Chemical Engineering Thermodynamics
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Lecture 21
Multivariable Calculus

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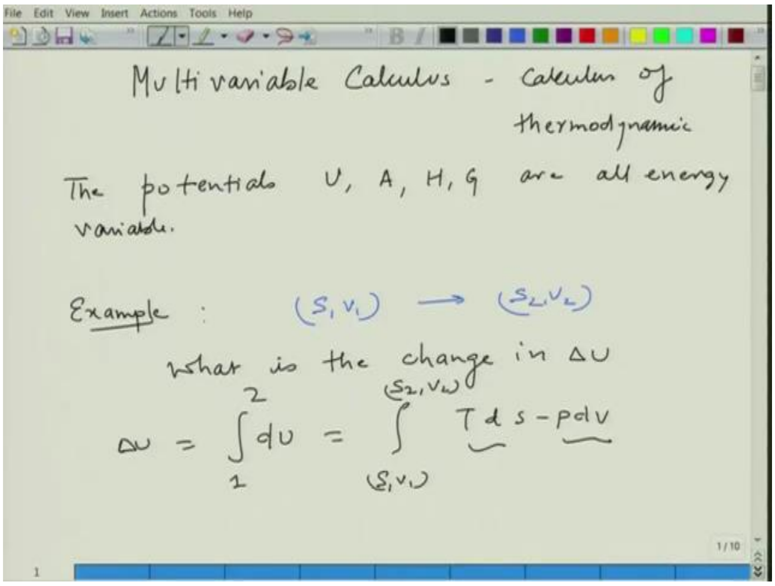

Welcome back, today's class we will be starting with the multivariable calculus and this will be over basis for later on connecting different expressions in thermodynamics particularly in a derivative form which are going to be extremely valuable in our ways to obtain properties. So, one of the important thing which we have done in the last class is to define the potentials, we have developed the potentials here, and so we need about of course U, but we develop the thermodynamic potentials A, H and G and for A the Helmholtz Free energy the natural variables as we know is T, V, N number of moles and similarly for H and G they are certain natural variables.

But these are all energies, so these are all energies and energy variables basically, and there is one of the important thing is there is nothing call like energy 0, that is a something which we must understand that, so what we typically calculate is, if there is a change in the state then the corresponding the change in the variables we are interested in such as delta U delta A delta H and delta J.

So, what we will be dealing with in thermodynamics is most was the time is basically change in the such kind of favorables. So for example, if you look at simple example like say we can talk about state process where we change from state from S1, V1 to S2, V2. The question would be, what is the change in delta U, so this could be one of the questions because for U the natural variables is S, V and assuming that the number of moles remains the constant and hence with this question is very obvious and in that case what we going to do is you are going to do just write down this as integral of delta U from let us say 1 to 2, and you are going to write the thermodynamic expression of dU which is T ds minus P dv, now this both we know it is depends on the path.

$$\Delta U = \int_{1}^{2} dU = \int_{(S_1,V_1)}^{(S_2,V_2)} TdS - PdV$$

So, you can come up with the various variety or different path enough to achieve this process change from S1, V1 to S2, V2. Now in order to achieve this we need to first understand some aspects of calculus and that is what I am going to do, kind of quick review of that, which is going to be extremely useful in the later part of this lecture or in general the understanding of this multivariate calculus should be quit useful.

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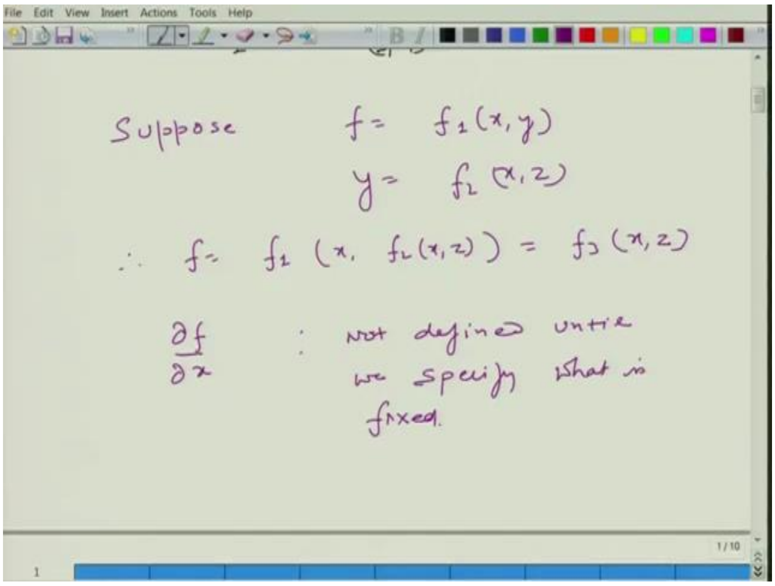

So, let us suppose: $f = f_1(x,y)$ $y = f_2(x,z)$

$$Therefore, f = f_1\big(x, f_2(x,z)\big) = f_3(x,z)$$

$$\frac{\partial f}{\partial x} \; is \; not \; defined \; until \; we \; specify \; what \; is \; fixed$$

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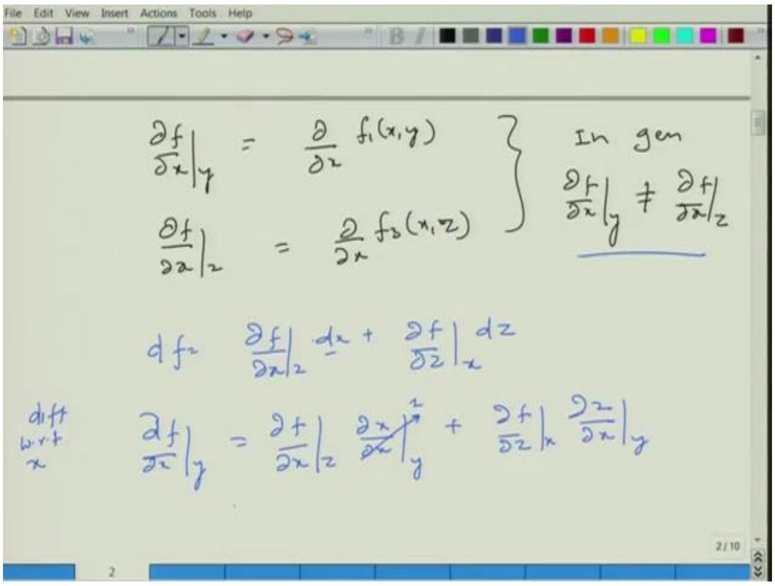

So,

$$\frac{\partial f}{\partial x}|_y = \frac{\partial}{\partial x} f_1(x, y)$$

$$\frac{\partial f}{\partial x}|_z = \frac{\partial}{\partial x} f_3(x, z)$$

In general,

$$\frac{\partial f}{\partial x}|_y \neq \frac{\partial f}{\partial x}|_z$$

Now you can clearly see that this mean that in general del f by del x at constant y need not be equal to del f by del x at constant z. So what is relation between these 2 partial derivatives? So in order to calculate the relation we can do a simple exercise and we can write:

$$df = \frac{\partial f}{\partial x}|_z dx + \frac{\partial f}{\partial z}|_x dz$$

$$differentiating\ wrt\ x,\ \ \frac{\partial f}{\partial x}|_y = \frac{\partial f}{\partial x}|_z \frac{\partial x}{\partial x}|_y + \frac{\partial f}{\partial z}|_x \frac{\partial z}{\partial x}|_y$$

$$\frac{\partial f}{\partial x}|_y = \frac{\partial f}{\partial x}|_z + \frac{\partial f}{\partial z}|_x \frac{\partial z}{\partial x}|_y$$

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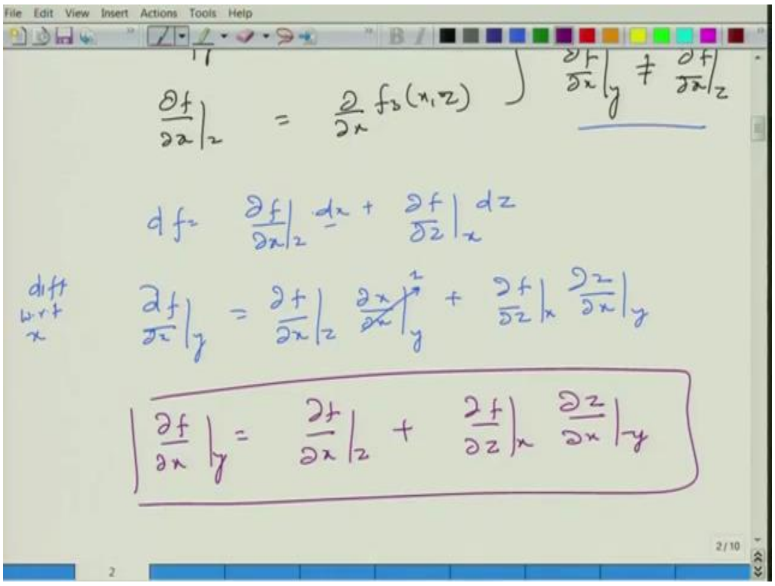

So, this is the relation between these 2 partial derivatives, so, this was the question which we raised here, so this is one example, or one particular relation which we can use in solving some of the problems. But many times we are interested as said, I am going for one state to another and this may require some kind of contour integrals, that is something which I am also going to now, describe that.

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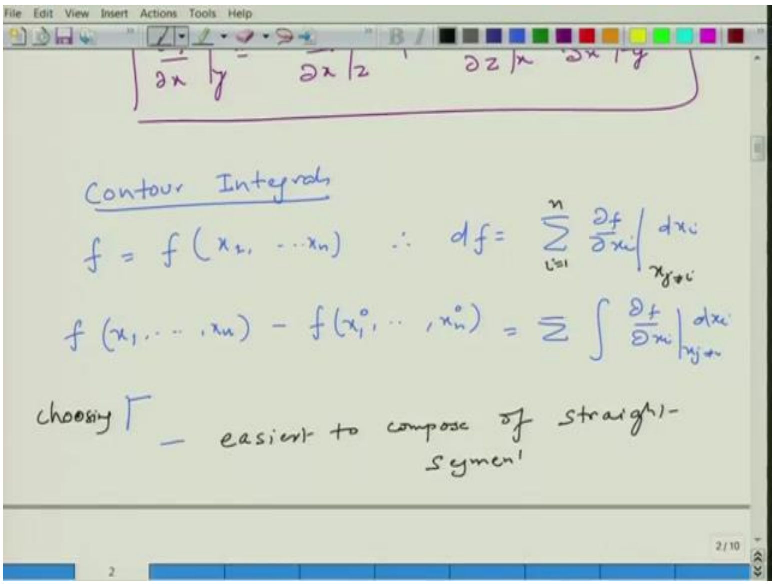

So in that case particularly which is relevant for thermodynamics would be something like where f is that say function of many variables, in that case, I can write, df as summation del f by del x i and here j is not a equal to i, where we look through, so that means for all or rather I should write this as for all xi is xj not equal to i and this is now, dx i.

$$f = f(x_1, \dots, x_n) \quad therefore, df = \sum_{i=1}^{n} \frac{\partial f}{\partial x_i} |_{x_{j \neq i}} dx_i$$

So, this is the differentiation in this form of a multivariable, now if we integrate this, between two to such that we have two specific state point then I have this left hand side has x 1, x n this is a kind of state point which have multiple planes and then the difference will be f x1 to some other initial point, and this is going to be summation integral of this del f del xi, xj equal to i dxi.

$$f(x_1, \dots, x_n) - f(x_1^0, \dots, x_n^0) = \sum_{i=1}^{n} \int \frac{\partial f}{\partial x_i} |_{x_{j \neq i}} dx_i$$

Now, the question is how so you find this path, how do we find the path or in other words if I define this path this symbol gamma, so how do we decide the path from going to 1 point to another? One of the easiest way if there is a 2 dimensional, or 2 variables state then it will be a simple collection of straight lines, so that is something which we can demonstrate for a simple problems, so choosing gamma or path is sometimes tricky business, but the easiest would be to compose this path or this particular path is composed of straight lines, or straight segments.

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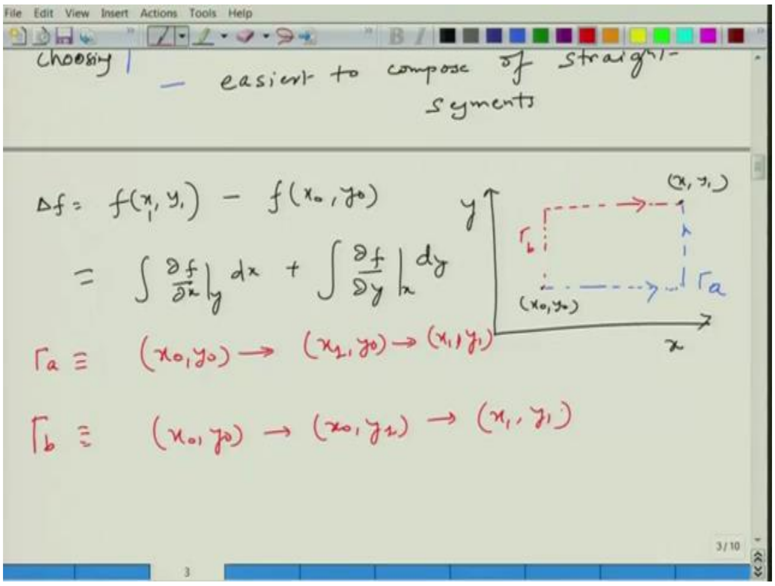

So, let us try to demonstrate this so, we can consider let us say this y and x and you have a initial point is x0, y0 and finally we would like to go through x1, y1 so that kind of two state point on a y and x. Now what we interested is to find out the delta f which is the function of x and y, so initially this is 1, 1 or in the final state is 1, 1 or and this is initial x0, y0 right.

$$\Delta f = f(x_1, y_1) - f(x_0, y_0) = \int \frac{\partial f}{\partial x}|_y dx + \int \frac{\partial f}{\partial y}|_x dy$$

Now here I can choose many paths so as I said the easiest gamma would be composed of straight segments, so there are 2 possible ways to do that, one is of course I can take it here, keeping y 0 constant and then, I take the vertical path and that would be where I keep x1 constant. So, this is something which we have going to say is gamma, gamma a, the other possibility is the that we keep this x0 constant and then we take this path where we say this is gamma b so we go from here till y1 and then keep the y1 constant and go along this path from x0 to x1. So there is a two different paths, so let me write it out write this here:

$$\Gamma_a: (x_0, y_0) \rightarrow (x_1, y_0) \rightarrow (x_1, y_1)$$

$$\Gamma_b: (x_0, y_0) \rightarrow (x_0, y_1) \rightarrow (x_1, y_1)$$

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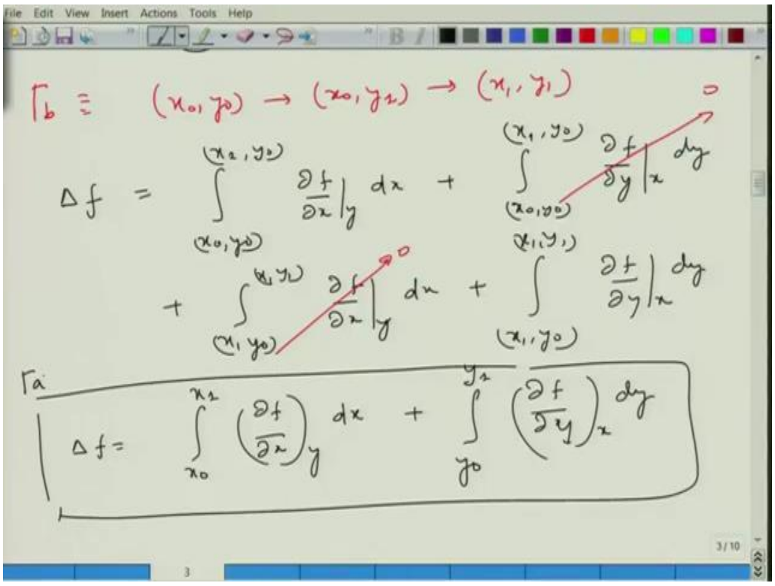

So, let us consider the gamma a as our possible path which we would like to use it in order to obtain delta f and let us try to develop the expression finally.

$$\Delta f = \int_{(x_0,y_0)}^{(x_1,y_0)} \frac{\partial f}{\partial x}|_y dx + \int_{(x_0,y_0)}^{(x_1,y_0)} \frac{\partial f}{\partial y}|_x dy + \int_{(x_1,y_0)}^{(x_1,y_1)} \frac{\partial f}{\partial x}|_y dx + \int_{(x_1,y_0)}^{(x_1,y_1)} \frac{\partial f}{\partial y}|_x dy$$

$$\Delta f = \int_{x_0}^{x_1} \left(\frac{\partial f}{\partial x}\right)_y dx + \int_{y_0}^{y_1} \left(\frac{\partial f}{\partial y}\right)_x dy$$

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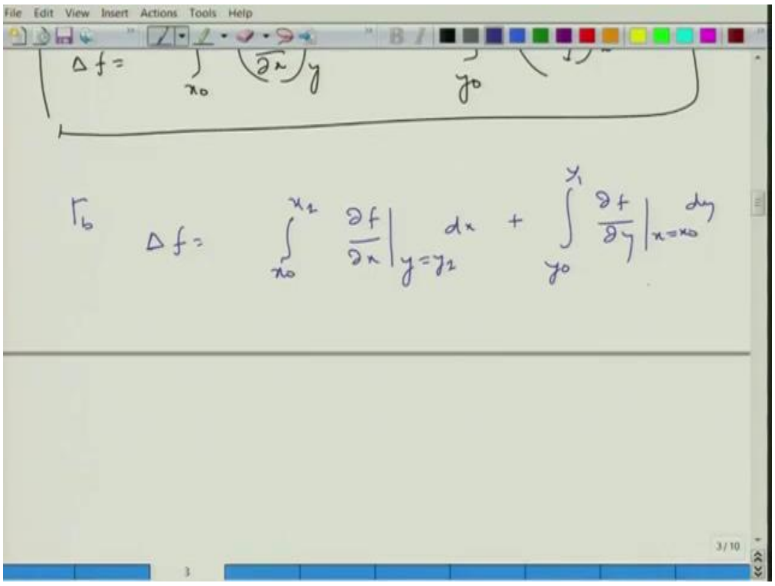

Similarly, I can use gamma b, if I use gamma b I am going to get a different expression. So without deriving it I am actually writing it here, so these are two different expressions, but since, is a thermodynamics, if we apply to the thermodynamic conditions the change is in the potentials or the variables which are state dependent, their value should be same, it respective of whatever the segments or the path we have taken

$$\Gamma_b: \quad \Delta f = \int_{x_0}^{x_1} \left(\frac{\partial f}{\partial x}\right)_{y=y_1} dx + \int_{y_0}^{y_1} \left(\frac{\partial f}{\partial y}\right)_{x=x_0} dy$$

Now, let us for the continue this exercise and try to develop a relation again something called change rule and as well as the inverse rule, so this is also relevant in variety or different calculations which we are going to do.

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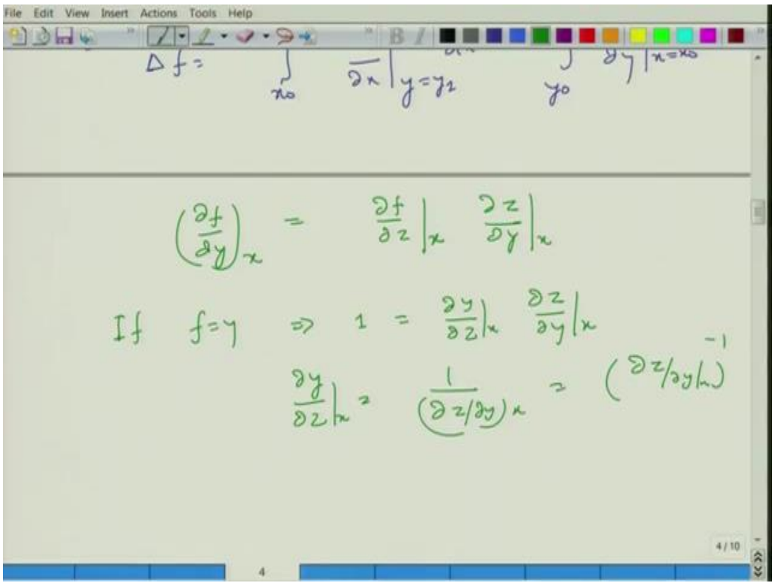

So, this is, so let me start with the inverse rule.

$$\left(\frac{\partial f}{\partial y}\right)_x = \frac{\partial f}{\partial z}|_x \frac{\partial z}{\partial y}|_x$$

$$If\ f = y \quad 1 = \frac{\partial y}{\partial z}|_x \frac{\partial z}{\partial y}|_x$$

$$\frac{\partial y}{\partial z}|_x = \frac{1}{\frac{\partial z}{\partial y}|_x} = \left(\frac{\partial z}{\partial y}|_x\right)^{-1}$$

So ,this is sometime is called inverse rule or minus 1 rule here. So ,what we are saying is simply that this is nothing but we can just inverse it in this way.

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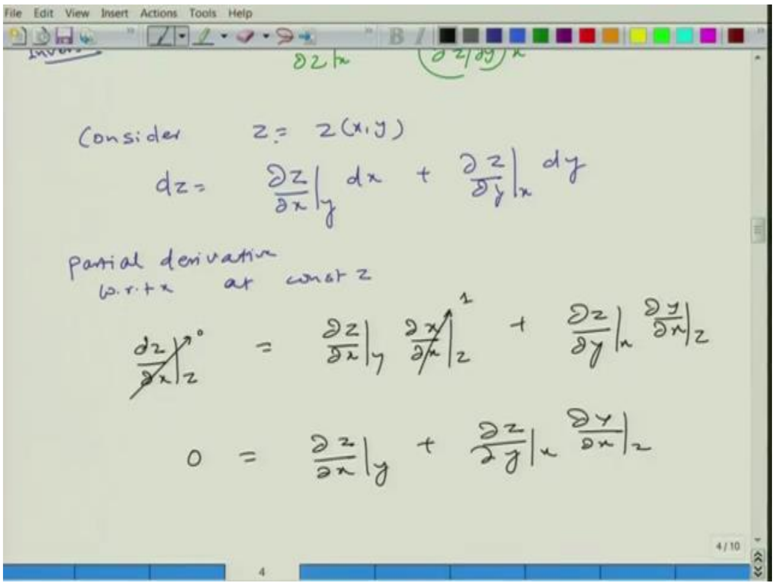

Consider z is a function of z x, y so this is inverse rule and then now I am going to develop a relation for which we call it minus 1 rule.

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

$$dz = \frac{\partial z}{\partial x}|_y dx + \frac{\partial z}{\partial y}|_x dy$$

Partial derivation wrt x at constant z, $\frac{\partial z}{\partial x}|_z = \frac{\partial z}{\partial x}|_y \frac{\partial x}{\partial x}|_z + \frac{\partial z}{\partial y}|_x \frac{\partial y}{\partial x}|_z$

Now, if you take a partial derivative with respect to x at constant z so, if we do this the following expression will comes, so we talking about partial derivative with respect to x keeping z constant, so essentially this is nothing but 0, this should be del z by del x so this must be 1 plus del z by del y keeping x constant del y by del x, z here. So, you have an expression as:

$$0 = \frac{\partial z}{\partial x}|_y + \frac{\partial z}{\partial y}|_x \frac{\partial y}{\partial x}|_z$$

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

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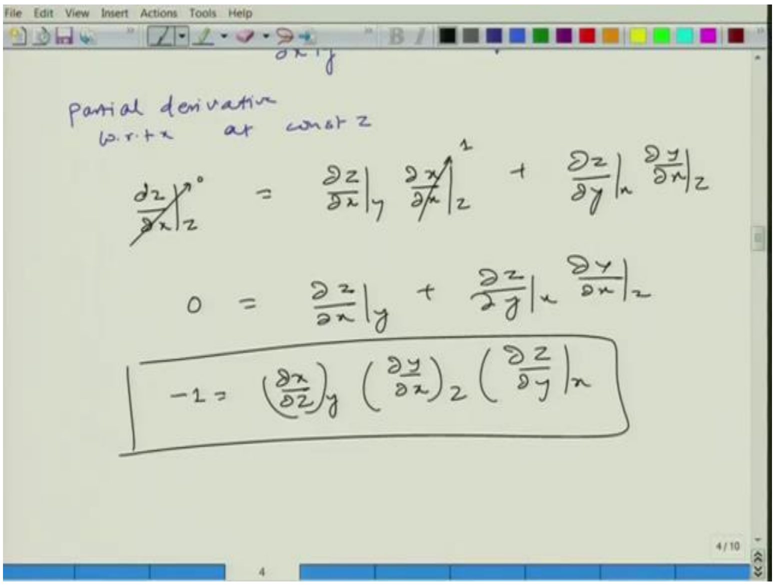

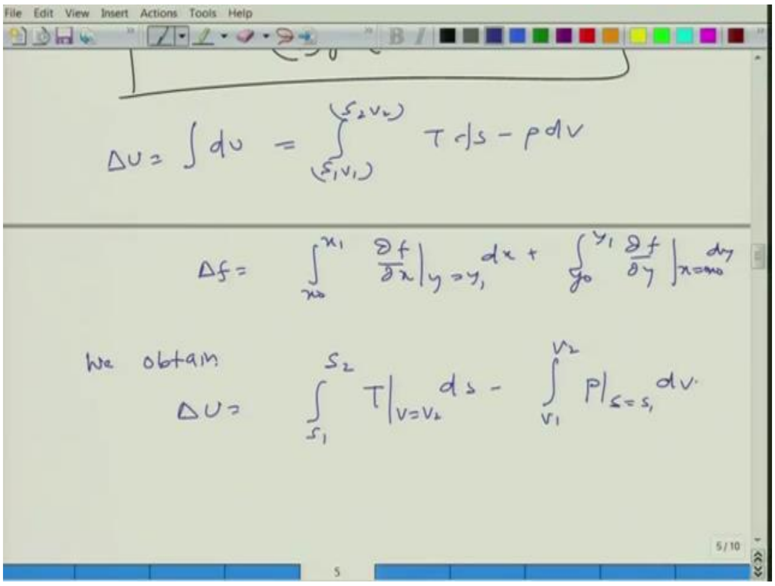

This expression is sometimes we called a chain rule also.

So these are very we know valuable expressions and something which we can now demonstrate in our calculations.

$$\Delta U = \int dU = \int_{(S_1,V_1)}^{(S_2,V_2)} TdS - PdV$$

$$\Delta f = \int_{x_0}^{x_1} \frac{\partial f}{\partial x}|_{y=y_1} dx + \int_{y_0}^{y_1} \frac{\partial f}{\partial y}|_{x=x_0} dy$$

$$We\ obtain,\ \ \Delta U = \int_{S_1}^{S_2} T|_{V=V_1} dS - \int_{V_1}^{V_2} P|_{S=S_1} dV$$

So, if we do this exercise if we make use of this expression, expression which you have used here, in here and then we should obtain del U as s1, s2 T at constant v is equal to v2, v1, v2 P as constant s is equal to s1, dv. Now this is something which clearly obtain from the expression of the contour integral, what if we have to find out delta U for a different set of variables so s and v are natural variables for U but, what if we, if we interested or if we wish.

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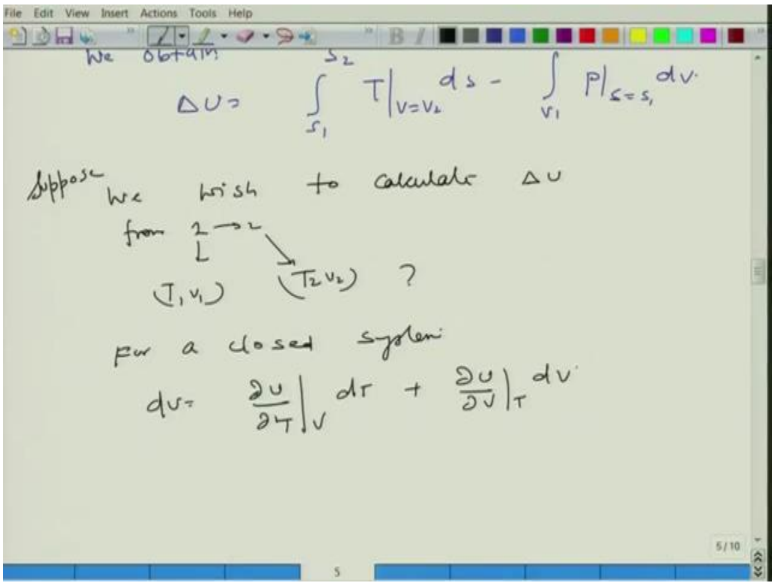

Suppose we wish to calculate delta U from state 1 to 2, but these are defined as T1 v1 and this is as T2 v2. So, how do you calculate because these are not the natural variables corresponding to thermodynamic function U. So for a closed system I can write:

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

$$dU = \frac{\partial U}{\partial T}|_V dT + \frac{\partial U}{\partial V}|_T dV$$

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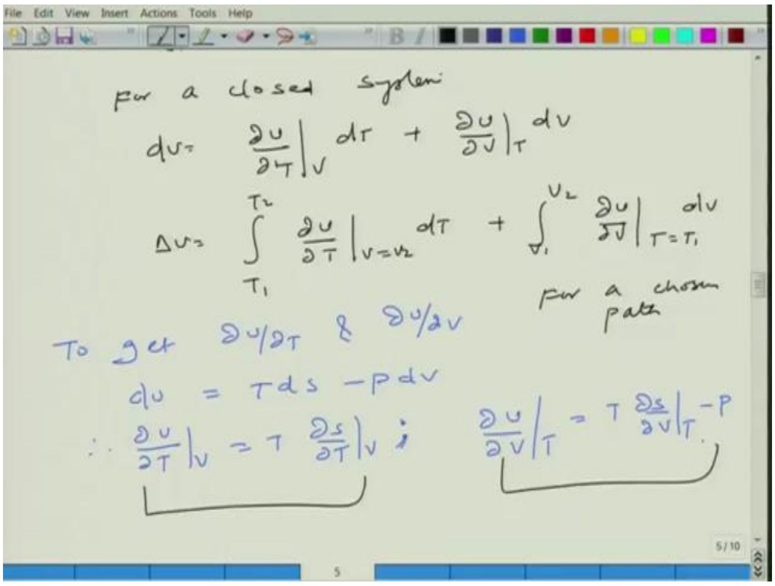

So if we integrate this:

$$\Delta U = \int_{T_1}^{T_2} \frac{\partial U}{\partial T}|_{V=V_1} dT + \int_{T_1}^{T_2} \frac{\partial U}{\partial V}|_{T=T_1} dV$$

$$To\ get\ \frac{\partial U}{\partial T}\ and\ \frac{\partial U}{\partial V}, \quad dU = TdS - PdV$$

$$Therefore, \quad \frac{\partial U}{\partial T}|_V = T\frac{\partial S}{\partial T}|_V; \quad \frac{\partial U}{\partial V}|_T = T\frac{\partial S}{\partial V}|_T - P$$

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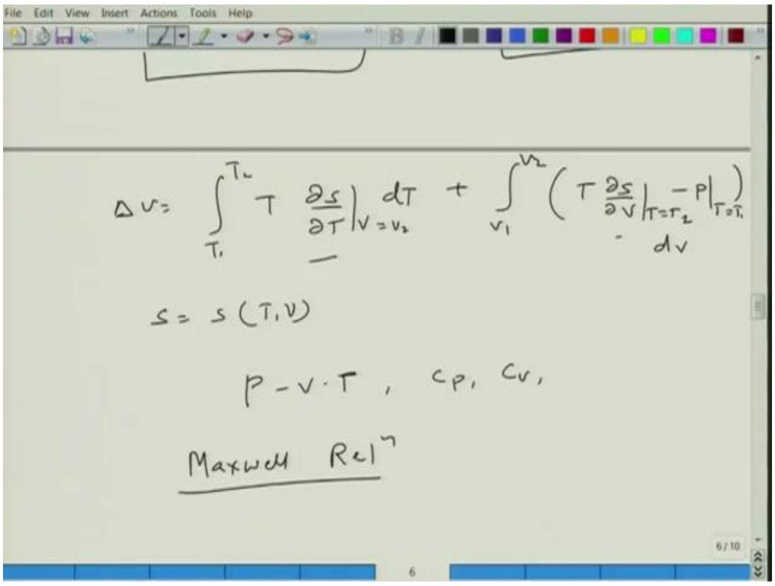

So, we have:

$$\Delta U = \int_{T_1}^{T_2} T \frac{\partial S}{\partial T}|_{V=V_1} dT + \int_{V_1}^{V_2} (T \frac{\partial S}{\partial V}|_{T=T_1} - P\, |_{T=T_1}) dV$$

Now this becomes more complicated further the issue is that we do not usually know s as function of T and V and what we want do is we want to express this delta U finally in terms of something which we can measure experimentally.

So what we can measure experimentally? We can measure experimentally P V T relations, we can change the pressure and observe the change in the volume in terms density, we can change the temperature again find out the changes in the P V T expression, but in addition we can also calculate CP heat capacity at constant pressure Cv and we can also obtain something isothermal compressibility and other terms which I am going to mention it in a later part.

So one of the important thing is that, which comes directly from this expression, that we would like to finally convert this all this partial derivative which is not accessible directly into something which we can measure experimentally, and this is where we need to know how to do that, and one of the way is making use of something called Maxwell relations. So this is where it comes very valuable to make use of this in order to express this, of this derivatives into something which we can measure and this is something which I am going to describe in the next lecture, I will stop here, so I will see you in the next lecture.