Mechanics, Heat, Oscillations and Waves
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Lecture – 39
The laws of Thermo Dynamics

We talked about the idea begin Thermo Dynamics and we also looked at a specific instance about thermodynamics system, even though it is an ideal one called the ideal gas, the ideal classical gas. Now, we are ready to look at the laws of thermodynamics in sense and explore a few of the consequences. The first step in doing the thermodynamics of a system is to identify all the variables, the thermodynamic variables.

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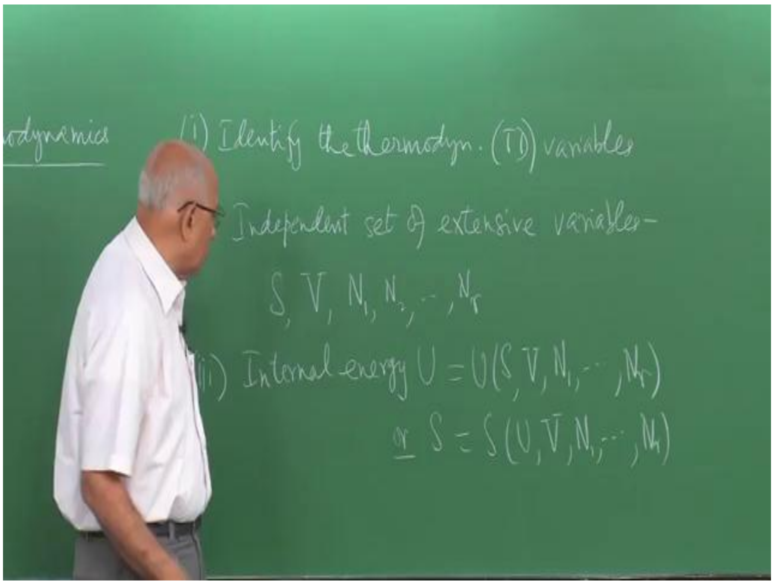

So, let us start by writing step 1 identify the thermodynamic, I will use the abbreviation TD for Thermo Dynamics every, now then, variables both extensive and intensive variables. So, we identify the set of variables, macroscopic variables in terms of which the description of the system is possible and complete. Then, step 2 and this is slightly more difficult step is to identify those extensive variables, which provide a complete description of the system.

So, we may have a large number of a intensive and extensive variables. On the other hand a smaller set among this set of variables are going to be the independent variables, they define in some sense the responsible system to various stimuli. So, we need to identify the independent set of extensive variables and there are several ways of doing this, this is not unique, one way of doing this is the following and a very common one and the one that standard, so to speak is the following.

If you have a thermodynamic system compressing say several chemical components, several kinds of molecules species are mixed together, then one has so called entropy of the system S, we will come back to this and explain lot more about this, together with a volume of the system and then, you have to specify how much of each of the substances there is. So, in some sense you need to know, what are the number of moles, number of moles each of this chemical components or the number of particles of each molecules species.

Let us call them N 1, N 2 up to N sub r, now under normal circumstances this provides a completes set at least for the kind of systems we are going to look at, this is a full set of variables in terms of which you can explicit everything else. And we have to say lot more about what this S is, I mention the couple of times that if you label in equilibrium statistical mechanics. If you enumerate all the possible microstates of the system, namely you tell me what each detail, details of all the relevant details about what each element it constituent of the system is doing at any instant of time.

You are given a microstate; I now list all the microstates and take it is log and that essentially the entropy of the system. In lose terms it is the measure of the disorder in the system, but it is called a precise definition and we will see by experience. Actually we will see, what it is in certain explicit cases. Now, given this set of variables, the idea is that you form, what is called an energy function out of this.

So, we have a basic quantity called the internal energy of the system, one should use a symbol like E for it as I done on occasion, but U is the standard thermodynamic symbol the internal energy U of the system. And this is a function of all these variables in general, this is called the energy representation, but it is possible to have another representation in which U, it is so called entropy representation by you write S as a function of U V N 1 N 2 N r.

So, let me write that down just for r S as a function of U V N 1 N r, these are equivalent waves of doing thermodynamics and whichever is convenience that is the one we choose. So, once you done this and you got all the variables here etcetera, we have the concept of what is called a state function.

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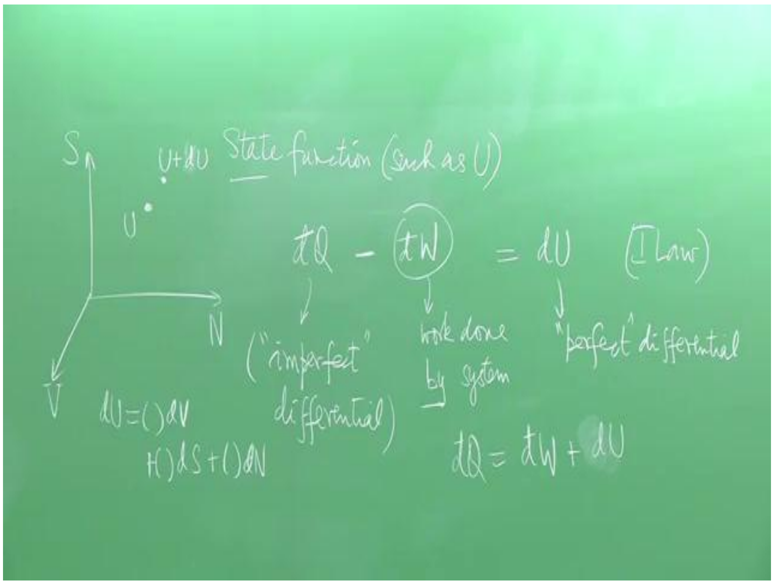

So, what one does is in the space of these independent variables for instance in the case that I wrote down here U as a function of S V N etcetera, etcetera, if you plot all these variables, you get a space, a certain space. So, here is for instance S, here is may be V and here is the typical N. So, if you had just one component that would be the, so called state space of the system. Then, this function U here is a state function in the sense that at any given point in this space, for specified values of S V and N you have certain energy of the system, internal energy of the system.

So, there are every state function, state function such as U is a function of these variables, these state variables. And the idea is that these functions in general most of the time would be smooth functions for which there may be partial derivatives with respect to each of these independent variables and so on. So, the value at each of these point in the state space of the function U is said to be, is supposed to be unique here.

So, this much for the mathematical part of it, but what use this is going to be put to will come in a minute; that is why the laws of thermodynamic coming. The first law as you all known as you heared probably is just the law of conservation of energy, but we need to write this down in most specific form in the case of thermodynamics and the way it is written as follows. It says, if you take a thermodynamic system and you supply a quantity of heat to it, delta q and incremental quantity of heat.

And let me write this amount supplied as d Q, not the usual kind of differential, but something called an imperfect differential. So, I put a little slash there that is just a notation, imperfect and I will explain what this means in a minute, but for the moment it is an infinite decimal quantity of heat supply to this system. And suppose the system does some work for you and let us suppose the amount of work it does is d w, then d Q minus d W that too is an imperfect differential in a certain technical sense, which again I explain very, very shortly, this is work done by the system.

When the remarkable thing is that the difference between these two imperfect differentials is a perfect differential which turns out to be d U here; that is the first law of thermodynamics, this is the so called perfect differential. And what is meant by that, what is meant by saying d U is the perfect differential is the same as saying that U is the state function. In other words, if at this point you have a certain value U and at this point, you have a value U plus d U, which is this point is attained by moving N a little bit, V a little bit and S a little bit and all the independent variables a little bit.

Then, the statement is this is a perfect differential, if you can write this d U as a linear combination of increments in V, N, S and all the other independent variables. So, as long as you can write d U equals to something times d V plus something times d S plus something times d N. In this picture it is a perfect differential, where these coefficients these something's or nothing but, the partial derivatives of U with respect to V, S and N respectively and then, again seconds function of S V and N.

So, called perfect differential is simply statement that this is a nice function of these variables and the value at this point depend on the values of S, V and N at this point. An imperfect differential on the other hand such as this would be a function, which is not a static function. In other words, this incremental value here depends on the part, which you have taken in order to get to the new point.

So, if you have a certain Q here and the q plus d Q d slash Q here, this value of the d slash Q would depend on how you went from U to d U, it would actually depend on the specific path. Unlike the case of the state function, where it does not depend on what path you choose, the general formula for d U is simply this linear combination here with these well defined partial derivatives. So, when you do not have this path dependence, you have what is called an impulsive, when you have this so called path dependence, then you have an imperfect differential.

The work done is an imperfect differential, the heat is an imperfect differential, the incremental heat, but the difference of the two happens to be a perfect differential. Now, this is the way we stated mathematically and of course, this is look abstract, but the point is all these this law was arrived that purely empirically from experiment. So, lot of experimentation and empiricism went into writing the laws of thermodynamics. By Einstein, now the benefit of Einstein, we can now write what the actual mathematical quantities are.

And they, turn out to be the difference between two imperfect differentials is given by the increment of the state function called the internal energy of the system and it is increment is a perfect differential on that side. So, that is the content of the first law, you could rewrite it in various other ways; you could write it as d Q equal to d W plus d U. So, in a supply heat to a system it does a certain amount of work and the rest of it goes in it is increment of it is internal energy; this could be positive or negative.

So, this work could actually exceed this and this will become negative and so on. So, there is no restriction on this quantity at all, it is just that the sin convention I have chosen is such that d W is the work done by the system. Therefore, minus d W is the work done on the system, but I prefer to use this convention here, because it is easier and more physically easy to understand. Because, it says you supply heat the system does some work and then, rest of it goes in changing it is internal energy, so that is the content of the first law. Now, the most common example of d W will immediately make the position clear.

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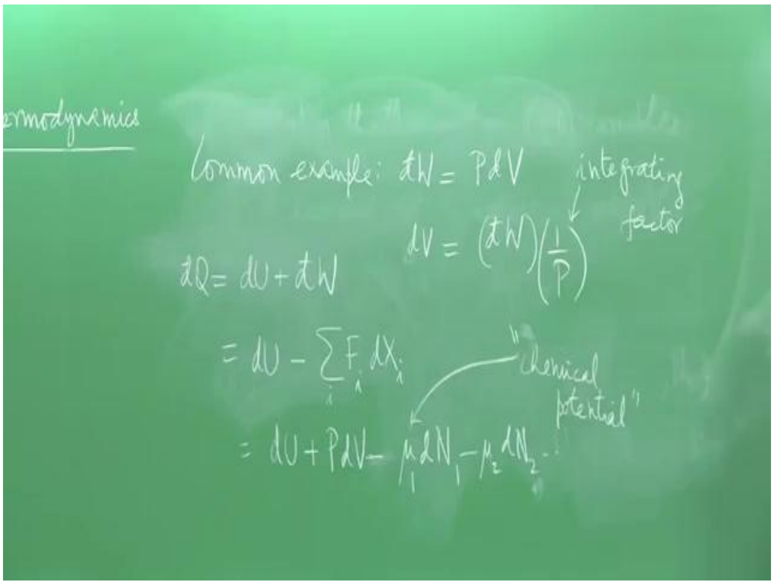

The most common example is the case, in which d W arises from the gas for instants, which undergoes expansion equal to P d V P is the pressure of the gas d V is the change infinite as change my in the volume of the gas when does some work from instants by expansion and then, d W is P d V. But, what you must note here is the d V is the differential is the perfect differential is the differential one of this independent state variables.

So, it actually says that d V equal to d W times 1 over P and it terms of mathematics. What it means is that, when you have an imperfect differential like this you can multiplied by, what is called an integrating factor to make it a perfect differential. So, the statement in general is that when you have an imperfect differential it might be possible be multiplied by an integrating factor, which is itself some there function of some thermodynamic variables, which will make it a perfect differential in this case.

So, the way the first law is return in general for this case of this gas for instance is d Q equal to d U plus P d V. Actually it is a little more general, then that the most general form of write in the first law is as follows. You identify a set of intensive variable, which a called field variables and a set of extensive variables or response variables, which a first state variables.

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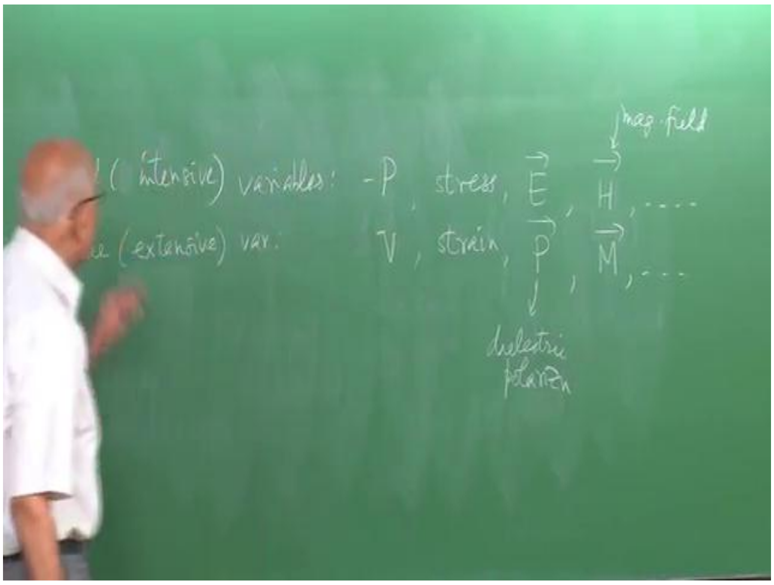

So, you have the, so called field or intensive field variables happens to be intensive variables I give a examples write a way. And then, you have this state are extensive variables and example most common example P here and then V minus P for instance. So, that are sine compendious is kept straight in general stress, strain out here you could applying electric field to a dielectric. So, that is the field variable E, and then the dielectric would respond by get in polarize.

So, the dielectric polarization P that is a field state variable as the response. Then, you could perhaps at supply a magnetic field H this system would response by inquiring the magnetization M and so on. So, you have a set of field variables and the set of extensive variables called the state variables, which is represents the response of the system to the application of this field variables.

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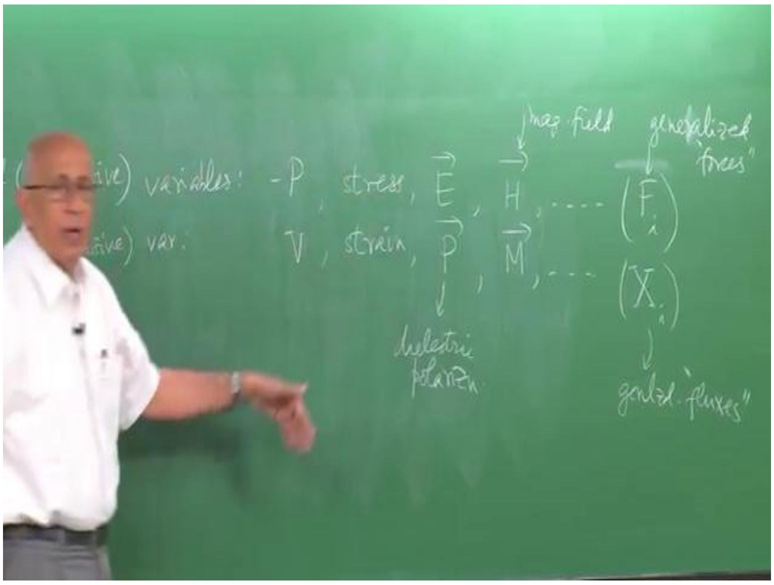

So, in general one could called this some generalize forces F lets called it a generalized forces and these variables lets denote this by X sub i and these are generalized they called generalize fluxes. So, you have forces and fluxes are stimuli and responses in general. When the first law in its generality actually says d Q equal to d U plus d W, which is equal to d U minus summation over i F i d X i. And the first of this F is minus P, so this thing becomes equal to d U plus P d V plus various are the terms of this kind.

For instance, if you had an electric field it would be E and then, this should be dotted it would be dotted d with d P are H dot d N and so on. So, it have a whole lot of this terms, which would tell you, what is the kind of work being done by the system and a various kinds of stimuli are applications of fields that is a generalize first law. A very important one, which is normally, neglected an elementary treatment, but which is important very important is the following even in the absence of an external field right magnetic fields electric fields and so on.

You could consider you should really consider a thermodynamic system, in which the number particles itself can vary. Now, thermodynamic system these are of three kinds first you have an isolated system, which as no exchange either heat or energy with the surroundings no exchange of matters with the surroundings. Then, you have a close system which can exchange heat or energy with the surroundings; such as a beaker of water kept in this atmosphere at close beaker no water can get out no water can no air can get in that is a close system, but energy can be change it can be heated of it can be cooled and so on.

And then, you have and open system, where the number of particles itself can it can change for metric and it be a same with the surrounding and vice versa in addition to energy. So, in the case of open systems you must also allow for variation in the number of particles itself that is, why used in as one of the variables when I said S V and N. So, when you use that when you do that, then this law reads a little differently this is equal to the first term here is minus mu d N.

And you must use one of this for each chemicals component in therefore, really the law is minus mu 1 N 1 minus mu 2 d N 2 etcetera, where this mu, which is the conjugate variable to the N corresponding N just as P is the conjugate variable thermodynamic conjugate of the volume V this a mu is called the chemical potential corresponding to the chemical component one that I labeled as one the molecules spices is one has a chemical potential.

If you had an unknown molecular spices is also in the mix share, then it would be mu two and so on and so for that. So, that is the sort of general form of the first law of thermodynamic and do will write this in the following way for all purposes, let me write it, let us look at the single component system.

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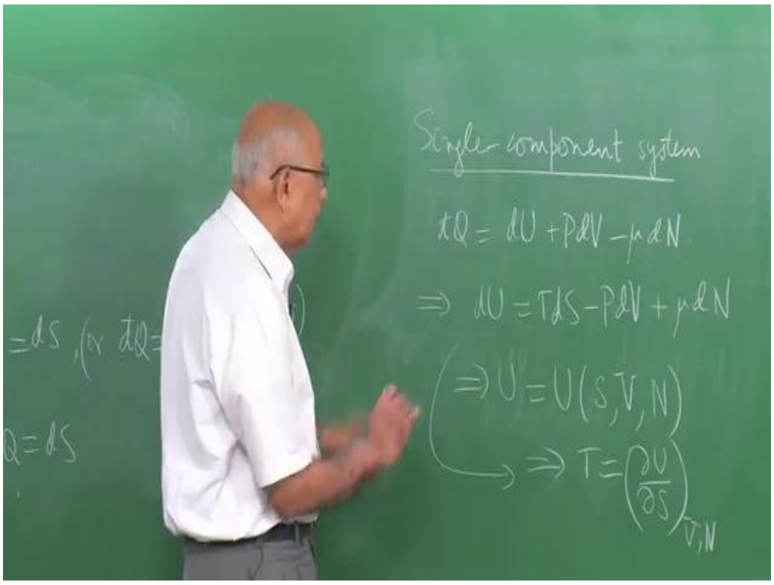

So, the first law of thermodynamics then is d Q equal to d U plus P d V minus mu d N a single component with chemical potential mu its equal to this, this quantity mu has the following significance as it stands. It some kind of rate of change of this quantity with respect to N; that is the first point we see immediately, but it is got a better significance on that it will turn out that this is the, so called gives free energy of this thermodynamic system per particle.

So, that is the physical interpretation of this mu are to put it in a simpler terms it is the coasting energy for adding one more particle to the thermodynamic system and a specific external conditions. And a conditions, in which the temperature and the pressure at kept constant you add one more particle to the collection of objects collection of molecule and that a cost an energy do show is essentially the chemical potential of the system. So, it is not a force that you can apply in the sense that you can apply pressure on electric field a magnetic field.

But, it is a generalize force in this sense that it is one of the F that we can write down in the first law of thermodynamics. When not going to look at this very much we going to restrict are self to cases very of fixed amount of gas or fixed amount of fluid, in which case this term drops out, because N is constant in this cases. But, just for completeness this is the more general we have writing this. So, much for the first law, now, what is the second law if thermodynamic in that is a very performed one in a very deep one.

Now, several ways of enunciating that a many ways and the elementary text books ways are doing. So, put tell you things like it is impossible to get to the absolute 0 of temperature in a finite number of operation and so on and, so forth. But, actually one should write this a little more pressingly and, let us do it in terms of the various thermodynamic variables we talk to about here.

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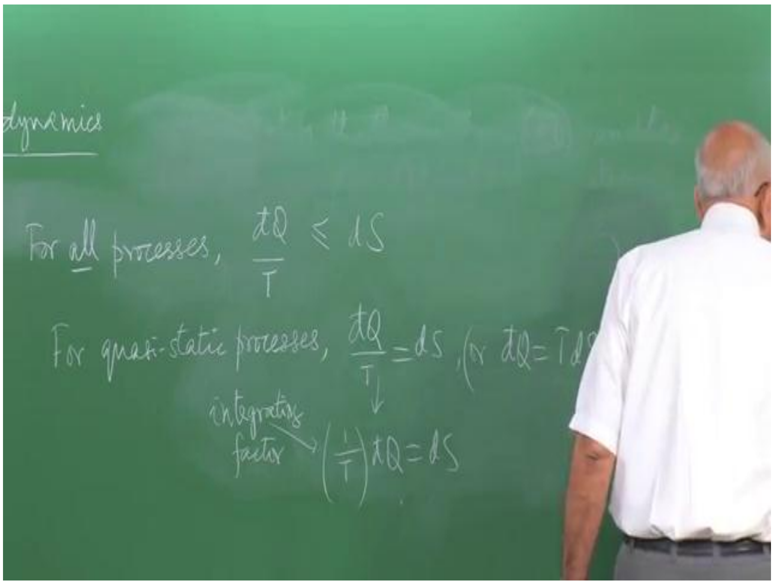

Before that I need to mention, what is meant by a quasi static process I have already talk about this I said that when you make a change of state when you take a thermodynamic system and you do something to it are it change a state. If it does show in a sequence of sleek of states; such that at any given times its in thermal equilibrium. Then, this process is a quasi static process.

In general, what it implies is that very roughly speaking you do not do to in sudden things it your own make many rapid changes although that is not necessarily something which guarantees a quasi static process. But, we if already seen, what is mean by thermal equilibrium, a thermal equilibrium state is one, in which all time averages at time independent all averages of microscopic quantity at time independent. Now, when you make a change of state if you ensure that you go through a sequence of equilibrium states, then we have a quasi static process.

In a quasi static process certain remarkable things happen one can show that in all such process d Q this quantity is less than equal to if you divide by the absolute temperature this is less than are equal to the perfect differential of a state function is less than equal to the differential of the entropy this if you like is the content of the second law of thermodynamics. So, for all quasi static processes where I should say this little more carefully for all processes d Q over T is less than equal to d S.

And for quasi static processes d Q is over T is equal to d S, so that is the write it to say. And, if you like this is the second law of thermodynamics the formulation in this a form it is most convenient for us to produce further. So, the any equality we says the change in the entropy is always greater than equal to d Q over T becomes in equality in the case of quasi static processes, so it say r d Q equal to T d S. So, the significance one significance of a quasi static process is that 1 over T acts like an integrating factor.

So, note is that this thing here is 1 over T and integrating factor times an imperfect differential becomes a perfect differential. So, this quantity is in integrating factor just as 1 over P it was an integrating factor, which multiplied d W to give you d V in exactly the same way d Q this imperfect differential multiplied by this integrating factor gives you the derivative gives you the differential of the entropy. So, if you put that in this is second law, if you put that in this implies that du is T d S minus P d V plus mu d N could I write this as T d S.

And then, you see immediately that this implies that U as promise is the function of the state variables the internal energy of this system is a state function and it is a function of the extends a variables the entropy the volume and the member here. This is the content of thermodynamics essentially another law is by the way a 0th out law and this a third law and I mention that very briefly very shortly. But, this specifying this specifies as for as a single component is concern a system is concern with thermodynamics completely that is it.

Once you tell me, what this function is I tell you everything about the system that is thermodynamically movable about the system. So, this is the content of wooding in the first two law's now just one quick remark about the 0th law the 0th law helps to define the temperature in terms of this quantity is, because it says if use a function of S V and N and you keep V and N constant its clear by du is than T d S. So, therefore, this will imply immediately this implies the T is the rate of change of the internal energy with respect to the entropy given that the other two or kept constant.

So, this is the notation with says this two independent variables a I kept constant and then this co efficient must necessarily be the rate of change of U with respective S all you got do to put this 2 equal to 0 and divide by d U and take in a divide by d S an take the limit.

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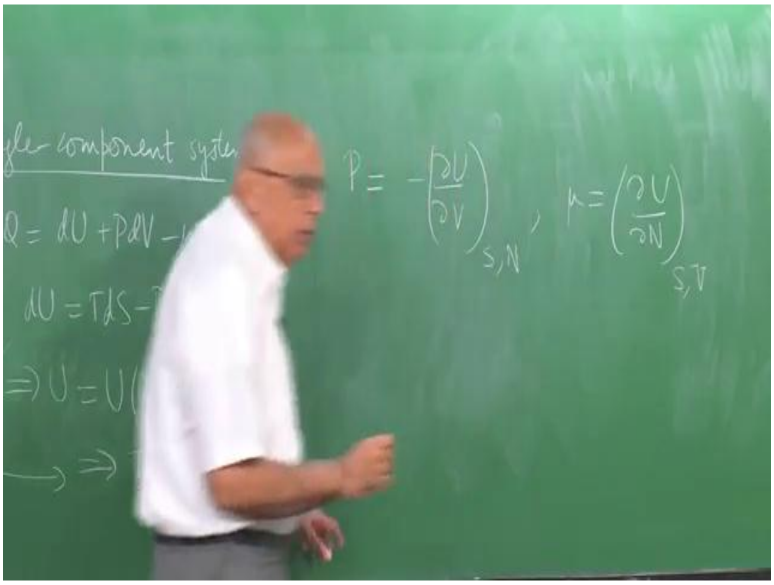

Similarly, in exactly the same way you immediately find also that the pressure, in the pressure is equal to minus delta U over delta V keeping S and N constant. And the, so call chemical potential is the derivative of d U with respect to N keeping S and V constant this is at this stage purely mathematical. Because, you may ask in physical practice how do I keep the entropy constant, how do I keep I can keep the volume constant we can physically see this, how do I keep the entropy constant that is the non trivial question this can to express.

But, in mathematical terms it is clear that the partial derivatives actually give you the coefficients here. So, this is the content of the first two laws of thermo dynamics if you like the third law of thermodynamics actually says the first law say the 0th law says that there exist a quantity call with temperature etcetera. I mention that in thermodynamics we use the ideal gas equation of state define a Kelvin's scale of temperature.

If you like this defines the temperature here this quantity here defines a rate of change of the internal energy with expect to the entropy at constant V and N helps you to define the temperature not a very useful definition as it stands here. But, when you go to statistical mechanics it becomes an obvious kind of definition. Similarly, for the pressure and in the chemical potential there the third law of thermodynamics is something different it is says that if this derivative is 0 there exist a state, in which the entropy also vanishes.

That is, equivalent to saying that the entropy of the system vanishes at absolute 0 of temperature we will come back to that I am talk about little later. So, we not going to use the third law of the thermodynamics as such, but I thought I should mention it and interest of completeness you will get back to this.