High Speed Aerodynamics

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Module No. # 01
Lecture No. # 03
Review of Thermodynamics (Contd.)

So, we will discuss second law of thermodynamics today. Of course, since it is not a course on thermodynamics we will not have a full proper discussion on second law; we will just have just brief discussion in the form of recapitulation. Now, second law of thermodynamics is very important physical law. See the first law that, express the conservation of energy or in a change, what type of change the energy will experience, but it does not say whether a particular physical process, is possible or not. It simply says that in a physical process, the energy will be conserved, the heat added to the system, and work done on the system, will increase the energy of the system. But, there is nothing in this law, which clearly say whether a particular physical process is possible or not, and the second law exactly does that, that is second law tells us, whether a particular process will be possible or not. The second law of thermodynamics are expressed in some classical statements, but exactly in those classical forms, they will not be very useful to us. So we will try to get the expressions that are directly useful to us.

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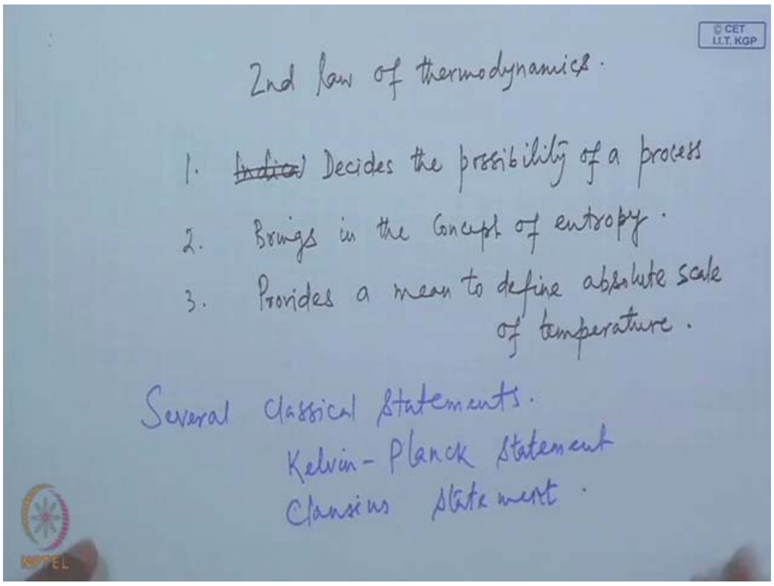

2nd law of thermodynamics.

1. ~~Indicat~~ Decides the possibility of a process
2. Brings in the Concept of entropy.
3. Provides a mean to define absolute scale of temperature.

Several Classical Statements.

Kelvin - Planck Statement

Clausius Statement.

This indicates the possibility of a process, or decides the possibility of a process, and in doing so, it brings in the concept of a new state variable, known as entropy, as the first law brings in the concept of inter line energy. Similarly, the second law brings in the concept of entropy. It also provides a mean to, define absolute scale of temperature, that is that the zeroth law brought in the concept of temperature. However, the actual measure of absolute scale temperature is given by the second law. As we have mentioned that, there are several classical statements of second law, there are several classical statements of second law, and the several classical statements, and the most important of them are Kelvin Planck Statement and Clausius Clapeyron or Clausius Statement. Now, Kelvin Planck statement said, that it is impossible for a heat engine to produce network, working in a complete cycle. If it exchanges heat only with bodies at a single fixed temperature. It is impossible for a heat engine to produce network, in a working in a complete cycle, if it exchanges heat only with bodies at a single fixed temperature; that is what, is the Kelvin Planck statement.

And similarly, the Clausius Clapeyron statement, says that it is impossible to construct a device, which operating in a cycle, will produce no other effect than the transfer of heat from a cooler body to a hotter body. Just repeat the Clausius statement once again, that it is impossible to construct a device, which operates in a cycle, and produces no effect other than the transfer of heat from a cooler to a hotter body. Now, as we said that these classical statements are, not directly useful in our context, and of course these, from these classical statements we can obtain the useful statements or useful form of the law, which are of direct use to us, but that is a subject matter of a full course and thermodynamics, and here we will not go in that approach, rather we will straight away get what it says. Now, let us think about any change and again come back to our indicator diagram.

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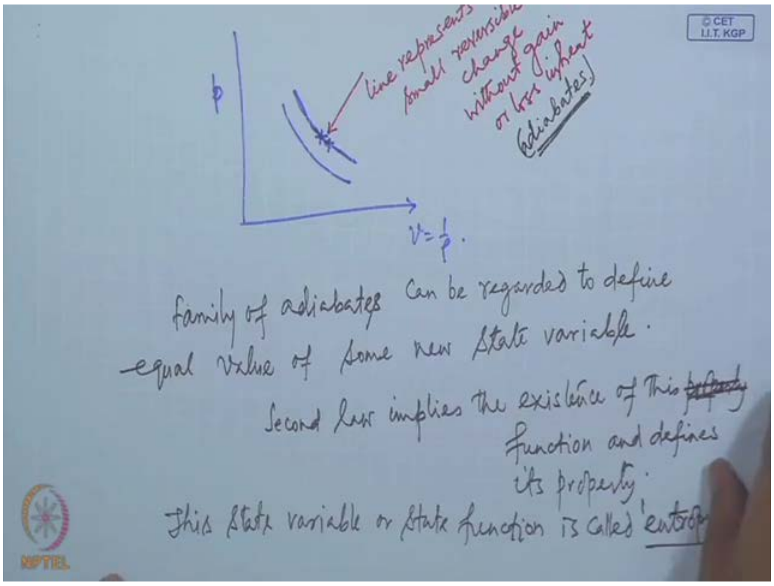

family of adiabates can be regarded to define equal value of some new state variable.

Second law implies the existence of this ~~property~~ function and defines its property.

This state variable or state function is called 'entrop

we know in the indicator diagram, let us say it is that indicator diagram p and v or one by rho. Any point represents a state, and, so if we consider any line that represents a succession of change. Now of course, we can draw lines which define the direction of a small reversible change, and also we can define lines; which gives small reversible change without gain or loss on heat. See let us say that, this as an example, let us think about a line, say this line represents small reversible change, without gain or loss in heat. Let us say this is what is defined from this point. Now of course, it is possible to define such lines from each point, and get a family these lines. So line drawns from each point, will give us a family of such lines and these lines are, of course called adiabates. These lines are called adiabates, because they represent adiabatic reversible change. Now if we define, then say again from this point, goes on like this, and consequently we have, if we define from each point, of course we will have a family of such lines, and so on.

Now on these lines, the changes represents have reversible change, if we think about changes in succession, every time a small change very slow change. Then these lines, can be regarded to define equal value of some new function of state. So these lines can be or this family of adiabates, can be regarded to define, equal value of some new state variable. And the second function, discuss the property of this; the second law, discuss the property of this function. Now, second law implies the existence of this property, second law implies the existence of this property, existence of sorry, existence of this function, and defines its property. This state variable or state function, is called entropy. Entropy is of course, an extensive property, that it depends on the mass, but we can have specific entropy.

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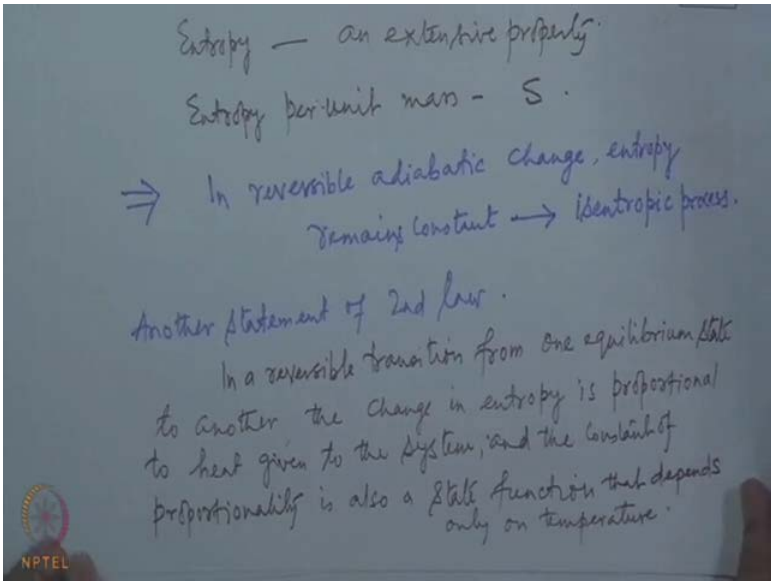

Entropy — an extensive property.

Entropy per unit mass - S.

$\Rightarrow$ In reversible adiabatic change, entropy
remains constant → isentropic process.

Another statement of 2nd law.

In a reversible transition from one equilibrium state
to another the change in entropy is proportional
to heat given to the system, and the constant of
proportionality is also a state function that depends
only on temperature.

The specific entropy, which is intensive property and extensive property. And the intensive property that is specific entropy or entropy per unit mass, we will let us denote it now by S. So, the second law actually tells us that, those families of adiabates, are lines on which this entropy is constant. So the reversible adiabatic, those lines as you have seen that those particular adiabates represents a reversible change. So it says that, in a reversible adiabatic change, entropy remain constant. So it says that in reversible adiabatic change entropy remain constant. Now, any process in which the entropy remains constant, is isentropic process. The process in which there are no heat transfer, and the process are reversible, those process are called isentropic processes. And with the help of this, the second law can be expressed also in this form, that in a reversible transition from one equilibrium state to another equilibrium state, the increase in entropy is proportional to the heat given to the fluid. So another statement or other in a more useful form, so another statement of.

Of course as we mentioned before that this statement of can be obtained from those classical statements, due to Kelvin Planck and Clausius. This says that in a reversible transition, from one equilibrium state to another, that is let us write in a reversible transition from one equilibrium state to another in a reversible transition , from one equilibrium state to another. The change in entropy, is proportional to heat given to the system. And the constant of proportionality is also a state function, that depends only on temperature. What it says that, if there is a reversible transition from one equilibrium state to another, then the change in entropy will be proportional to the heat given to the system, if no heat is given the entropy will not change. And the constant of proportionality is also a state function, and it depends only on temperature. And the reverse, the inverse or reciprocal of this constant of proportionality, is defined as the absolute temperature.

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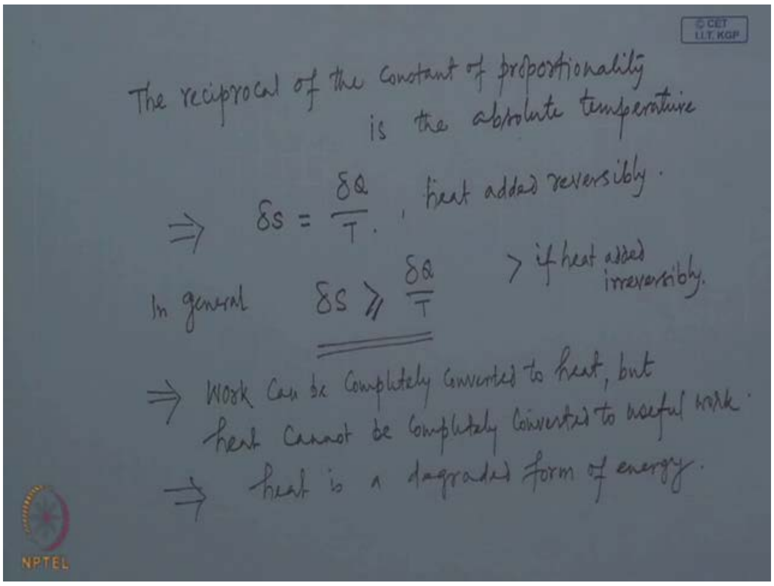

The reciprocal of the constant of proportionality is the absolute temperature

$\Rightarrow \quad \delta s = \frac{\delta Q}{T}.$, heat added reversibly.

In general $\quad \delta s \geqslant \frac{\delta Q}{T}$ $\quad >$ if heat added irreversibly.

$\Rightarrow$ Work can be completely converted to heat, but heat cannot be completely converted to useful work.

$\Rightarrow$ heat is a degraded form of energy.

The reciprocal of the constant of proportionality, is the absolute scale temperature. So we see that it defines the absolute scale temperature also, and mathematically this is written as, that change in entropy delta S is delta Q by T, heat added reversibly. And in general, however the greater than sign implies, irreversibly add equal T is for when heat added reversibly. These are also possible to get from those Kelvin Planck statement or Clausius

Clapeyron statement. Now this also has another significance. It also says that, it also implies that work can be converted completely to heat, but heat cannot be converted completely to work, or heat is a degraded form of energy. That is this also implies, this as an implication, that work can be completely converted to heat, but heat cannot be completely converted to work. Meaning; heat is a degraded form of the energy.

So, you see that the second law gives us various possibilities, that if a process is adiabatic and reversible then there will be no change in entropy, that is adiabatic reversible changes are isentropic change. In any other reversible change, the change in entropy will be proportional to the heat added. In other if the change is irreversible, then the relationship will change to this form, that is delta Q will be less than T times delta S, but for reversible case delta Q will be T times delta S. Now, particularly we interested in that reversible adiabatic or isentropic processes, and a second law consequence of second law that in adiabatic reversible change, entropy will remain constant, will not change. And in adiabatic second law reversible change, the entropy cannot decrease, diminish, the entropy will increase.

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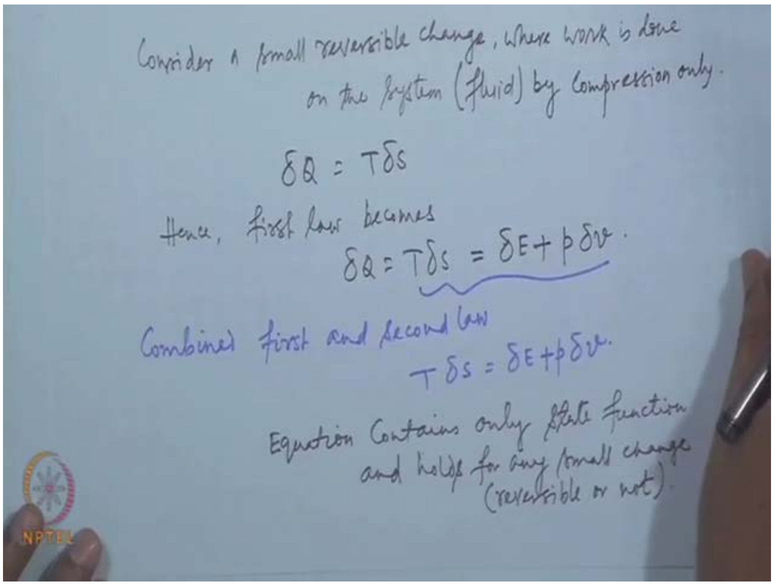

Consider a small reversible change, where work is done on the system (fluid) by compression only.

$$\delta Q = T\delta s$$

Hence, first law becomes

$$\delta Q = T\delta s = \delta E + p\delta v.$$

Combined first and second law

$$T\delta s = \delta E + p\delta v.$$

Equation Contains only state function and holds for any small change (reversible or not).

Now, let us consider a small reversible change, where work is done by compression on the system. The system in our case, will always consider fluid, by compression only. Since you are considering our small reversible change, then delta Q is T delta S. Hence that first law, delta Q is T delta S, that equal to delta E plus p delta v. So this is a combined form of first and second law. So combined form second law. Now, in this equation all the variables are state variables, all the variables are state variables, and hence this relation, must be ready for any infinitesimal transition, in which work is done by compression, whether reversible or not. So all are state function, contents on equation contains only state function, and holds for any small change, reversible or not. The only restriction is, that the work must be compression work. It is not valid for any other type of work done on the system. Now of course, if the process is not irreversible, that is the equation holds, as we mentioned that, even if the change is not reversible. In other way that these equation will holds, even if the change is not reversible, but if the change is not reversible, then this is not the heat and this is not the work.

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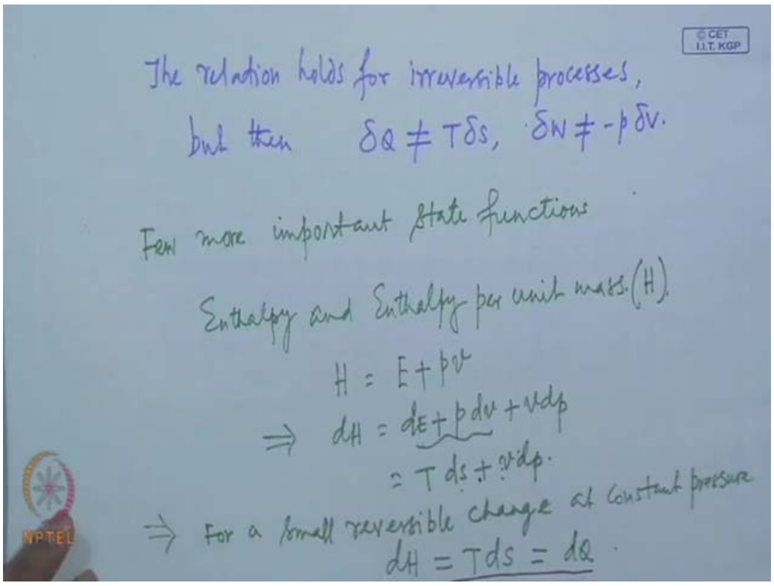

The relation holds for irreversible processes,

but then $\delta Q \neq T\delta s$, $\delta W \neq -p\,\delta v$.

Few more important state functions

Enthalpy and Enthalpy per unit mass. (H)

$$H = E + pv$$

$$\Rightarrow dH = \underbrace{dE + p\,dv} + v\,dp$$

$$= T\,ds + v\,dp.$$

$\Rightarrow$ For a small reversible change at constant pressure

$$\underline{dH = T\,ds = dQ}.$$

That is the relation holds for irreversible process also, but then, and that is these are not true, the heat added is not T delta S. The work done is not minus p delta v, but the total change; that is T delta S is equal to delta E plus p delta v still holds. We will now define few more important state variables or state functions, and one very important state function; let us say few more important state functions, enthalpy. Enthalpy is also again an extensive property. So we have a specific enthalpy, which is the intrinsic property. And enthalpy per unit mass. So this enthalpy per unit mass will denoted by H, since here we are defining all capital letters, let us use letter. So this H is defined as E plus p v, which gives in the differential form d H is d E, plus p d v plus v d p, and we have already seen that d E plus p d v is T d s, so that is. And this imply that, for small reversible change at constant pressure, d H equal to T d s is equal to d Q. ((no audio 37:06 to 37:53)) And, since it is reversible T d s is. And, this imply that the enthalpy, basically represents the total heat content of the system, and also if you look to these equation, this also involves only state variables, and hence apply for both reversible and irreversible changes.

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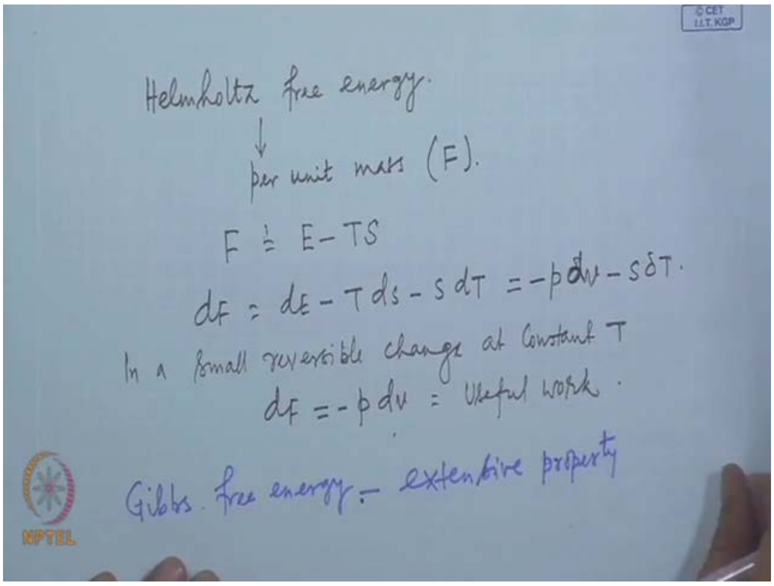

Helmholtz free energy.

$\downarrow$

per unit mass (F).

$F \doteq E - TS$

$dF = dE - T\,ds - s\,dT = -p\,dv - s\,\delta T.$

In a small reversible change at constant T

$dF = -p\,dv$ = Useful work.

Gibbs. free energy - extensive property

One more important state function is Helmholtz free energy, and this per unit mass, we define this by say F, and the definition of this F is E minus T S. So this be d F equal to d E minus, minus d E minus T delta S is p d v minus. So, then in a reversible small change, at constant temperature d F equal to minus p d v or equal to the compression work or useful work. So, in a small reversible change at constant T, we see that if, we have an isothermal small change or isothermal small reversible change, then the gain in free energy is work done by the work done on the system. So work done on the system in a reversible manner at constant temperature, is actually the gain in free energy or Helmholtz free energy of the system, and thus the Helmholtz free energy is related to useful work. The other free energy function is called Gibbs free energy, this is once again an another extensive property. This is also an extensive property like Helmholtz free energy enthalpy or entropy.

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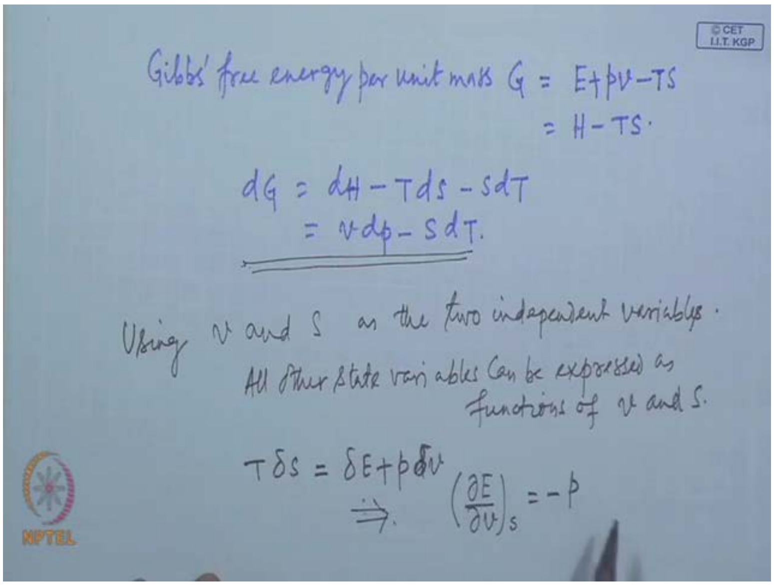

Gibbs' free energy per unit mass $G = E + pv - TS$

$= H - TS.$

$$dG = dH - Tds - sdT$$
$$= vdp - sdT.$$

Using v and S as the two independent variables.

All other state variables can be expressed as functions of v and S.

$$T\delta s = \delta E + p\delta v$$
$$\Rightarrow \left(\frac{\partial E}{\partial v}\right)_s = -p$$

And Gibbs free energy per unit mass, G is defined as E plus p v minus T S, or you can write H minus T S, and hence you can write d G equal to d H minus T d S, minus S d T, and from the definition of enthalpy d H minus T d S becomes v d p minus s d T. And this Gibbs free energy also is, associated with or the available work output. Now with this, now we will try to derive few more important relationships. First of all let us consider that, we will be using say v and S, as the two independent variables. We have already stated that for any pure substance, any two state variables can be considered as independent variables, and all other state variables or state functions can be obtained in terms of those two. Earlier we expressed pressure and specific volume as two such independent variables, and express all other as a function of pressure and volume. But, now let us take v and v and s are the two independent variables, and hence all other can be expressed as functions of v and S. All other state variables can be expressed as functions of v and S, and this already we have. Now, this imply that we have d E d v at constant entropy equal to minus p.

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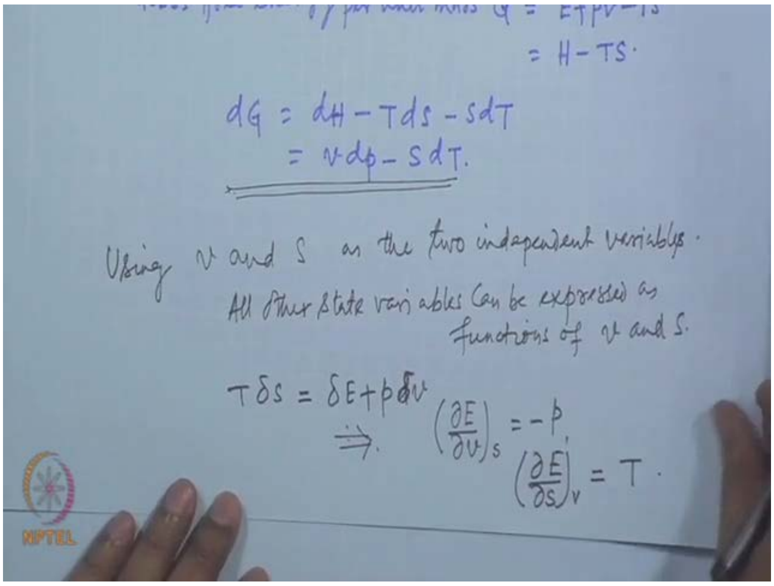

$G = E + pv - Ts$

$= H - TS.$

$dG = dH - Tds - sdT$

$= vdp - sdT.$

Using v and S as the two independent variables. All other state variables can be expressed as functions of v and S.

$T\delta s = \delta E + p\delta v$

$\Rightarrow \left(\frac{\partial E}{\partial v}\right)_s = -p,$

$\left(\frac{\partial E}{\partial s}\right)_v = T.$

And, also d E d S at constant volume equal to T. So we have obtained new definitions of pressure and temperature. Now, we can evaluate the second derivative of.

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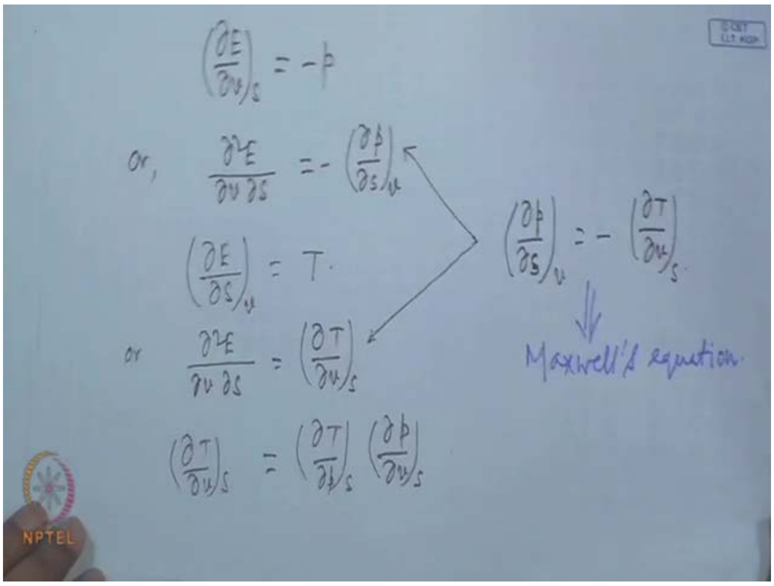

$$\left(\frac{\partial E}{\partial v}\right)_s = -p$$

$$\text{or,} \quad \frac{\partial^2 E}{\partial v \partial s} = -\left(\frac{\partial p}{\partial s}\right)_v$$

$$\left(\frac{\partial E}{\partial s}\right)_v = T.$$

$$\text{or} \quad \frac{\partial^2 E}{\partial v \partial s} = \left(\frac{\partial T}{\partial v}\right)_s$$

$$\left(\frac{\partial p}{\partial s}\right)_v = -\left(\frac{\partial T}{\partial v}\right)_s.$$

$$\Downarrow$$

Maxwell's equation.

$$\left(\frac{\partial T}{\partial v}\right)_s = \left(\frac{\partial T}{\partial p}\right)_s \left(\frac{\partial p}{\partial v}\right)_s$$

We can differentiate the first relation; that is d E d v at constant entropy as minus p, so we differentiate it again with entropy now, so this makes. Similarly, we have d E d S at constant volume is T. Now, we differentiate this again with v at constant entropy, and that gives us, and combining these this gives us d p d S v as minus d T d v S. This is one of the Maxwell’s law. Now, also from here this d T d v S, can be written as d T d p at constant entropy, into d p d v at constant entropy.

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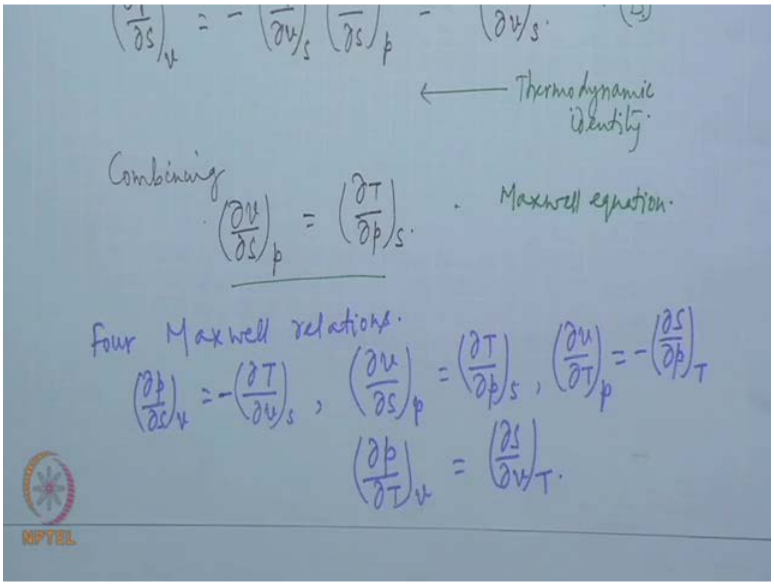

Thermodynamic identity.

Combining

$$\left(\frac{\partial v}{\partial s}\right)_p = \left(\frac{\partial T}{\partial p}\right)_s . \quad \text{Maxwell equation.}$$

four Maxwell relations.

$$\left(\frac{\partial p}{\partial s}\right)_v = -\left(\frac{\partial T}{\partial v}\right)_s , \quad \left(\frac{\partial v}{\partial s}\right)_p = \left(\frac{\partial T}{\partial p}\right)_s , \quad \left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T .$$

Similarly, we have d p d S at constant volume is minus d p d v S, into d v d S p, and that is becomes minus d T d v S. This is a thermodynamic identity. Now you can mark this first equation as A, and this as B, and combining we get d v d S at pressure is d T d p at S. This is also another Maxwell law. This relation can also be obtained in an another manner, that is we could have defined second derivative of H in two different manner, as we have done here for second derivative of E in two different manner. Similarly, we can define second derivative of H in two different manners. Second derivative of F and G also into two different manners, and get total four relations, and all these four relations are called the Maxwell’s relations. So we have four Maxwell’s relations or four Maxwell equations. We have d p d S at constant volume is minus d t d v at constant entropy.

We have d v d S at constant pressure into d T d p at constant entropy, d v d T at constant pressure, will do minus d S d p at constant temperature. And the last one d p d T at constant volume is. These four relations are known as Maxwell’s relations, and they are quiet useful in many thermo dynamical relationship, and at least in one or two cases we will use them. So what we have done today, first we have discussed about second law, and the concept of entropy, and the absolute scale of temperature, and based on that we have subsequently defined, few more important thermo dynamical state functions, enthalpy Gibbs free energy, and Helmholtz free energy, and final we have obtained the Maxwell’s equations. So further useful relations that are often used in high speed aerodynamics we will derive subsequently in our next class.