Chemical Engineering Thermodynamics
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Lecture 23
Jacobian Method and its applications

Welcome back, so let us start with the Jacobian method this will be quite simple approach in order to remember the Maxwell relation as well as to apply to obtain various different thermodynamic relations.

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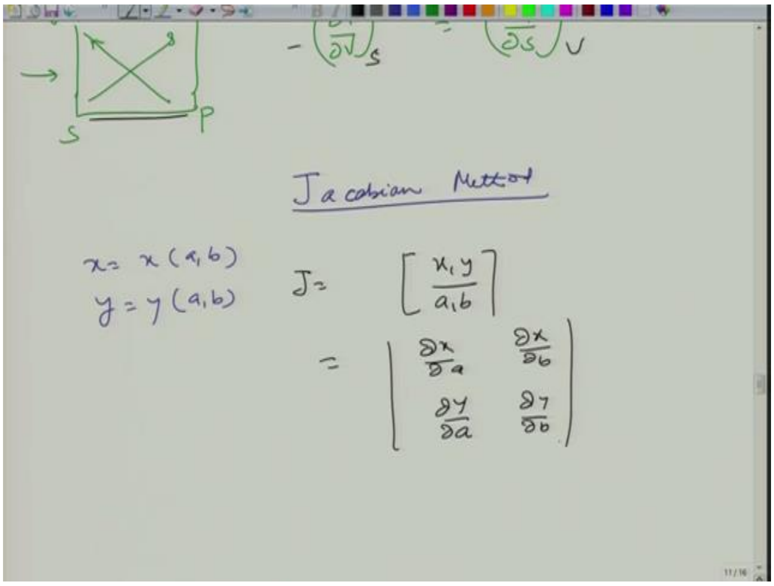

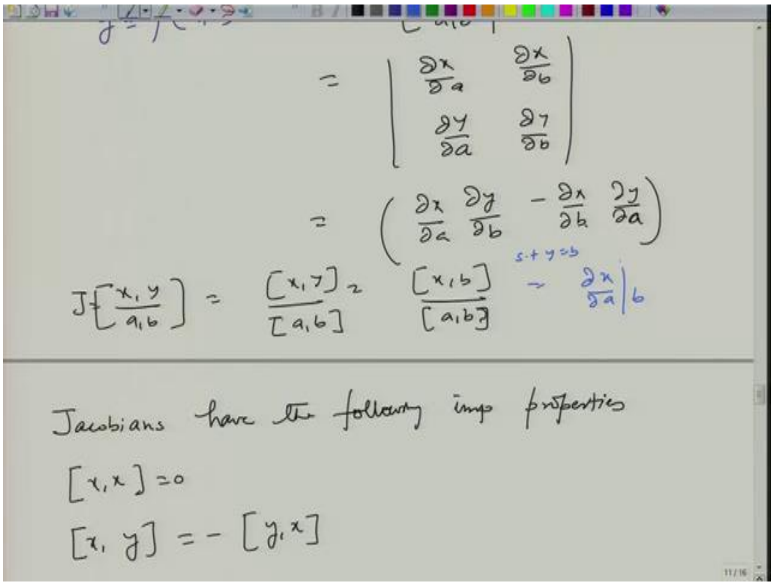

So, if you can see such method corresponding or, with respect to the one which is just based on just derivatives. So, let us consider X is equal to X A B and, Y is equal to Y A B. So, what

I am going to do in now is write down the properties of this Jacobian method. So, Jacobian is defined as follows.

$$x = x(a, b)$$

$$y = y(a, b)$$

$$J = \left[\frac{x, a}{y, b}\right] = \begin{vmatrix} \frac{\partial x}{\partial a} & \frac{\partial x}{\partial b} \\ \frac{\partial y}{\partial a} & \frac{\partial y}{\partial b} \end{vmatrix} = \left(\frac{\partial x}{\partial a}\frac{\partial y}{\partial b} - \frac{\partial x}{\partial b}\frac{\partial y}{\partial a}\right)$$

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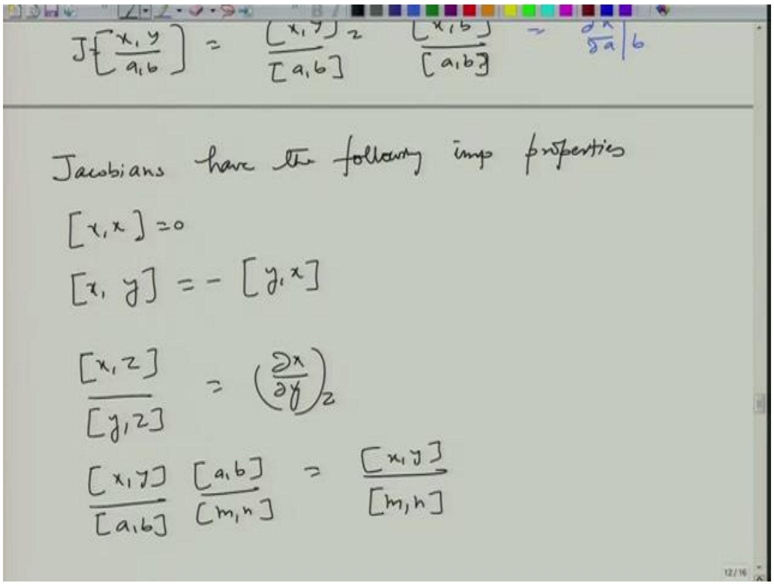

So, Jacobian has the following properties, important properties.

$$[x, x] = 0 \qquad [x, y] = -[y, x]$$

$$\frac{[x, z]}{[y, z]} = \left(\frac{\partial x}{\partial y}\right)_z$$

$$\frac{[x, y]}{[a, b]}\frac{[a, b]}{[m, n]} = \frac{[x, y]}{[m, n]}$$

So, you may ask question what does this particular mean. So, this will be more like a differential of X keeping X constant or differential of X keeping Y constant. And, essentially this is directly related to the determinant in their approach. For example, in this case if I had to replace this by B, A by B by considering such that Y is B than it essentially means del X by del A by B.

Now, this you can prove it by using this. So, you can plug in this and essentially you can show that, this is indeed this expression from the Jacobian expression. You can derive it. So, without as i said without going to details we are going to write these expressions and then we will make use of it in our thermodynamic derivations.

So, X of Z, Y of Z, is nothing but del X by del Y keeping Z constant. For convenience we write it in this way, it is easy for us to make use of our analysis. So, for the case of this X Y, A B and so A B, A B get cancel so this is nothing but X Y, this okay. So, these are the properties here now how do we use it?

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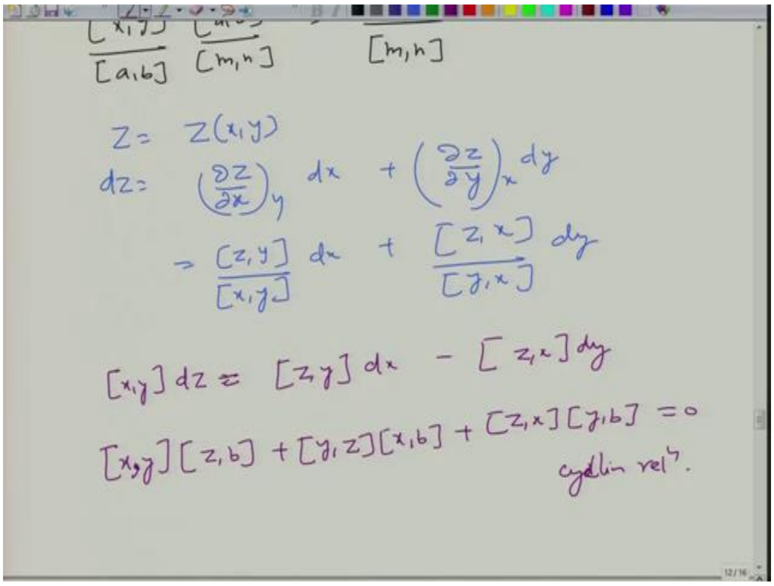

Let us try to do some examples here so, let us say consider Z is equal to function of X and Y. And we would like to take the Z into the differential form D Z, which I can write it in the following way. Now here what I would like to do is I would like to represent this expression that the partial derivatives in the form of Jacobian.

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

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

$$[x,y]dz = [z,y]dx - [z,x]dy$$

$$[x,y][z,b] + [y,z][x,b] + [z,x][y,b] = 0 \; (cyclic\ relation)$$

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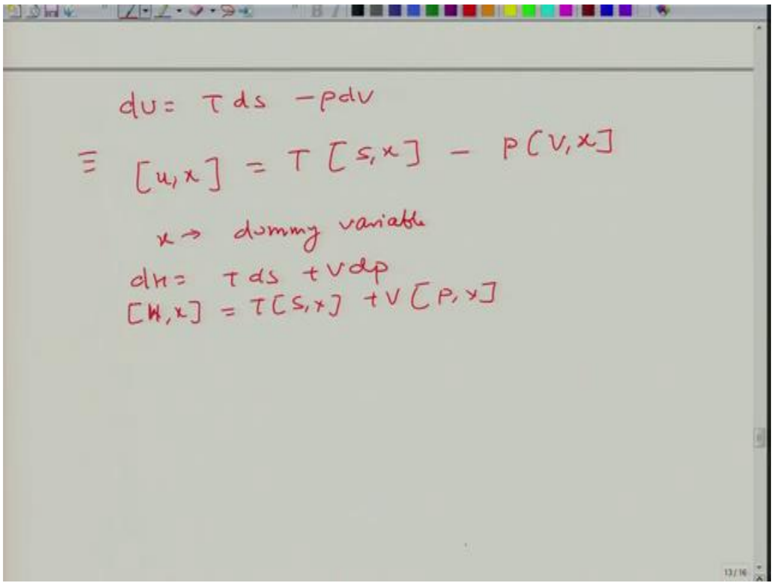

So if you apply this thing for thermodynamic potentials in the derivative form:

$$dU = TdS - PdV$$

$$[u, x] = T[s, x] - P[v, x] \quad x \; is \; a \; dummy \; variable$$

$$Similarly, \qquad dH = TdS + VdP$$

$$[h, x] = T[s, x] + V[P, x]$$

Similarly, I can do that for other variables. Now, let us apply this concept of Jacobian to the Maxell relation and see what kind of expression we get when we apply to Maxwell relation.

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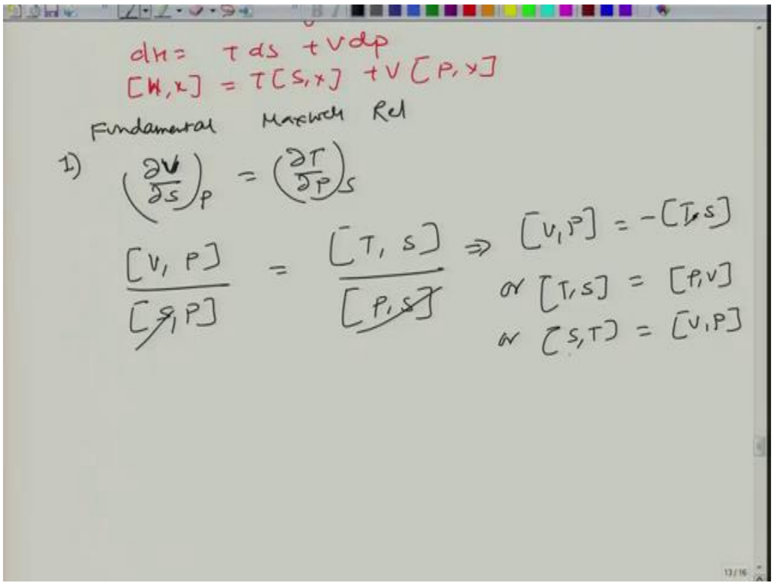

So, let us start with the first Maxwell relation. So, I am going to write this as del V by del S P is equal to del T by del P, S. So, this is first Maxwell relation which we have. And now, I would like to see how this will yield, what can of expression it will yield, if we apply the Jacobian method. So, Jacobian method if you apply this is V so this will be your V, P, S, P and this is your T, S and P, S. Now we know that S, P is nothing but minus of P, S.

So hence, this would mean that V, P is equal to minus T, S because this will cancel out with a negative sign here, so this will be minus A. Now or I can write this as T, S is nothing but P, V, or I can write as S, T is nothing but V, P so these are equivalent. So, I have one relation now from this particular Maxwell relation in terms of a Jacobian.

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$$

$$\frac{[V,P]}{[S,P]} = \frac{[T,S]}{[P,S]}\ or, [V,P] = -[T,S]\ \ or, [T,S] = [P,V]\ or, [S,T] = [V,P]$$

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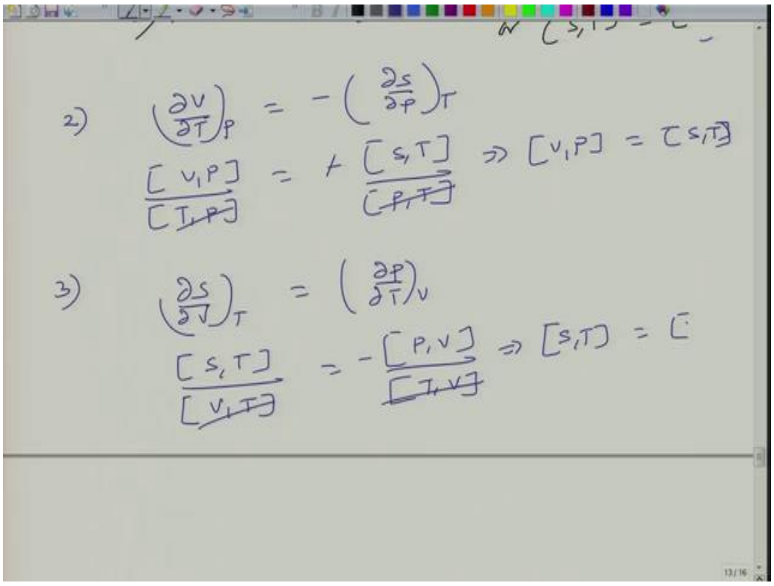

$$Similarly, from,\ \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

$$[V,P] = [S,T]$$

$$From, \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$[S,T] = -[P,V]$$

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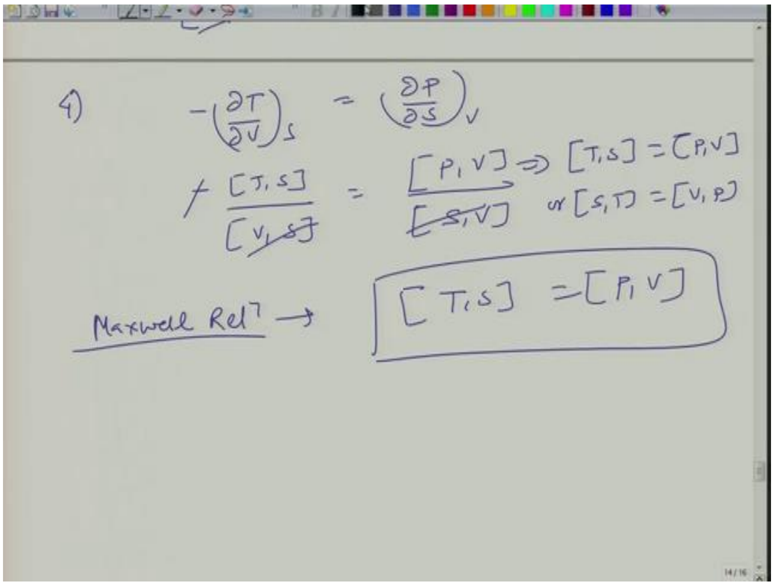

Let us look at the final Maxwell relation we have from this fundamental relation.

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

$$[T, S] = [P, V]$$

So, it turns out that all the four Maxwell relation yielded the same in the form of Jacobian variable. So, finally one can summarize that Maxwell relation in Jacobian expression is just one expression that is T, S is equal to P, V.

You do not have to remember the four expressions, you just have to remember the one in Jacobian that solves the problem significantly. So, how do you adopt a method of Jacobian in solving thermodynamic problems as well as the relation the derivative which we have to evolve or derive?

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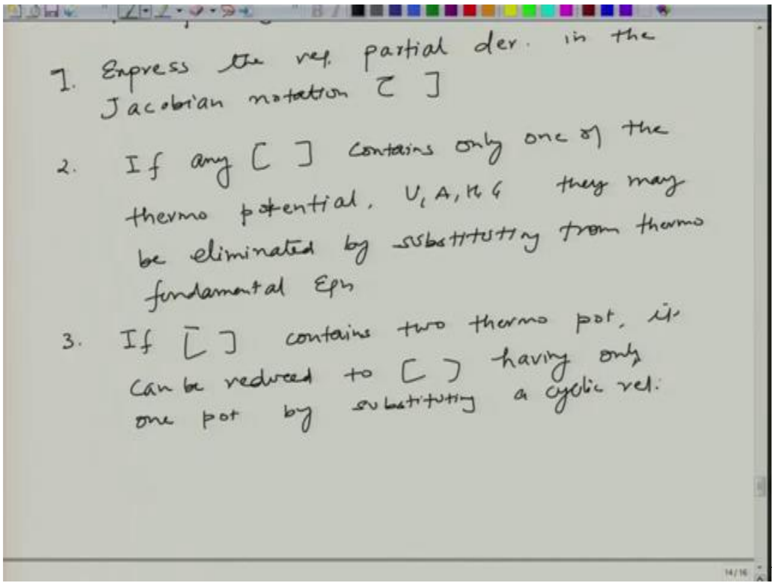

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Now one can write down a summary of this kind of a procedural form. So, the following procedure can be adopted may be adopted. So, express the required partial derivative in Jacobian notation. So that will be the first step. The second step is, if any notation or Jacobian expression contains only one of the thermodynamic function or potential, that is U, A, H and G they may be eliminated by substituting from thermodynamic fundamental equation. So that is a point number 2.

Point number 3 is, if contains a two thermodynamic function or thermo potential. It can be reduced to expression having only one potential by substituting or by making use of cyclic relation. So in such case you have to use cyclic relation.

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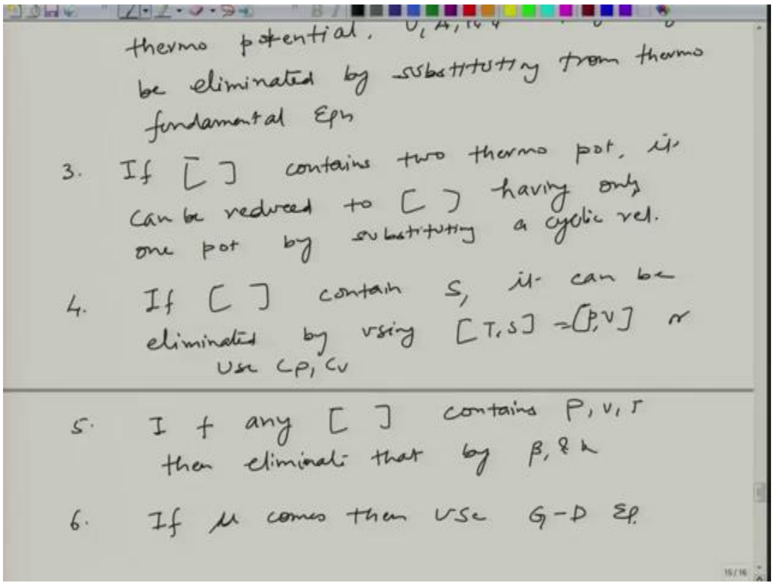

Now forth, if the notation or the expression contains entropy S, then it can eliminated by using Maxwell relation. T, S is equal to P, V or use C, P or C, V. If any notation contains P, V, T then you can eliminate that by using beta and kappa. Finally, if chemical potential comes in use Gibbs–Duhem equation. So, this is something which one can summarize how one have to use the Jacobian in order to solve problem.

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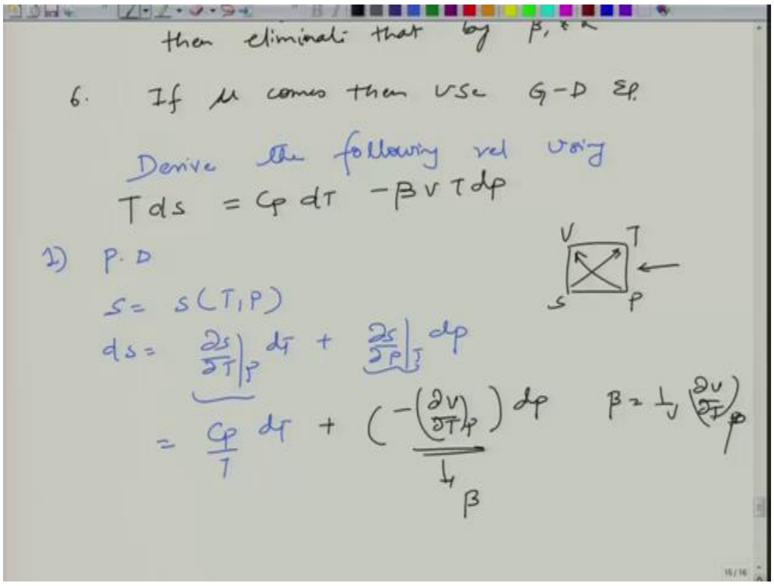

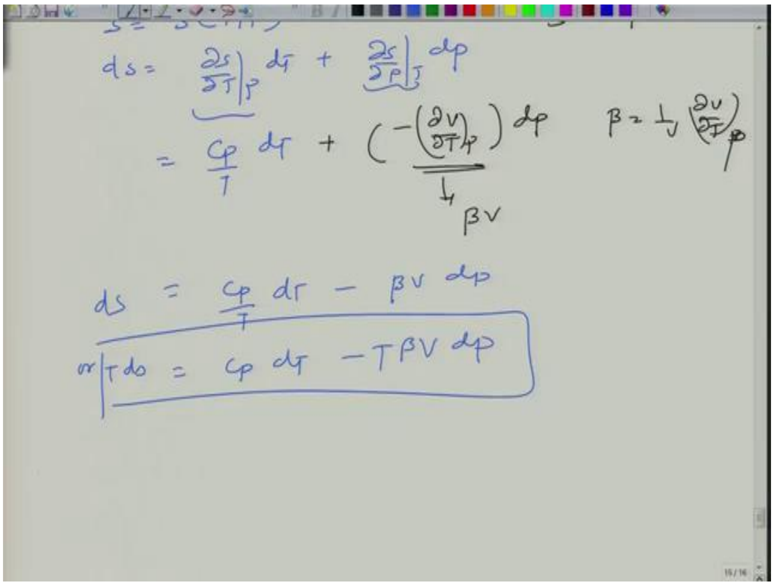

So, before I close this section our lecture. Let me try to solve a final example using both the methods the method which is partial derivative one, and the other one is Jacobian method. So you have derive this expression, so the first which we will try is partial derivative based.

$$S = S(T, P)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP = \frac{C_P}{T} dT + \left(-\left(\frac{\partial V}{\partial T}\right)_P\right) dP$$

$$TdS = C_P dT - \beta VTdP$$

So, this is from your partial derivative approach.

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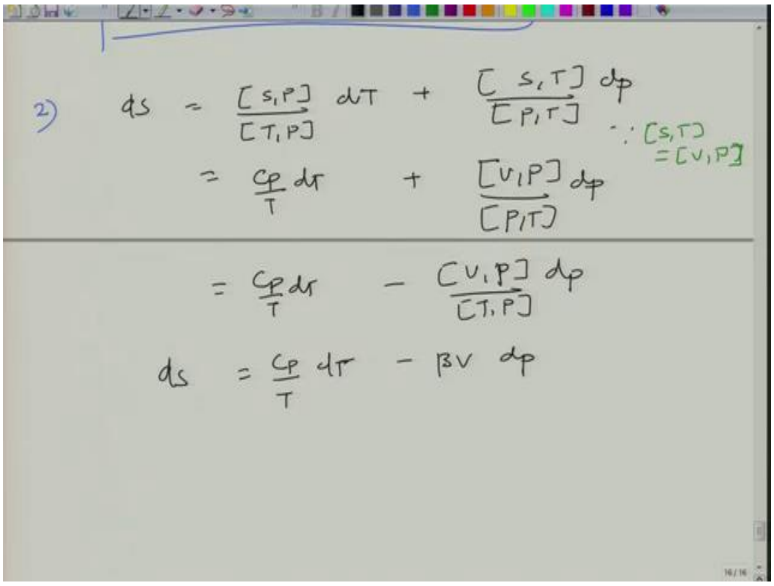

Now let us see how we do when we make use of Jacobian. So, now looking at this expression again we go back to this expression. So this, we have the partial derivative, we have to represent the partial derivative with respect to the Jacobian notation. And this is what I have written here also express the required partial derivability in the Jacobian notation.

Now, this we know anyway this is a C P by T. There is nothing great about that, but what about this? Now we have to replace S. Now, we know the Maxwell relation, Maxwell relation for this is straight forward S, T is nothing but V, P. So, remember that S, T is nothing but V, P. So, I have got this relation straight forward I do not have to worry about bond diagram or anything else.

Now this V, P if you replace this sign rather in here P. Then I can get negative sign here I can write P and this is T, P. So this is nothing but del V by del T at constant pressure. And this something which we can now replace by beta V. So you still have to remember the definitions of the beta and K and, C, P and C, V and that is necessary.

$$dS = \frac{[S,P]}{[T,P]} dT + \frac{[S,T]}{[P,T]} dP$$

$$= \frac{C_P}{T} dT + \frac{[V,P]}{[P,T]} dP$$

$$= \frac{C_P}{T} dT - \frac{[V,P]}{[T,P]} dP$$

$$dS = \frac{C_P}{T} dT - \beta V dP$$

And in addition of course you have to remember or, you can derive this on the fly the thermodynamic functions. But otherwise, there are two different approaches which you can make use of it to calculate their derivatives or the expressions of thermodynamic functions. So I hope that I have given a comprehensive way to solve problems in thermodynamic property relation making use of the partial derivatives Jacobian and the definitions are C, P, C, V, alpha, kappa this would help perhaps, you will see that later part you will be using this.

And of course with the help of some certain assignments you will also practice. And hopefully you will gain the solid foundation for using these expressions or this understanding to derive the derivations for complex expression as well. So I think I will stop here and in a next lecture I will move to equilibrium, stability and other kind of concepts. Okay, so I will you see in the next lecture.