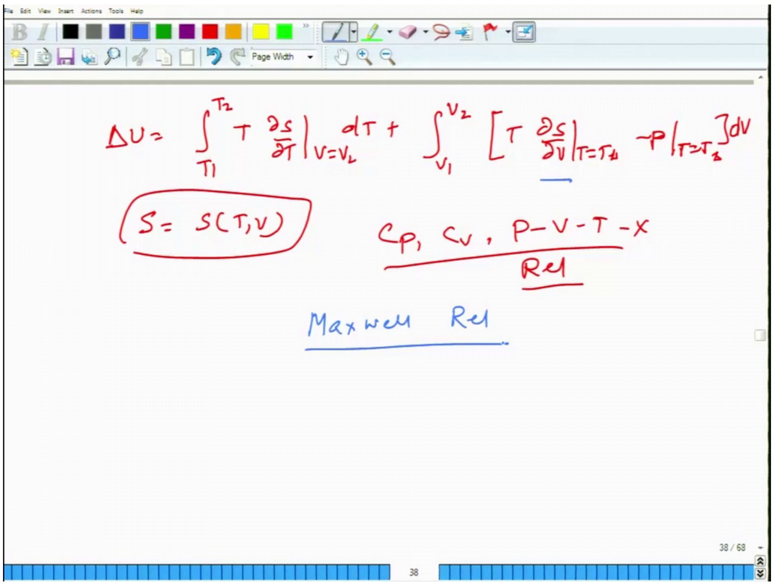
Thermodynamics of Fluid Phase Equilibria
Dr. Jayant K. Singh
Department of Chemical Engineering
Indian Institute of Technology, Kanpur

Lecture – 16
Maxwell Relation

In the last class, we discussed about the importance of relations in order to solve problems such as what we describe here, delta U.

(Refer Slide Time: 00:24)



$$\Delta U = \int_{T_1}^{T_2} T \left.\frac{\partial S}{\partial T}\right|_{V=V_2} dT + \int_{V_1}^{V_2} \left[T \left.\underline{\frac{\partial S}{\partial V}}\right|_{T=T_1} - P\Big|_{T=T_1} \right] dV$$

$$\boxed{S = S(T,V)}$$

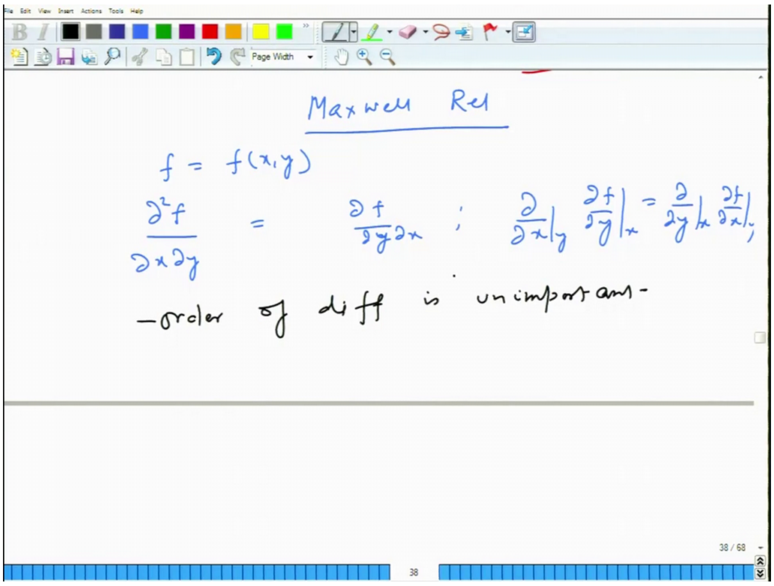
$$\underline{C_P,\ C_V,\ P-V-T-x}$$

$$\underline{\text{Rel}}$$

$$\underline{\text{Maxwell Rel}}$$

And in order to get this expression, we need to convert such a, such an expression in something measurable quantities ok? And that is what we are going to discuss today. And this is something which we can make use of Maxwell's relation.

(Refer Slide Time: 00:52)



Maxwell Rel

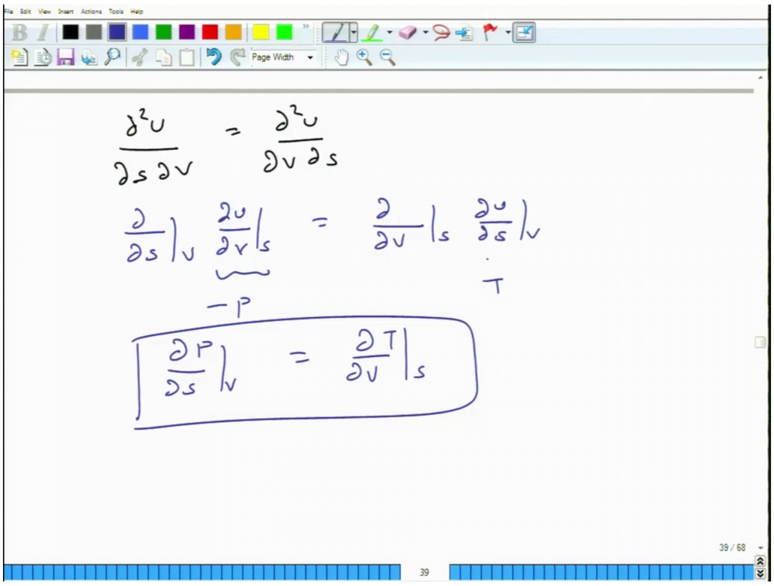
$f = f(x,y)$

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial f}{\partial y \partial x} \; ; \; \frac{\partial}{\partial x}\Big|_y \frac{\partial f}{\partial y}\Big|_x = \frac{\partial}{\partial y}\Big|_x \frac{\partial f}{\partial x}\Big|_y$$

-order of diff is unimportant-

So, I will just quickly describe this and then we will try to get back to this particular expression. So, let me just take a function f ok. And what we are interested is; so, this we can write it this as del f, del y, del x. Or you can also write this as; so, the point is that, order of differentiation is unimportant ok. So, we can make use of this, this expression in our thermodynamic relation. So, I will just take a case of U, U is a function of S V N. So, f is basically U and let us say, x and y are V and S N V, right?

(Refer Slide Time: 02:09)



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

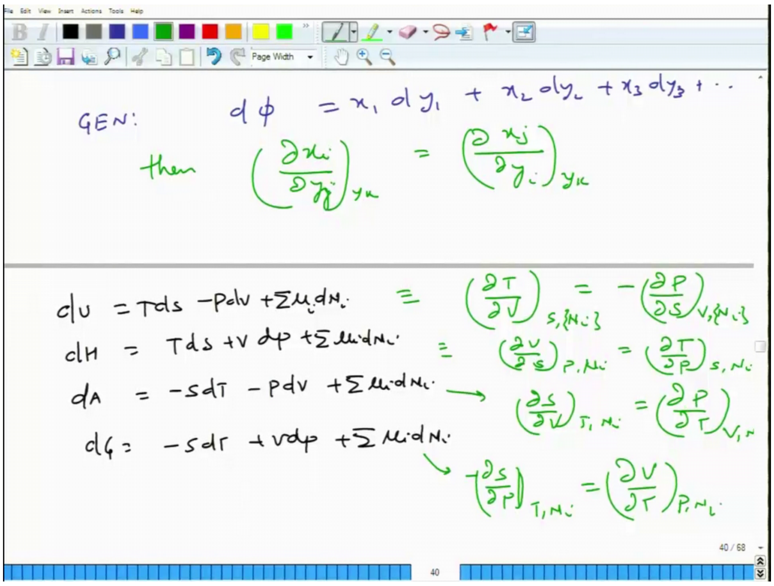
$$\frac{\partial}{\partial S}\Big|_V \underbrace{\frac{\partial U}{\partial V}\Big|_S}_{-P} = \frac{\partial}{\partial V}\Big|_S \underbrace{\frac{\partial U}{\partial S}\Big|_V}_{T}$$

$$\boxed{\frac{\partial P}{\partial S}\Big|_V = \frac{\partial T}{\partial V}\Big|_S}$$

So, f is nothing but U and x is let us say, you have S and V. So, we are just dropping N here, considering this to be a pure case. So, this is going to be, I can write it in this way.

So, let me make use of this expression here, this one. Now what is this? Minus P and this is going to be T. So, essentially what you got is del P by del S at V, is equal to del V by del T at S. So, this is one thermodynamic relation, or Maxwell relations we call it ok. Now this we can generalize it also. So, you see the way I did was, I made use of this, this order of differentiation ok. Now you need not do this in this, in this way.

(Refer Slide Time: 03:35)



GEN: $d\phi = x_1\,dy_1 + x_2\,dy_2 + x_3\,dy_3 + \cdots$

then $\left(\frac{\partial x_i}{\partial y_j}\right)_{y_k} = \left(\frac{\partial x_j}{\partial y_i}\right)_{y_k}$

$dU = T\,dS - P\,dV + \sum \mu_i\,dN_i \equiv \left(\frac{\partial T}{\partial V}\right)_{S,\{N_i\}} = -\left(\frac{\partial P}{\partial S}\right)_{V,\{N_i\}}$

$dH = T\,dS + V\,dP + \sum \mu_i\,dN_i \equiv \left(\frac{\partial V}{\partial S}\right)_{P,N_i} = \left(\frac{\partial T}{\partial P}\right)_{S,N_i}$

$dA = -S\,dT - P\,dV + \sum \mu_i\,dN_i \rightarrow \left(\frac{\partial S}{\partial V}\right)_{T,N_i} = \left(\frac{\partial P}{\partial T}\right)_{V,N}$

$dG = -S\,dT + V\,dP + \sum \mu_i\,dN_i \searrow -\left(\frac{\partial S}{\partial P}\right)_{T,N_i} = \left(\frac{\partial V}{\partial T}\right)_{P,N_i}$

40 / 68

40

You can simply make use of the fundamental equation in differential form for different thermodynamic functions and directly use a basic general properties such as, what I am going to write here. If phi is a function which can be written as, x 2 divide 2 plus x 3 divide 3 and so forth, then del x i by del y i for a given y K is same as, del x j by del y i for the same y k. That is what he’s trying to say ok.

Now, you can relook at, from this perspective, that I am going to write this different fundamental equation; del U is equal to T d S minus P D V plus mu d N ok. So, mu i let us say.

Student: d i.

d i. So now, for this you can clearly get the expression because, this is what is talked about, del x i del y i this form ok. So, you have del x i del y. So, this is nothing but, equivalently you can say this is nothing but, del T by del V, del T by del V y j ok. So, this would be same as minus of del P by del S.

Now, what would be constant here? So, for this one, this would be S and all N is, right? And this is going to be your V and all N is ok. So, many times I may be writing just like an i, it means basically all, or I can use the curly bracket to say that, that is all the N is as of now. We can easily write for others quickly without too much of thinking ok.

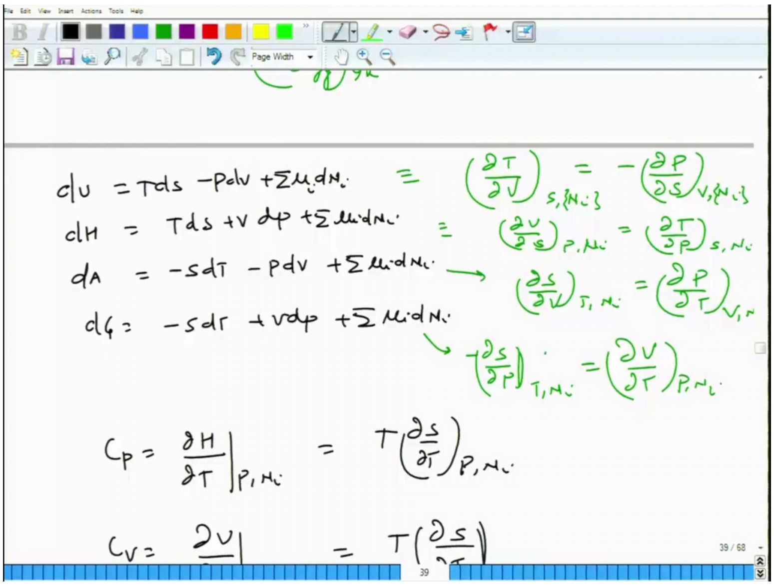
So, I am going to write this as, del V by del S P N i.

Student: Constant.

Constant V; no, this has to be del V by del S and del T by del P at constant S ok. Now, you can also use inversion. You can make it this as to be del P by del T ok? That would be equivalent to, del S by del V right. So, this will be using expression, using inversion rules. So, here we get more important terms; here we get del S by del V T N i is equal to del P by del T V N i. And here, we get minus del S by del P T i ok. So, these 2 terms, which means quite important, if you look into the last 2 Maxwell relation, this relates the entropy to the P V T data; a P V T data you can extract from the experiment ok.

So, this is why it becomes a very, very important expressions first.

(Refer Slide Time: 07:50)



$$dU = TdS - PdV + \sum \mu_i dN_i \quad \equiv \quad \left(\frac{\partial T}{\partial V}\right)_{S,\{N_i\}} = -\left(\frac{\partial P}{\partial S}\right)_{V,\{N_i\}}$$

$$dH = TdS + VdP + \sum \mu_i dN_i \quad \equiv \quad \left(\frac{\partial V}{\partial S}\right)_{P,N_i} = \left(\frac{\partial T}{\partial P}\right)_{S,N_i}$$

$$dA = -SdT - PdV + \sum \mu_i dN_i \rightarrow \left(\frac{\partial S}{\partial V}\right)_{T,N_i} = \left(\frac{\partial P}{\partial T}\right)_{V,N_i}$$

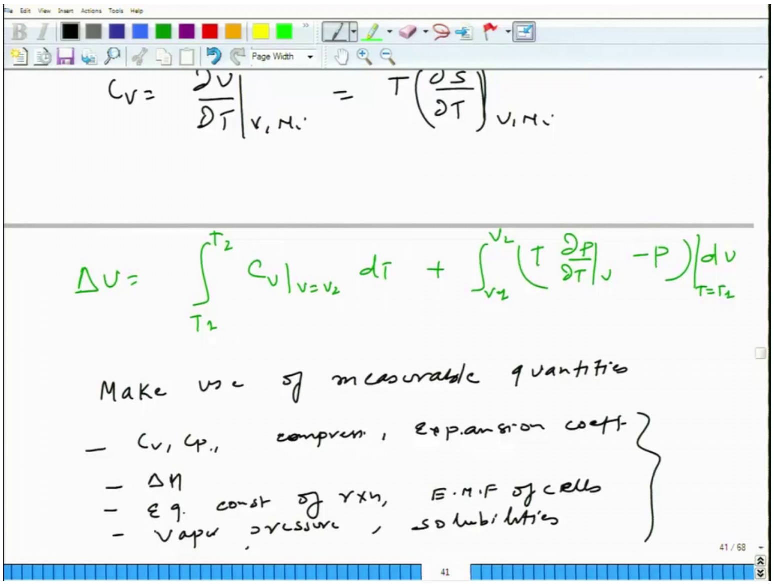
$$dG = -SdT + VdP + \sum \mu_i dN_i \searrow -\left(\frac{\partial S}{\partial P}\right)_{T,N_i} = \left(\frac{\partial V}{\partial T}\right)_{P,N_i}$$

$$C_P = \left.\frac{\partial H}{\partial T}\right|_{P,N_i} = T\left(\frac{\partial S}{\partial T}\right)_{P,N_i}$$

$$C_V = \partial U \Big| = T\Big(\partial S$$

So, in addition, we are going to also write down the other variables, which we are often going to use that is del, the definition of Cp and Cv ok. Now, let us go back to the expression of del U. So, what we needed, we needed to get this and this. So, this is nothing but this whole thing is Cv, right. What about this del S by del V?

(Refer Slide Time: 08:51)



$$C_V = \left.\frac{\partial U}{\partial T}\right|_{V,N_i} = T\left(\frac{\partial S}{\partial T}\right)_{V,N_i}$$

$$\Delta U = \int_{T_1}^{T_2} C_V\Big|_{V=V_2} dT + \int_{V_1}^{V_2}\left(T\left.\frac{\partial P}{\partial T}\right|_V - P\right)\Big|_{T=T_1} dV$$

Make use of measurable quantities

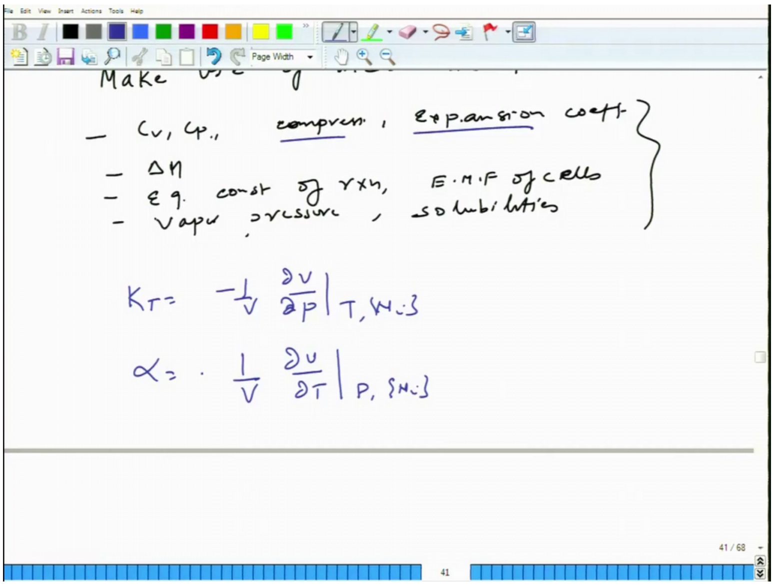
- Cv, Cp., compress., expansion coeff
- ΔH
- Eq. const of rxn, E.M.F of cells
- Vapor pressure, solubilities

Let us look at del S by del V expressions. So, del S by del V is nothing but, it is del P by dou P by dou T or del P by del T. So, we can directly tell now write this expression ok. So, what we have now, final expression is delta U in terms of measurable variables ok. We add some value V 2. This is one path ok, the expression will be slightly different ok. The only thing is that the constants are going to be different ok, if we use another path

So, this whole thing will be at constant T is equal to T 1. This is one path which I have considered. So, one way I have considered V constant taken to a temperature T and then, the other one is we consider T constant ok. So, remember that, what we are interested is to make all this, this exercise is to make use of measurable quantities such as, C V, C P, and we are going to define compressibility, expansion coefficient, delta h changes enthalpy because, you can use calorimetry and all this thing to get a delta h.

Then, you can also use this equilibrium constant. This is also easy to find equilibrium constant of reaction EMF of cells, vapor pressure, solubility. These are all, this you can find out from experiment; these are measurable quantities. So, we have to make use of our thermodynamic variable changes in terms of this quantities.

(Refer Slide Time: 10:54)



Make

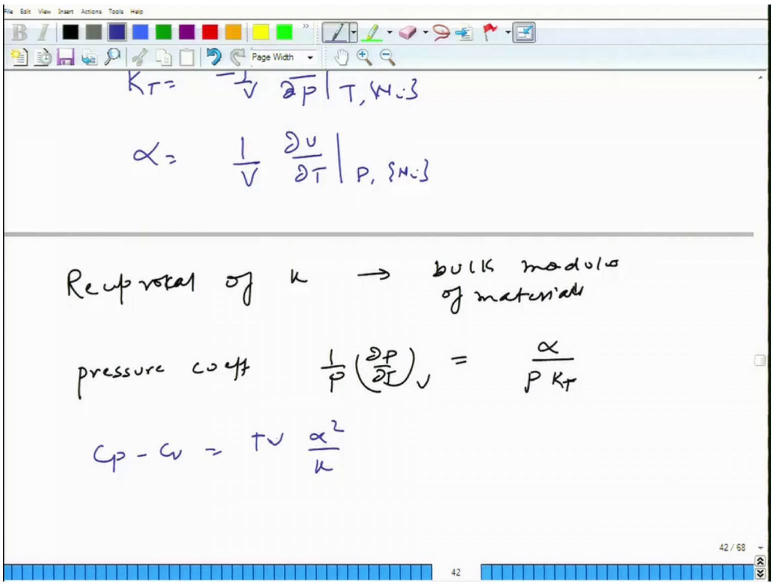
- C_v, C_p, compress, expansion coeff
- ΔH
- Eq. const of rxn, E.M.F of cells
- Vapor pressure, solubilities

$$K_T = -\frac{1}{V}\frac{\partial V}{\partial P}\Big|_{T,\{N_i\}}$$

$$\alpha = \frac{1}{V}\frac{\partial V}{\partial T}\Big|_{P,\{N_i\}}$$

So, let me try to comment here because, we talked about compressibility and expansibility. So, K T is minus 1 by V dou V by dou P, at some temperature and of course, you have all other thing constant and then, alpha is 1 by V del V by del T at constant P. Now, these are positive values, these are these are positive values, and, we can show that later also that, what del V by del P should be negative for stability and so forth, and hence K should be positive.

(Refer Slide Time: 11:39)



$$K_T = -\frac{1}{V}\frac{\partial V}{\partial P}\Big|_{T,\{N_i\}}$$

$$\alpha = \frac{1}{V}\frac{\partial V}{\partial T}\Big|_{P,\{N_i\}}$$

Reciprocal of κ → bulk modulo of materials

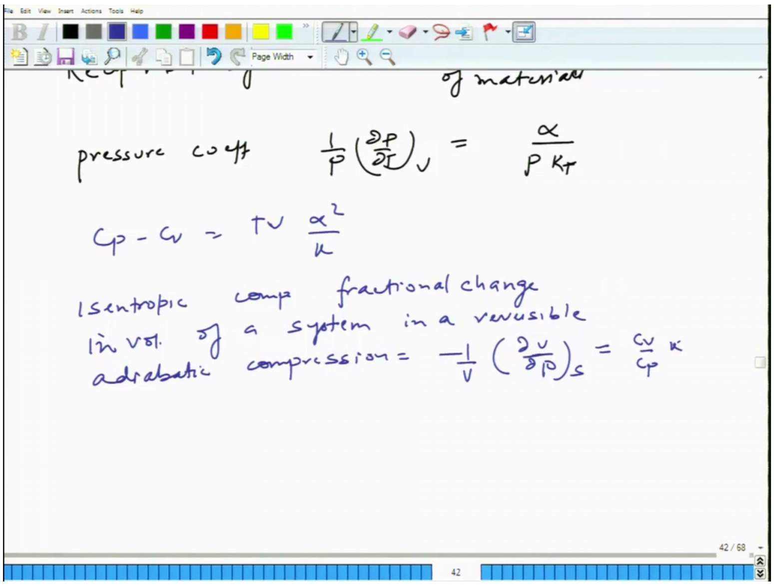
pressure coeff $\frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{P K_T}$

$$C_p - C_v = TV\frac{\alpha^2}{\kappa}$$

Now remember this also that, this compressibility, inverse of the compressibility reciprocal of K; sometimes is also called bulk modulus of the material. You can show that, similar to the way we have done this expansion coefficient, you can show that the pressure coefficient expansion is, volume is basically expanding so pressure coefficient, which would be 1 by P del P by del T at constant V, can be shown that, this is nothing but alpha by P K T ok. So, you can show that, you can also prove that ok.

So, this; it is also useful to see how the pressure is changing as you change the temperature for a constant volume ok. You can also prove or show that the C P minus C V is T V alpha square by K. And for ideal gas you can show this, this is nothing but, r.

(Refer Slide Time: 12:51)



of material

pressure coeff $\frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{P K_T}$

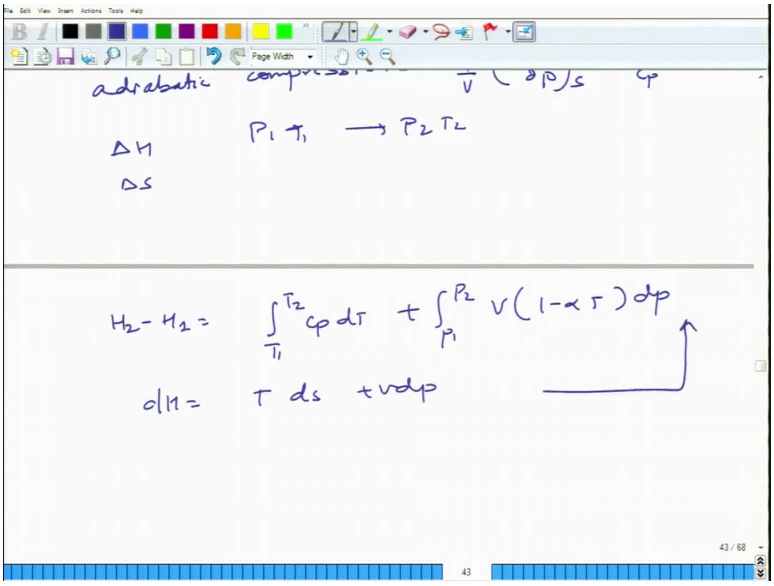
$C_P - C_V = TV \frac{\alpha^2}{K}$

Isentropic comp fractional change in vol. of a system in a reversible adiabatic compression $= -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S = \frac{C_V}{C_P} K$

Other expression which you can derive is something called isentropic compressibility fractional change in volume of a system undergoing a reversible adiabatic compression. And you can show that, this is nothing but minus 1 by V. Basically the expression here is minus 1 by V del V by del P because, you are compressing it entropy constant adiabatic compression, entropic constant reversible adiabatic is entropic constant. And this expression, you can show this is nothing but, C V by C P multiplied by K. So, you can prove that.

So, all these things you can connect to the measurable quantities; whatever you desire to do that ok.

(Refer Slide Time: 14:07)



adiabatic

ΔH $\quad P_1 T_1 \longrightarrow P_2 T_2$

ΔS

$$H_2 - H_1 = \int_{T_1}^{T_2} c_p \, dT + \int_{P_1}^{P_2} V(1-\alpha T)\, dp$$

$$dH = T\, ds + v\, dp$$

So, this, the way we have done or derived for delta U, in a similar way you can actually also calculate the expression of delta H, going from P 1 T 1 to P 2 T 2. And similarly, for delta S in a, in a measurable quantities; so, I will just do, just to try to put down the equation ok. So, for example, in the case of delta H, H 2 minus H 1, you can show that, this is nothing but T 1 T 2 C P d T plus P 1 P 2 V 1 minus alpha T d P ok. When it is very easy to actually derive, you can always do a path-based calculation because, you can start from d S is equal to d H, is equal to T d S plus V d V. And from here, you can do the next few steps to get to this expression.

So, I think as far as the maximal relation is, the derivatives are concerned as usage is concerned, I will stop here ok. And just, in the next lecture we will talk about, quickly, on the stability aspect of it.