Chemical Principles II
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Thermodynamic Relations: Jacobian Method Part 01

Okay, so we have seen Maxwell relations that actually originates from the fact that the thermodynamic potentials, which are of course the Legendre's transformation of the internal energy. So, the thermodynamic potentials being an exact differential give rise to 4 different Maxwell relations. However, as you know that there are many possible thermodynamic potentials are there or many possible thermodynamic quantities are there, I can write some of them.

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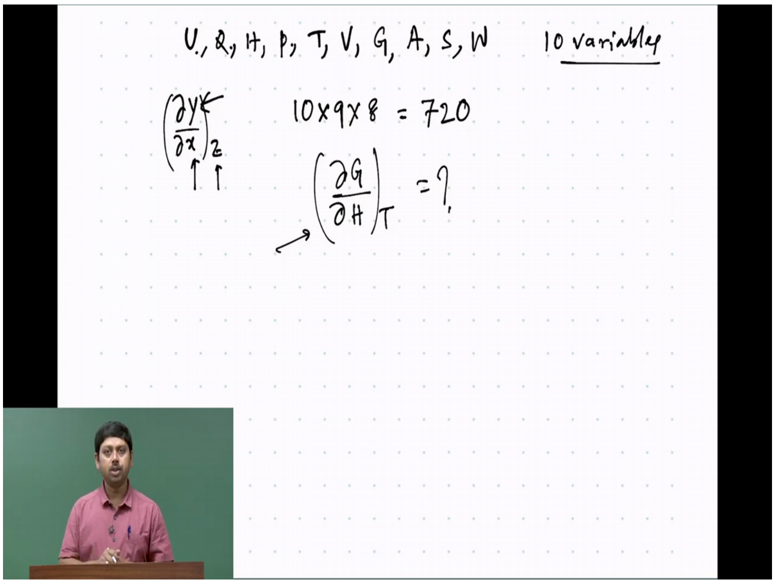

For example, internal energy U, then Q, as heat, then enthalpy, pressure, temperature, volume, Gibbs free energy, Helmholtz free energy, entropy, work done and many other things, so, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, let us say there are 10 different variables 10 different variables or parameters. Now, once you write, when you write a particular partial differentiation, for example dy by dx at a constant z, you need 3 variables y, x and z. So, therefore I can take y as any of the 1st 10 and then acts as any of the next 9 and then z as any of the next 8, giving me 720 possible partial derivatives.

Now, once you take these 720 possible partial derivative and in order to equate with similarly more, number of another set of 3 partial derivatives, there are huge number of partial derivative that can be formulated. And therefore in order to convert one partial derivative to another partial derivative can become a really humongous task or a very difficult task. However, why do we need to calculate such partial derivatives? For example, why do we need to calculate something like dell G by dell H at a constant T. Why do we need even these kind of quantities?

So, you will see that, as I mentioned also earlier that any of these partial derivatives ultimately can be cast into the few heat capacities that we discussed. For example, specific heat at a constant pressure, specific heat at a constant volume, then isothermal compressibility or adiabatic compressibility and coefficient of thermal expansion. So, these are the quantities through which any of the partial derivative can be expressed. And since those quantities are experimentally measurable, therefore we can always relate to any of these quantities to those experimentally measurable quantities.

Because it is not easy to perform an experiment where we change the enthalpy of the system and calculate free energy at a constant temperature, it may not be possible. As you know that it may not be possible to directly measure and entropy of the system. And therefore we need to calculate free energy at different temperatures in order to get the value of entropy. So, something like an indirect relation. So, in order to do that we have to know how to break these partial derivatives what I mentioned into those heat capacities and thereby we can estimate experimentally those partial derivatives.

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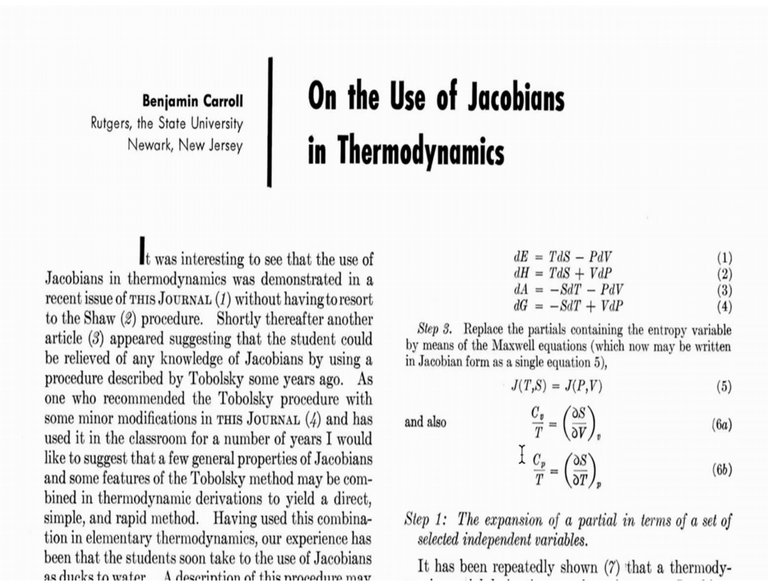

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On the Use of Jacobians in Thermodynamics

It was interesting to see that the use of Jacobians in thermodynamics was demonstrated in a recent issue of THIS JOURNAL (*1*) without having to resort to the Shaw (*2*) procedure. Shortly thereafter another article (*3*) appeared suggesting that the student could be relieved of any knowledge of Jacobians by using a procedure described by Tobolsky some years ago. As one who recommended the Tobolsky procedure with some minor modifications in THIS JOURNAL (*4*) and has used it in the classroom for a number of years I would like to suggest that a few general properties of Jacobians and some features of the Tobolsky method may be combined in thermodynamic derivations to yield a direct, simple, and rapid method. Having used this combination in elementary thermodynamics, our experience has been that the students soon take to the use of Jacobians as ducks to water. A description of this procedure may

$$dE = TdS - PdV \quad (1)$$
$$dH = TdS + VdP \quad (2)$$
$$dA = -SdT - PdV \quad (3)$$
$$dG = -SdT + VdP \quad (4)$$

Step 3. Replace the partials containing the entropy variable by means of the Maxwell equations (which now may be written in Jacobian form as a single equation 5),

$$J(T,S) = J(P,V) \quad (5)$$

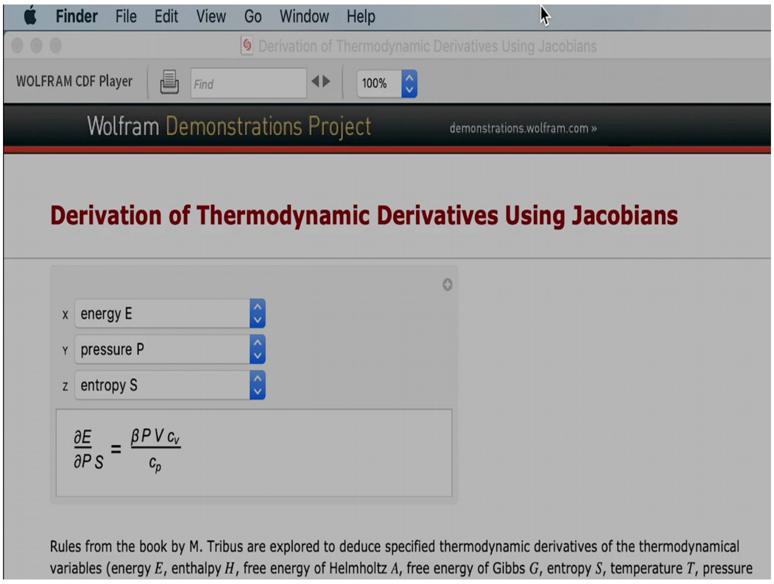
and also

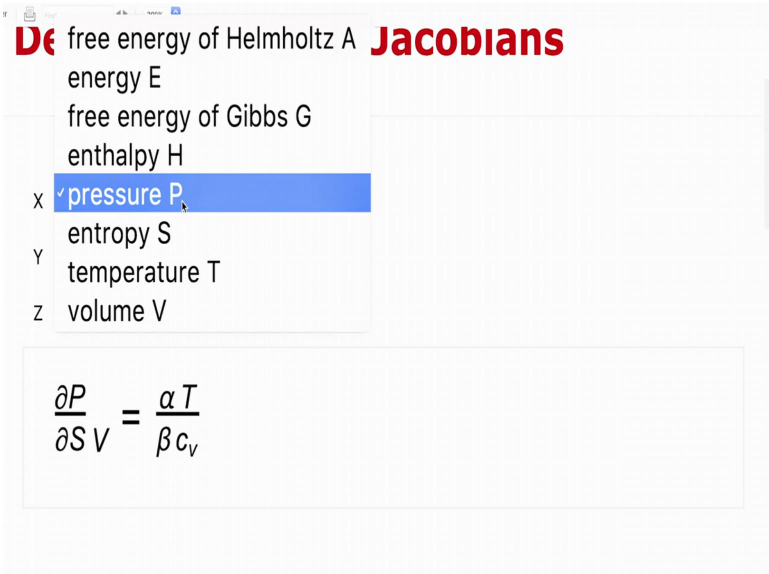
$$\frac{C_v}{T} = \left(\frac{\partial S}{\partial V}\right)_v \quad (6a)$$

$$\frac{C_p}{T} = \left(\frac{\partial S}{\partial T}\right)_p \quad (6b)$$

Step 1: The expansion of a partial in terms of a set of selected independent variables.

It has been repeatedly shown (*7*) that a thermody-





And therefore this particular subject of conversion of partial derivatives or transformation of partial derivative is very important in thermodynamics. And we are going to discuss that today. So, in the textbook there are a standard techniques often I find it very difficult to convert one partial derivative to another. However, I encountered a software, like Mathematica, which I talked to you before, that it can convert you know partial derivative from one form to another form very easily.

And when I looked into that, and I will show you a moment that thing, how to convert one set of partial derivatives to another using Mathematica, when I encounter that, I tried to find out the logic behind it. Remember, Mathematica is just a computer program and therefore it must have a very definite logic by which it can convert one form to another form. And then I saw that it follows a procedure called Jacobian technique or Jacobian Method of conversion of partial derivatives. And we are going to talk to you about that.

This method is not so popular in books, however there are papers associated with it and I am going to show you the paper and also I am going to show you the conversion of partial derivative using the Mathematica briefly. So, okay, so this is the, this is the paper that can be followed on the use of Jacobian in thermodynamics by Benjamin Carroll and this came in the Journal of chemical education. This is the technique that I am going to discuss today for conversion of partial derivatives and you can refer to this particular paper in order to this method in more detail.

And I am going to show you also using Mathematica that we can convert that. Okay, so you see I am hoping something equivalent to Mathematica, called computable document format, which is freely available, you do not have to have a license or anything. So, that you can also test it, for example you can look at a particular partial derivatives written as, so as you can see, this is a partial derivative of dE by dP at a at S which is, I can show you a, dE by dP or dU by dP at a constant S. Once you do that, you get beta PV CV by CP.

So beta is again isothermal compressibility as I see, let me see what is mentioned as beta. See, coefficient of thermal expansion is alpha, and compressibility is beta. So, beta is compressibility, which is you know as -1 by V dell V by dell P at a constant temperature. So, isothermal compressibility and sometimes it is also written as kappa T, I mentioned is Kappa T. And alpha is coefficient of thermal expansion, which is 1 by V dell V by dell T at a constant P. And PV are just pressure and volume and CP and CV also you know are specific heats.

So, you can see that the change in internal energy E as a function of P is at constant S is nothing but this particular quantity. All of them are measurable and therefore one can measure this particular partial derivative. So, if I change it, I can also show you some other example. So, if I change E to let say something like G and if I change the pressure to something like S and if I take it at a constant V, I get to see another different expression as mentioned here. So, Mathematica can quickly calculate that, I can also calculate dell P and I can also show you some of the Maxwell's relations.

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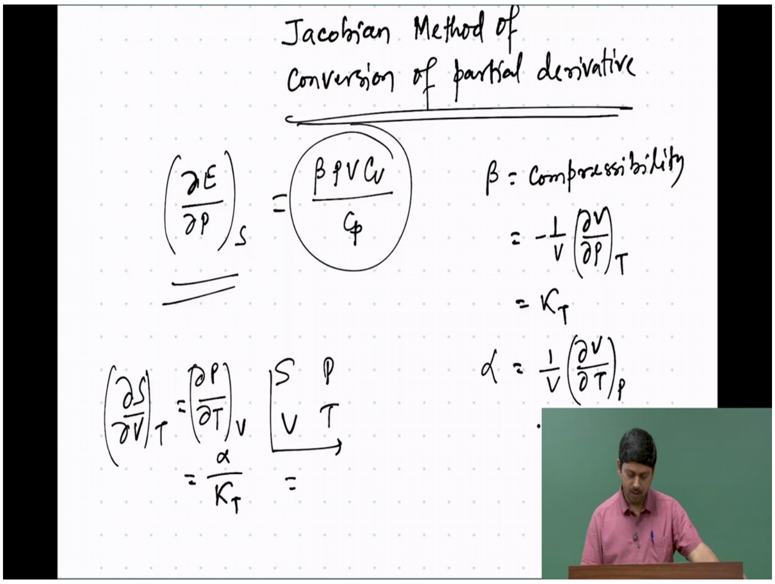

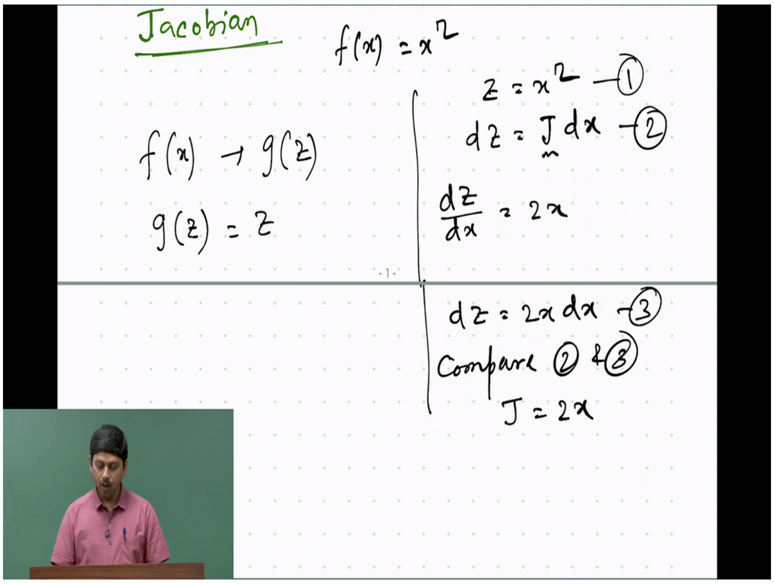

So for example, I can show you dell S, so dell S by dell V at a constant temperature, so we know that dell S by dell V at a constant temperature is nothing but dell P by dell T at a constant volume and that is coming as Alpha by beta which is Alpha by Kappa T. So, you know that dell S by dell V at a constant temperature is dell P by dell T at a constant volume from this Maxwell relations we can we can calculate that. dell S by dell V at a constant temperature is dell P by dell T at a constant volume and that is coming out to be Alpha by Kappa T.

So let us see dell P by dell T at a constant V also. dell P by dell T at a constant volume and that is also alpha by kappa T. So, you can see that whatever the Maxwell relation gives, thermodynamics position also gives the same thing. So, now we have to find out a general way to get all possible partial derivative and that is what we are going to discuss today. So, 1st of all we want to understand what is Jacobian. So, let us see what is Jacobian. Jacobian is something that changes the variable from one to another. For example, Fx is x square and I want to convert it to a function, another function of z.

So I want to change x to z. So, let us say I write z as x square, so in that case if I take a derivative of z, I will write that dz as J Jacobian into dx. So, Jacobian is the quantity that will convert one variable to another variable. So, what will be the value of z? So, let us take a derivative of this particular equation 1. So, dz by dx we know is 2x. So, therefore dz is nothing but 2x dx. Now, when you compare equation 3 with equation 1, equation compare 2 and 3, what do we get? We get to be 2x.

So, Jacobian is something that, again, as I said convert one variable to another variable. And therefore we can write the Fx function as some, we can convert Fx to some Gz function where my Gz will be just simple z because I am converting just x square mapping Fx to another variable z. And whenever we want to take a derivative of that, we need to use the Jacobian form. Now, we do not use the Jacobian for the 1st, when the function is dependent on one variable only. Then we do not need to use the Jacobian because we can get directly by taking the derivative with respect to the function.

But let us say I have a function that depends on 2 variables. Often we know that our function U or internal energy U depends on let us say able to variables x and y. When that happens, we know that we can write dU as, the total differential as dell U by dell x dx at a constant y of course, dx + del U. And I am betting U is a small thing, it does not necessarily mean that it is the internal energy, it is just some function U, just a function U of x and y variables. So, del U by dell y dy. So, U is a function and also lets say x is also a function of x and y.

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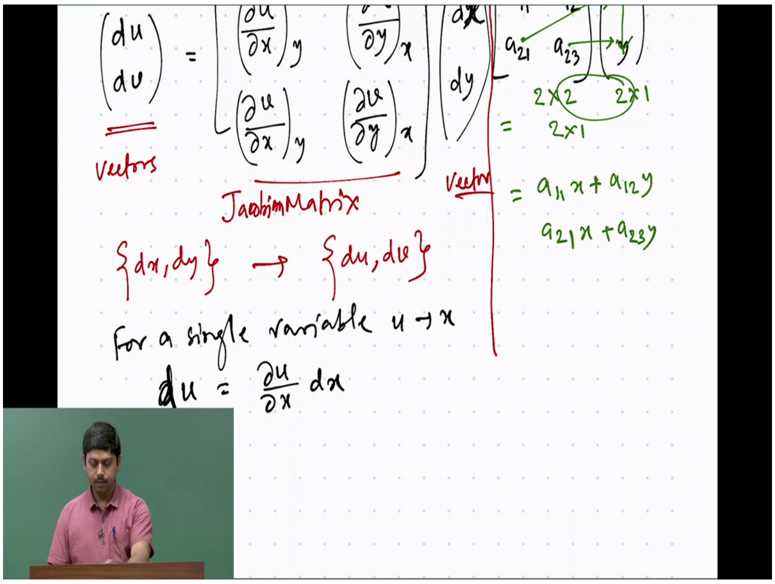

So, I can write dv as dell V dell x at a constant y + dell V dell yx dy. Now I get equation 4 and equation 5. At this point you need to know something called matrix multiplication. So, if you do not know matrix multiplication, you do not have to worry because we are not going to talk about too many variables, we are going to talk about only 2 variables only. Okay, I forgot to write the dx. So, now we have these 2, now you need to know matrix multiplication. So, I will just briefly tell you about matrix multiplication. So, let us say I talk about a 2 by 2 matrix A 11, a 12, a21, a 23 and when you multiply with let us say 2 variables x and y, then we have to multiply in this way.

you go, I will just draw with a different line. This, this way. And so, so if I multiply this matrix, this is 2 cross 2 matrix and this is just 2 cross 1 matrix, that will give me 2 cross 1 matrix. And if I write that, it will be a 11 x + a 12 y, one term, another term will be a 21x + a 23y. So, there also I am going this to this and + this to this, the disciple matrix multiplication. So, if I used matrix multiplication, it is very easy and convenient to write multiple variables in matrix form.

So, I am going to write this equation 4 and 5 with the matrix form as this. So, dU by dV, dU and TV, these 2 variables on the left-hand side, so it is a matrix of 2 cross 1. And right-hand side I have a matrix of this 2 cross 2 term, dU by dx y, dU by dy x, dV by dx y, dV by dy x. And then I have this dy dx and dy, okay. I will just put a line here in order to denote the separation of the space. So, you see I got now a matrix form of an equation. This is typically called as vectors, this is matrix and this is also a vector.

So what essentially we are doing is that I have this pair of variable x and y, which I am converting to a pair of variable U and V, that is what we are doing. And this is a Jacobean matrix. If I had only one variable, you see it will reduce down to only one term. So, if I did not have to variables, then you know I will get just 1 as you can see. I will get let us say du and let us say there is, converting U to x, I will simply get dU equal to dU by dx dx.

For a single variable, let us say U going to x, I will simply get dU equal to dell U by dell x dx. So, you can see for 3 variables I can get 3 by 3 matrix, for variables, 4 by 4 matrix and things like that. And I will get a Jacobean matrix and using that Jacobian matrix it will be helpful really to get the desired changes in thermodynamic variables. How, that we are going to discuss. Before we do that, we will discuss some notations.

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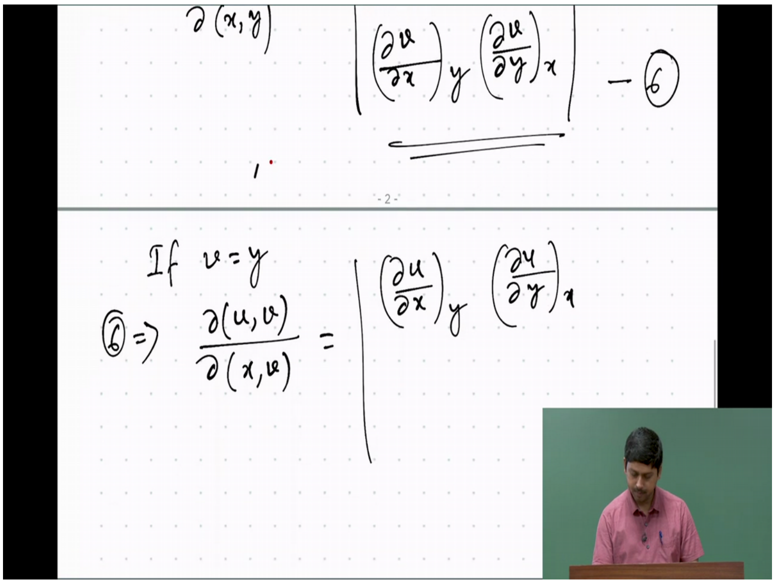

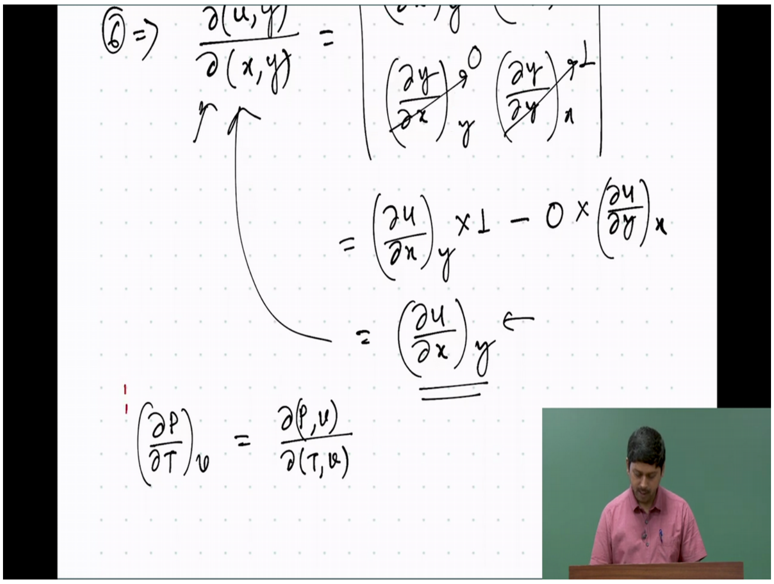

One notation is that this matrix that we talked about, Jacobian matrix can be written in a much simpler form as this one. So, this means dU by d x constant y, dU by dy at a constant x and then dV by dx at a constant y and dV by dy at a constant x. Whatever the Jacobian matrix we discussed, this is our Jacobian matrix. So, this is just a shorthand notation, till now we only know dy by dx kind of thing. But, here you see, I am using a pair of variables dUV by d xy. And that I have to write in this form.

So, you can see that immediately some properties will come up, let us say if V equal to y, so what will happen, so let us call that as equations number 6. So, if V equal to y, then from 6 what we will get is d U, V by dell UV by dell xV. And I will write it on the right-hand side, dell U by dell x, V equal to y, right, so y dell U by dell V x, dell y by dell x, if I say V equal to y, then I can write dV as y and I can write that as dell y by dell yx. Now, you see what is the consequence of this particular thing? dUy by dx at a constant y is nothing but 0.

And this dell y by dell y is nothing but one. So, again in the matrix multiplication, you have to multiply these 2 corners, for example a 11, a 12, a21 and a22, the matrix multiplication product will be this - this. So, it will be a 11 into a 22 - a 12 into a 21, that will be the multiply product. So, similarly here what will happen is that it will be del U by dell x fixed y into 1- 0 into del U by dell y at a constant x. So, it will give you dell U by dell V's at a constant y. So, only thing is that have to just I would like to change this V to y because we said V equal to y, which means that either I keep V or I keep y, so I kept y.

So, you see what just happened. If the 2nd variable, so for example I am converting, I was converting earlier x y to UV, now I am converting xy to Uy Foster so, instead of 22 new variables, I have introduced only 1 new variable U, in that case it is simply the partial derivative. So, we can always write the partial derivatives in terms of Jacobian like this. So, I will give an example. Let us say I am talking about dell P by dell T at a constant V which is in this particular form, then I can write in this particular form as dell PV by dell TP. Okay, so this is very important because we need to convert it again and again to this kind of format. Okay.

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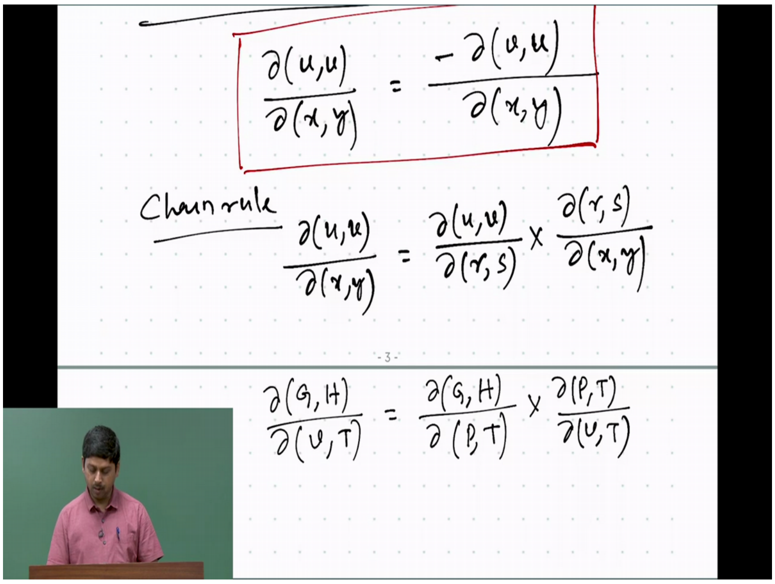

So, now the 2nd rule is element interchange. Let us say I have d U, V by Sorry dell U, V by by dell x, y. If I interchange U and V, it will become - of dell V, U by dell x, y. And that interchange basically happens due to matrix dulquer. you know, in matrix a free change one row, than the determinant becomes, so this Jacobian is determinant by the way, this Jacobian matrix, but the value Jacobian is the determinant. 5 example, here we are writing as determinant and this is the determinant of this particular matrix is this one. So, this is determinant, just matrix product.

Once you understand this role, you will see later on it will become very easy but right now it might be little bit learning curve for some of you. So, when you interchange the element, V becomes U and U becomes V, we are essentially interchanging the rows. So, V becomes U and U becomes V, means I am interchanging one row. And the rule of the matrix is that the determinant will become negative and that is why it becomes negative when you change that. So, now we are going to use chain rule, okay, so I will just border it.

I am going to use the chain rule now. Chain rule says that dell U, V by dell x, y can be written as dell U, V by dell new quantity R, S a new variable multiplied by dell R, S by dell x, y. So, often it will be necessary to introduce 2 more new variables, often it is let us say P, T. So, I can give an example for that, let us say we are trying to convert dell GH and dell V, T, I can always write GH by dell P, T multiplied by dell P, T by dell V, T. C, it is not necessary that you need to completely change both R and S, you can change one of them and that is what we have done here. So this is an example for the above chain rule.

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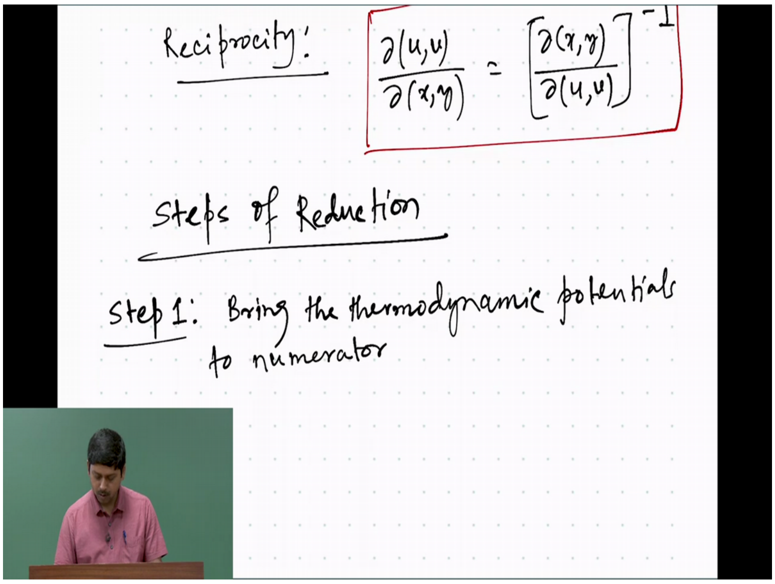

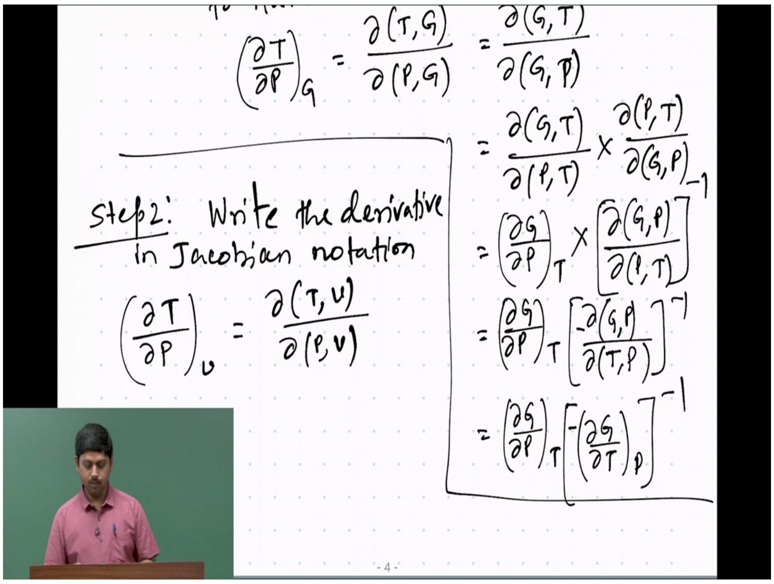

And then the final one is reciprocity, reciprocity, then the final one reciprocity. dell U, V by dell x, y is inverse of that, which means dell xy by dell UV to the power -1. Okay, so once we have that, we now need some steps, okay, so I will just border it also. So, without about reciprocity, reciprocity, we talked about chain rule, without about element interchange and we talked about that if one of the variable is less, like if enough for the nursery, then we can write like that.

So, once we have that, now we are going to tell you the steps of reduction of these variables. So, 1st of all will talk about step 1. Steps of production, now there are some rules for reducing the thermodynamic variables. So, we are going to do that. So, for example if the thermodynamic variables contain, thermodynamic derivatives contain some thermodynamic potential like G and U and all, so bring it to the numerator. So, bring the thermodynamic potentials to numerator.

For example if you have dell T by dell P at a constant G, you can write that as dell T, G by dell P, G okay. And then you can write that as, you can write that of course as G, T and dell G, T because you are converting both of them in the numerator and the denominator, so the negative cancels, GP, sorry. And then you can introduce a new variable, let us say P, T and then you can write P, T by dell G, P and then you can write dell T by dell P at a constant temperature. So, you have brought G to the numerator. And here you can write that as dell G, P by dell P, T to the power -1.

you can write even more, you can write dell G, P by dell, okay, so you can write that as T, P but with a - and that is, there is an inverse sign. So, you can write dell G by dell P at a constant temperature and this one you can write as dell V by dell P at a constant pressure, of course there is a - sign an inverse of that. So, you see that we can write, we can bring the thermodynamic potential to the numerator because that will help because many of the derivatives contain, while the thermodynamic potentials are in the numerator.

Now, step 2 of the reduction, that, write the derivative, the Jacobian notation, that is already I discussed, that write the derivative in Jacobian notation. For example, if you have dell T by dell P at a constant volume V, you can write that as T, V by dell P, V. Remember I showed that if one of the variables is same, then it will come like that, so you can show that.

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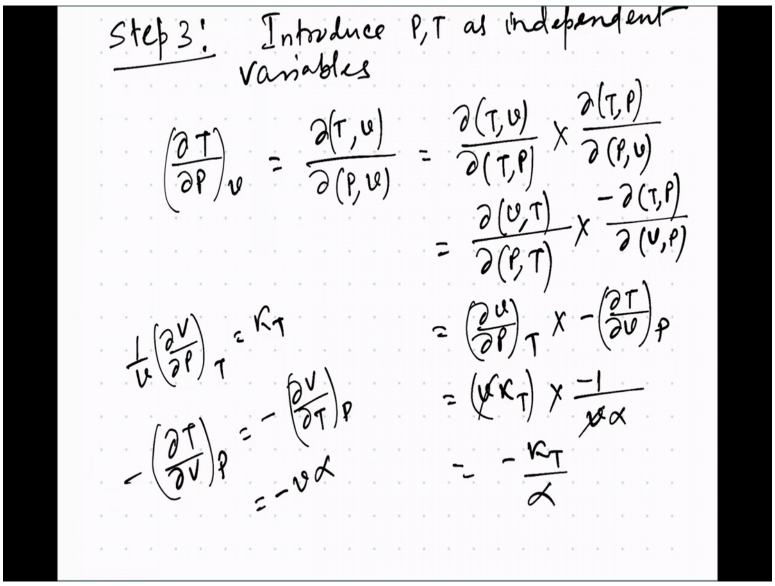

Now step 3. Introduce P and T as independent variables. you will see it is extremely beneficial to introduce these 2 variables as independent variables because many of the heat capacities used P and T. So, for example if you have dell T by dell P at a constant volume, you can write that as dell T, V and dell P, V and then you can have dell T, V and dell T, P you can bring it for which you have to multiply with dell T, P and you have the P, V. And you will see, immediately you will get some interesting thing. So, it can be written as V, T by dell P, T and this can be written as - of dell T, P by dell V, P.

Now, you know this one is dell V by dell P at constant temperature and this is - of dell T by dell V at a constant pressure. If you identify this quantity dell V by dell P, you know that 1 by V dell V by dell P is compressibility, right, isothermal compressibility, which is kappa T. So, this is nothing but V into kappa T and this one is dell T by dell V at a constant P, it is just inverse of del V by dell T at a constant P. So, this is you can see that it is - of V into coefficient of thermal expansion. And of course we have taken inverse of that. So, it is -1 by V into Alpha, if you see it as - Kappa T by alpha. So, that it becomes very very easy when you do that.

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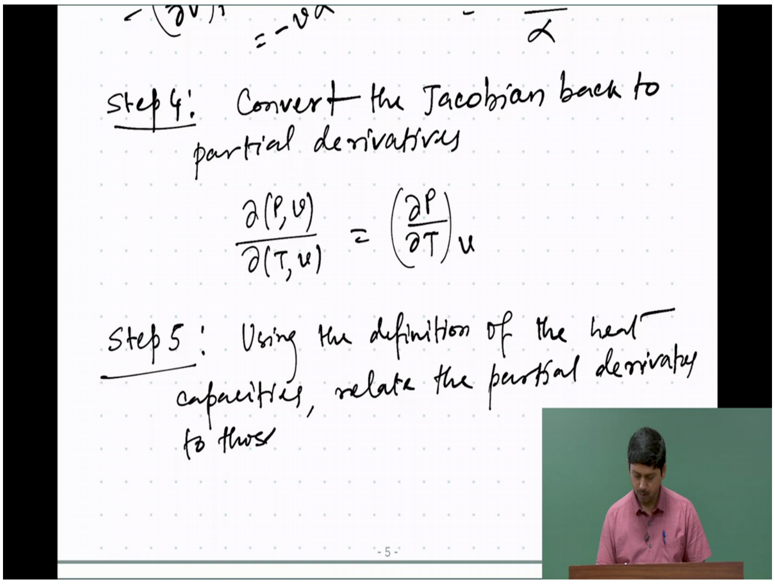

So, now step 4, okay. So, step 4 is, once you write that, of course step 4 is obvious that convert the Jacobian back to partial derivatives, which we have done as you can see here, from this step to this We have done that. Okay, Sir will give you a comfort back example, the example is let us say you have dell P, V and let us say you encounter this kind of situation that means it is nothing but dell P by dell T at a constant V, which we have used above. And then say 5 the final one, so using the definition of the heat capacities, relate the partial derivatives to those.

For example, here we have identified that, here we have done that these quantities are that. So, these are the rules for Jacobian and once you have the rule, you can convert more and more difficult partial derivative to, change from one form to another form and I am going to give you an example of that.