Lecture - 40
Specific Heat of an Ideal Gas

We talked about the combination of first and second laws of thermodynamics.

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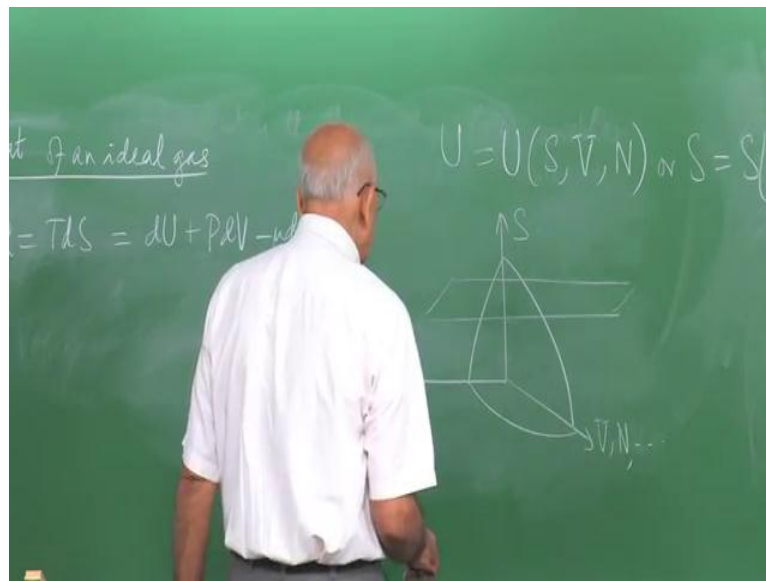
And we discover that you could write them down as d Q is T d s, assuming that we are talking about processer which are in quasi static equilibrium all the time, when this is equal to that and this is equal to d U plus P d V minus mu d N and so on here. Now, the question is, what happens in a state of thermodynamic equilibrium, any state of thermodynamic equilibrium, I said already that the basic point about thermodynamics is that, you have a U express as the function of the internal energy, expressed as a function of S, V, N.

For instance, for a single component system or S could be expressed as the function of U, V, N and so on and in a state of thermal equilibrium, what happens is that, this quantity is at a minimum. In other words, these thermodynamic variables have values such that, they minimize this energy here or they maximize this S and this is most easily seen in terms of the picture.

So, if I would try to draw picture with S coming out there and let say U going here and then, all these other extensive variables V, N etcetera, I do not have enough axis to draw

all these things. When this represents some kinds of surface in this space and this surface would look roughly like this, just very schematically, it would look like convex surface of this kind.

Such that in a thermal equilibrium state, if for instance, you looked at an equilibrium state in which the entropy is kept fixed at some point. Then, it would correspond to a section of this kind and let us do this better.

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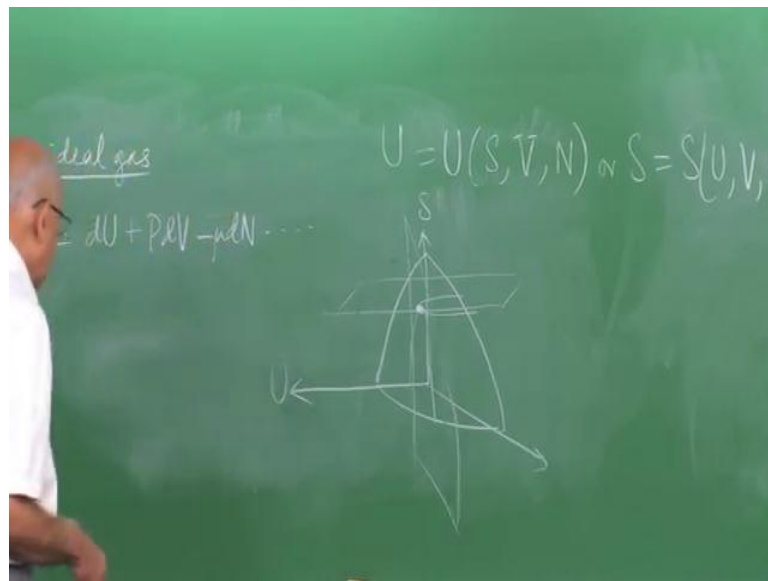
For better representation it have been looking like this, exactly I do before and if you looked at the section of this, here is S and here is U. If you looked at the section of it by cutting it in a perpendicular section for instance, I am not going to draw this, then you have a state on this surface, which is at a maximum value of the entropy. On the other hand, as far as cutting it in this direction is concerned, it would correspond to a minimum of the entropy here.

So, you have an equilibrium state is one, where either this is minimized or that is maximized, the way it is drawn here. So, that is the idea behind thermal equilibrium state. Now, it depends on the external conditions always, what are the variables, had I choose in a field variable here, instead of the state variable like V, had I choosing pressure here or had I choosing the chemical potential here. Then, these thing should be different is not this quantity; that is minimum or this quantity; that is maximum in those thermal states and I will give an example very, very shortly.

But, the idea is that, thermal equilibrium corresponds to the minimum or in a certain case

in the case of the entropy a maximum of a certain thermodynamics potential or state function, if you like. Energy is easy to understand, because mechanical equilibrium the energy is minimize, so it is convenient to say that the internal energy is a minimum in the case, where U is a function of S, V, N and the other fluxes in this problem.

Now, let us go to the case of an ideal gas, which is the familiar instance and ask, what this gives us. So, let us look at an ideal gas, a fixed amount of this gas, so that one mole says, so that this goes away and we haven equation of this kind and I like to know, what the specific heat.

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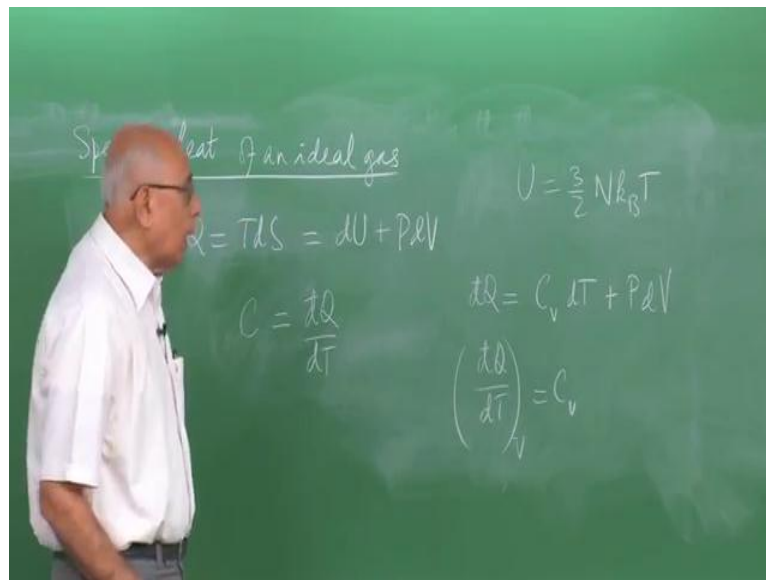
As you know the specific heat under any condition is denoted by C, it is just the capacity of the system to change it is temperature on the absorption or emersion of a certain amount, extraction of a certain amount of heat. So, it is just d Q over d T under conditions to be specified. Now, when the volume is constant, then it is clear that d Q by d T is going to give you, this is goes away goes to 0 is going to give you the specific heat at constant volume.

Now, in an ideal gas, the internal energy we know is the function for ideal gas, this is equal to the 3 half N k Boltzmann T and it is derivative with respect to the temperature gives you immediately the specific heat at constant volume. So, for in ideal gas this thing here becomes d Q equal to C v d T plus P d is gives and if I keep the volume constant and differentiate with respect to temperature d Q over d T at constant volume equal to C v, so that figures. What happens at constant pressure?

Well, the same equations says d Q over d T at constant pressure is C v, because I divide by d T here plus P times d V over d T, but I am skip the pressure constant. On the other hand, for an ideal gas and one mole of it as be looking at here, we have P V equal to R T, which implies P d V plus V d P equal to R d T at constant pressure.

If P equal to constant, then this term goes away and it says P d V equal to R d T here. So, d V over d T is R over P or this gives you C v plus P times R over P plus R, which implies that for an ideal gas C p minus C v equal to R. A relation which you are already familiar with, where that is part of a more general relation that d Q is C v d T plus P d V, the immediately follows that and a constant pressure, you have this relation C p is C v minus R.

One can now ask, what happens if the process to which I subject this gas is not necessarily under constant pressure or constant volume or anything. Something in between, such as an isothermal or adiabatic or any other process, where the pressure and volume vary in a prescribe manner, they are related to each other in a prescribe manner. So, let s look at a more general case, let us look at the following case of which all these are special cases.
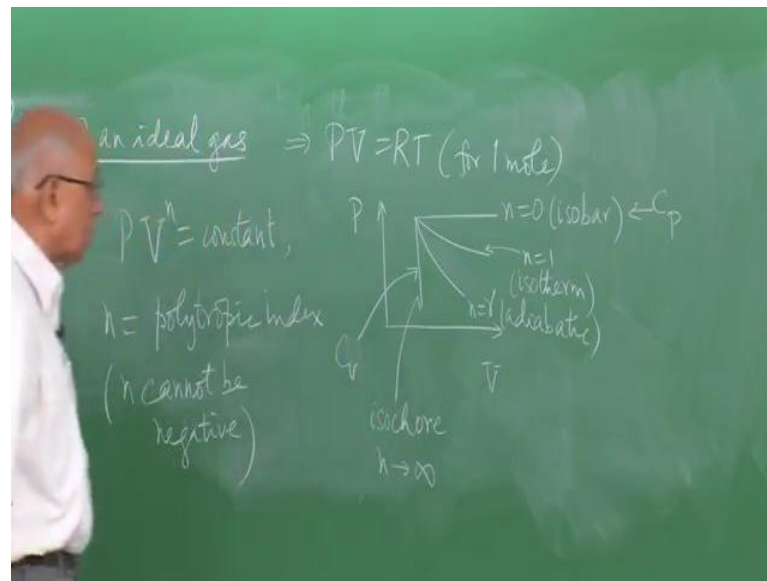
So, we look at a case, where a process quasi static process, which means that you go through the succession of equilibrium states, such that P times V to the power n equal to constant. And n is so called polytrophic index, all the while, the equation of state is still valid. So, an ideal gas implies that P V equal to R T for one mole, I am now, looking at what happens, when P v to the n is constant. So, in the space of P and V, the plot P here and V here, this can be negative. So, in the first quadrant is involve, then as you know, if I put n equal to 1, I get an isothermal process; that is Boyle's law says P v equal to constant, when T is constant.

So, you end up with this corresponds to n equal to 1, P v equal to constants. So, this is isothermal; that is an isothermal. On the other hand, you could have also had P v to the gamma equal to constant, which is an adiabatic and since, gamma is greater than 1, so you have a thing like that, when says n equal to gamma; that is an adiabatic. Adiabatic process, you can have a constant volume process, you will keep the volume constant.

So, you end up with something with changes in this fashion, this is an isochore corresponding to constant volume and what can of n would it correspond to, well it means n must an to infinity. Because, infinite decimal change is in, when n is infinity here, this thing dominates out here. So, and when n is 0, P is constant; that is an isobar, so you can have any number between 0 and infinity for n and then, you get so call polytrophic process in which n is the polytrophic index anything in between.

As you can see, when n increases over positive values to infinity the curve bends down

and comes down pull it like this a limiting value, n cannot be negative. If n is negative, it says P is proportional to V to a positive power, which means, if you increase P, the volume increases that violates thermodynamics stability, which is also known to you as Le Chatelier's principle.

You increase a pressure on a gas, it is volume cannot increase, it most move in the direction of decreasing volume; that is an equivalent way of saying that you are at the minimum of some thermodynamic potential and I mention what this is a little later. But, it is obvious from this principle of stability that n must only be a positive number. And now, I ask, what is the specific heat if the gas under goes this process here, for a general value of n, which is positive, somewhere between 0 and infinity.

Well, we know the answer already, when n is 0 an isobar, the specific heat is the specific heat at constant pressure, so we know, what it is here, this is C p and we know, what it is here on this curve, the specific heat is the specific heat at constant volume C v. This is 3 halves R for the monotonic ideal gas; that is 5 halves R, because C p is C v plus R. What is it is in between, well, let us look at it, see, if we can write both this out.

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So, we have P v to the n equal to constant that implies that P n P v to the n minus 1 d V plus V to the power n d P equal to 0 or if you cancel out V to the n minus 1, it says n P d V plus V d P equal to 0. Now, it also know that P v is R T, so we know that the P d V plus V d P, this quantity is equal to R d T in general by differentiating this equation force. So, it says V d P is R d T minus P d V this implies n P d V plus R d T minus P d V equal to 0

R d T, write it in other way n minus 1 P d V equal to minus R d T or let us write this as plus or R d T input a 1 minus 1; that is the general relation.

And now, we need to know, what the loss of thermodynamics tell us, the loss of thermodynamics tell us that d Q is equal to, I do not in need to use the second law, this is equal to d U, which is C v d T plus P d V. Therefore, the specific heat for a given value of n, which I denote as C sub n for a given isotropic process P v to the n is constant. This is equal to C n by definition equal to C v plus P d V over d T for this process for a given n for this process.

But, we know from this equation that d V over d T for this process, this implies that d V over d T for a given n process at P times implies that P times this for a given process is equal to R d T, R divided 1 minus n. So, that is all we got a put in here and then, the problem is solved.
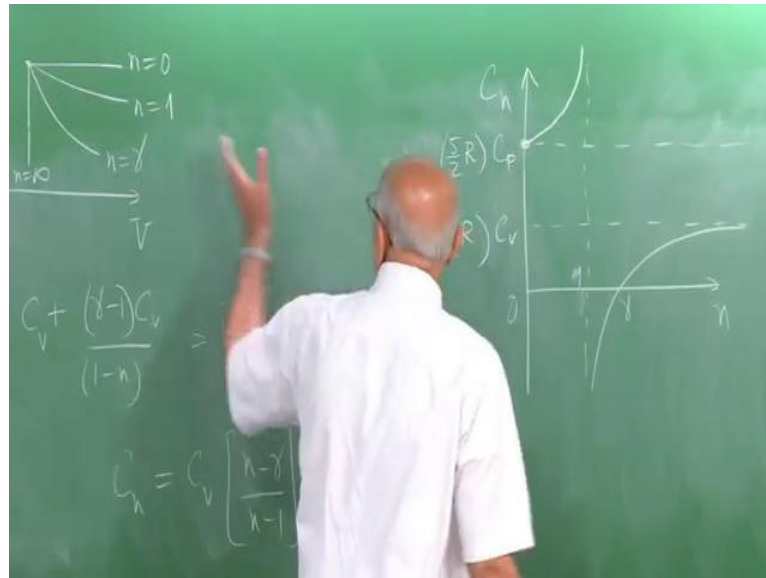
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So, we have C n for this process, this implies that C n for such a process is equal to C v plus R divided by 1 minus n. But, this is the same as C v plus C p minus C v divided by 1 minus n, because C p minus C v is R for a mole of ideal gas and C p is gamma time C v. So, this is equal to C v plus gamma minus 1 C v divided by 1 minus n, which is equal to C v times 1 minus n plus gamma minus 1 divided by 1 minus n and the 1 cancels out.

And therefore, I have my final answer which says C n equal to C v times let us write this as n minus gamma over n minus 1 and that is it; that is a general answer here. So, we have an expression for the specific heat for a general polytrophic process for an ideal

gas, one mole of an ideal gas which is C v times something or the other. Now, physical dimensions implied that this thing must also have the same dimensions has d Q energy over temperature, which is that C v has. So, this is a dimensionless ratio here and that is the general formula and it tells as that all the special cases should be merge automatically and let see if that happens.

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So, let us plot as the function of this index n, let us plot the specific heat C sub n, this is what happens. Now, at n equal to gamma, it varnishes, this thing vanishes here, when n tends to infinity.

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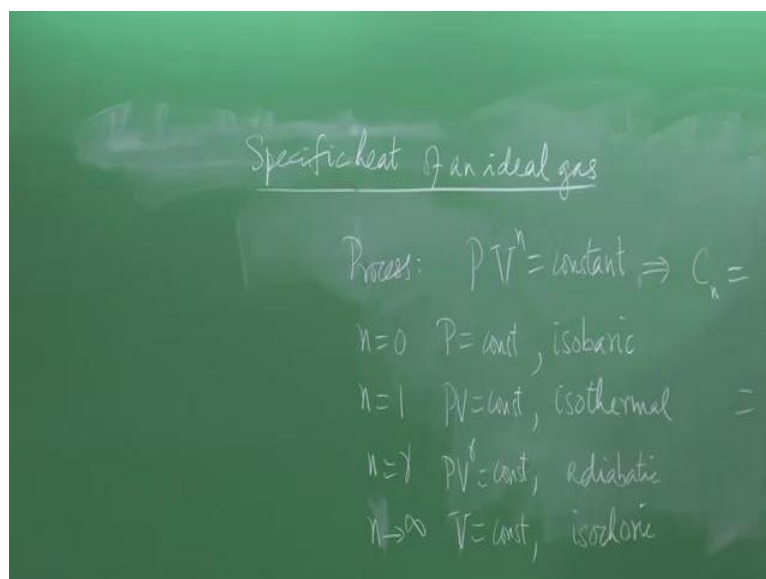
So, let us recall what these things were n equal to 0 corresponded to in isobar P equal to constant. Isobaric process, n equal to 1 corresponded to an isothermal process, n equal to gamma corresponded to P v to the gamma equal to constant, which corresponded to an adiabatic process. Actually, I should say isentropic process, because the entropy kept constant, remember that that is the definition, since d Q is T d s for quasi static processes if d Q is 0, d S is also 0, which means, it is an isentropic process.

And n tending to infinity corresponded to V equal to constant which is an isochrome, isochoric process. Now, let us see what happens here when n terms to infinity this ratio goes to 1 and you do indeed get C infinity is C v; that is what you have here. So, that some number 3 halves are in this case, this is 3 over 2, this is C v in this point and that is a attain when n terms to infinity according to this formula.

When n is 0, we have here and isobaric process. So, when n is 0, you have C n is gamma time C v; that C p, so this recover C p correctly and C p is sitting somewhere here ((Refer Time: 20:29)), C p that is 5 halves are and it says when n is 0, you there at this point. When n is 1; that this isothermal process, it says C n is infinite. Of course it is, because remember the definition of C n, the general C n was equal to d Q over d T for a given value of n and when n is 1, you are an isotherm, which means T does in change this go to 0 and therefore C goes to infinity.

So, it is very reasonable that it 1, it goes to infinity, this is the point 1 and therefore, it is start here and goes of the infinity in this fashion. When n is between 1 and gamma ((Refer Time: 21:29)) this numerator is negative, but the denominator is positive. So, C is actually negative, C is n is negative. So, it is start of at minus infinity here crosses this axis at the value gamma, this is the value 1 out here and n tends to infinity it tends to C v the value C v here.

Notice that for n polytrophic process can this specific heat have a value between C v and C p ((Refer Time: 21:59)), this is 3 halves and this is 5 halves. But, it could actually have for certain processes, it could actually have a value of n, which is between, which is less than C v or greater than C p on this side, depending on the polytrophic index, we wrote down. So, all the four limiting cases if we go back to the P v diagram ((Refer Time: 22:29)), here is V, here is P, remember that for started this point and I talk only about the part of the process for the volume increases.

Then, this should be are increases are remains constant, this should be n equal to infinity,

this should be n equal to 0, this is n equal to 1 and this is n equal to the R, corresponding to these four processes, you have specific heat here, which are respectively C p in this case, C v in this case. When, a n tends to infinity, n is 1, it is 0 and when n is gamma, it should be 0 on an adiabatic, because d Q is 0, d S is 0 for an isentropic process.

So, at n equal to gamma this specific heat should vanish and indeed it does so for in gamma. So, even the simple ideal gas classical ideal gas can have early complicated behavior depending on the kind of process to way choose subject this system. Normally, one restricts oneself to isothermal and adiabatic processes, but there is no reason why you cannot consider a more general family a process is such as this process here.

One could ask is there a general relation, which express as the different C p minus C v, we found it was equal to R in the case of the classical ideal gas, but I leave it as exercise for you do show that the following in his true. This requires a little bit of partial differential in differential and so on playing around with this differentials.

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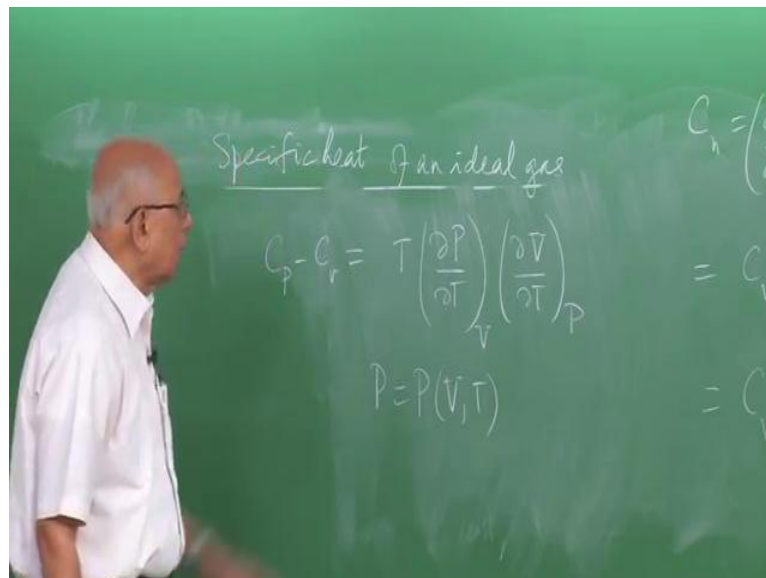
But, in general, it terms out that C p minus C v is equal to on this side T times delta P over delta T at constant volume times delta V over delta T at constant pressure. In other words, if you give me the equation of state, which corresponds to saying that you give me P as a function of V and T for a given amount of the gas, then I can compute this partial derivatives and that is what C p minus C v is in general.

For an ideal gas it will reduced to whatever we are talk to about, this is reduces this whole thing reduces to R for an ideal gas, but this is the general formula which is valid

from more general cases, then the ideal gas itself. Next, I mentioned that you can have other kinds of independent thermodynamic variables not just the once that we have chosen which were S, V and N, you could look at other kinds of thermodynamic variables and keep those constant and ask, what is the equilibrium state of the system etcetera.

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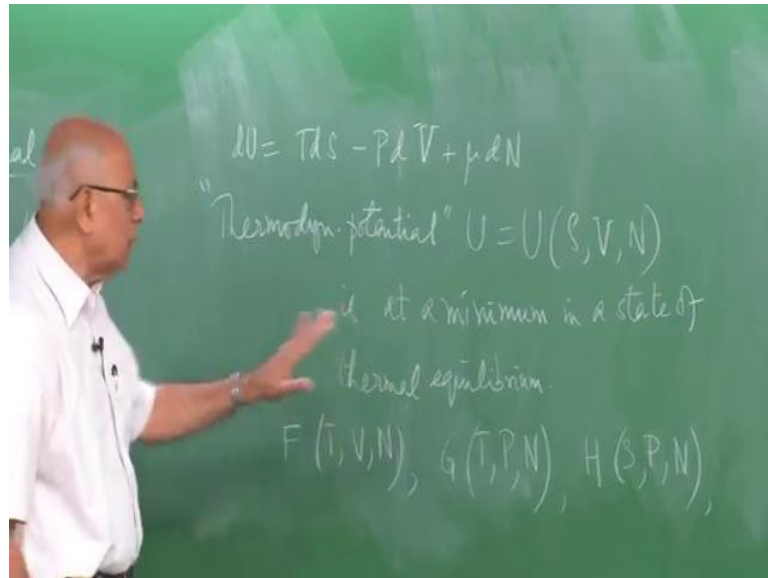
So, remember that we start it with something with said du was T d s minus P d V plus mu d N. So, that is the generalized first and second was together and this corresponded to a thermodynamic potential U, which is the function of S, V and N and at a minimum is at a minimum in a state of thermal equilibrium. So, look at the structure of this, it says this perfect differential is a product of differentials this T times d S, P times d V, mu times d N.

These two T and S thermodynamically conjugate variables, P and V are thermodynamically conjugate variables, mu and N are thermodynamically conjugate variables. So, the question arises, suppose this is choice of variables is not what I want, I do not know have to control the entropy may be at like control the temperature. Can I find the new thermodynamic potential, which is at the minimum in a state of thermal equilibrium at a given value of T, V and N rather than S, V and N?

So, I would like to eliminate as in favor of T, in other words somehow being this around and write it has S d T. Similarly, I may be able to control the pressure rather than the volume. So, I should able to write some other thermodynamic potential in which the

differential of that potential involves not P d V, but V d P or N be the mu for that matter is this possible or not. And the answer is yes, this is the way thermodynamics is one of the beautiful parts of thermodynamics.

There are other such potential, they corresponds to other kinds of free energies. For instance, if you had as independent variables T, V and N, then the potential that is at a minimum for given values of T, V, N is a so called Helmholtz free energy, which is denoted by F. In the same way you have T, P and N, this is denoted by the Gibbs free energy G you could have S, T and N here. So, you retain this, but you consider S P and N, you change this from P d V to V d P, then you have the so called enthalpy denoted by H. And then, you can also have which in this 2 P, So, could have T, P and N; that is done.

So, we did not change this, we change this, we change this here may that also change and then, you could have a system, where and in the internal energy. While, you can also make other changes, you can also write it in terms of N d mu here, but since are not in focusing on change of N, let me not do that for the moment, these are the other commonly used thermodynamic potential, there are a couple more, but these are the most commonly used ones.

So, you can either use U or F or G or S depending on what you can control, what are your variables, which you can vary and keep a constant. We will talk next about how this and this helps as understand different phases of matter, because that is the next and last topic, we do not deal with, namely the change of state for which we need little more information about this.