Statistical Mechanics
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Lecture - 05
Extensivity of Entropy and Internal Energy, Gibbs Duhem Relation

So, we are briefly going to review what we had done so far.

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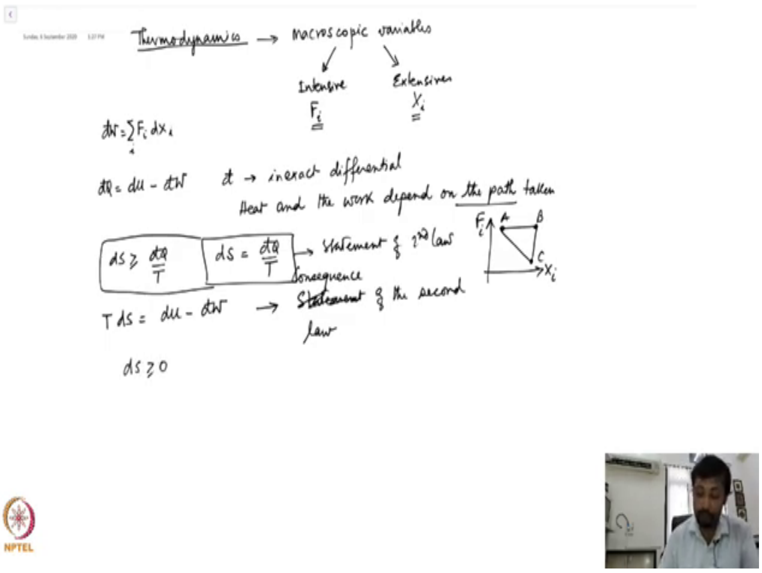

Thermodynamics → macroscopic variables

Intensive F_i

Extensive X_i

$đW = \sum_i F_i dX_i$

$đQ = dU - đW$ $đ \rightarrow$ inexact differential

Heat and the work depend on the path taken

$\boxed{dS \geq \frac{đQ}{T}}$ $\boxed{dS = \frac{đQ}{T}}$ → Statement of 2nd law

Consequence ~~Statement~~ of the second law

$T dS = dU - đW$ →

$dS \geq 0$

We are looking at thermodynamics and we said that; if I want to describe a system then I want to describe it I need to describe it in terms of a set of macroscopic variables. And, these macroscopic variables are essentially of two kinds, they are intensive or extensive. The intensive ones we understood are the forces F i and the extensive arms are the ones, which we understood to be the coordinates X i.

And, then using the analogy of mechanics we wrote down the work done as F i dx i with a sum over i. The first law the zeroth law of course, comes into playing saying that, I can define a temperature. An empirical temperature therefore, I can pick up isotherms in the p v or in the coordinate space.

Similarly, comes the first law that tells you that d cut Q is equal to d u minus d cut w. The cut means it is an in exact differential, that is the heat and the work depend on the path taken. Once again the path we clarified what does the path mean. Path means essentially the trajectory of the thermodynamic systems in the coordinate plane. So, this path would be typically the path that is taken in the force and the coordinate plane, so, X i and F i.

So, F i which is the force is conjugate to the coordinate. So, this can be like this, this can be like this, this can be like this, this can be like this, it goes from state 2 A to B and then B to C something like this way. Then enters the second law which tells you that d s must be greater than equal to d cut Q by T for any process.

If it is an reversible process, then I know that the equality holds and write down d cut Q by T as d s which gets which modifies the first law as T ds is equal to d u minus d cut w. And, this is the statement of the second law. Yet the another statement of the second law tells you or not a statement of the second law, but this is a consequence of the second law, this rather is the statement of the second law.

What it also particularly tells you, that if you have an adiabatic system. And, if the subsystems which were in equilibrium come to a joint equilibrium, then you know that d s must be greater than equal to 0, which effectively means, that entropy must be maximized for an isolated system.

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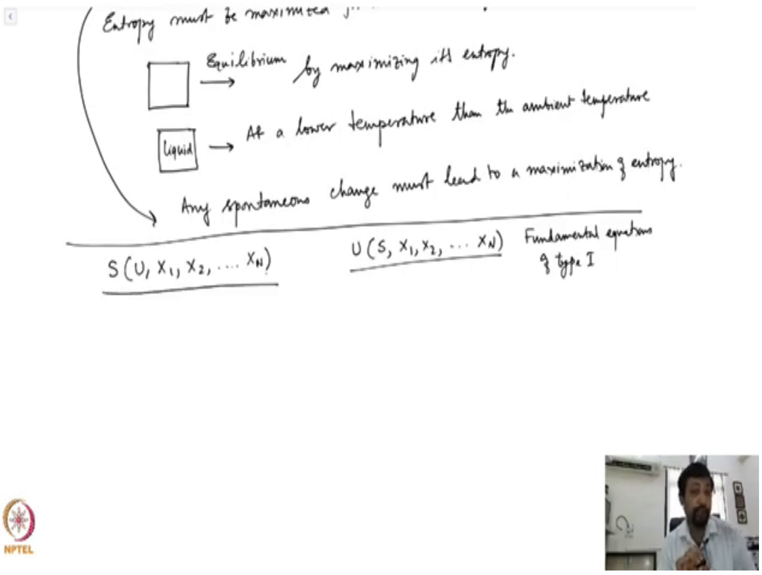

Entropy must be maximized

→ Equilibrium by maximizing its entropy.

liquid → At a lower temperature than the ambient temperature

Any spontaneous change must lead to a maximization of entropy.

$S(U, X_1, X_2, \ldots X_N)$

$U(S, X_1, X_2, \ldots X_N)$ Fundamental equations of type I

This means that, if you have an isolated system and if you take the system out of the equilibrium, then it goes to the equilibrium state, it should go to the equilibrium state by maximizing its entropy right. The most common example that you can visualize is that you have a can of gas or a liquid and you cool the liquid, you put it in the freezer. So, that it is it comes to kind of an equilibrium, which is a different equilibrium and then you bring it out.

So, you have a liquid and which is at a lower temperature, when you bring it bring this liquid this can of liquid from the freezer and set it outside, then it is at a lower temperature, than the ambient temperature. The ambient means the surrounding temperature then you know that the temperature of the liquid rises and thereby since the temperature of the liquid rises things becomes more mobile.

So, this also molecules also start to move more vigorously and therefore, the entropy increases we shall later on look at these things, this also means that any spontaneous change, if you have an adiabatic system any spontaneous change must lead to a maximization of entropy. So, perhaps this was a very not such a well-suited example, if you can imagine that you have a can of gas contained within an adiabatic walls and then you press there is a top part is a piston you press it below. So, that it gets suppressed.

But, this is not a spontaneous change, because you have supplied energy. This means a spontaneous change would mean that there is a spontaneous change within the system that would lead to the contraction of the volume that is not allowed. Because, that is a decrease in energy any spontaneous change can lead to a expansion of the wall right.

So, then comes the fact that now that we have introduced entropy, we know we write down the entropy as a function of the internal energy and the generalized coordinates, or in the internal energy as a function of entropy and the generalized coordinates. You should note over here for example, if you just look at this. So, these expressions that we have seen are the fundamental equations of type 1.

And, this is the pillar of thermodynamics; if you know these relations then it gives you everything. The limitation of thermodynamics is that these equations must be given to you, you cannot derive them. Statistical mechanics on the other hand tells you how to derive them. So, we shall see how to do that, when we do statistical mechanics.

Now, coming back to this if you see I have written down internal energy as a function of entropy and the generalized coordinates.

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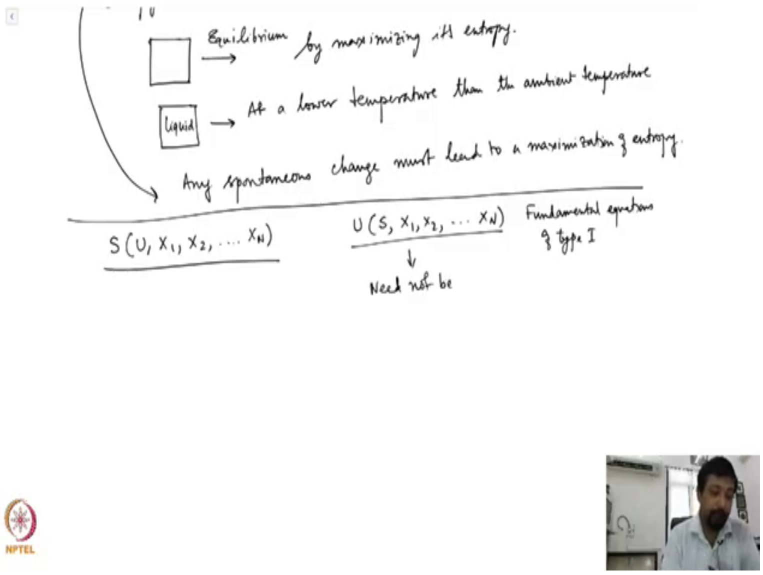

Liquid

→ Equilibrium by maximizing its entropy.

→ At a lower temperature than the ambient temperature

Any spontaneous change must lead to a maximization of entropy.

$\underline{S(U, X_1, X_2, \ldots X_N)}$

$\underline{U(S, X_1, X_2, \ldots X_N)}$ Fundamental equations of type I

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Need not be

This need not be true. In the sense, so, let me first see what I try to say that your internal energy, it may not be that it is a function of all the thermodynamic extra coordinates the extensive variables. I can replace this each any of these thermodynamic variables by it is conjugate force.

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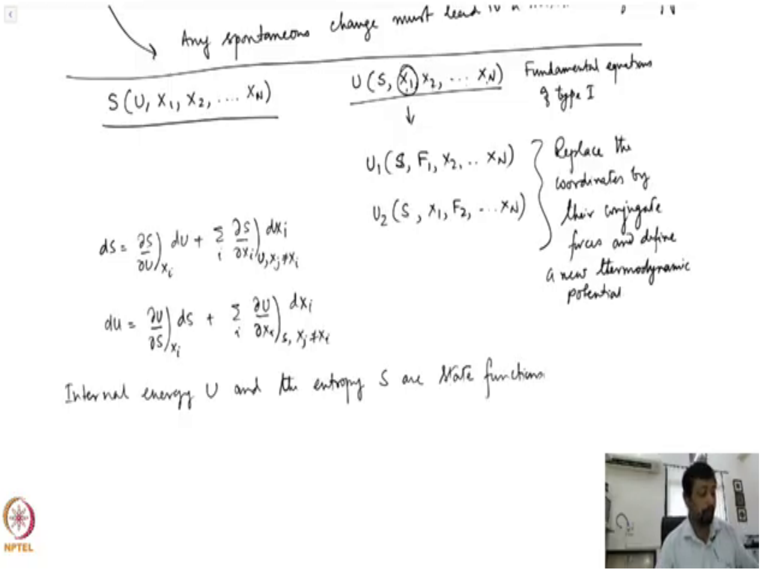

Any spontaneous change must lead to a

$S(U, X_1, X_2, \ldots X_N)$

$U(S, \textcircled{X_1} X_2, \ldots X_N)$ Fundamental equations of type I

$\downarrow$

$U_1(S, F_1, X_2, \ldots X_N)$

$U_2(S, X_1, F_2, \ldots X_N)$

Replace the coordinates by their conjugate forces and define a new thermodynamic potential

$$dS = \left.\frac{\partial S}{\partial U}\right)_{X_i} dU + \sum_i \left.\frac{\partial S}{\partial X_i}\right)_{U, X_j \neq X_i} dX_i$$

$$dU = \left.\frac{\partial U}{\partial S}\right)_{X_i} dS + \sum_i \left.\frac{\partial U}{\partial X_i}\right)_{S, X_j \neq X_i} dX_i$$

Internal energy U and the entropy S are state functions

F 1, x 2, x N, I can define some thermodynamic free energies let us say U 1, U 2 S, X, 1 F 2 so on and so forth. So, you can see that various possible combinations that are possible. So, I can replace the internal replace the coordinates by their conjugate forces. And, define a new thermodynamic potential. So, that is allowed right. For example, you can look at Helmholtz free energy right or Gibbs free.

So, once you know all these functions then clearly you can write down d S as del S del U the X i's are held constant d U plus sum over i del S del X i U and X j not equal to X i are held constant d X i. And, similarly you can also write down d U as del S sorry del U del S x i are held constant d S plus sum over i del U del X i S and X j not equal to X i d X i. Recall that both internal energy U and the entropy S are state functions.

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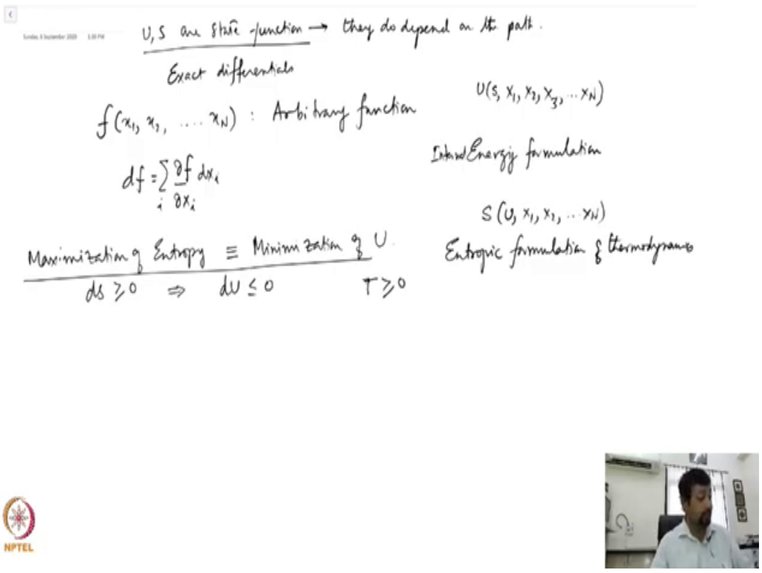

U, S are state function → they do depend on the path.

Exact differentials

$f(x_1, x_2, \ldots x_N)$: Arbitrary function

$$df = \sum_i \frac{\partial f}{\partial x_i} dx_i$$

$U(S, x_1, x_2, x_3, \ldots x_N)$

Internal Energy formulation

$S(U, x_1, x_2, \ldots x_N)$

Entropic formulation of thermodynamics

Maximization of Entropy ≡ Minimization of U

$dS \geq 0 \Rightarrow dU \leq 0 \qquad T \geq 0$

Which means, U and S are state functions, this means they do not depend on the path. In other words these are what are called exact differentials. And, the property of the exact differentials are such that you can write down the differential form if U let us say, if U we will not write down U. So, we will consider any arbitrary function f which is a function of x 1, x 2, x N.

So, this is an arbitrary it is a function, then if it is an exact differential I can write down del f del X i, d X i. So, you can clearly write down this for U and S and therefore, we wrote down the earlier forms that you could see. When you look at so, when you deal with the thermodynamic system and, you write it down in this you start off from this relation; you are doing the energetic formulation or internal energy formulation of thermodynamics.

If, you rather do it like this way you are doing the entropic formulation of thermodynamics. Both are valid descriptions there is no difference between them and we have seen earlier also, that this relation delta S must be greater than 0 or in it is differential form let us say d S is greater than equal to 0 is implies that d U must be less than 0.

So, maximization of entropy is equivalent to minimization of U. And, the reason for this is basically that the temperature is a positive quantity. And, the temperature is a positive quantity is a consequence of Kelvin statement, it is a consequence of second law which tells you that you cannot have a negative temperature right.

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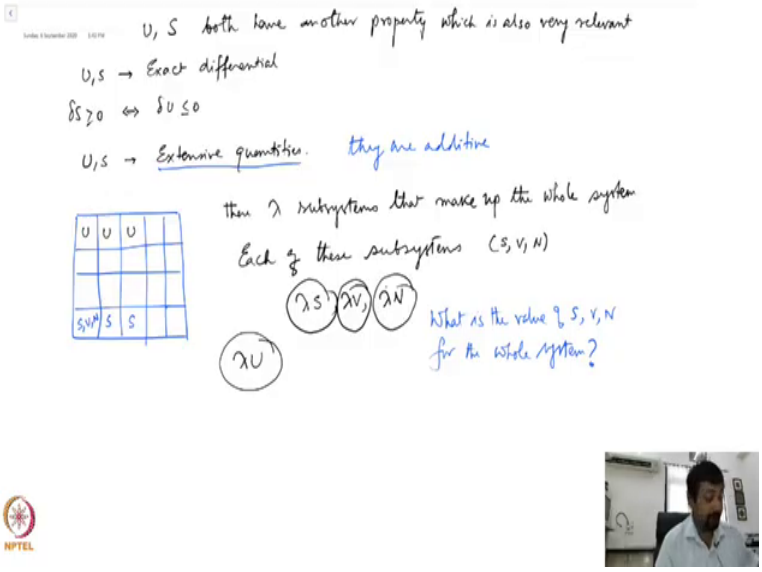

U, S both have another property which is also very relevant

U, S → Exact differential

$\delta S \geq 0 \Leftrightarrow \delta U \leq 0$

U, S → Extensive quantities. they are additive

then λ subsystems that make up the whole system

Each of these subsystems (S, V, N)

What is the value of S, V, N for the whole system?

So, once we know this U and S both have another property, which is very interesting, which is also very relevant. So, we want to just list down the so, U and S are exact differentials delta S greater than 0, implies or is equivalent to delta U less than 0. Further, U and S are extensive quantities, what does this mean?

So, let us look at a system, let us take a system, big system we can imagine and let us divide this into subsystems right. So, what we see is that there are lambda subsystems that make up the whole system. Now, each of these subsystems, have each of these subsystems, the entropy is S, volume is V and particle number is N.

So, this means, that if I want to find out what is the value for the whole system, the obvious is lambda V and lambda N. And, the extensive property of the (Refer Time: 15:15) of the entropy means that the entropy is additive. So, it is lambda S. But, the extensivity property of U what does it mean that, if this one has U this one has U, this one has U, then the whole system should have the internal energy U.

So, let me repeat my argument again, any of if you have just missed it out; the let us look at the system which is made up of lambda subsystems, this looks little ugly. So, let us just draw it properly here yeah. So, each of these subsystems have S, V and N. This is a hydrostatic system we are talking about. So, I have a gas which is contained in a container and I sub divide the volume of the whole container into lambda subsystems. Each of these subsystems have the entropy S, the volume V and the particle number N.

Then, my question is what is the value of S, V, N for the whole system? Well, the two obvious answers for V and N I know, I will simply add up the volume and I will get the volume of the whole system. I will simply add up the particle number for each of these subsystems and then I will get the whole the particle number for the whole system.

Now, comes the entropy, what happens to the entropy? The extensive property of the entropy implies that, they sorry they are additive, which means that if this system has an entropy S, this system has an entropy S, this system has an entropy S, then I simply keep on adding the entropies to find out the total entropy.

U is also extensive, that is the property that we are trying to say, then it also means that the internal energy are also extensive quantities. So, I will simply add up. Therefore, the internal energy of the system becomes lambda times 2. On the other hand, the entropy of the system whole system becomes lambda times S, volume becomes lambda time V and particle number becomes lambda times N.

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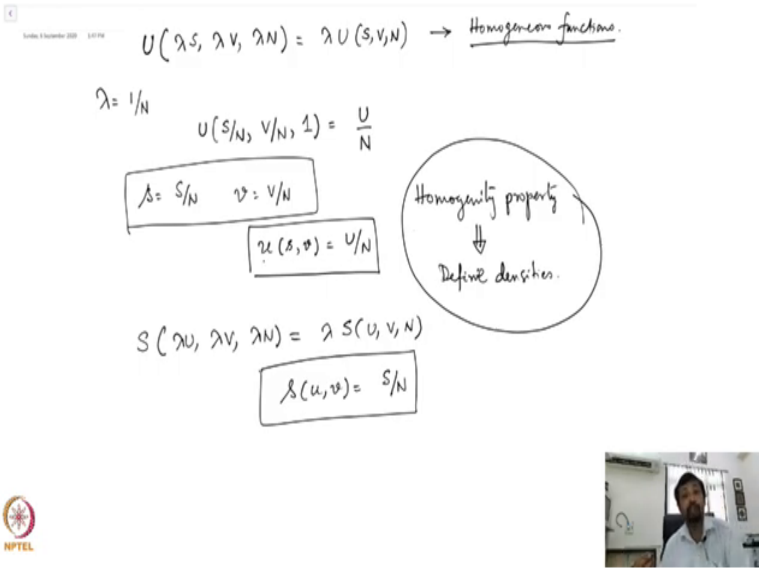

$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N) \rightarrow$ Homogeneous functions.

$\lambda = 1/N$

$U(S/N, V/N, 1) = \frac{U}{N}$

$\boxed{s = S/N \quad v = V/N}$

$\boxed{u(s, v) = U/N}$

Homogenity property

$\Downarrow$

Define densities.

$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N)$

$\boxed{s(u, v) = S/N}$

Therefore, if I write down this equation lambda S, lambda V, lambda N must be equal to lambda times U, S, V, N correct. So, this means the internal energy of the whole system, which has an entropy of lambda S, volume of lambda V and particle number of lambda N would be simply lambda times the internal energy of each of this subsystem.

Functions which obey such a relation are called homogeneous functions ok. So, before we want to understand what homogeneous functions are what we want to write down is let us choose lambda is equal to 1 by N right. Then it follows U of S by N, V by N and 1 is equal to U by N.

So, therefore, you see the number 1 is not very important. So, if I define small s as capital S over N, small v as capital V over N, then u of small s and small v is U by N right. So, the homogeneity property allows me to define densities. You could have started the argument in other way round you could have said that look my system has an internal energy U volume V and particle number N.

So, subsystem therefore, what is it for the total system? And, you would have you could have carried it out for the whole system and you would have come up with the relation that lambda U, lambda V, and lambda N must be equal to lambda times S, U, V, N. And, again you would have done the same procedure then you would have defined the entropy as this.

So, it is a homogeneity property of the internal energy and the entropy that allows you to the to write down the to write down or to define densities for these two quantities. Remember we are talking about internal energy here you can do it for any extensive quantity. For example, for free and any free energy can also be defined in terms of densities, because that is a property of it, because it is a homogeneity homogeneous function right.

So, what does a homogeneous function mean?

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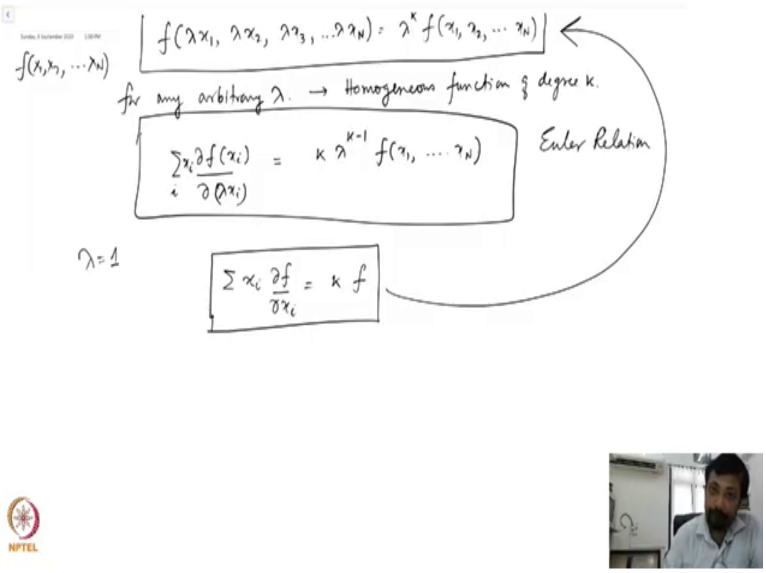

$f(x_1, x_2, \cdots x_N)$

$$\boxed{f(\lambda x_1, \lambda x_2, \lambda x_3, \ldots \lambda x_N) = \lambda^k f(x_1, x_2, \cdots x_N)}$$

for any arbitrary λ. → Homogeneous function of degree k.

$$\boxed{\sum_i x_i \frac{\partial f(x_i)}{\partial(\lambda x_i)} = k \lambda^{k-1} f(x_1, \ldots x_N)}$$

Euler Relation

$\lambda = 1$

$$\boxed{\sum x_i \frac{\partial f}{\partial x_i} = k f}$$

Mathematically, if I have x 1 so, once again I consider a function of many variable and I write it down in this way. So, it is lambda to the power k x N. If a function obeys such a relation for arbitrary lambda, then this is called a homogeneous function of degree k right.

This is the mathematical definition, one can take a derivative with respect to lambda on both sides, if I take a derivative with respect to lambda, then basically del f of x I, del lambda x i times x i this is just manipulating the derivative on the left hand side is k lambda k minus 1, f of x 1 x N right.

This is what is called an Euler relation. It obeys any homogeneous function must obey an Euler relation. Now, if you put lambda is equal to 1, which you are allowed to do because any arbitrary values of lambda are allowed, then it means that sum over x i del f del x i must be equal to k times f x i. It is understood that this is a function of ok, let us just see all of this particular relation follows from this relation right.

And, there is nothing cleverness or nothing ambiguous about it. If a functional relation, if a function satisfies this relation, then it must satisfy this.

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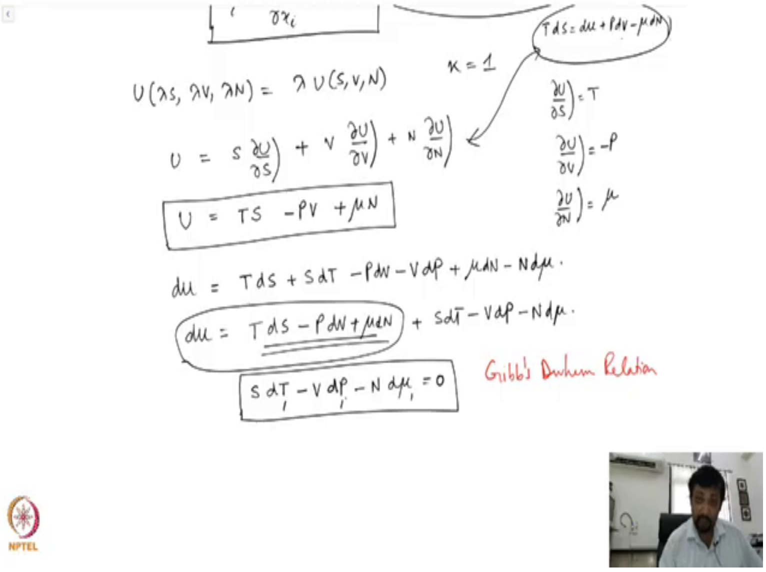

∂x_i

$TdS = du + PdV - \mu dN$

$\kappa = 1$

$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)$

$U = S \left.\frac{\partial U}{\partial S}\right) + V \left.\frac{\partial U}{\partial V}\right) + N \left.\frac{\partial U}{\partial N}\right)$

$\left.\frac{\partial U}{\partial S}\right) = T$

$\left.\frac{\partial U}{\partial V}\right) = -P$

$\left.\frac{\partial U}{\partial N}\right) = \mu$

$\boxed{U = TS - PV + \mu N}$

$du = TdS + SdT - PdV - VdP + \mu dN - Nd\mu.$

$du = \underline{\underline{TdS - PdV + \mu dN}} + SdT - VdP - Nd\mu.$

$\boxed{SdT - VdP - Nd\mu = 0}$

Gibb's Duhem Relation

But, now I know my internal energy obeys this particular relation. And, this is strikingly similar to this particular the relation that you see over here with k equal to 1. If, this is the case then I will also have a similar relation over here.

So, let us write down the Euler form or the Euler relation for this. So, this means it is a function of s V and N therefore, I should have if I write down explicitly U must be equal to the right hand side, S del U del S the rest of the x i's are fixed which I am not going to write it is implied that they are fixed V del U del V plus N del U del N correct.

But, what is U del U del S, I know that del U del S from the first law is equal to T. And, del U del V is equal to minus P right. If, you want if you have forgotten how to write it down you always write down the first law for the hydrostatic system p d V minus mu d N, and then you can see that del U del V is minus P and del U del N is equal to mu.

So, let us write down this means that T S minus P V plus mu N. So, if I combine this equation with the first law together with the first law I come up with this particular relation.

Now, I want to take a differential of this equation. So, write down d u, d u would be T d S, plus S d T, minus P d V, minus V d P here when you write down the differential in U you allow for all the variations of the thermodynamic variables.

There is no restriction plus mu d N minus N d mu, which I can simply collect terms together plus S d T minus V d P minus N d mu. Remember your first law, if you now look at your first law you have exactly this. The left hand side d U cancels with the right hand side the three terms in the right hand side.

Therefore, you see S d T minus V d P minus N d mu must be equal to 0. This relation is called Gibbs Duhem relation. It is surprisingly simple, but it is very very powerful see. If, you look at the first law which is this one over here, then if I want to vary the generalized coordinates, I cannot vary it arbitrarily, I mean their variations are constrained V and N are constrained right. So, if it is an adiabatic wall, then d U plus P d V minus mu d N must be equal to 0 right.

So, in the first law restricts the variations or constraints of variation of your generalized coordinates. If, you look at the Gibbs term relation it does opposite that, it restricts the variation in your generalized forces. T is conjugate to the entropy which is an extensive quantity and therefore, a thermodynamic coordinate the conjugate force is the temperature.

So, the Gibbs Duhem relation does nothing, but it restricts the thermodynamic forces. So, you cannot arbitrarily vary T P and mu. You can arbitrarily vary any of these 2, but arbitrarily you cannot do that. So, if you fix T, if you fix P, then the chemical potential is also fixed the Gibbs Duhem relation.

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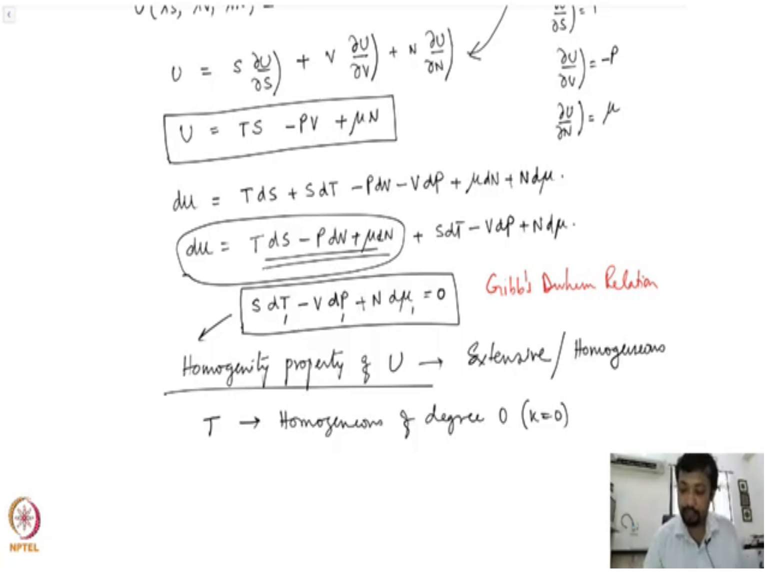

$$U = S\frac{\partial U}{\partial S}\Big) + V\frac{\partial U}{\partial V}\Big) + N\frac{\partial U}{\partial N}\Big)$$

$$\frac{\partial U}{\partial V}\Big) = -P$$

$$\frac{\partial U}{\partial N}\Big) = \mu$$

$$\boxed{U = TS - PV + \mu N}$$

$$dU = TdS + SdT - PdV - VdP + \mu dN + Nd\mu.$$

$$dU = TdS - PdV + \mu dN + SdT - VdP + Nd\mu.$$

$$\boxed{SdT - VdP + Nd\mu = 0}$$

Gibb's Duhem Relation

Homogenity property of U → Extensive / Homogeneous

T → Homogeneous of degree 0 (k=0)

Now, what is also interesting to know is that this is nothing but a consequence of the homogeneity property of U. If, U was not extensive, it was not it would not be homogeneous and therefore, you cannot write down. This you cannot write down a Gibbs Duhem relation if you say U was an intensive variable. Temperature is an intensive variable therefore, temperature is homogeneous of degree 0 that is kappa is equal to or k is equal to 0 ok.

So, I am sorry this has to be plus this has to be plus please rectify I mean I miss the sign over here. So, we did it with the internal energy.

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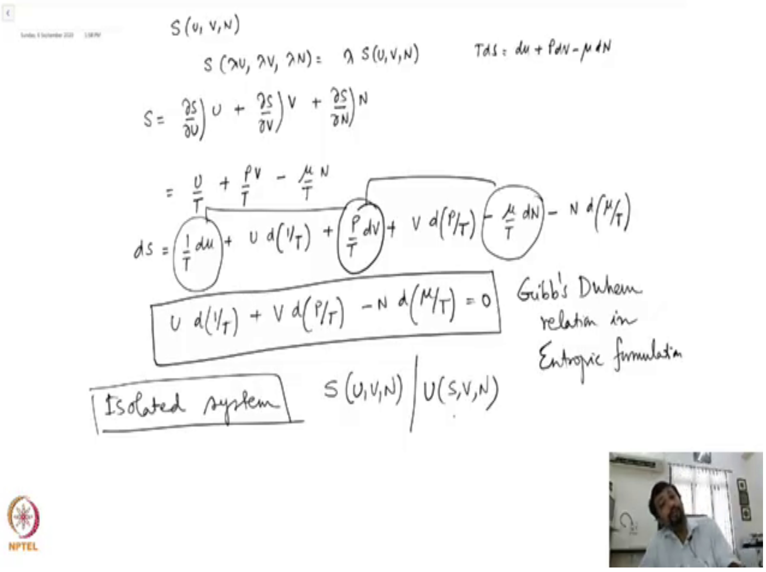

$$S(U,V,N)$$

$$S(\lambda U,\lambda V,\lambda N) = \lambda S(U,V,N) \qquad TdS = dU + PdV - \mu dN$$

$$S = \left.\frac{\partial S}{\partial U}\right)U + \left.\frac{\partial S}{\partial V}\right)V + \left.\frac{\partial S}{\partial N}\right)N$$

$$= \frac{U}{T} + \frac{PV}{T} - \frac{\mu}{T}N$$

$$dS = \frac{1}{T}dU + U\,d(1/T) + \frac{P}{T}dV + V\,d(P/T) - \frac{\mu}{T}dN - N\,d(\mu/T)$$

$$\boxed{U\,d(1/T) + V\,d(P/T) - N\,d(\mu/T) = 0}$$

Gibb's Duhem relation in Entropic formulation

Isolated system $\quad S(U,V,N) \,\big|\, U(S,V,N)$

One can again do it with the entropy, where I have U, V, N and I know that S of lambda U lambda V and lambda N must be equal to lambda times S of U, V, N. So, therefore, if I want to apply the Euler Theory Euler relation over here this would mean that s because it is a homogeneous function of degree 1 S is going to be del S, del U times U plus del S del V times V plus del S del N times N, please note that there are quantities which are held fixed which I am not writing explicitly, but it should be obvious to you.

But, del S del U is U over T sorry the del S del U is 1 by T therefore, this is what you get and then del S del V is minus P over T right, del S del V is plus P over T sorry. Because, if you write down Tds is equal to du plus Pdv minus mu dN and the pressure is defined as the force which is conjugate to the volume is defined as minus P.

And, then minus mu over T arbitrary if you carry out the differential, then this means du 1 by T plus U d of 1 by T plus P by T dv plus I want to write down V d of P by T there is minus mu by T d N minus N d of mu by T. Look at this term, this term and this term, together they form the first law.

So, therefore, you are left out with the variation sorry just getting a little bit sloppy here plus V of d P by T minus N d of U by T must be equal to 0. This is the Gibb's Duhem relation in entropic formulation. Entropic formulation would mean that you have started off with entropy as a you have started off with the fundamental relation where your entropy is a function of U. And, the coordinates and internal energy formulation would mean that you have started off with the internal energy the fundamental equation of type 1, where internal energy is just a function of entropy and the importance right.

So, you might wonder that why are we restricting ourselves to U and S, what we are always trying to talk about here is an isolated system, which is not connected to any kind of a environment. So, you do not have a bath. So, we will come to that later on how to treat such systems?

Because in reality we do get the environment whenever you do experiments it is coupled to the surrounding, but we are typically talking about the isolated system where the entropy is the only as a function of U, V, N or the internal energy as a function of S, V, N are the quantities of a interest.

So, now I have U of again.

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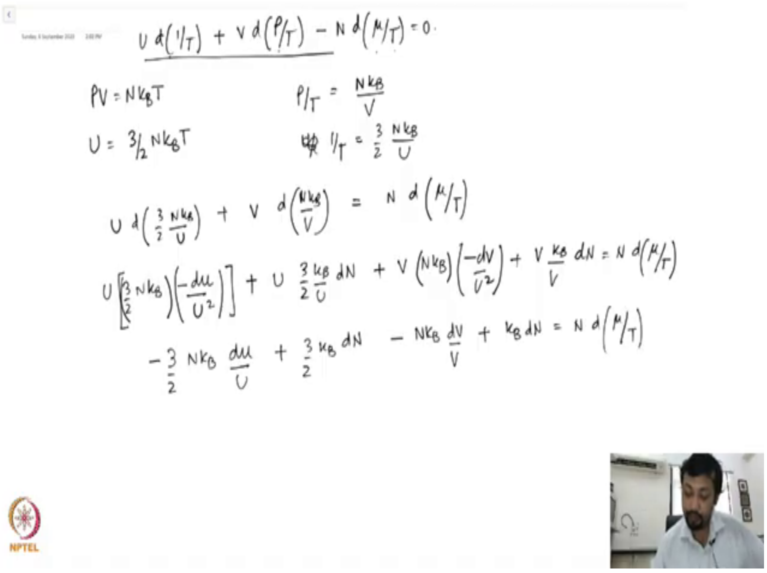

$$\underline{U\,d(1/T) + V\,d(P/T)} - N\,d(\mu/T) = 0.$$

$$PV = Nk_BT \qquad P/T = \frac{Nk_B}{V}$$

$$U = 3/_2\, Nk_BT \qquad 1/T = \frac{3}{2}\frac{Nk_B}{U}$$

$$U\,d\left(\frac{3}{2}\frac{Nk_B}{U}\right) + V\,d\left(\frac{Nk_B}{V}\right) = N\,d\left(\mu/T\right)$$

$$U\left[\left(\frac{3}{2}Nk_B\right)\left(\frac{-du}{U^2}\right)\right] + U\,\frac{3}{2}\frac{k_B}{U}\,dN + V\left(Nk_B\right)\left(\frac{-dV}{V^2}\right) + V\,\frac{k_B}{V}\,dN = N\,d(\mu/T)$$

$$-\frac{3}{2}Nk_B\,\frac{du}{U} + \frac{3}{2}k_B\,dN - Nk_B\,\frac{dV}{V} + k_B\,dN = N\,d\left(\mu/T\right)$$

So, U d of 1 by T plus, V d of P by T, minus N d of U by T is equal to 0 right. Let us see, how strong or how powerful this equation is so, I want to apply this for an ideal gas. I want to see what the ideal gas gives me. This also gives you the third equation of state if you know only these 2 right. So, if I have P V is equal to N k B T and U is 3 half N k B T right.

Then, P by T is equal to N k b by V and U by so, 1 by T is equal to 3 by 2 N k B by U. Let us substitute over here then I have d of 3 by 2 N k B over U plus V d of N k B over V is equal to N d mu over T ok. So, let us do the differentials now U, 3 by 2 N k B d of 1 by U is minus du over U square. So, this term multiplies this term plus U 3 by 2 k B by U d N plus V N k B multiplying minus d V over U square plus V N k B sorry should not be N here, k B over V d N is equal to N d of V by T.

Let us simplify it is a little bit of an algebra, but it is doable. So, this tells you minus 3 by 2 N k B, du by U, plus 3 by 2 k B d N plus. So, again we will have a minus sign because of the derivative we will have minus N k B d V by V, plus k B d N is equal to N d mu by T divide throughout by N.

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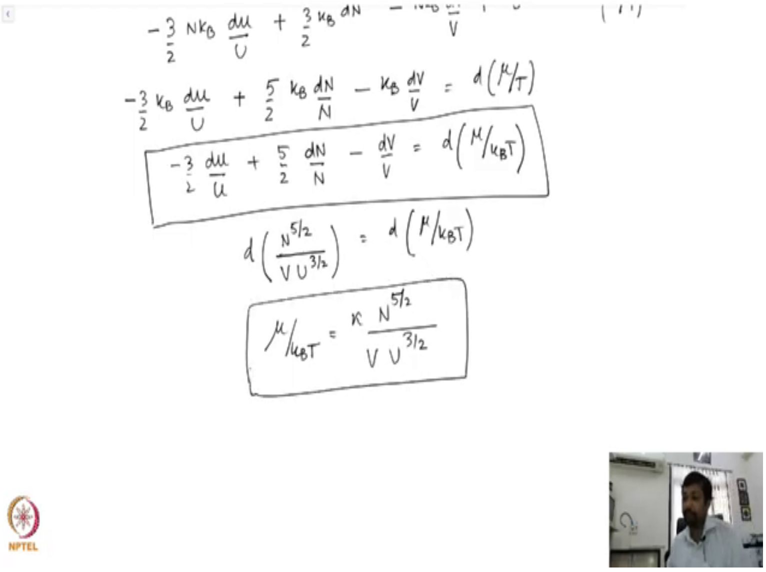

$$-\frac{3}{2} N k_B \frac{du}{U} + \frac{3}{2} k_B \, dN - \frac{\quad}{V}$$

$$-\frac{3}{2} k_B \frac{du}{U} + \frac{5}{2} k_B \frac{dN}{N} - k_B \frac{dV}{V} = d\left(\mu/T\right)$$

$$\boxed{-\frac{3}{2} \frac{du}{u} + \frac{5}{2} \frac{dN}{N} - \frac{dV}{V} = d\left(\mu/k_BT\right)}$$

$$d\left(\frac{N^{5/2}}{V U^{3/2}}\right) = d\left(\mu/k_BT\right)$$

$$\boxed{\mu/k_BT = \kappa \frac{N^{5/2}}{V U^{3/2}}}$$

If, I divide throughout by N, then I have minus 3 k B 3 by 2 k B, du by U plus there is a 3 by 2 k B over here and there is a k B over here that makes it 5 by 2 k B d N, over N minus k B d V over V is equal to d of mu by T. I can take care of the k B also. So, what I will do is I will simply write it down like this way plus 5 by 2 d N by N minus d V by V is d of mu by k B T.

So, that the right hand side becomes a dimensionless thing. Look at this equation now. If, I look at this equation then the left hand side I can write down as N to the power of 5 by 2, V times U to the power 3 by 2 must be equal to d of mu by k B T. Which means mu over k B T is N to the power 5 by 2 V U to the power 3 by 2 and there is an arbitrary constant, which I put it like this way.

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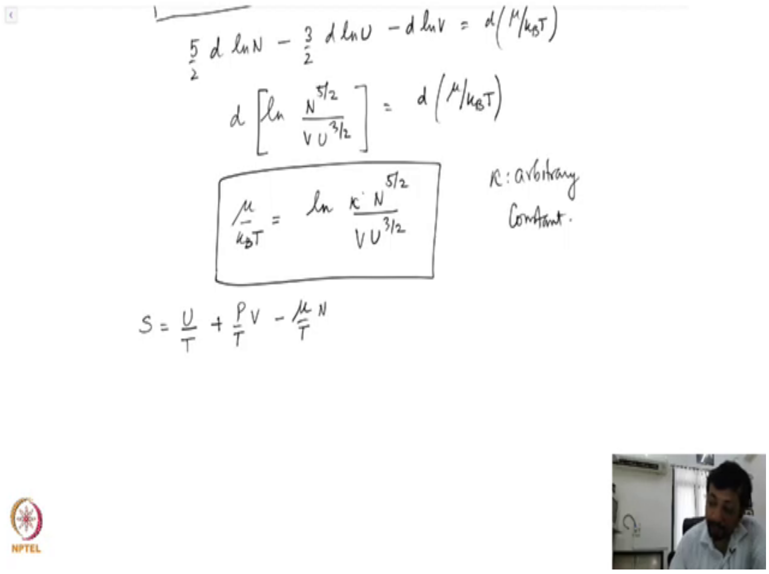

$$\frac{5}{2}\, d \ln N - \frac{3}{2}\, d \ln U - d \ln V = d(\mu/k_BT)$$

$$d\left[\ln \frac{N^{5/2}}{V U^{3/2}}\right] = d(\mu/k_BT)$$

$$\boxed{\frac{\mu}{k_BT} = \ln \frac{\kappa N^{5/2}}{V U^{3/2}}}$$

κ : arbitrary Constant.

$$S = \frac{U}{T} + \frac{P}{T}V - \frac{\mu}{T}N$$

So, sorry there is now so, look at this equation then the left hand side is 5 by 2 d of ln N minus 3 by 2 d of ln U minus d of ln V is d of U over k B T. So, which means I can write down this as d ln N to the power 5 by 2 by V U to the power 3 by 2 is equal to d of mu over k B T. So, it follows mu over k B T is equal to ln kappa N to the power 5 by 2 over V U to the power 3 by 2 right.

Now, you see this quantity kappa is an arbitrary constant. And, thermodynamics cannot give you any idea about this kappa you have to go to statistical mechanics to determine what is going to be your kappa right. So, now, what was S it is a homogeneous function. So, S was if you recall U by T plus P by T V minus mu by T N right, but I know what is U by T?

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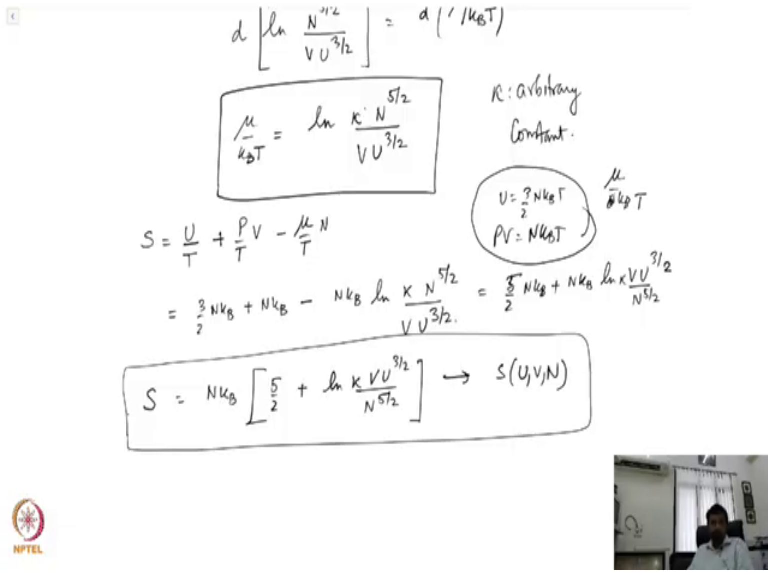

$$d\left[\ln \frac{N^{5/2}}{VU^{3/2}}\right] = d(\,/k_BT)$$

$$\boxed{\frac{\mu}{k_BT} = \ln \frac{\kappa N^{5/2}}{VU^{3/2}}}$$

κ: arbitrary Constant.

$U = \frac{3}{2}Nk_BT$

$PV = Nk_BT$

$\frac{\mu}{k_BT}$

$$S = \frac{U}{T} + \frac{P}{T}V - \frac{\mu}{T}N$$

$$= \frac{3}{2}Nk_B + Nk_B - Nk_B \ln \frac{\kappa N^{5/2}}{VU^{3/2}} = \frac{5}{2}Nk_B + Nk_B \ln \kappa \frac{VU^{3/2}}{N^{5/2}}$$

$$\boxed{S = Nk_B\left[\frac{5}{2} + \ln \kappa \frac{VU^{3/2}}{N^{5/2}}\right] \longrightarrow S(U,V,N)}$$

U by T has been given to you; U is 3 by 2 N k B T. So, this becomes 3 by 2 N k B, P V by T is N k B minus mu by T is N k B l N kappa N to the power 5 by 2, V 2 e to the power 3 by 2. So, I can take N k B outside. So, I can just rearrange this to write down this as 5 by 2 N k B plus N k B, ln V U to the power 3 by 2, kappa times N to the power 5 by 2.

Where, I have now defined redefined the kappa that is all it is just a multiplicative constant it does not matter, whether it sits in the numerator or denominator. So, I can do it like this plus ln kappa V U to the power 3 by 2 over N to the power 5 by 2. You see surprisingly using the Gibbs how strong this equations are, how closely tight thermodynamics is that. I have now constructed the fundamental equation S as a function of U, V, N starting from these two equations.

So, from these two equations I have calculated mu the third equation of state and I have so, mu over k B T, I have determined the third equation of state and from there I have calculated the fundamental relation S of U, V, N. So, most of the exercise in thermodynamics is essentially this. That either this relation is given to you and you look at all the thermodynamic processes starting from this equation.

If, you need the equation of state you derive the equation of state from this equation. If you need to calculate the change of entropy you can calculate the or the heat taken, or given out you can calculate this from this equation right. Or the other way round is you are given the equations of state either all of them if all of them are given to you then it is very very trivial you can just substitute this in the Gibbs Duhem relation and you can find it out.

So, sometimes the equations of states were not going given in the more easier form that you would prefer, but one has to do is little bit algebra to bring them to this form, not to the form that you want essentially. And, you can substitute this in the equation that we have just seen the Euler relation for the entropy and you can get the fundamental relations.

If, 2 equations are given to you and if the third is not given to you then of course, you can eliminate the other equation, and sorry not you can eliminate you can determine the third equation of state from the Gibb's Duhem relation and find out the fundamental relations.