Chemical Engineering Thermodynamics
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Lecture - 18
Mathematical properties of fundamental equations

Welcome back. Today we are going to start a new set of lectures on particularly mathematical properties of fundamental equations. In the first 2 weeks we looked into the fundamental thermodynamic equations as basic derivations and the concept behind that. And subsequently we looked into the equilibrium properties, the driving force for different changes in the thermodynamic properties. And then we spent some time to revise First Law and Second Law. So, with that background now we can start little bit more mathematical aspects of thermodynamics.

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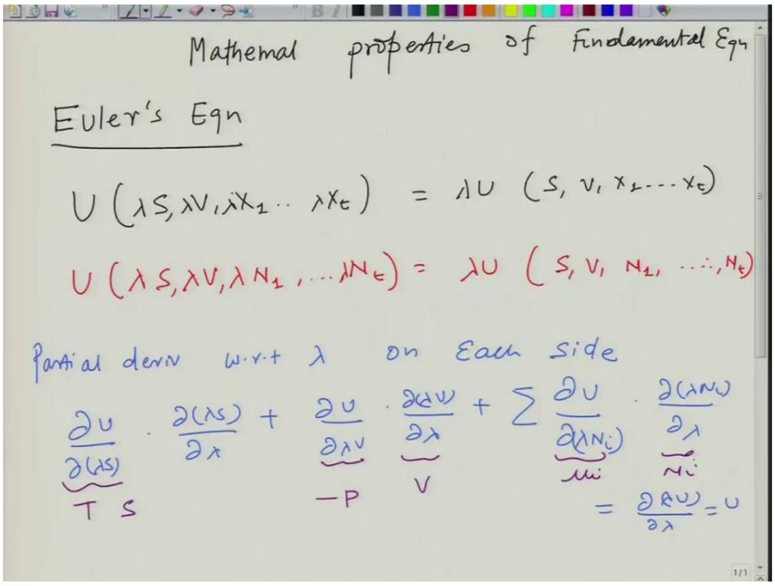

So, this lecture will specifically focus on mathematical properties of fundamental equation, okay. Now we will start with the Euler's equation, okay. So we will look into the thermodynamic function or the potential which is usually a function of S, V and some other variables. So we are considering all these variables are extrinsic. Now the Euler's Equation or Theorem says that if you are going to consider a different size of the system such that the entropy is multiplied by lambda and the volume corresponding is also multiplied by lambda.

$$U(\lambda S, \lambda V, \lambda X_1 \ldots \lambda X_t) = \lambda U(S, V, X_1 \ldots X_t)$$

$$U(\lambda S, \lambda V, \lambda N_1 \ldots \lambda N_t) = \lambda U(S, V, N_1 \ldots N_t)$$

So this comes directly from the extensive properties of these thermodynamic potentials which are extensive in nature. So where x could be, because it is extensive property, x could be something such as moles of the component. So we can consider something like this where we have U, lambda S, lambda V and instead of x I can put number of number of moles, okay and in that case this will be lambda U, S, V, okay.

Now if you take a partial derivative, partial derivative with respect to lambda on each side, in that case I can get this:

$$\frac{\partial U}{\partial(\lambda S)}\frac{\partial(\lambda S)}{\partial\lambda}+\frac{\partial U}{\partial\lambda V}\frac{\partial(\lambda V)}{\partial\lambda}+\sum\left(\frac{\partial U}{\partial(\lambda N_i)}\frac{\partial(\lambda N_i)}{\partial\lambda}\right)=\frac{\partial(\lambda U)}{\partial\lambda}=U$$

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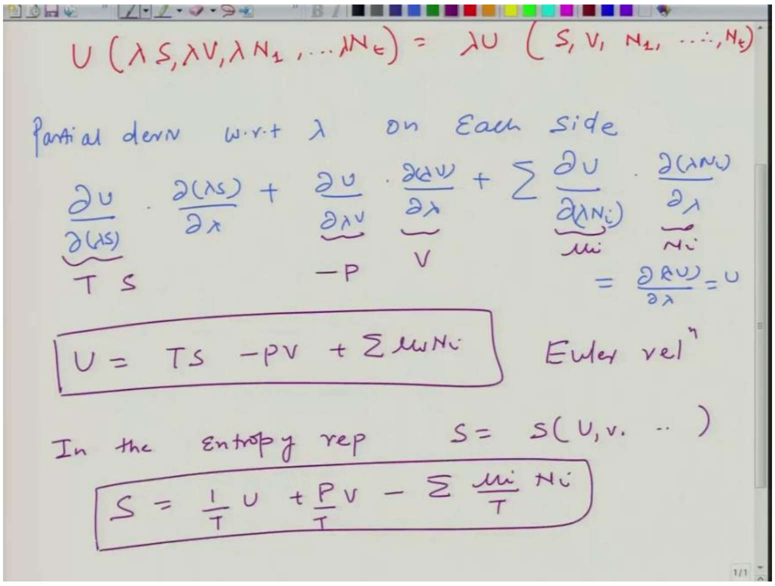

So in that case, so what you have now is your U, okay. This is right hand side so I brought it here.

$$U=TS-PV+\sum\mu_iN_i$$

This is the standard Euler relation. So we started with a property of the extensivity of the thermodynamic functions from there we can obtain Euler equation, okay. Now you can do the similar exercise not just considering the internal energy but if you consider this as entropy also, entropy as a function of U, S, V and so forth.

Then essentially you should be able to obtain a different expression for Euler which would be your something like this. So if we consider in the, based on the entropy relation representation that is S is equal to S of U, v and so forth, then S, the corresponding other relation would be, you would do the similar exercise as we have done for the U and you would now obtain the expression of S in the same sense or the same line as we did for internal energy and I would write it directly without deriving it.

So you can obtain this as Euler relation based on that.

$$S = \frac{1}{T}U + \frac{P}{T}V - \sum\left(\frac{\mu_i}{T}N_i\right)$$

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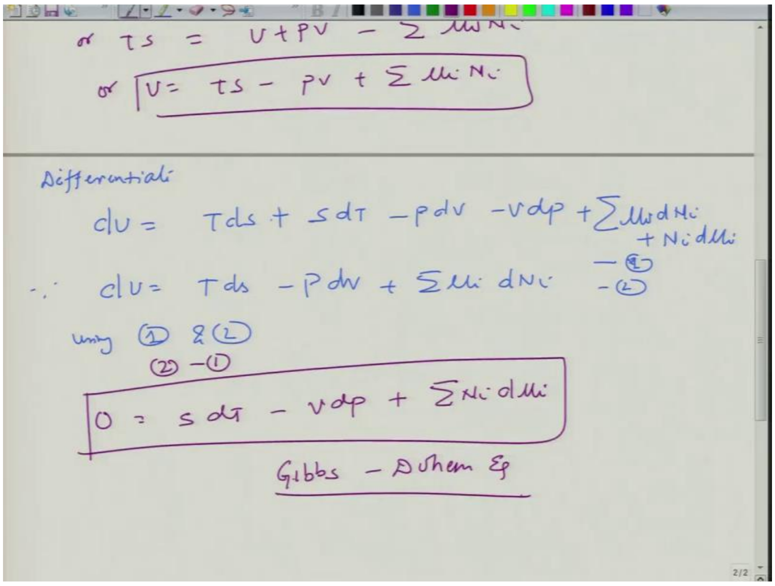

Now if you take this relation, okay so now you can take the derivative of this expression. okay let me just, so we do differentiation, differentiate the above expression we get

$$dU = TdS + SdT - PdV - VdP + \sum\mu_i dN_i + N_i d\mu_i$$

Now earlier we know that fundamental expression of internal energy in a differential form:

$$dU = TdS - PdV + \sum\mu_i dN_i$$

So if we use this expression, so this is let us say 1, this is 2, so using 1 and 2 I am going to get this if you just subtract this then I can get 0, so that means 0, it is like the following:

$$0 = SdT - VdP + \sum N_i d\mu_i$$

So now this expression puts the constraint on the intensive variable. You can clearly see this. It says that the differential amount of T is connected to the other variables. So it gives you a relation or constraints of the internal of the intensive variable among the intensive variables.

So essentially it gives a relation between T, P and mu i. So this expression is called Gibbs-Duhem equation, okay.

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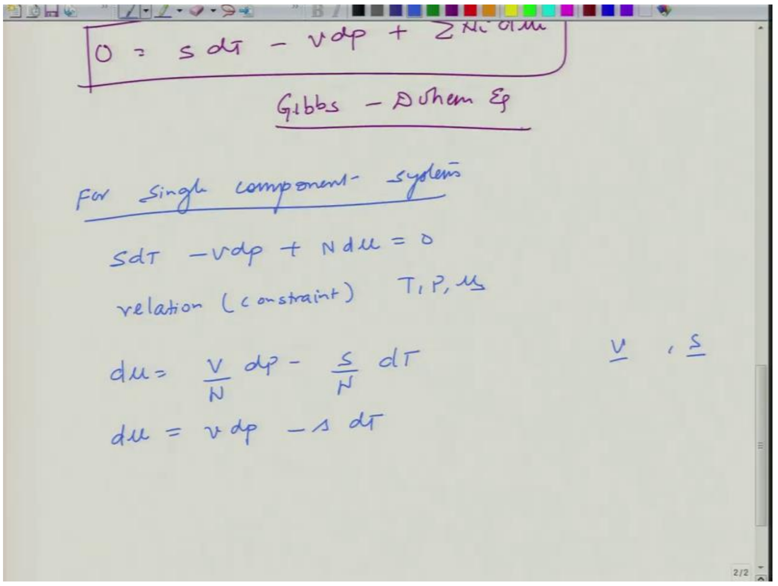

Now let us consider for a single component. So if it is for single component:

$$SdT - VdP + Nd\mu = 0$$

Now as I said this gives you a relation or constraints between T, P and mu.

$$d\mu = \frac{V}{N}dP - \frac{S}{N}dT\ (Rearranging)$$

$$d\mu = vdP - sdT\ (in\ terms\ of\ molar\ variables)$$

Now this is for the case of expression based on the internal energy, right. Now I can use the similar kind of exercise. Or I can do the similar exercise based on entropy, okay. So if you start, or let us try to do this.

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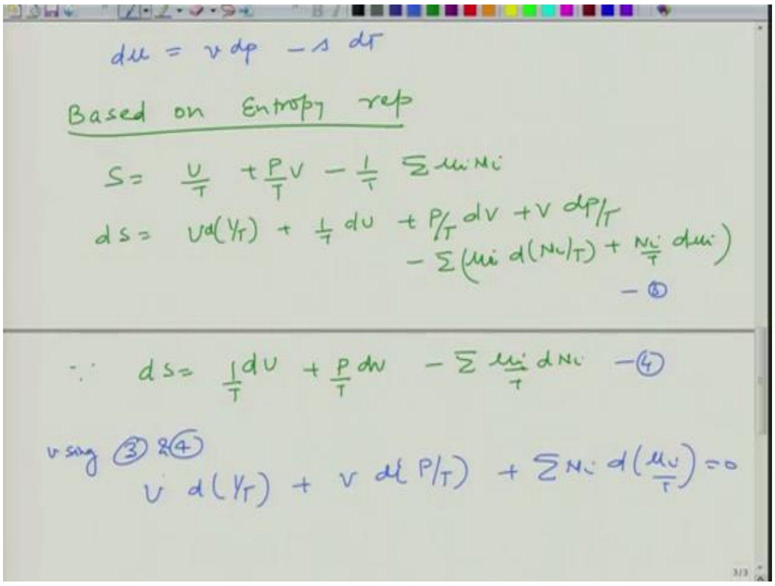

So let us say this is based on entropy relation if we try to come up with the expression. Then I will start with the S here, this I would rewrite again in this way:

$$S = \frac{U}{T} + \frac{P}{T}\,V - \frac{1}{T}\sum(\mu_i N_i)$$

$$dS = Ud\left(\frac{1}{T}\right) + \frac{1}{T}dU + \frac{P}{T}dV + \frac{VdP}{T} - \sum\left(\mu_i d\left(\frac{N_i}{T}\right) + \frac{N_i}{T}d\mu_i\right)$$

$$Fundamental\ relation, dS = \frac{1}{T}dU + \frac{P}{T}dV - \sum\left(\frac{\mu_i}{T}dN_i\right)$$

$$Using\ above\ expressions, Ud\left(\frac{1}{T}\right) + Vd\left(\frac{P}{T}\right) + \sum\left(N_i d\left(\frac{\mu_i}{T}\right)\right) = 0$$

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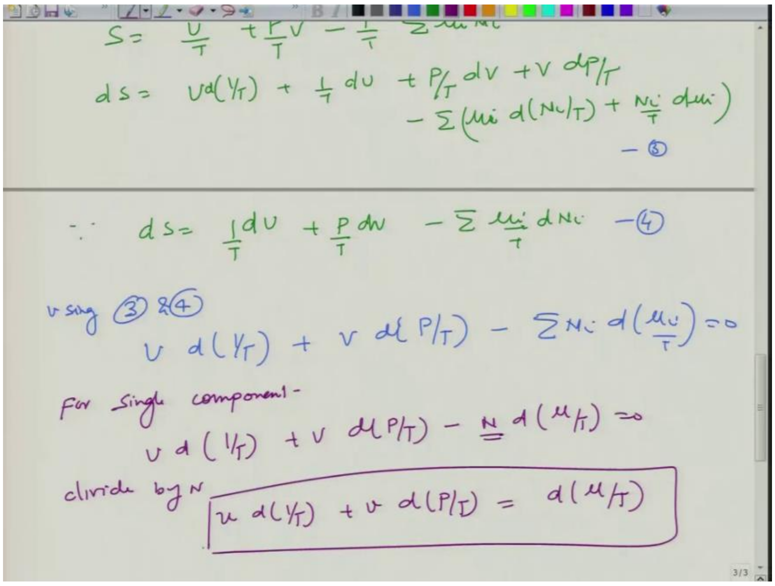

Now, if you consider for a single component,

$$Ud\left(\frac{1}{T}\right) + Vd\left(\frac{P}{T}\right) - Nd\left(\frac{\mu}{T}\right) = 0$$

$$u\,d\left(\frac{1}{T}\right) + v\,d\left(\frac{P}{T}\right) = d\left(\frac{\mu}{T}\right)$$

So this is the expression which we are going to get based on the entropy, okay. Now what I am going to do is I am going to apply a bit of, what I am going to consider is a simple case and try to extend this understanding.

So Euler again, let us summarize this, so the purpose of this exercise is to demonstrate the expression which connects between the intensive variables. So it gives you the constraints between the intensive variables, okay. And the Euler expression which we made use of it here, okay later on we use these Euler expressions, okay which was based on the extensivity of the variable and later obtain the expression of the Gibbs-Duhem relation. So the Gibbs-Duhem relation basically is nothing, which provides the constraints on the intensive variables.

You can come up with the internal energy based expression or you can come up with the entropy based expression. That is why we did these both the exercises and clearly you see these relations are different. So this is the one which is entropy-based, and this is the one which is internal energy based. Both provides or both gives you the constraints between intensive variable, okay. So taking this forward, now let us consider an ideal gas.

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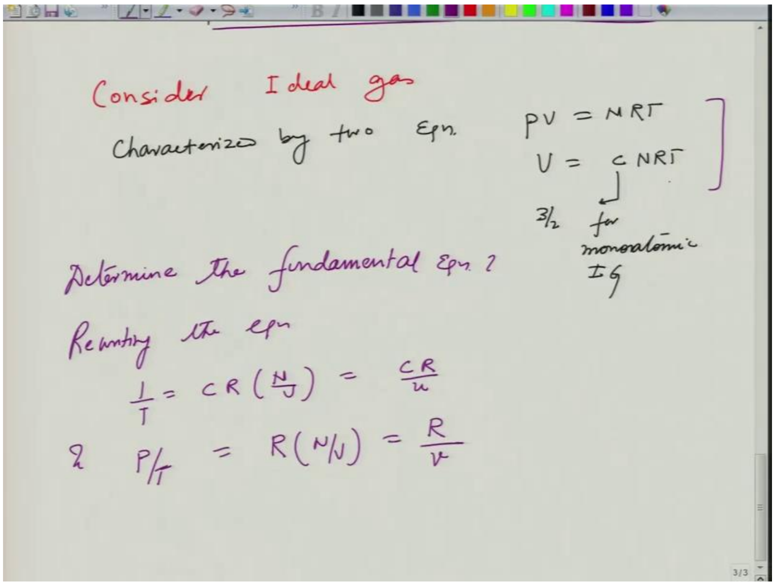

So consider a simple ideal gas, a monatomic in some sense, okay. Now this is characterized by two equations. One is of course we know the equation of state which is:

$$PV = NRT$$

$$V = cNRT \quad \left(c = \frac{3}{2}\, for\ monoatomic\ ideal\ gas\right)$$

So remember that this is for high temperature and low pressure, right. So that is the definition which, or rather the validity of ideal gas, high temperature and low pressure.

Now the question which we are interested in is to determine the fundamental equation, okay where in this case U is explicitly expressed, U expression is given. So we need to use this expression to obtain a fundamental, x equations. So let us try to do this exercise. So we will rewrite this expression.

So rewriting the equation in the corresponding appropriate form, so what would be appropriate form? We will write:

$$\frac{1}{T} = CR\left(\frac{N}{V}\right) = \frac{CR}{u}$$

$$\frac{P}{T} = R\left(\frac{N}{V}\right) = \frac{R}{v}$$

Now these are the expressions which come directly from here. So, we are going to use certain relation which brings this intensive variable or connects this intensive variable.

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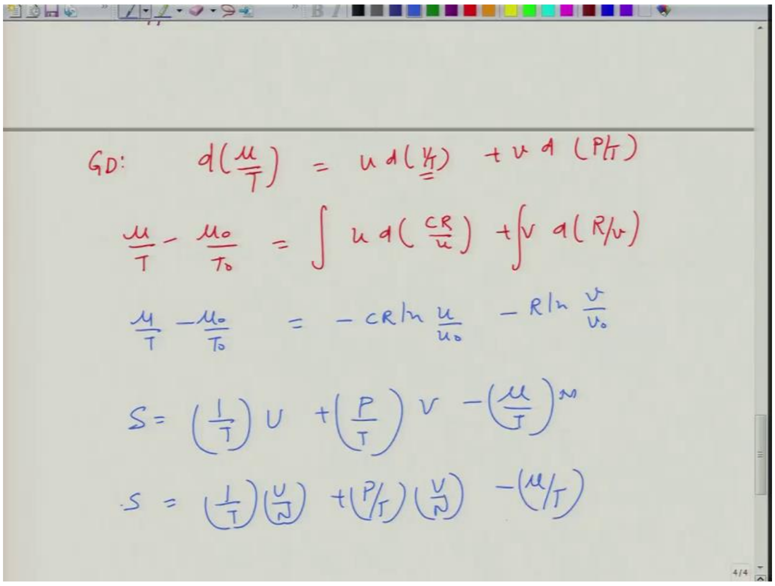

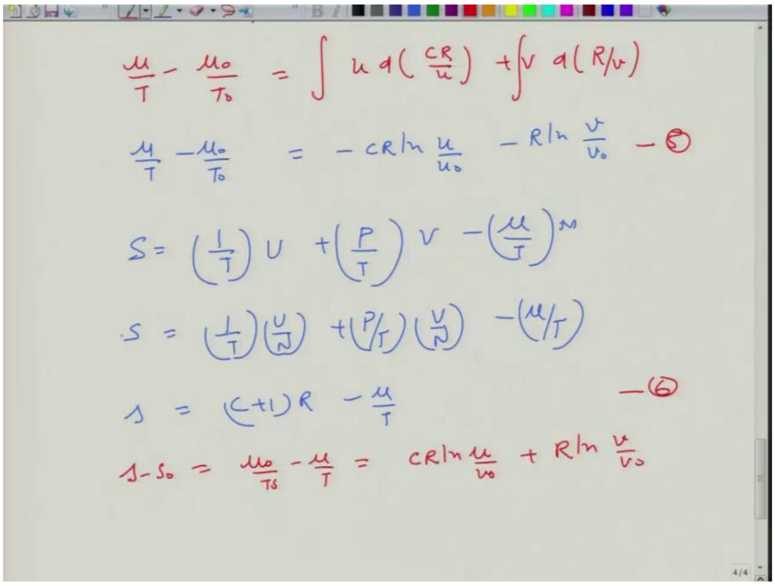

So let us look at Gibbs-Duhem relation to start with. So we will take Gibbs-Duhem relation here. So Gibbs-Duhem relation says that following:

$$d\left(\frac{\mu}{T}\right) = u\, d\left(\frac{1}{T}\right) + v\, d\left(\frac{P}{T}\right)$$

So this is directly from the, which came from the Gibbs-Duhem relation based on the entropy relation and now I can integrate this:

$$\frac{\mu}{T} - \frac{\mu_0}{T} = \int u\, d\left(\frac{CR}{u}\right) + \int v\, d\left(\frac{R}{v}\right)$$

$$\frac{\mu}{T} - \frac{\mu_0}{T} = -cRln\frac{u}{u_0} - Rln\frac{v}{v_0}$$

But Euler equation of the entropy is S is equal to:

$$S = \left(\frac{1}{T}\right) U + \left(\frac{P}{T}\right) V - \left(\frac{\mu}{T}\right) N$$

$$S = \left(\frac{1}{T}\right)\left(\frac{U}{N}\right) + \left(\frac{P}{T}\right)\left(\frac{V}{N}\right) - \left(\frac{\mu}{T}\right)$$

$$s = (C+1)R - \frac{\mu}{T}$$

$$s - s_0 = \frac{\mu_0}{Ts} - \frac{\mu}{T} = CRln\frac{u}{u_0} + Rln\frac{v}{v_0}$$

So that is your, basically the fundamental equation which comes for the ideal gas system which we have just described, for the simple one. So, this is what we have made use of two things. We have made use of the Gibbs-Duhem relation, that number 1. Number 2 is we have made use of the Euler relations also. So, with that I will stop in today's lecture and I will continue this exercise and bring more mathematical relations to obtain variety of different ingenuity which normally we see in thermodynamics course.

So, we will build it upon what you have learnt today and in the next lecture we will take up something called generalized thermodynamic function. So, I will see you in the next lecture.