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

Lecture – 12
Thermodynamic Calculus – 3

In the last lecture we were trying to cover up. We looked at multivariate calculus relevant for a thermodynamic such as in this course we will continue this exercise.

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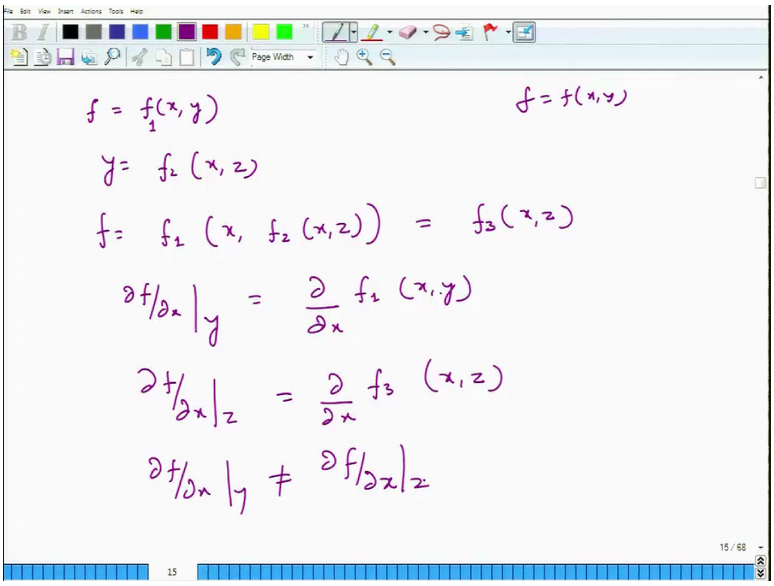

So, let us assume functions f is a function of x y, let us say f 1, where y is dependent on x and z ok. So, in other word f is function of f, x, f 2, x, z or some function f 3 x z ok.

So, the reason we are considering such a complicated function, because typically thermodynamic functions are not just f is equal to x and y, where y x and y are independent. So, most of the time we have more complicated functions. Now in this case if you want to find out partial derivatives such as f n del x, it has no meaning until you specify what is fixed for example, del f by del x at constant y is del by del x, f 1 x comma y or del f by del x at constant z is del f by del x because this is s and z we are going to consider f 3 exit. So, clearly in this case del f by del x, y is not equal to del f by del x z. So, what is the relation between this 2 ok?

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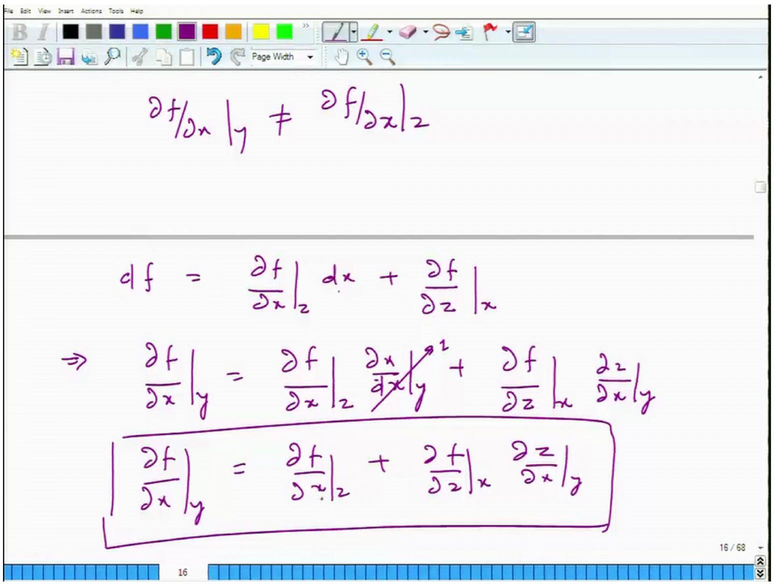

So, we are going to consider the differential of f can be written as del f by del x, z at constant z multiplied by dx plus del f by del z at x ok. Now this can be further differentiated such that del f by del x at y is del f by del x, z and this is written as del x by y plus ok. So, this is of course, going to be 1 and this you can write del f 1 del x at constant y, del f by del x at constant z, plus del f by del z constant x del z del x at constant y. So, this is a relation between these 2 partial derivatives ok.

So, we can further continue particularly now considering f as a function of more variables, something which is what we are going to encounter in thermodynamics.

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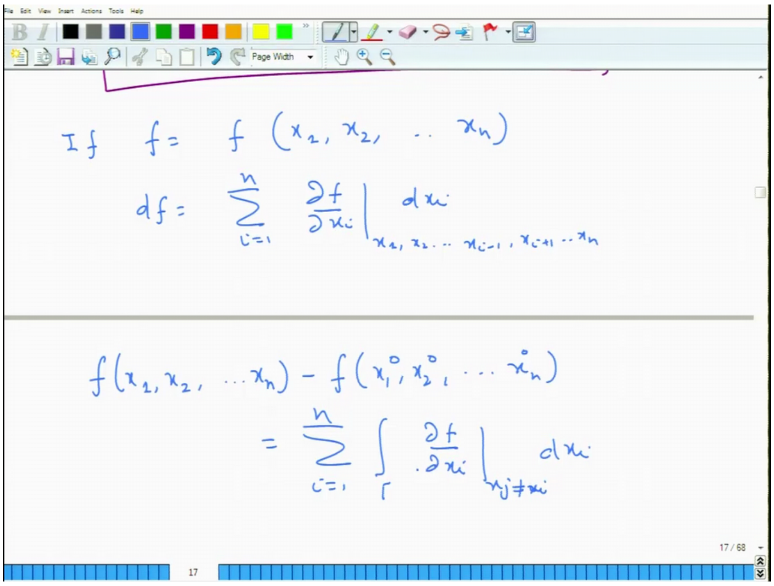

So, let us assumed that f is a function of x 1 x 2 and so forth. In that case d f can be written as summation of partial derivatives of f with respect to x i, where i is equal to 1 to n at and this derivative is at keeping x 1, x 2, x i minus 1 x i plus 1 till x n constant ok. So, this is something which we can write the differentiation or differential amount of f in terms of the summation of the partial derivatives ok.

We can integrate this also all right. So, if you integrate this from x 1 0's to x 1, then we can get something like this minus f of x 1 0, x 2 0 this is nothing, but summation of I equal to 1 to n, integral across the path we want to take del f by del x i, x 0 its not equal to x i d x i. Now remember that the left hand side is independent of the path, but this right hand side the expressions will depend on which path you want to take. So, in order to illustrate we will take some example.

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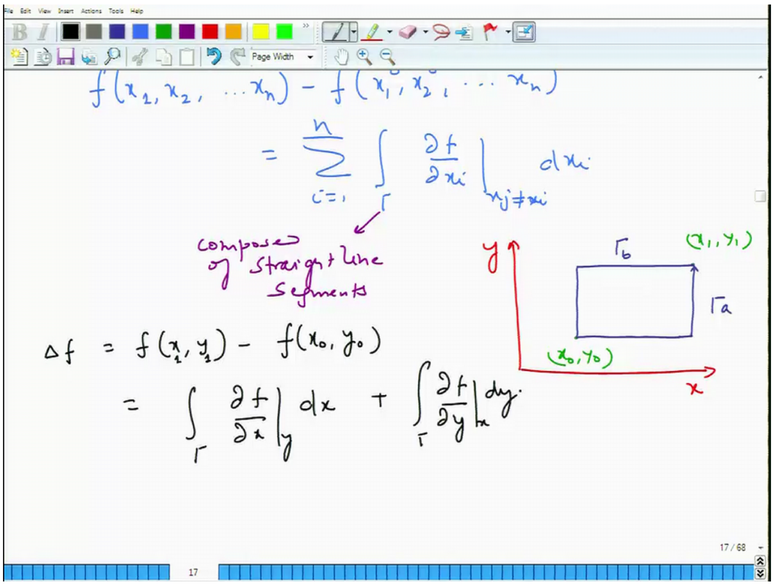

So, let us consider plot y against x where we have x 0, y 0 and somewhere here is x 1 y 1. So, the easiest path we can consider is basically composed of straight line segments ok. So, what we can do is, we can consider straight lines such as this ok. This is one path composed of 2 line segments, let me say this is gamma a and there is another one from here till here. So, in this case we are keeping x constant in this case we are keeping y constant. This would be another side path composed of 2 segments and let me say this is gamma b.

Ok and. So, what we are interested in is delta f ok. So, delta f is in this case since its a function of 2 variables. So, this is going to be f x comma y. So, this will be x 1, y 1 minus f x 0, y 0 ok. So, based on this definition which we have put it here, this delta f you can be written as del f del x y dx plus del f by del y x divide ok.

So, now since we can consider 2 different path we are going to derive this expression for 2 different path, and you can clearly see that the expressions are going to be different ok. So, let me consider this a all right.

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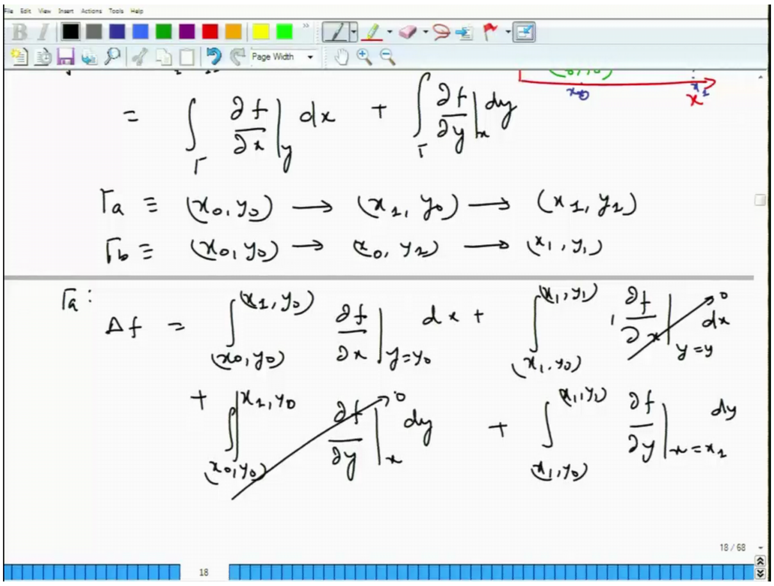

So, this will be x 0, y 0 to x 1, y 0 and finally, x 1, y 1 and this is going to be x 0, y 0 to x 0, y 1 to x 1, y 1. So, just to make this clear we this is going to be 0, x 0 and this is going to be x 1, this is going to be y 0, and this is going to be y 1 ok. So, let me just further write it now my expression now this is going to be for gamma a path del f by del x in this case y 0 is constant. So, this is nothing, but y equal to y 0 dx plus. So, this is part 1 and similarly you can also integrate x 0, y 0 to x 1, y 1 sorry y 0, del f by del y, x device. So, this is going from x 0 y 0 to x 1 y 0 plus. So, this is again plus here, plus you have another path another line segment from x 1 y y 0 to x 1 y 1.

So, its going to be x 1, y 0 to x 1, y 1 del f by del x. So, this is basically again y is equal to y dx, since x 1 is fixed and y is variable which means this term is going to be 0 considering that x is fixed. And the second term is going to be again x 1, y 0 x 1 y 1 del f by del y x divide where x is nothing, but x 1 ok. So, what I did was I actually you have 2 parts or 2 partial derivatives. So, this is basically the partial derivative integration over first line segment, this is the derivation over the line second line segment. In the first line segment y is equal to y is constant. So, the first derivative is this one and the second derivative this one since is y is constant this should be also 0 assimilate this for the second side line segment.

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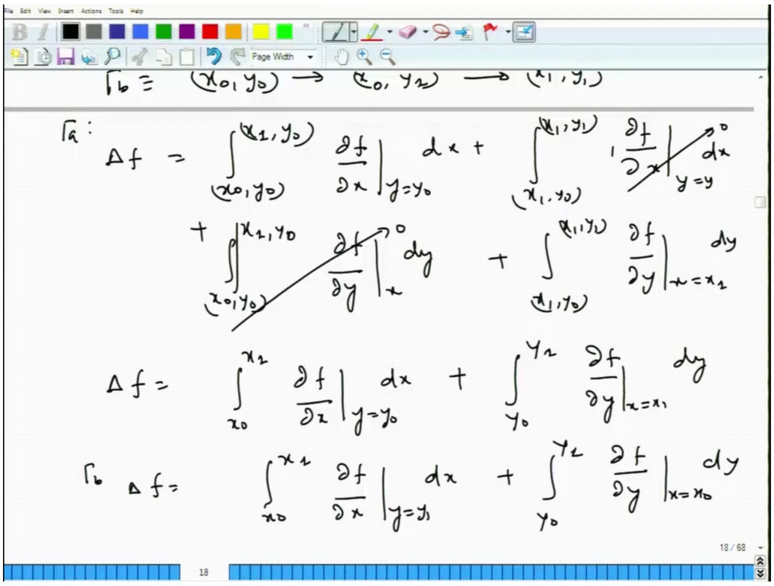

So, when you simplify this expression delta f turns out to be x 0, x 1 since y is constant here, I can simply write del f by del x, y is equal to y 0 dx, plus this one which is going to be since x 1 is constant I can simply write y 0 to y 1, del f by del y x is equal to x 1 dy ok. So, this is one expression, now if you had used gamma b you could show that del f is x 0 x 1 del f by del x y is equal to y 1 dx plus y 0, y 1 del f by del y, x is equal to x 0 dy ok.

So, the constants are different ok. So, this is a simple way of finding out changes in the functions using paths, which are broken into different line segments ok. So, we are going to continue this exercise now, and now we are going to look at Euler theorem for homogeneous function ok.

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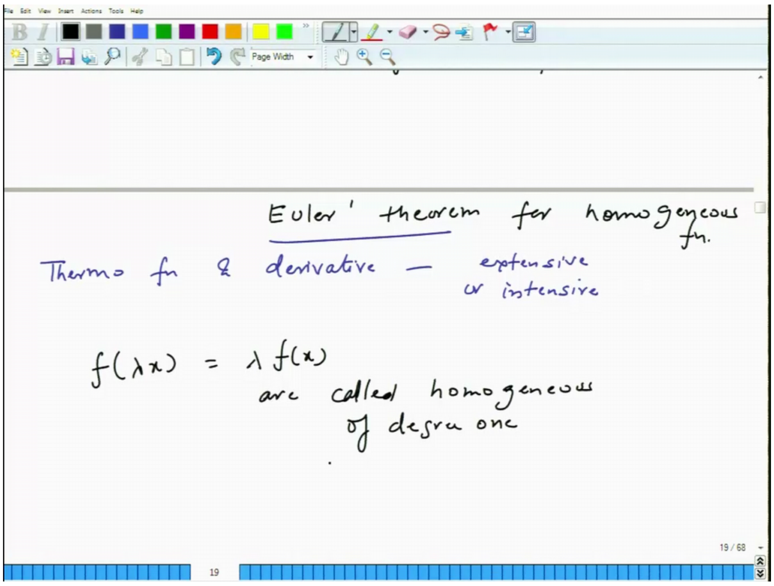

Now this is the important component of classical thermodynamics. So, let us make a comment here, the thermodynamic function and its derivative are either extensive or intensive. So, this is something which we observe that all these functions are either extensive or intensive that we have already defined. Now mathematically a function which satisfies a relation such as this, for all values of x are called homogeneous function of degree 1 ok.

So, this is a typical extensive property of which we know from thermodynamics ok. So, the intensive property would be a homogenous function of degree 0 ok.

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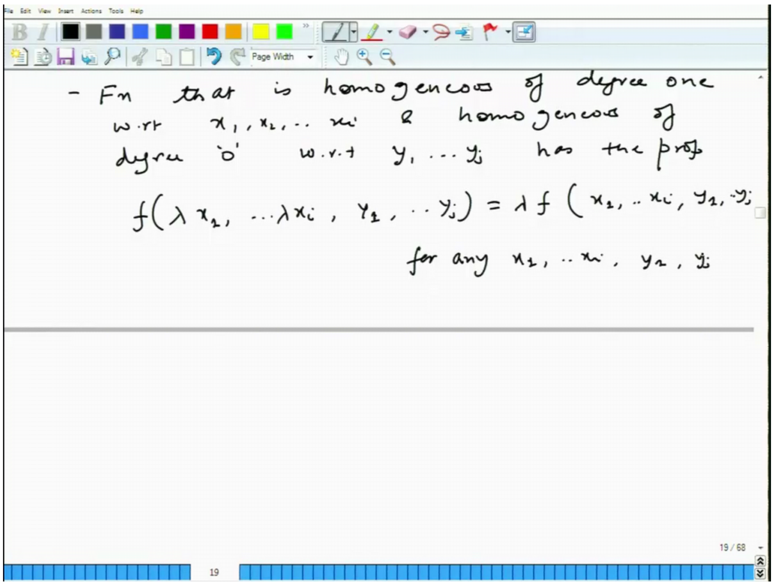

So; that means, the function that is homogeneous of degree 1 with respect to variable let us say x 1, x 2, x i and homogeneous of degree 0 with respect to variables y 1 till y j has the following property, has the property that you can write the following as this ok. So, what I did basically nothing, but the lambda which is multiplied here in this variables, have been taken out I multiplied the whole function by a lambda that is what basically nothing, but Euler theorem ok.

So, this is true for any x 1, x i, y 1, y j ok. Now thermodynamic function a homogeneous function of degree 1 with respect to extensive variable and degree 0 with respect to intensive variable. So, this Euler theorem basically provides a link between its function is derivative, and we are going to show that we are going to prove that ok.

So, let us consider again this function, which we know f and just take it its derivative.

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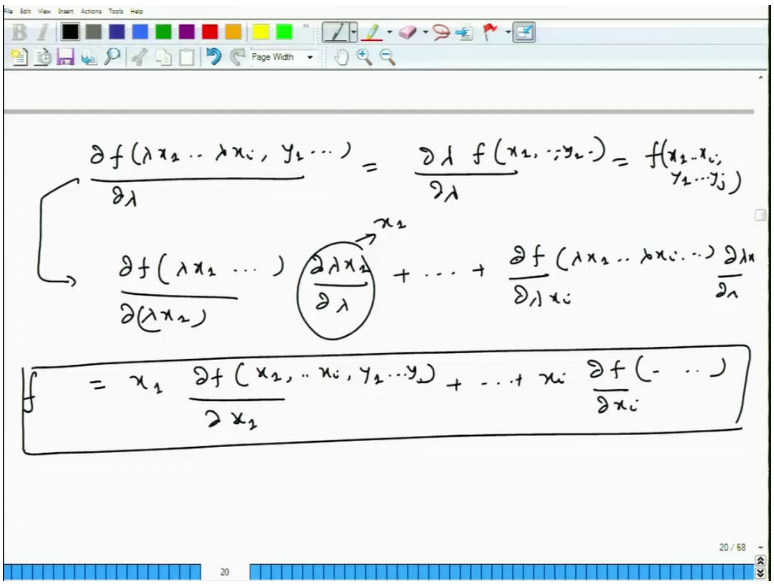

Del f lambda x 1 till lambda x i, and y 1 till x j y until y j with respect to lambda. So, we are taking a derivative of f with respect to lambda ok. Knowing this a Euler theorem, we can write this expression as del lambda f x 1 till y 1 and so forth ok.

Now, this is with respect to lambda, thus this is nothing, but f of x 1, x i comma y 1 till y j all right. So, this derivative of f with respect to lambda is nothing, but simple function f. Now you can also consider also rewrite this expression as follows this is nothing, but based on the differential information this is nothing, but del f lambda x 1 del lambda x 1 del lambda x 1 del lambda plus and so on until you have this del f lambda x 1 lambda x i del lambda x i del lambda x i, divided by del lambda. So, this is nothing, but x i ok.

So, this turns out to be nothing, but x 1 ok. So, what we have is and similarly that 1 is for x i, now this is just a multiplication of lambda lambda can be can come out here and similarly f can be written as f of this can be written as lambda times f and lambda lambda gets cancel. So, this is nothing, but equivalent of saying x 1 del f, x 1 x i y 1, y j divided by del x 1 plus x i del f again there is del x i and this is nothing, but f from this term. So, this gives us basically Euler theorem for homogeneous function in this form ok.

So, this is basically because x 1 to x i are homogeneous function of degree 1. Now having derived this expression we can also apply it to thermodynamic functions. So, let me just try that for internal energy. So, if you consider.

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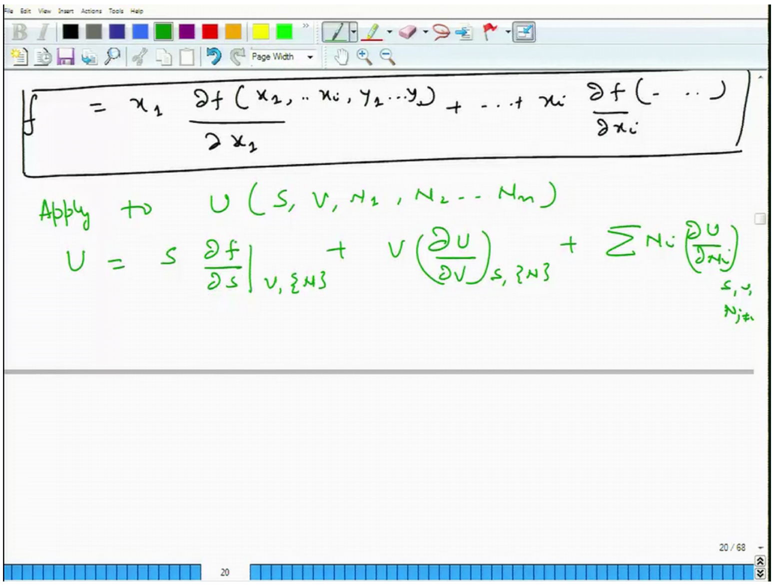

So, the objective now is to apply to let us say u as a function of u v and 1 and 2 and so forth ok. Now these are all our extensive variable. So, this is all homogeneous function of degree 1 ok. So, with respect to all the variable. So, in that case you can be written as u is nothing, but f can be written as x 1 is s del f by del s keeping all of the variable constant v plus v del u by del v keeping all variable constant plus summation N i del u by del N i keeping all available all other variable constant.

Ok. So, now, oh sorry this f should have been u. So, we want to write it here u ok.

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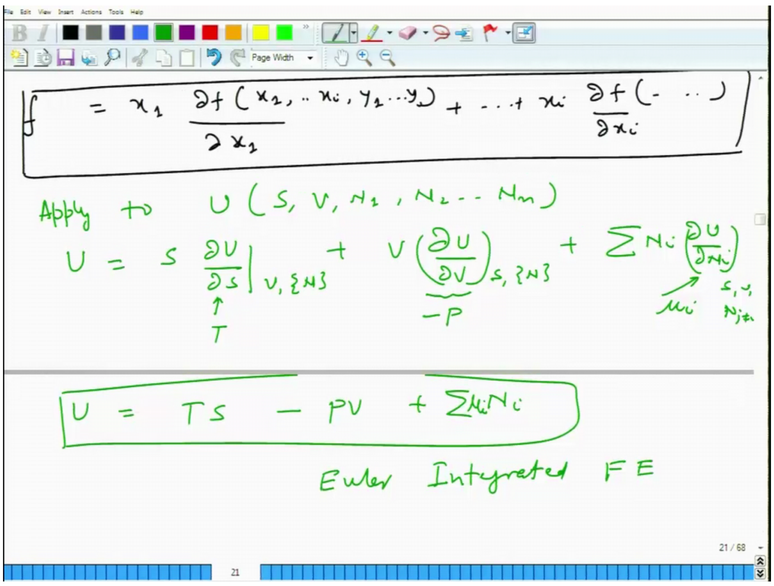

Now, what is del partial derivative of u with respect to s is nothing, but T, what is a partial derivative with respect to U, partial derivative with respect to V; this is nothing, but if you look at the first law of thermodynamics, you can derive that this is nothing, but minus p and this is nothing, but mu i.

So, we have now relation U is equal to TS minus PV plus summation N i or mu i N i. So, we have now got an equation which is Euler integrated fundamental equation ok. So, this is based on the very simple mathematics and this expression are going to be extremely useful to derive something called gives you an equation which you are going to talk in the next lecture. So, with that I am going to stop and we will see you in the next lecture.