Thermodynamics of Fluid Phase Equilibria
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Lecture – 11
Thermodynamic Calculus-2

In the last lecture we derived this expression of entropy in the differential form in, as a function of u v n. So, what we going to do is we are going to make use of this and develop an equation of state for a simple example. So, this is an example.

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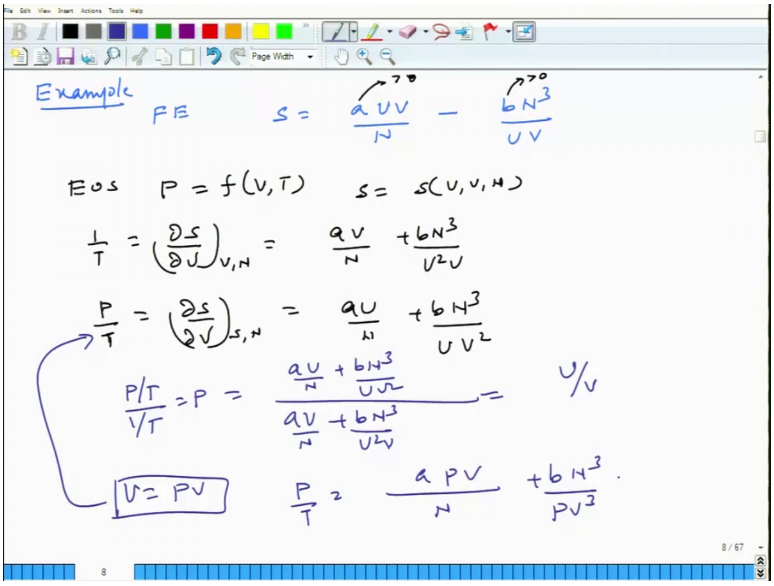

So, for a pure fluid, the fundamental equation is given as s is equal to a u v divided by N and b N cube u n v.

So, this is something which is given, and what is being asked is to obtain the equation of state P as a function of V and T for this material where a and b are positive quantities ok. So, this is greater than 0 greater than 0. So, what we are going to do is we are going to make use of fundamental equation the equation which we have derived here.

So, we have we know this s as a function of U, V, N. So, we can write d s in differential form and since d s is already given here ok. So, you will have d s s del s by del u for constant v and d u and so forth.

So, this will be your 1 by T and this information we can make use of it here this will be your a v by N plus b N cube q u square v and similarly P by T which is this part can be written as in terms of partial derivative with respect to v at constant N and this is given by a u N plus b N cube u v square.

So, now with this equation, you can take the ratio of this P by T divided by 1 by T which is nothing, but P and this can be now written as a u by N plus b N cube by u v square, and this is a v by N plus b n cube u square v this after rearranging you should be able to get u by v ok.

So, in other word u is nothing, but p v ok. You can plug in here this information on the right hand side we get P by T as a p v by N plus b N cube p v cube ok..

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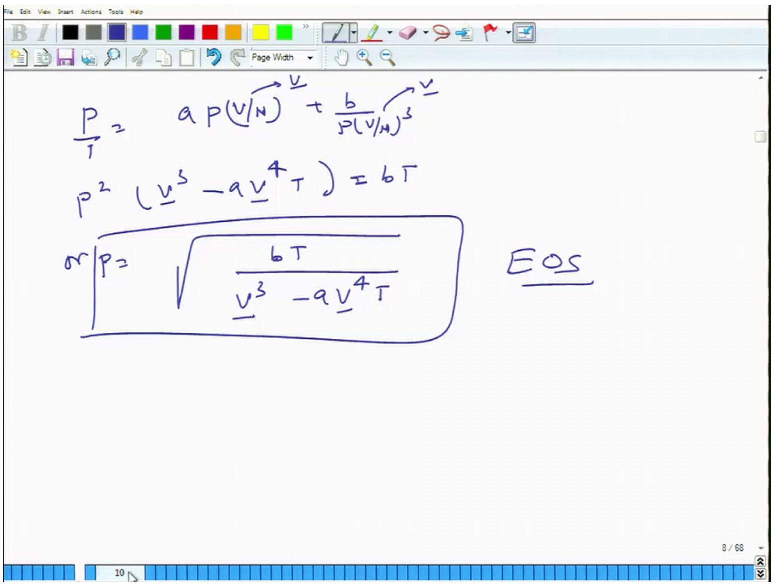

So, we can write in terms of molar property ok. So, if we consider molar property as v by N ok.

This would be b P v by N cube. So, sometimes its also written as v underscore bar and that case you can write P as this equal to b T or P is. So, this is your basically the equation of state based on the fundamental equation which is given to us ok.

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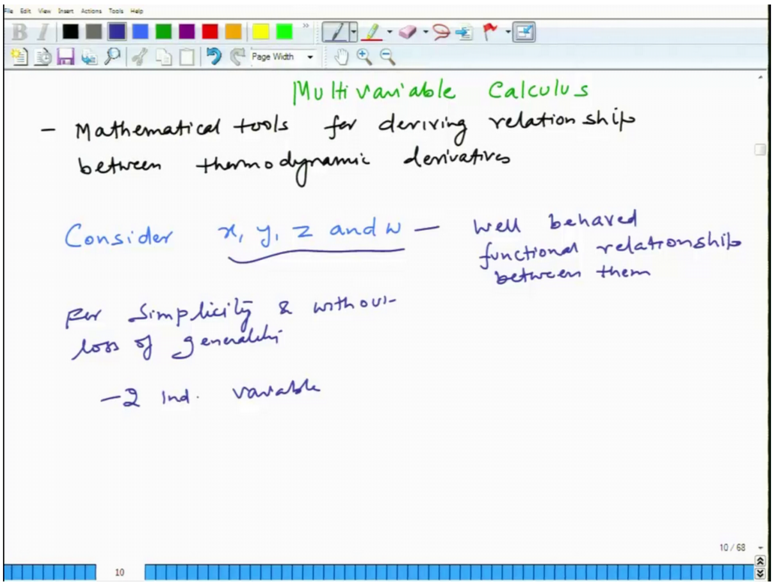

So, now we move on to a multivariate calculus, multivariate calculus is nothing, but a mathematical tools for deriving relationship between thermodynamic derivatives. So, what we are going to consider is let us say x y z and w as a kind of a variable ok.

So, this is the variable which we are going to consider as well behaved functional relationship between them. So, for simplicity and without loss of generality, we will assume that among the 4 they are two independent variables.

Any two of them can serve independent variables, then the following rule general mathematical relations can be used often in manipulating derivation of the functions which are commonly used in thermodynamic classical thermodynamics.

So, mathematical relations we are going to make use of often are the inversion.

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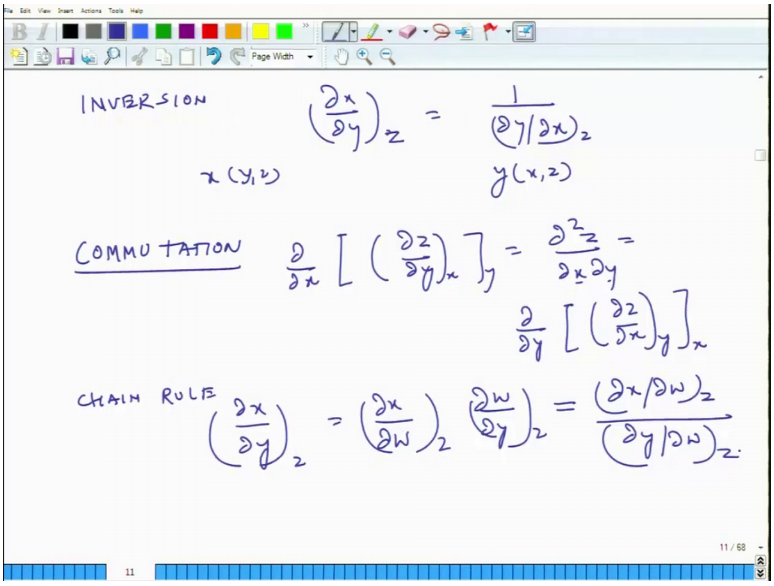

Relation which is nothing, but del x by y z is 1 by del y by del x z. Now note there this is the partial derivative or this is x equal to y z is being differentiated.

Whereas in this case y is equal to as a function of x z is being differentiated ok. Now in addition to inversion we will be often using commutation and this can be written as del z, del square z, del x and del y ok..

And this can be rearranged also this sequence of derivative as del y by del by del y, del z by del x the constant y n here this is content x. So, this is a commutation expression, now chain rule is often used. So, del x by del y at constant z can be written as del x by del w constant z and del w by del y at constant z and this is by making use of inversion rule here, we can also write as del x by del w at constant z divided by del y by del w at constant z ok. So, this is a inversion rule.

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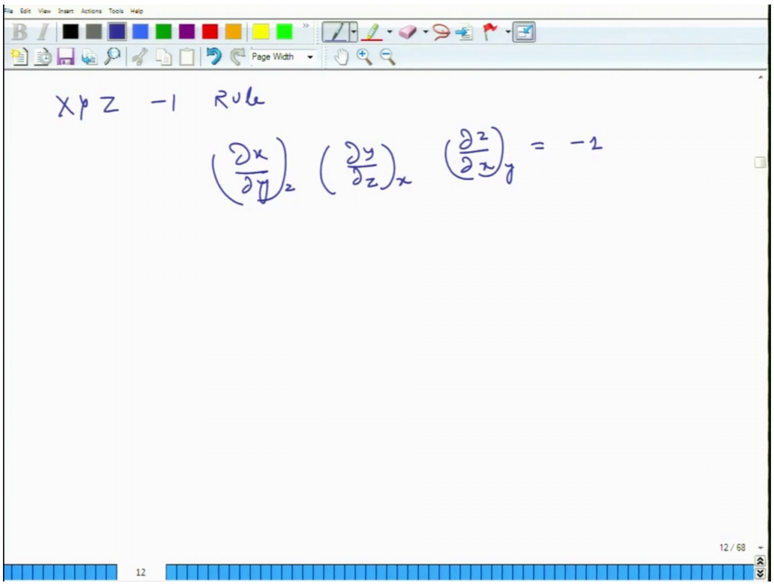

Now in addition you have this x y z minus 1 rule which is nothing, but a cyclic permutated derivative del x by del y del y by del z x. So, what we are doing is basically nothing, but x y z here its y z x and; that means, del z by del x at constant y, this is nothing, but minus 1. So, these are the three important mathematical relations, which we are going to often use it.

So, let me now move on and now we consider case in order to understand the dependency of the path let us assume the function f 0.

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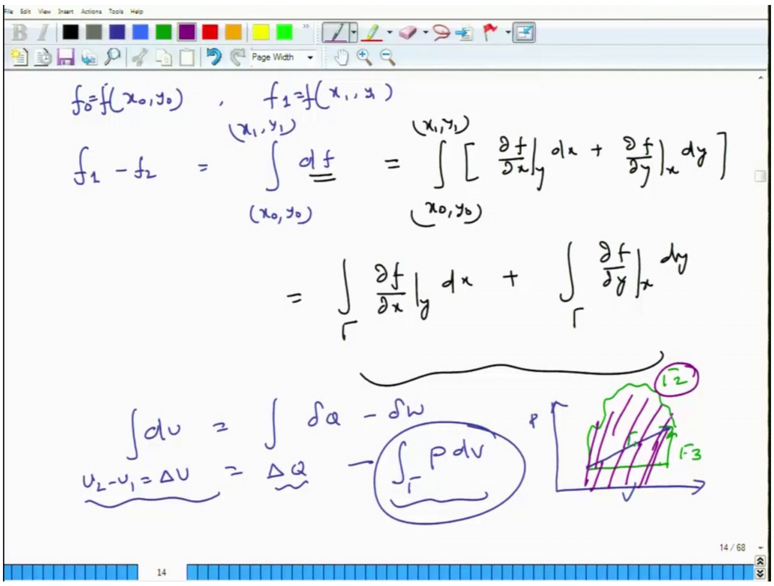

Which is a function depends on initial a function which is basically nothing, but let us say a state variable or in general this could be a property.

So, basically f 0 is nothing, but the function value at x 0 and y 0, and we are going to consider f 1 which is a function value at x 1 and y 1 and what we are interested is f 1 minus f 2 ok. This is a commonly occurring instances in thermodynamics. So, this can be evaluated by integrating t f from x 0, y 0 to x 1 y 1 ok. Now we can write this in partial derivative form and then as follows.

So, we can write as del f by del x constant y, d x plus del f by constant x d y ok. Or in other word you can also rewrite this as del f by del x y d x and this integration is along this path plus del f by del y constant x, again its integration is along this path.

That means some of these two integral is independent of the path, because f depends on the initial and the final information. So, that is you are taking the difference of the functions at different point on a phase space and thus left hand side is just depends on the initial and the final values.

Whereas the right hand side individual components does depend on the path, but when you add it up its become independent of path. You can understand from the point of view of d u, if we can integrate along a certain path this could be written as del u del w and this would be delta u delta Q minus let us say if P v work is there than P d v along this path gamma ok. And this will be your this would be your delta u which would be u 2 minus u 1 ok. Left hand side does not depend on the path, but this depends on the path and thus in order to achieve the same delta u and this will have to complement with each other in order to achieve the same. So, one can see that the though this particular work will depend on the path you gone it to consider for example, you have this p v and essentially the initial state is here and final state is here. So, this could be a one particular path ok.

Let us say may gamma 1, and there could be another part and there could be another path here this will be gamma 2 and gamma 3 ok. Now naturally this is area under the curve. So, of course, the value that depends on what particular path you are going to consider for gamma 2 the work is more gamma 1, the work is less gamma 3 the work is further less and thus this value depends on different gammas.

On the other hand delta Q will have to also vary in order to maintain the same u 2 minus u 1 ok. So, this is just a simple example to understand these functions.

So, let me end this lecture and we will continue this mathematical calculus review in the next lecture as well ok. So, see you in the next lecture.