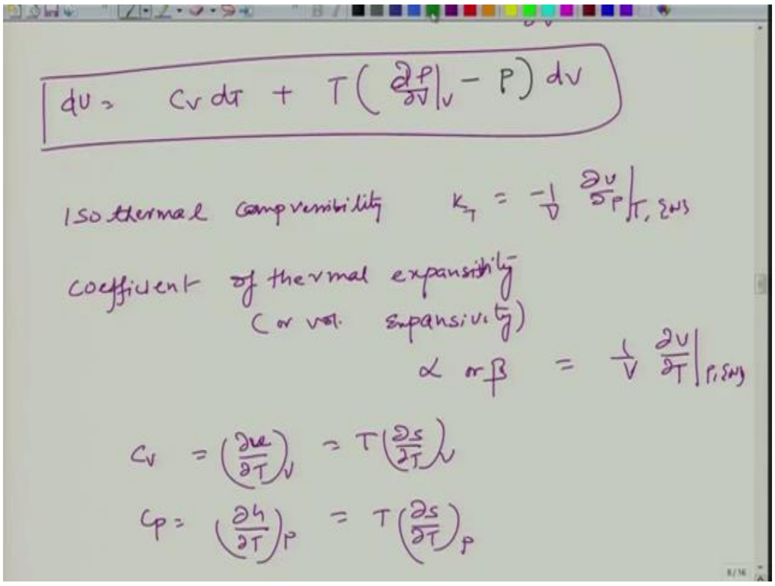

Now in addition to this Maxwell relation as I said we are going to make use of a other thermodynamic properties or the variables and one of the important variables are isothermal compressibility and the coefficient of expansivity, many times it is because of isothermal its symbol is k and t is to identify that it is basically at a constant temperature and this is 1 by v del v by del p because you are trying to look at what is the rate of compression as you change your pressure, that means basically the amount of the volume which is changed as you change the pressure at a constant temperature and the negative sign is meant because is added because this should be negative, here the k must be positive and this is something which we would like to prove it also later for a stability analyses during when we are going to talk about stability of the system.

In addition to this we would be also interested to have this variable because we can calculate this in the experiment coefficient of thermal expansion or expansivity. And many times this is also called volume expansivity, usually symbols Alfa is used sometimes or beta is also used okay so Alfa or beta could be used here, but the meaning remains the same that you are looking at how the volume gets affected as you change the temperature at a constant pressure, okay.

And it is a important variable which we use so in addition to your beta k you have of course c v, and c p. So, this is by definition.

$$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P}|_{T,\{N_i\}} \quad Isothermal\ compressibility$$

$$\alpha \text{ or } \beta = -\frac{1}{V}\frac{\partial V}{\partial T}|_{P,\{N_i\}} \quad Coefficient\ of\ thermal\ expansivity$$

$$C_V = \left(\frac{\partial u}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

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

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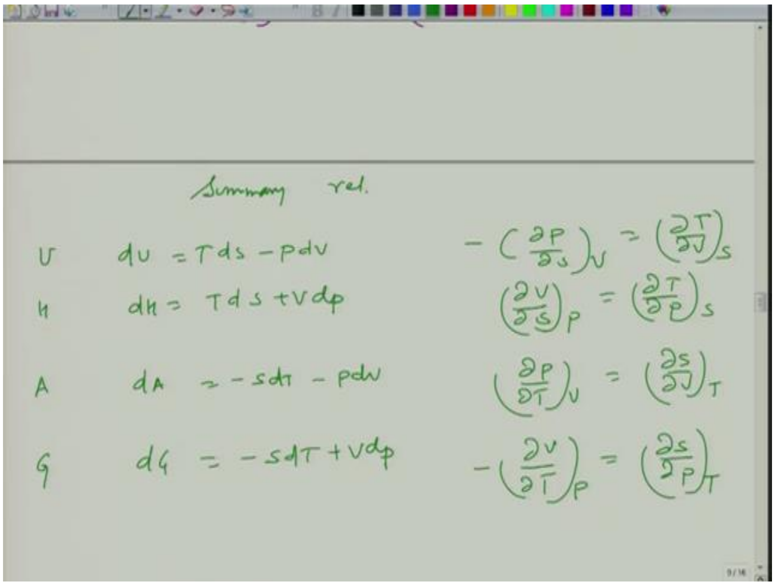

So again let me summarize Maxwell relation. So we have obtained 4 Maxwell relations okay. Summary of Maxwell relation, okay. From the expression u, t u is equal t d s m minus p d v and the Maxwell relation is minus of del p by del s del p by del s at constant volume, this must be equal to del t here by d v at constant s minus sign is there because one of the coefficient of this here is minus, okay.

Then you have this a function h which gives you d h is equal to t d s plus v d p and from here I can get del v by del s at constant p this is equal to del t by del p at constant s, okay. Then we have function a, okay sometimes people use f also but let me just use a here minus s d t minus p d v okay. and here I have del p by del t at constant v is equal to del s by del v at constant t again negative signs here gets cancelled and so you have this relation and then finally you have G del G is equal to minus s d t plus v d p and this is del v by del t at constant p and this is negative here, this is equal to del s by del p by constant T, okay. So these are the 4 important relations which we have, okay.

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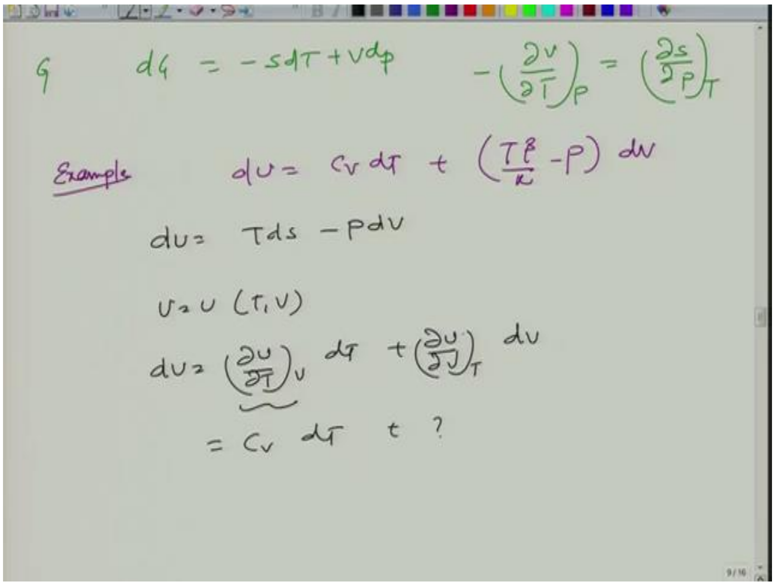

Now having derived this expressions, now let us try to do some examples making use of this Maxwell relation in order to simplify the expressions or the changes in the thermodynamic variables in terms of something which we can calculate experimentally okay.

So one of the example could be, let us say this is an example and so the question is to derive this expression, okay. So this is the expression here, so here of course beta is same as volume expansivity. So let us start with du

$$dU = TdS - PdV$$

$$U = U(T, V)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V dT$$

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

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

$$Maxwell's\ Relation, \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P}|_T \qquad \beta = -\frac{1}{V}\frac{\partial V}{\partial T}|_P$$

$$Chain\ rule, \quad \left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial V}{\partial P}\right)_T = -1$$

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{1}{\left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial V}{\partial P}\right)_T} = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = -\frac{\beta V}{-\kappa V} = \frac{\beta}{\kappa}$$

$$dU = C_V dT + \left(T\frac{\beta}{\kappa} - P\right)dV$$

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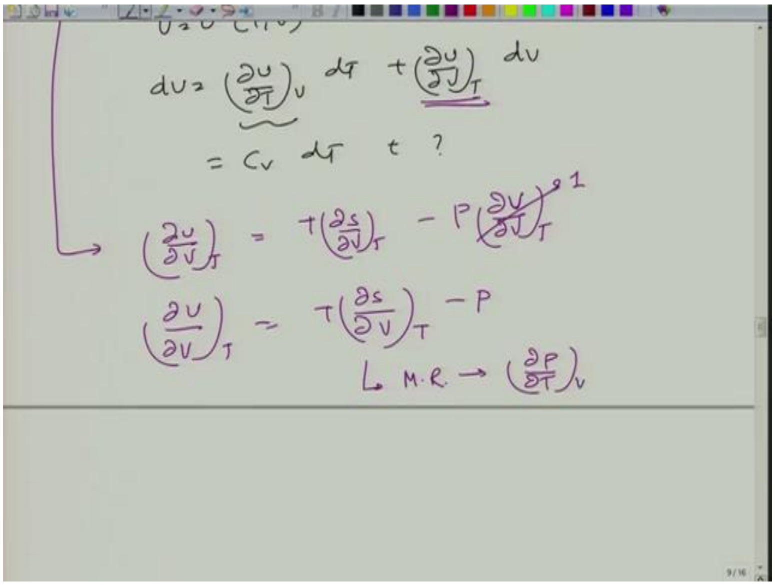

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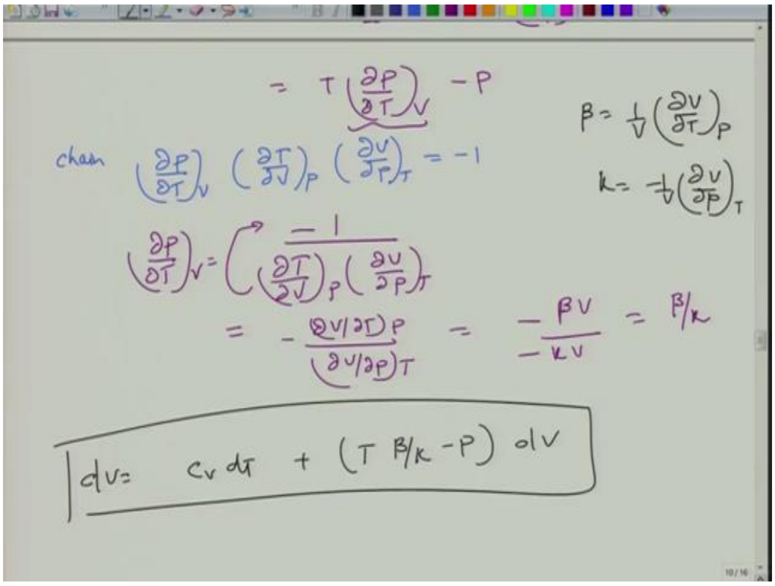

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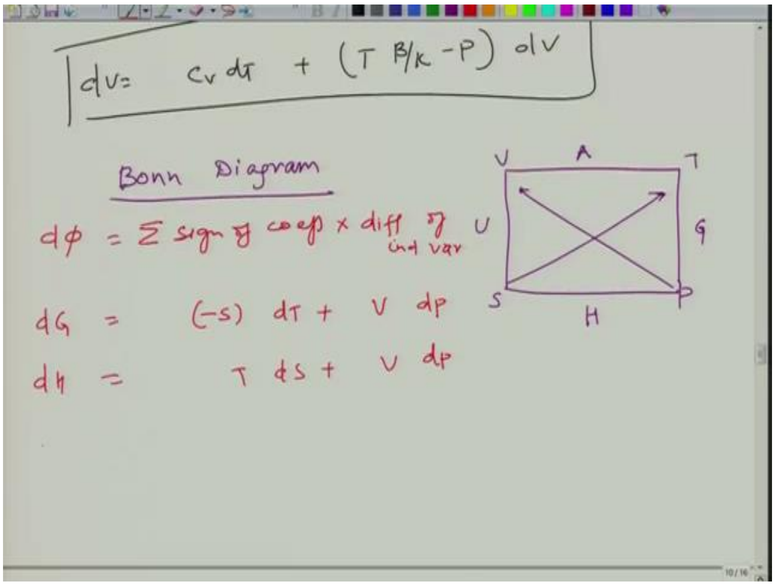

So you can write do this, but there could be other ways which you can remember if you want to do that and one of the often used approach is something called bond diagram okay. The way it is a written or it works as a following, that a you draw this kind of a square such that you have this s v t and p which is a corners of this square and then you can draw these two lines which one going from s to t and the other going from p to v and this are the independent variables okay so appropriate independent appropriate thermodynamic functions can be added now H is for s and p and if you look at t and p this has to be G, if it is v and t then this is A, if it is v and s is nothing but U, okay.

So what we have done is we have written something like this. Now you can write down let us say thermodynamic function also in the way in the following way let us say if a generic thermodynamic function is Phi, then this is nothing but a sign of coefficient multiply by the differential of independent variable, okay.

So you can demonstrated this so let us consider let us say d of G, okay so G has independent variables t and p, so this is your d t and this is your d p so that is part of it and then you need to have sign of coefficient, so the coefficient sign are written in this way so essentially for t the conjugate variables goes to s, so essentially here I am going to write is the minus of s okay plus from p it going from p to v but since its going from originate from p in this direction this is a positive in this case, we have to written negative because its coming towards t and hence it is written minus s that is what the sign stands for. So sign and the here it would be your for p it is v.

Similarly, I can write here d of h here, okay. So it goes toward from both the corners or both the vertices and hence is going to be positive so here I can write d s with t here plus p and this is v p so this is by definition and similarly you can write the other terms. Now since our interest is basically to get the Maxwell relations a from this diagrammatic approach, let us look at how it can be done.

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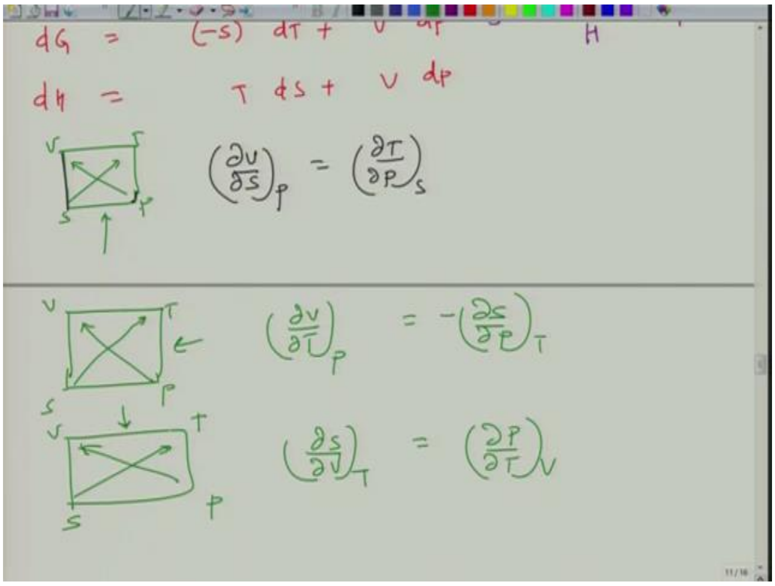

So a the idea is the same you write it in this small thing s v t p okay, right, so this is how it is written. Now when you look at from here from the one of the sides okay then essentially what you have to do is you have to look at the edges, okay. here for example in their edge you have v and s and the corresponding vertices here which is connected to s because you are looking from it, so essentially you can write it here as del v by del s okay, keeping this p constant. And similarly, this would be your h here del t by del p, but the corresponding the other side is s here and since both arrows are towards the other sides and hence it is a is basically there is no negative sign here.

Similarly, so until I do not show you the other examples you will not be clear, so let me just demonstrate it for the other side, okay. So now we are looking at from this side right so this side has 2 edges here, this is the one, the other one is this, so it is going to be del v by del t this must be equal to del s by del p, okay.

Now if you look at it what should be here in a constant for the case of a del v by del t should be p, for the case of del d by del p it should be t, okay. But the other things is that weather it is going to be positive or negative here, so if you look at it by here again one of them is approaching towards the edge okay. So hence, there has to be some negative you can put it here or here does not matter okay.

Now let us look at the other sides also, so we put it here, so this is going to be del s by del v should be equal to del p by del t again del s by del v should be the constant as t, for this constant is v and both the sides both the arrows are pointed towards this hence this will be positive.

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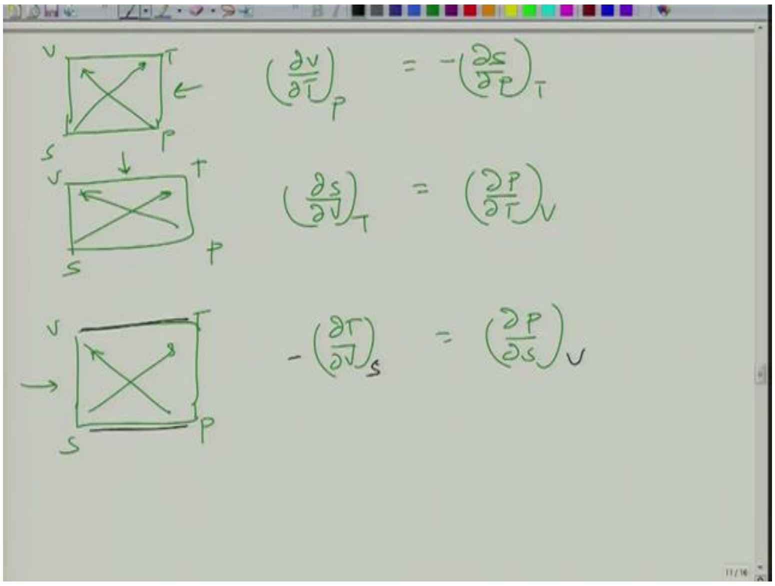

Similarly I can so the last one, so this is your del t by del v del p by del s okay, these are the two edges, okay two points here del t by del v del p by del s and now for the case of del t by del v we have kept s as constant, for the case of del p by del s the v is constant, but if you look at from this side one of the arrow is pointing towards itself so there has to be negative sign somewhere, okay.

So these are the 4 Maxwell relations which have evaluated from the Bond Diagram Approach which could be very useful if you are not able to understand or directly extract it from the thermodynamic expressions the way I was trying to do that. But I will try to show you another way to solve problems or remember this Maxwell relation that will be your Jacobean approach and I will take that approach in the next lecture, so that will be the end of today’s lecture.