Basic Thermodynamics

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Lecture – 14

Thermodynamic Property Relations-II

Good morning. I welcome you to this session. In the last class, we started the discussion on important thermodynamic property relations. We will do that in this class, continue that. Just we started the discussion.

Today, what we will do, before continuing that, these thermodynamic property relations, just we will recapitulate two important mathematical theorems, very simple, which we know just as information, we have to recapitulate. These theorems are like that.

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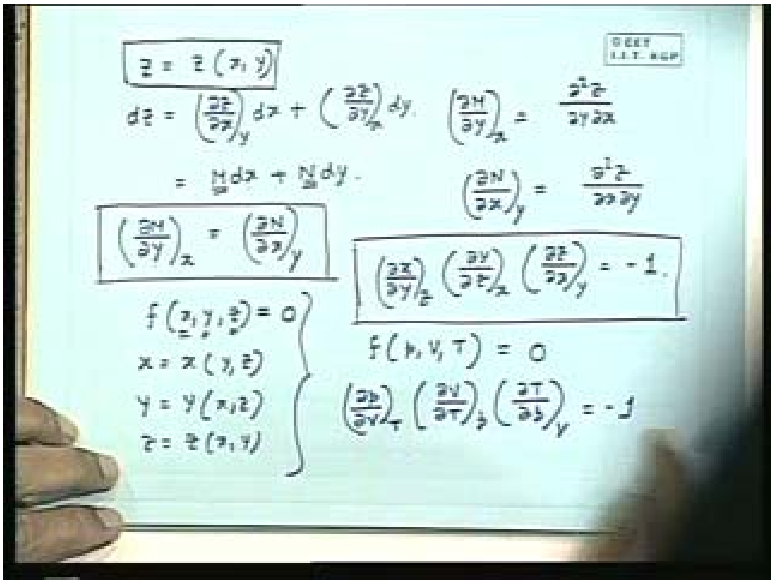

$$\boxed{z = z(x, y)}$$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$= \underline{M}dx + \underline{N}dy$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial y \partial x}$$

$$\left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial x \partial y}$$

$$\boxed{\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y}$$

$$\left.\begin{array}{l} f(\underline{x}, \underline{y}, \underline{z}) = 0 \\ x = x(y, z) \\ y = y(x, z) \\ z = z(x, y) \end{array}\right\}$$

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1}$$

$$f(p, v, T) = 0$$

$$\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_v = -1$$

Let us see that if z is expressed as a function of two independent variables x, y. It is a very simple mathematical theorem. z is expressed as two independent variables x and y. Then the total differential of z, dz can be written like this; Del z divided by del x at constant y dx plus del z divided by del y at constant x dy. Now, if this coefficient I write as M and del z divided by del y at x N dy, then it can be written that del N divided by del y; that means, the differentiation of this coefficient with respect to y at constant x is equal to del N divided by del x at constant y.

It is very simple, because M is nothing but this one; del z divided by del x at y that means, other way, we can see that if we differentiate this with respective y at constant x, what will happen? Del M divided by del y at constant x means the differentiation of this with respective y. That means del square z at constant x, that means this restriction will go. That means del y divided by del x. Very simple mathematical theorem.

Similarly, if we write for del N divided by del x at y, that is differentiate this expression with x at constant y. This constant x restriction will go. This becomes equal to del square z divided by del x del z. We know that if z is a continuous function of x and y then these two double differentials are equal, even if the order is different; that is del square z divided by del y del x is del square z divided by del x del y. In any order, the second order differentiations are taken. They are equal, provided z is a continuous function of xy. Therefore, this is one of the very important relationships in mathematics which is used in deriving some important thermodynamic property relations.

If dz is expressed as M dx plus N dy, where M stands for the differentiation of z with respect to x at constant y and N stands for differentiation of this variable with respect to y at constant x. Then the differentiation of this with respect to y at constant x has to be differentiation of this coefficient with respect to x at constant y. Another important mathematical theorem is there. It will be very much useful in deriving different thermodynamic property relations.

Three variables x, y, z can be expressed as a functional relationship like this; x, y, z, the three variables are dependent on each other. It can be expressed by a functional relationship of that so that any of these variables, for example, x can expressed as the function of other. Similarly, y can be expressed as a function of other two and z as a function of other two. Each one of these is related to the other two. If these three variables are related by a functional relationship so that one can be expressed as a function of the other two then there occurs a relationship like that, is cyclic. This is known as cyclic relationship.

If we differentiate x with respect to y at constant z then del y divided by del z del at constant x and del z divided by del x with these at constant y. They equal to minus 1. Let us prove this theorem is beyond the scope of this course. So I am not going to prove it because this is not a mathematics class, you have done it in mathematics class. But this information will be required.

So, similarly, just an immediate consequence of this in thermodynamic property relations, first I will tell that if x, y, z is replaced by p, V, T. We know, these three, pressure, volume and temperature are the basic measurable and sensible properties of a system. Pressure and temperature are sense process and they are directly measurable properties. Sometimes, we call these three are the primary properties or fundamental properties of a system. They are related by a functional relationship for any system which is known as equation of state. We will see afterwards that the relationship between pressure, volume and temperature for a given mass of a system that means for a close system is known as the equation of state of that system.

Therefore, an immediate application of this mathematical theorem tells us that del p divided by del V at constant T into del V divided by del T at constant p into del T divided by del p at constant V is minus1 which is again a very important relationship because this is derived using this mathematical theorem for our thermodynamic property relation. Sometimes, this is known as cyclic relations; del p divided by del V, del V divided by del T and del T divided by del p. So, this is one of the very important thermodynamic relations.

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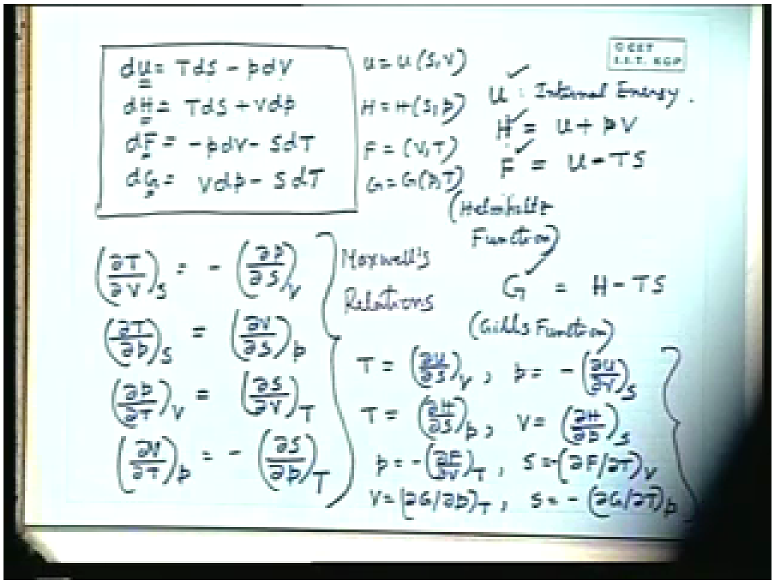

$$du = Tds - pdV$$
$$dH = Tds + Vdp$$
$$dF = -pdV - SdT$$
$$dG = Vdp - SdT$$

$u = u(s,V)$

$H = H(s,p)$

$F = (V,T)$

$G = G(p,T)$

u : Internal Energy.

$H = u + pV$

$F = u - TS$

(Helmholtz Function)

$G = H - TS$

(Gibbs Function)

$$\left.\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_s &= -\left(\frac{\partial p}{\partial s}\right)_V \\ \left(\frac{\partial T}{\partial p}\right)_s &= \left(\frac{\partial V}{\partial s}\right)_p \\ \left(\frac{\partial p}{\partial T}\right)_V &= \left(\frac{\partial s}{\partial V}\right)_T \\ \left(\frac{\partial V}{\partial T}\right)_p &= -\left(\frac{\partial s}{\partial p}\right)_T \end{aligned}\right\} \text{Maxwell's Relations}$$

$$\left\{\begin{aligned} &T = \left(\frac{\partial u}{\partial s}\right)_V, \quad p = -\left(\frac{\partial u}{\partial V}\right)_s \\ &T = \left(\frac{\partial H}{\partial s}\right)_p, \quad V = \left(\frac{\partial H}{\partial p}\right)_s \\ &p = -\left(\frac{\partial F}{\partial V}\right)_T, \quad s = -(\partial F/\partial T)_V \\ &V = (\partial G/\partial p)_T, \quad s = -(\partial G/\partial T)_p \end{aligned}\right\}$$

Now, I come to the property relations which we started in the last class. We started with four very important extensive properties. One is the u that is the internal energy is basically the intermolecular energy which neglects the kinetic energy, internal energy. Another is the H that is enthalpy which equals to u plus pV. Another is the F. F is the Helmholtz function, Helmholtz energy, or sometimes it is known as Helmholtz function.

Helmholtz function or Helmholtz energy sometimes the concept energy comes, because the units are all energy. That way enthalpy is also an energy unit, but this is not exactly an energy quantity. That we must know. So, far we have learnt this thing, because the difference of enthalpy gives the energy quantity, heat and work interactions in an open system. So, enthalpy is very similar to the energy whose dimension is energy but is not exactly the energy.

Similar way, Helmholtz function is like this. That is why, sometimes it is known Helmholtz energy whose definition is u minus Ts. This is a system property. All these u, T, s are that of the system. Because earlier, we have seen that the availability function for a close system is u plus p_0V minus T_0s. So they are $p_{0,}$ T_0 at the surrounding properties, where F is u minus Ts. Similarly, G which is defined as Gibbs energy or Gibbs function;

this is defined as H minus Ts. This H, T, s are all of system; that means, they are all system properties.

u, H, F, G is four very basic properties of a system, where u is the internal energy which comes from the first law. H is by definition u plus p V. F, G come from the, actually this concept of physical implications or concept of significance of F and G. I told that this signifies the maximum amount of work that we can extract from a closed system when it interacts with the surrounding at an isothermal process and the temperature of system and surrounding remaining the same.

Similarly, when an open system interacts with the surrounding and isothermal process where the temperature of these surrounding and the system remains same, then the difference of Gibbs energy gives the maximum work done.

Similarly, the difference of Helmholtz function gives the maximum work done in closed system, as far as the physical explanation or physical significance of Helmholtz function and Gibbs function are concerned. But at this present moment, it will be sufficient to know, how these Helmholtz function and Gibbs function are defined.

Afterwards also, when we will start the reactive thermodynamics or thermodynamics of reactive systems, we will study this in this course. Then we will be able to find out the physical significance of Gibbs function in more detail. At the present moment, if we just recognize the definition of these four functions, now I can write the differential form or a differential expression of this. du is T ds minus p dV. This relationship we know T ds is du plus p dV is a property relations which have been found from the first law of thermodynamics.

Similarly, dH exploiting this, the du plus p dV plus V dp and du plus p dV is T ds. So, dH becomes T ds plus V dp. Next one, dF is equal to, now here if I use this definition dF is du minus T ds minus s dT. So, du minus T ds from here is minus p dV. Therefore, dF becomes minus p dV minus s dT.

Similarly for dG, by differentiating G is equal to H minus Ts equation both sides, dG is dH minus T ds. So, dH minus T ds is V dp. So dG becomes V dp minus s dT. From the definitions of these functions, I can write four expressions in terms of the differentials of all these properties u, H, F, G.

u, H, F, G are the point functions and they are expressed in terms of differentials of other point functions ds, dV. In this case, we can exploit this theorem. This means that u as a function of s V. This equation tells that u as a function of s V. H as a function of s p. F as a function of V T. If I start with u as a function of s V; then in that case, T is nothing but del u divided by del s at constant V into ds. Then minus V is del u divided by del V at constant s into dV. Similarly, if I could have expressed H as a function of s p, we could have written this expression.

Similarly F as function of V T, and G as a function of p T; This expression shows that these point functions are expressed in terms of the differentials of the other two point functions as independent variable.

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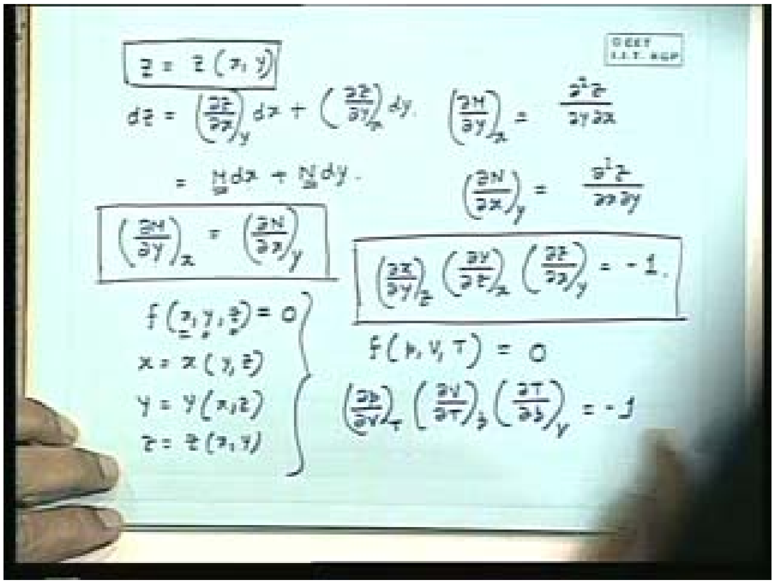

$$\boxed{z = z(x, y)}$$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \qquad \left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial y\,\partial x}$$

$$= M\,dx + N\,dy \qquad \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial x\,\partial y}$$

$$\boxed{\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y}$$

$$\left.\begin{aligned} f(x, y, z) &= 0 \\ x &= x(y, z) \\ y &= y(x, z) \\ z &= z(x, y) \end{aligned}\right\}$$

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1.}$$

$$f(p, V, T) = 0$$

$$\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V = -1$$

We can now just have a recapitulation that as z is a function of x, y and if it is written dz this M dx plus N dy, where M and N are these two coefficients. Then one can write, del M divided by del y at constant x is del N divided by del x at constant y.

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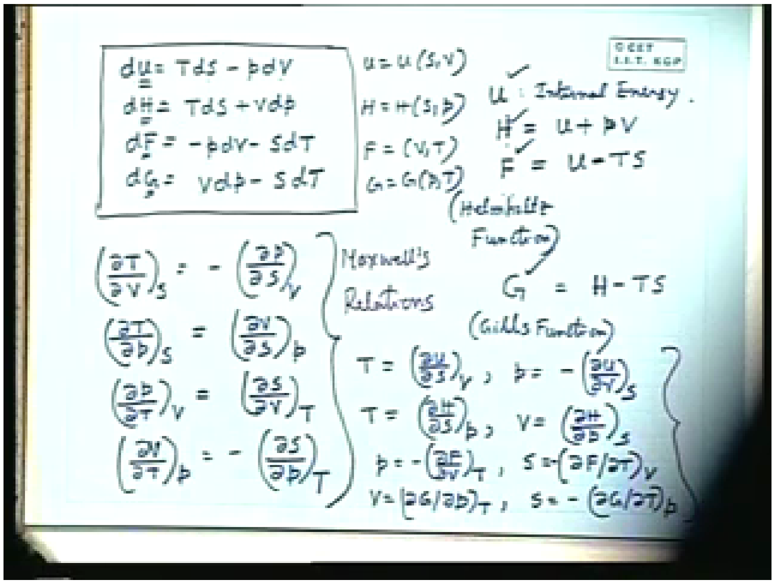

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u : Internal Energy.

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(Helmholtz Function)

$G = H - TS$

(Gibbs Function)

$\left(\frac{\partial T}{\partial V}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_V$

$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial V}{\partial s}\right)_p$

$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial s}{\partial V}\right)_T$

$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T$

Maxwell's Relations

$T = \left(\frac{\partial u}{\partial s}\right)_V, \quad p = -\left(\frac{\partial u}{\partial V}\right)_s$

$T = \left(\frac{\partial H}{\partial s}\right)_p, \quad V = \left(\frac{\partial H}{\partial p}\right)_s$

$p = -\left(\frac{\partial F}{\partial V}\right)_T, \quad s = -(\partial F/\partial T)_V$

$V = (\partial G/\partial p)_T, \quad s = -(\partial G/\partial T)_p$

So, exploiting that functional relationship from each of this equation, now we start with the first equation that del T divided by del V at constant s is equal to minus del p divided by del s at constant V. Now, here also, we see that del T, del p. Here also, from the second equation del T divided by del p at constant s is equal to del V divided by del s at constant p. From this equation, we get, del T divided by del p at constant s is del V divided by del s at constant p.

From the third equation, in this equation both are negative. So, we can write with positive things only; del p divided by del T at constant V is equal to del s divided by del V at constant T.

From the last equation, we can write, del V divided by del T at constant p is minus del s divided by del p at constant T. These four equations are very useful thermodynamic relations and they are known as Maxwell's relations or equations.

At the same time, we can write other few important relations. By recognizing that when I write this u as a function of s V then T is equal to del u divided by del s at constant V. Similarly, p is minus del u divided by del V at constant s. Then only, we can write the T ds minus p dV means T is del u divided by del s at constant V and del u divide by del V at constant s. Similar way, T is a function of s and p. So, this is del H divided by del s at constant p. Similarly, V is del H divided by del p at constant s. From here also, I can write, p is minus del F divided by del V at constant T and s is minus del F divided by del T at constant V. So, in the similar way, we can write, V is equal to del G divided by del p at constant T. Similarly, s is equal to minus del G divided by del T at constant p. Also from these equations, we can construct these relationships also.

So, in deriving certain important thermodynamic relations, some of the expression will be required. So, we can write all those equations from these four basics. If we can express these four equations in this form, these three, four basic functions then we derive these equations. These four sets of equations are known as Maxwell's equations.

This is the basic definition from which we wrote this, because this is del u divided by del s at constant V. This is del u divided by del V at constant S so that del T divided by del V at constant s is del p divided by del s at constant V.

[Conversation between Student and Professor minus Not audible ((00:17:36 min))]

Okay please third one, this one

[Conversation between Student and Professor minus Not audible ((00:17:36 min))]

Yes place where is the minus p is equal to this thing.

[Conversation between Student and Professor minus Not audible ((00:17:43 min))]

Oh! say yes, yes, yes, one this will be a minus.

Very good, there will be a minus, very good, and then it is all right?

Now, we will derive few other important equations in thermodynamics which are known as T minus ds equations.

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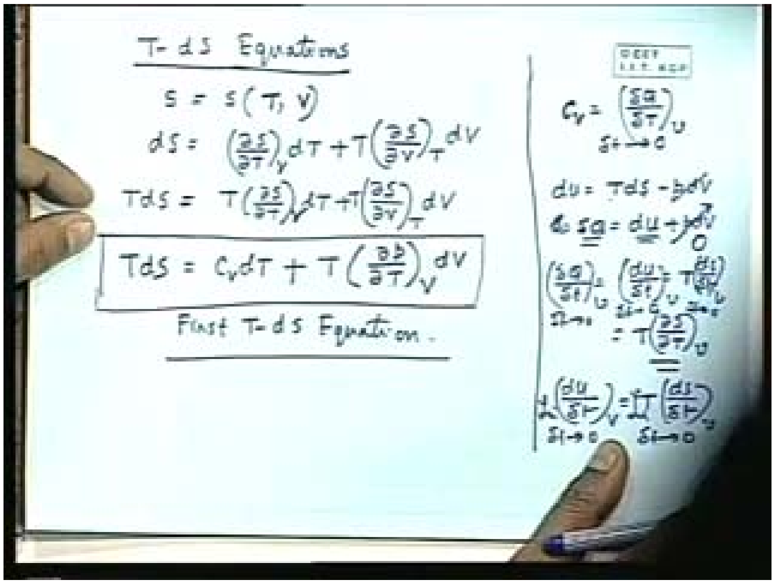

T- ds Equations

$$s = s(T, V)$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_V dT + T\left(\frac{\partial s}{\partial V}\right)_T dV$$

$$Tds = T\left(\frac{\partial s}{\partial T}\right)_V dT + T\left(\frac{\partial s}{\partial V}\right)_T dV$$

$$\boxed{Tds = c_v dT + T\left(\frac{\partial p}{\partial T}\right)_V dV}$$

First T-ds Equation.

$$c_v = \lim_{\delta t \to 0}\left(\frac{\delta q}{\delta T}\right)_v$$

$$du = Tds - pdv$$

$$\delta q = du + \cancel{pdv}^{\,0}$$

$$\lim_{\delta t \to 0}\left(\frac{\delta q}{\delta t}\right)_v = \lim_{\delta t \to 0}\left(\frac{du}{\delta t}\right)_v = T\left(\frac{ds}{\delta t}\right)_v = T\left(\frac{\partial s}{\partial T}\right)_v$$

$$\lim_{\delta t \to 0}\left(\frac{du}{\delta t}\right)_v = \lim_{\delta t \to 0} T\left(\frac{ds}{\delta t}\right)_v$$

These are very important equations, we must know. So, there is nothing much of thermodynamics in concept which we discussed earlier; the first law and second law and their corollaries. These are more towards primary label algebra rather than thermodynamic concepts. But we have to do, because we have to know the important property relations in thermodynamic.

The other most important property relations in thermodynamics are known as T minus ds equations. If I express now, first T minus ds equation, now let us express s as a function of T and V for a single face substance, s as a function of T and V then we can write ds is del s divided by del T at constant volume into dT plus del s divided by del V at constant T into dV. If I multiply both the sides by T then I get T into del s divided by del T at constant V into dT plus del s divided by del V at constant T into dV. I can write the first term as c_vdT, T into del s divided by del T as c_v.

[Conversation between Student and Professor minus Not audible ((00:19:54 min))]

V how? Yes, the question comes how definitely. So we cannot appreciate this.

Now $c_{v,}$ what is c_v? c_v is some delta Q divided by delta T at constant volume, when delta T tends to 0 per unit mass. Because it is a heat capacity or if it be becomes per unit mass delta Q divided by m, then it will be this specific heat.

Let us consider heat capacity, because we are considering about the whole system, not for unit mass. All are extensive properties. Now we know that this expression at del Q is T ds. Now T ds plus p dV now at constant, du is T ds minus p dV and we know that delta Q is du plus p dV. Now, when we heat it reversibly with only work, because in defining specific heat there will not be any work except p dV. But at constant volume p dV work will be 0. So, del Q is du, du is Tds.

So, del Q divided by del T will be du divided by by del T is equal to T into ds divided by del T and that is at constant volume. It becomes T; this can be expressed at del s divided by del T at constant volume. So, T into del s divided del T at constant volume gives the value of specific a heat capacity at constant volume, because small amount of heat del Q is a change in the du internal energy. So, del Q divided by del T is du divided by delta T, delta T tends to 0 at constant volume. This expression at constant volume when delta T tends to 0 becomes del s divided by del T. Here, delta T tends to 0. So, that is T into del s divided by del T. T is always there, So T into del s divided by del T. Clear or any doubt? Clear? du divided by delta T, limit delta T tends to 0 at constant volume is T into ds divided by delta T, limit delta T tends to 0 at constant volume. This becomes T into del s divided by del T plus. Now, what is del s divided by del V at constant T?

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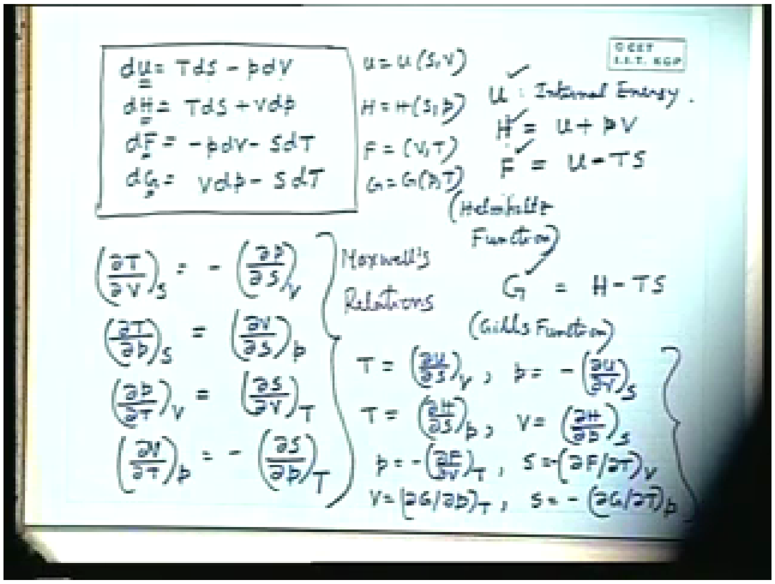

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$H = H(S,p)$

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U : Internal Energy.

$H = U + pV$

$F = U - TS$ (Helmholtz Function)

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Maxwell's Relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$$

$$T = \left(\frac{\partial u}{\partial S}\right)_V, \quad p = -\left(\frac{\partial u}{\partial V}\right)_S$$

$$T = \left(\frac{\partial H}{\partial S}\right)_p, \quad V = \left(\frac{\partial H}{\partial p}\right)_S$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T, \quad S = -(\partial F/\partial T)_V$$

$$V = (\partial G/\partial p)_T, \quad S = -(\partial G/\partial T)_p$$

Now, del s divided by del V at T is del V divided by del T at V; del s divided by del V at T is del V divided by del T at V, that is from Maxwell's equation.

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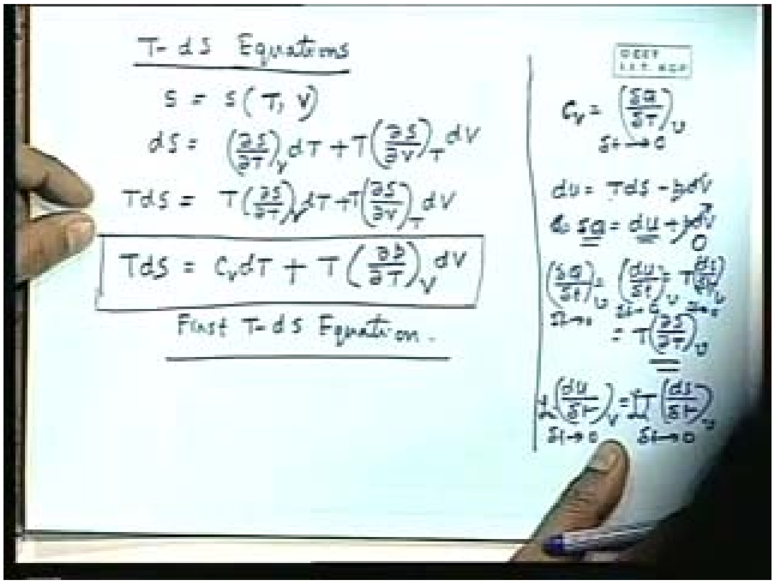

T- ds Equations

$s = s(T, V)$

$$ds = \left(\frac{\partial s}{\partial T}\right)_V dT + T\left(\frac{\partial s}{\partial V}\right)_T dV$$

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$$\boxed{Tds = C_v dT + T\left(\frac{\partial p}{\partial T}\right)_V dV}$$

First T-ds Equation.

$$C_v = \left(\frac{\delta Q}{\delta T}\right)_v \quad \delta T \to 0$$

$du = Tds - pdV$

$\delta Q = du + \cancel{pdV}^{0}$

$$\left(\frac{\delta Q}{\delta T}\right)_v = \left(\frac{du}{\delta T}\right)_v = T\left(\frac{ds}{\delta T}\right)_v = T\left(\frac{\partial s}{\partial T}\right)_v$$

$$\lim_{\delta T \to 0}\left(\frac{du}{\delta T}\right)_v = \lim_{\delta T \to 0} T\left(\frac{ds}{\delta T}\right)_v$$

Sorry one T will be there, you are correct, plus T into del p divided by del T at V. Any problem? You ask me. It is mathematics only that is nothing dV. Very good that is nothing to be exited and may be some silly mistake or you can just detect me. This is the expression known as first T minus ds equation. c_v dT in terms of T and V plus T into del p divided by del T at constant V into dV. Now, next we will derive the second T minus ds equation. This is first T minus ds equation.

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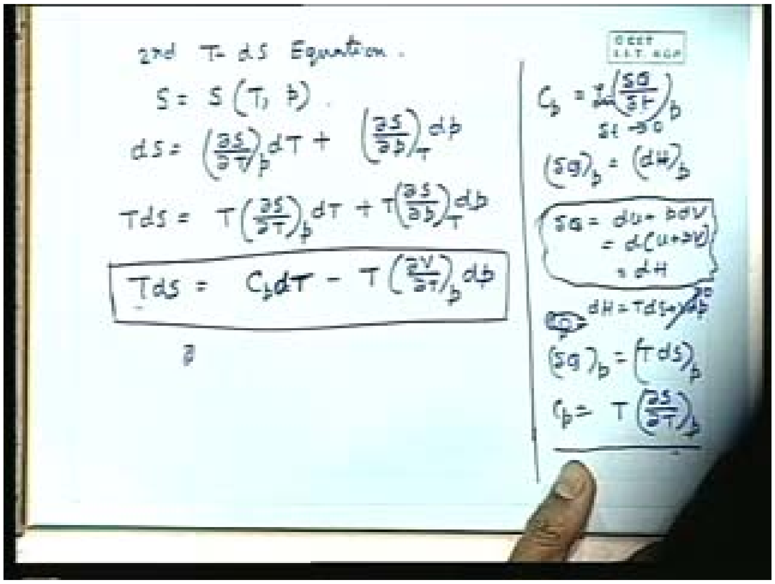

2nd T- ds Equation.

$s = s(T, p)$

$$ds = \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T dp$$

$$Tds = T\left(\frac{\partial s}{\partial T}\right)_p dT + T\left(\frac{\partial s}{\partial p}\right)_T dp$$

$$\boxed{Tds = c_p dT - T\left(\frac{\partial v}{\partial T}\right)_p dp}$$

$$c_p = \lim_{\delta t \to 0}\left(\frac{\delta q}{\delta t}\right)_p$$

$$(\delta q)_p = (dH)_p$$

$$\boxed{\begin{aligned}\delta q &= du + pdV \\ &= d(u + pV) \\ &= dH\end{aligned}}$$

$$dH = Tds + \overset{0}{\cancel{Vdp}}$$

$$(\delta q)_p = (Tds)_p$$

$$c_p = T\left(\frac{\partial s}{\partial T}\right)_p$$

Now, second T minus ds equation is T minus ds is expressed in terms of T and p; that means, we start with s as a function of T and p, temperature and pressure. So, we can write ds change in del s divided by del T at constant p into dT plus del s divided by del p at constant T $_{i0}$ dp.

So, if we multiply with Tds is T into del s divided by del T at constant p into dT plus T into del s divided by del p at constant T into dp. Again, I can write this as c_pdT. Let me again check, how I can write this c_pdT.

We know the definition of c_p is delta Q divided by delta T at constant pressure when delta T tends to 0. At constant pressure, delta Q is nothing but delta H; rather, I should write dH at constant pressure. That we have already know, because H by 1, the definition of H and del Q. We know that at constant pressure, heat addition is the change in the enthalpy, because delta Q is du plus p dV and d into u plus pV. Here, we have to remember that whenever we define this specific heat is a property of a system. How to define? It is very important.

Here is the concept. These are very simple. I am telling you through out your life you will see. Mathematics is just a tool, just to follow it a little bit of merit will do but what is tough is the physic that is the concept, the concept is clear everything is clear.

What is specific heat? Sometimes, by the basic definition, we are not clear. When we define the specific heat of a substance, we consider a closed system comprising that substance. Then add heat in such a way that there is no work transfer except a reversible work, because of the system boundary displacement. We add heat reversibly to infinite small temperature difference slowly, and allowing for no work transfer between the system and the surrounding, except the reversible displacement work. What is reversible displacement? P dV work.

So, when we heat is at a constant volume p dV, work automatically becomes 0. So, absolutely there is no work transfer. So, always we write the first law as del Q is du plus p dV. Because whenever I write the first law, del Q is du plus pdV. Probably in the examination, in the class test, there are so many expressions when we are told under what conditions they are right.

So, del Q is du plus dW is the general statement of first law, but del Q is du plus p dV. Whenever I write these as first law that means always we are assuming that closed system as work interactions, only through reversible displacement work that means pdV work.

When we define the specific heat at constant pressure, we allow the p dV work to maintain the pressure constant not by anything else. We cannot have any other work transfer to maintain the constant pressure. That is not the definition of the specific heat at constant pressure. Now, the pressure will be held constant by allowing only the reversible displacement work. So, p dV and when the pressure remains constant, this becomes this, this becomes dH. So, this is again and again recapitulation. If we recapitulate earlier things then our concept will be more or less clear.

Now, if we define this, with this if we write the expressions c_p then it will be simply coming as del H divided by del p. So, dH again we can write dH is Tds. Now, a property relation V dp, because at constant pressure dp is 0, so that dH, I can write ds. So, del Q at constant p is nothing but T ds at constant pressure. By this definition, del Q divided by del T at constant pressure T. We can write in terms of the differentiation; del s divided by del T at constant pressure.

No Book will derive this when they discuss the Tds equations. I am telling because they know that we should know these things from the very basic definition so that it may be little confusing that how they are substituting this, but I am doing it. Now be clear that T into del s divided by del T at constant p is c_p.

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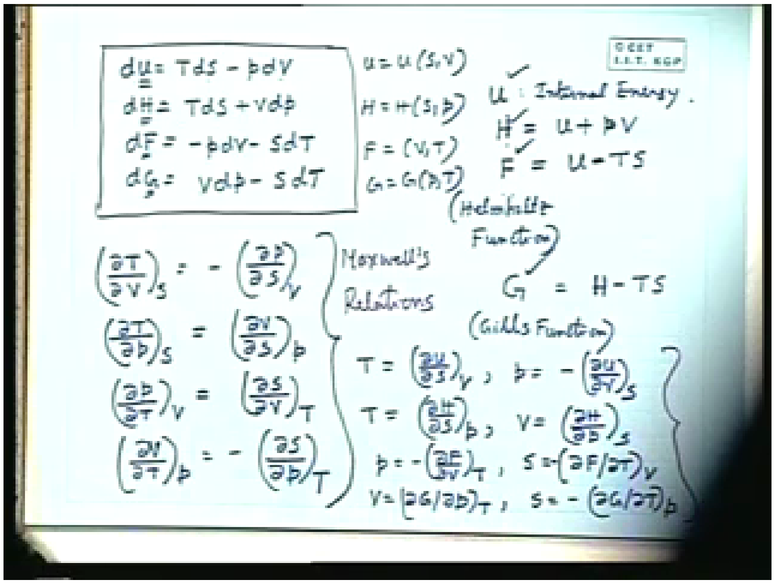

$du = Tds - pdV$ $\quad u = u(s,V)$

$dH = Tds + Vdp$ $\quad H = H(s,p)$

$dF = -pdV - sdT$ $\quad F = (V,T)$

$dG = Vdp - sdT$ $\quad G = G(p,T)$

U : Internal Energy.

$H = U + pV$

$F = U - TS$

(Helmholtz Function)

$G = H - TS$

(Gibbs Function)

Maxwell's Relations

$$\left(\frac{\partial T}{\partial V}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_V$$

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial V}{\partial s}\right)_p$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial s}{\partial V}\right)_T$$

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T$$

$$T = \left(\frac{\partial u}{\partial s}\right)_V, \quad p = -\left(\frac{\partial u}{\partial V}\right)_s$$

$$T = \left(\frac{\partial H}{\partial s}\right)_p, \quad V = \left(\frac{\partial H}{\partial p}\right)_s$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T, \quad s = -(\partial F/\partial T)_V$$

$$V = (\partial G/\partial p)_T, \quad s = -(\partial G/\partial T)_p$$

Again, the similar way this expression should be here. These expressions, del s divided by del p at constant T is minus del V divided by del T at constant p.

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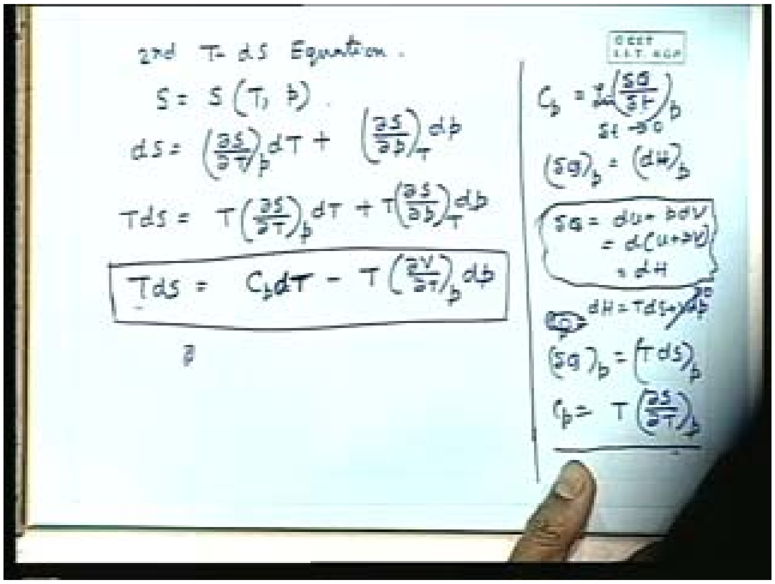

2nd T-ds Equation.

$$s = s(T, p)$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T dp$$

$$Tds = T\left(\frac{\partial s}{\partial T}\right)_p dT + T\left(\frac{\partial s}{\partial p}\right)_T dp$$

$$\boxed{Tds = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_p dp}$$

$$C_p = \lim_{\delta t \to 0}\left(\frac{\delta Q}{\delta t}\right)_p$$

$$(\delta Q)_p = (dH)_p$$

$$\boxed{\begin{aligned}\delta Q &= du + pdV\\ &= d(u+pV)\\ &= dH\end{aligned}}$$

$$dH = Tds + V\cancel{dp}^{\,0}$$

$$(\delta Q)_p = (Tds)_p$$

$$C_p = T\left(\frac{\partial s}{\partial T}\right)_p$$

So, I can write minus T del V divided by del T at constant p into dp and this is known as the second Tminusds equation. Now, from these two T minus ds equations, I will derive a very important relationship. Now, let us write the first T minus ds equation and second T minus ds equation side by side.

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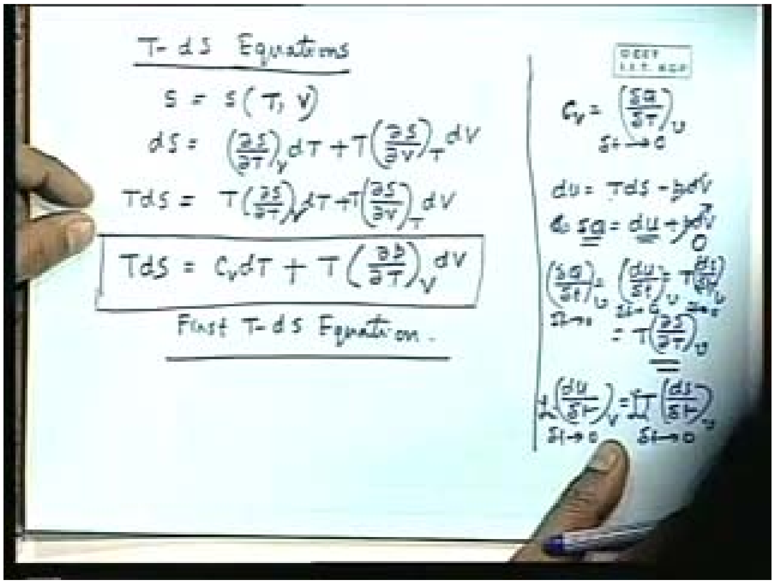

T-ds Equations

$$s = s(T, V)$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_V dT + T\left(\frac{\partial s}{\partial V}\right)_T dV$$

$$Tds = T\left(\frac{\partial s}{\partial T}\right)_V dT + T\left(\frac{\partial s}{\partial V}\right)_T dV$$

$$\boxed{Tds = C_v dT + T\left(\frac{\partial p}{\partial T}\right)_V dV}$$

First T-ds Equation.

$$C_v = \lim_{\delta t \to 0}\left(\frac{\delta Q}{\delta T}\right)_v$$

$$du = Tds - pdV$$

$$\delta Q = du + p\,\overset{0}{dV}$$

$$\lim_{\delta t \to 0}\left(\frac{\delta Q}{\delta t}\right)_v = \lim_{\delta t \to 0}\left(\frac{du}{\delta t}\right)_v = T\left(\frac{ds}{\delta t}\right)_v = T\left(\frac{\partial s}{\partial T}\right)_v$$

$$\lim_{\delta t \to 0}\left(\frac{du}{\delta t}\right)_v = \lim_{\delta t \to 0} T\left(\frac{ds}{\delta t}\right)_v$$

This is the first T minus ds equation T ds is c_v dT plus T into del p divided by del T at constant V into dV.

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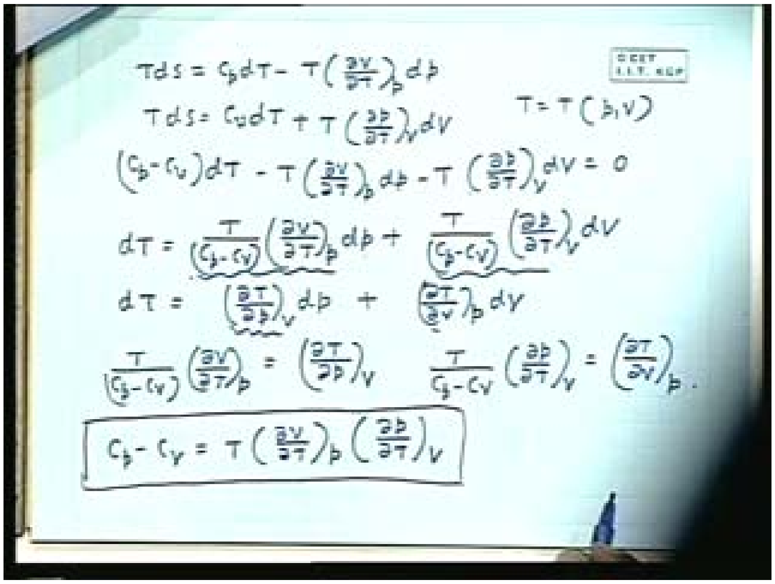

$$T ds = c_p dT - T\left(\frac{\partial v}{\partial T}\right)_p dp$$

$$T ds = c_v dT + T\left(\frac{\partial p}{\partial T}\right)_v dv \qquad T = T(p, v)$$

$$(c_p - c_v) dT - T\left(\frac{\partial v}{\partial T}\right)_p dp - T\left(\frac{\partial p}{\partial T}\right)_v dv = 0$$

$$dT = \underbrace{\frac{T}{(c_p - c_v)}\left(\frac{\partial v}{\partial T}\right)_p} dp + \underbrace{\frac{T}{(c_p - c_v)}\left(\frac{\partial p}{\partial T}\right)_v} dv$$

$$dT = \underbrace{\left(\frac{\partial T}{\partial p}\right)_v} dp + \left(\frac{\partial T}{\partial v}\right)_p dv$$

$$\frac{T}{(c_p - c_v)}\left(\frac{\partial v}{\partial T}\right)_p = \left(\frac{\partial T}{\partial p}\right)_v \qquad \frac{T}{c_p - c_v}\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial T}{\partial v}\right)_p.$$

$$\boxed{c_p - c_v = T\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_v}$$

I am writing the first T minus ds equation and second T minus ds equation. Let me write the second equation first. T ds is c_p dT minus T into del V divided by del T at constant p into dp, whereas first Tds set equation is this. Instead of that it will be c_v dT. It will be plus T and this will be del p divided by del T at constant V into dV. These are the two T minus ds equations.

Now, if we deduct one from other then we get c_p minus c_v into dT minus T del V divided by del T at constant p into dp minus T del p divided by del T at constant V into dV is equal to 0, or we can write dT is equal to T; T divided by c_p minus c_v, these things if we take this side, del V divided by del T at constant p into dp plus T divided by c_p minus c_v del p divided by del T at constant V into dV.

So now I am writing dT is equal to T this side or these two terms I am taking this side, T divided by c_p minus c_v del V divided by del T at constant p into dp plus T divided by c_p minus, I am not taking this as common, T divided by cp minus c_v. It can be written in that fashion, but I am writing in this fashion, del p divided by del T at constant V into dV.

This term, we can write this way, dT is equal to del T divided by del p by expressing T as a function of p and V. That means we can write del T divided by del p at constant volume dp plus del T divided by del V at constant pressure dV which means that this term is equals this, this term must equal this. I can write this term that T divided by c_p minus c_v into del V divided by del T at constant p must be equal to del T divided by del p at constant V.

Similarly, T divided by cp minus c_v into del p divided by del T at constant V is nothing but del T divided by del V at constant p. This coefficient can be written as del T divided by del p at constant V, as if T is expressed in terms of p and V. This coefficient can be written as del T divided by del V at p. Now, we get c_p minus c_v is T into del V divided by del T at constant p into del p divided by del T at constant V and the same thing we get from here.

c_p minus c_v is T into del V divided by del T at constant p and del p divided by del T at constant V. So, from both the equations, we arise equation is correct. We arrive the same expression for c_p minus $c_{v.}$ Now we go back well, any problem, again I am telling.

T is this del T divided by del p at constant V; del T divided by del V at constant p because this expresses T as a function of p and V. I can equate this with this one and I can equate this with del T divided by del V at constant p.

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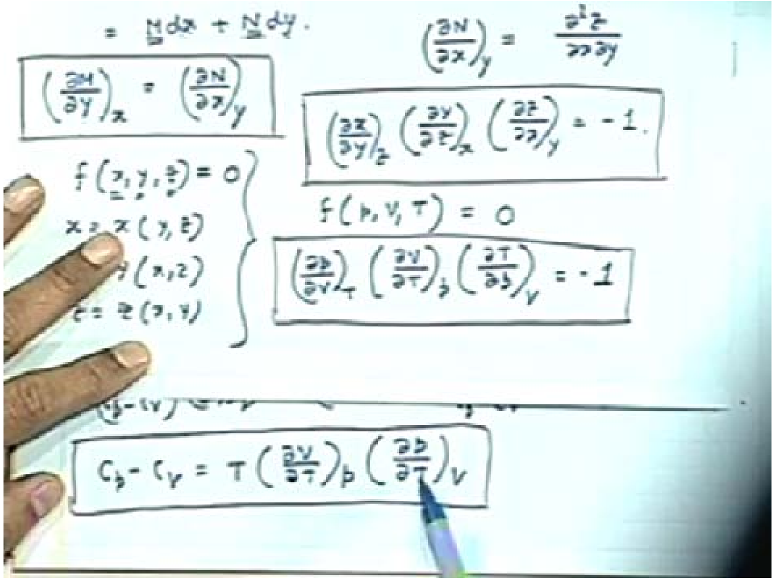

$$= M\,dx + N\,dy.$$

$$\left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial x \partial y}$$

$$\boxed{\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y}$$

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1.}$$

$$f(x,y,z) = 0$$

$$x = x(y,z)$$

$$y(x,z)$$

$$z = z(x,y)$$

$$f(p,V,T) = 0$$

$$\boxed{\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V = -1}$$

$$\boxed{c_p - c_V = T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_V}$$

So, if I just use this equation del p divided by del V, I want to substitute this. So, del p divided by del T is minus del p divided by del T at constant V. This side is minus del V divided by del T at constant p and del p divided by del V at constant T. I can write therefore c_p minus c_v.

Can you see all these three equations?

You can see this. You can also see this I think.

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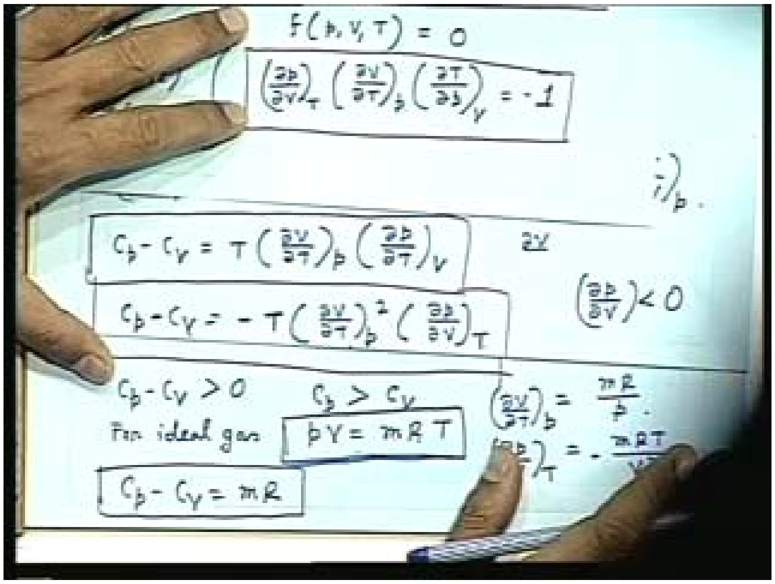

$f(p, V, T) = 0$

$\boxed{\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V = -1}$

$)_p$

$\boxed{c_p - c_v = T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_V}$ ∂V

$\boxed{c_p - c_v = -T\left(\frac{\partial V}{\partial T}\right)_p^2 \left(\frac{\partial p}{\partial V}\right)_T}$ $\left(\frac{\partial p}{\partial V}\right) < 0$

$c_p - c_v > 0$ $c_p > c_v$ $\left(\frac{\partial V}{\partial T}\right)_p = \frac{mR}{p}$.

For ideal gas $\boxed{pV = mRT}$ $\left(\frac{\partial p}{\partial V}\right)_T = -\frac{mRT}{V}$

$\boxed{c_p - c_v = mR}$

If I use this cyclic relationship to replace del p divided by del T at constant V by these two terms then I get c_p minus $c_{v.}$ There is a minus; minus T. This becomes square. del V divided by del T at constant p square into del p divided by del V at constant T. So, this is one of the very important relationships. This is c_p minus $c_{v;}$ that is, difference in heat capacity is minus T del V divided by del T whole square at constant p into del p divided by del V at constant T.

Now, we see this term is always positive. Square of any real term is always positive.

Now, del p divided by del V for all the substances are negative which means that c_p minus c_v is always greater than 0, which means c_p is greater than $c_{v.}$ Now this is a general thermodynamic relation. I can derive or small relationships can be derived in terms of the characteristic parameter of a system, if I know the equation of state. We know the equation of state is the equation between p, V and T.

For example, in case of an ideal gas, the equation of state tells that p into V is m into R into T. For an ideal gas of mass m, the equation of state states that in an ideal gas, the pressure of a close system into its volume equals to m into R is some constant known as characteristic gas constant into T. Therefore, in this equation, if we use this as equation of state and find out these parameters del V divided by del T at constant p then it becomes a very simple exercise; del p divided by del V at constant T, we will arrive c_p minus c_v is equal to mR.

We have to only find out del V divided by del T at constant p is equal to mR by p. Similarly, del p divided by del V at constant T is minus mRT by V square, because we take del p divided by del V at constant T. If we use this equation, then it can be shown that c_p minus c_v is m into R. this is a special case, if we have this equation between p V T. That means if we know the equation of state for different systems, I can find out c_p minus c_v in the simple expression, valid for that particular system. For an ideal gas, for particular system then ideal gas c_p minus c_v is mR, but this is the basic thermodynamic relation.

Now, another interesting fact we see that c_p is greater than c_v always, but there is a point where c_p exactly becomes equal to c_v when this becomes 0.

When will this become 0? del p divided by del V never becomes 0.

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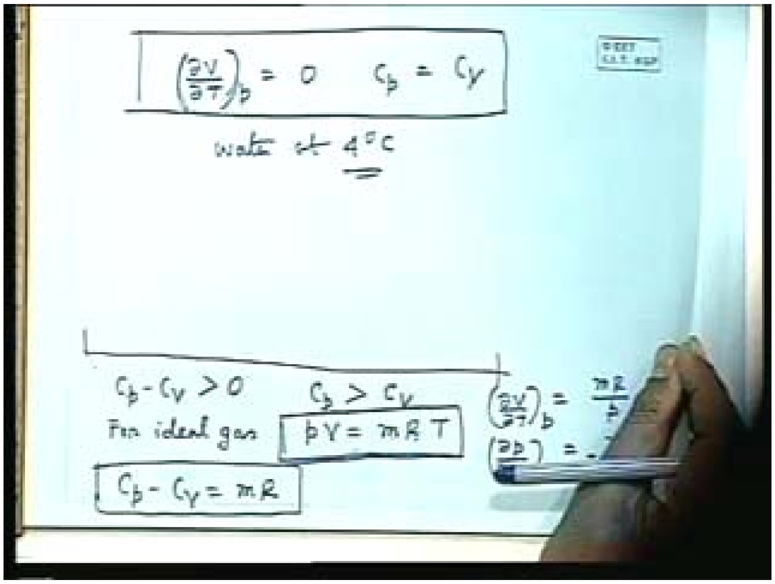

For example, when del V divided by del T at constant pressure becomes 0, $c_p = c_v$ and this is the case fulfilled by water at 4^0C because water reaches its minimum volume for a given mass that is minimum specific volume so del V divided by del T is 0. So these are few an important relationships.

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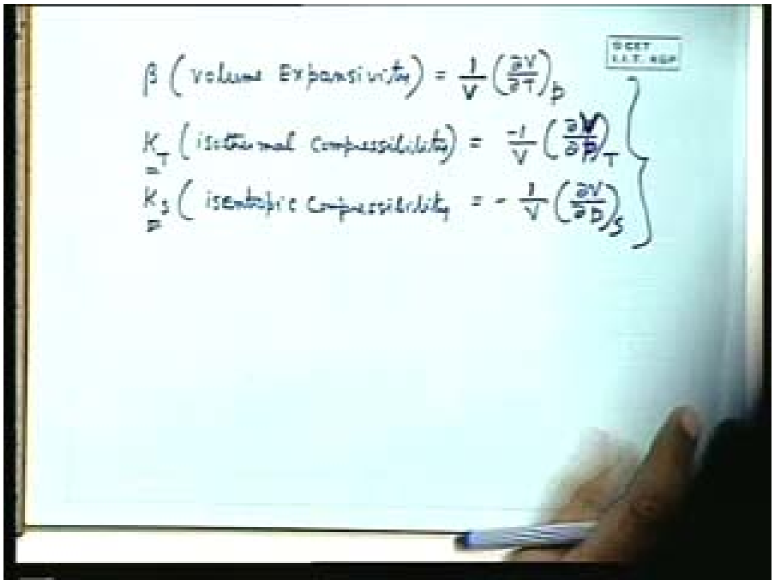

β (volume Expansivity) $= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$

K_T (isothermal compressibility) $= \frac{-1}{V}\left(\frac{\partial V}{\partial p}\right)_T$

K_s (isentropic compressibility $= -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_s$

Now, after that we define beta known as volume expansivity that is defined 1 by V into del V divided by del T at constant pressure with change in volume with respect to temperature is known as the volume expansivity.

Another expression is known as K_T that is isothermal compressibility. Now, we know, already we have read in fluid mechanics that when we compress a system that means the apply pressure to change its volume, the relationship between the pressure change and the change in volume depends upon the way which this change is brought. It depends upon the process constant; whether the temperature is kept constant or not, whether the temperature is not kept constant, some other properties kept constant or not, that depends upon the constant of the process, because when the pressure changes, the volume also changes and other properties may also change.

So, the relationship between change in pressure and change in volume which defines the modulus of rigidity or the compressibility depends upon the process constant. So, two such process constants are very important. One is isothermal compressibility.

If we change the pressure at constant temperature then this quantity, change of pressure with change of volume with respect to volume at constant temperature divided by the initial volume 1 by V. This is known as isothermal compressibility; that is, change in pressure divided by the change in volume per original volume at constant temperature.

Similar is the case that if we make it isentropic.

[Conversion between Student and Professor minus Not audible ((00:41:16 min))]

Yes please any question? No.

Isentropic compressibility, sorry, I am extremely sorry del V divided by del p.

Compressibility, with a minus sign, very good you are very thorough.

del V, I am extremely sorry otherwise this reverse is this the modulus of rigidity very good, minus 1 by V into del V divided by del p, because these are the scalar quantities with positive sign and the reciprocal of this are defined as modulus of rigidity. These definitions are very important.

Now, I will derive another one important relationship; that is, the ratio of c_p by $c_{v.}$

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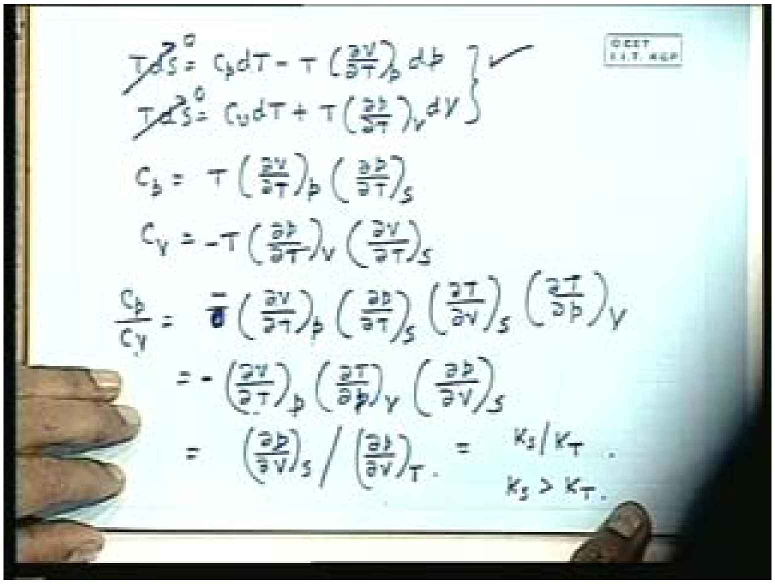

$$\left.\begin{aligned} \cancel{T\,ds}^{\,0} &= c_p\,dT - T\left(\frac{\partial v}{\partial T}\right)_p dp \\ \cancel{T\,ds}^{\,0} &= c_v\,dT + T\left(\frac{\partial p}{\partial T}\right)_v dv \end{aligned}\right\} \checkmark$$

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

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

$$\frac{c_p}{c_v} = \overset{-}{\cancel{T}}\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{\partial p}{\partial T}\right)_s\left(\frac{\partial T}{\partial v}\right)_s\left(\frac{\partial T}{\partial p}\right)_v$$

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

$$= \left(\frac{\partial p}{\partial v}\right)_s \Big/ \left(\frac{\partial p}{\partial v}\right)_T. = K_s/K_T.$$

$$K_s > K_T.$$

If I write the two T minus ds equations, that one is Tds is c_p dT minus T into del V divided by del T at constant p into dp and the first Tds equation Tds is c_v dT plus T into del p divided by del T at constant V into dV.

I can exploit these two equations to derive the ratio between c_p and c_v. If we consider isentropic process, ds is 0. From here, we get c_p is equal to T into del V divided by del T at constant p and this dp will be del p divided by del T at constant s, because I am using the constant entropy Tds that this becomes 0. So, dp divided by dT at constant s will be defined as del p divided by del T at constant s. I can write, from this equation at constant entropy, ds is equal to 0 at constant s.

Similarly, I can write from the second equation which is basically the first T minus ds equation that c_v is equal to T into del p divided by del T at constant V into del V divided by del T at constant s, with a minus sign; c_p will be minus.

So c_p by c_v will be T into del V divided by del T at constant p into del p divided by del T at constant s divided by this; that means, del T divided by del V at constant s. T will be cancelled, I am sorry, into del T divided by del p at constant V.

That is del V divided by del T at constant p into del p divided by del T at constant s into del T divided by del V at constant s into del T divided by del p at constant V.

So, this can be written as, these two together as, minus del V divided by del T at constant p and then del T divided by del p at constant V into del p divided by del V at constant s.

Now first of all we have to find out del p divided by del V at constant s; del p del Vs where from you get del p del Vs? well del p del Vs

[Conversion between Student and Professor -Not audible ((00:45:32 min))]

Just a minute del p del Vs, we find out del p del V, no, we have to find out del p del Vs is there, del T del pV, oh sorry I am extremely sorry. del T del pV has to be replaced from the equation del T from the cyclic equations. I am sorry, this is not be used, let me call the cyclic equations, cyclic equations, sorry del T del p del T del pV that means del T del pV del T del pV.

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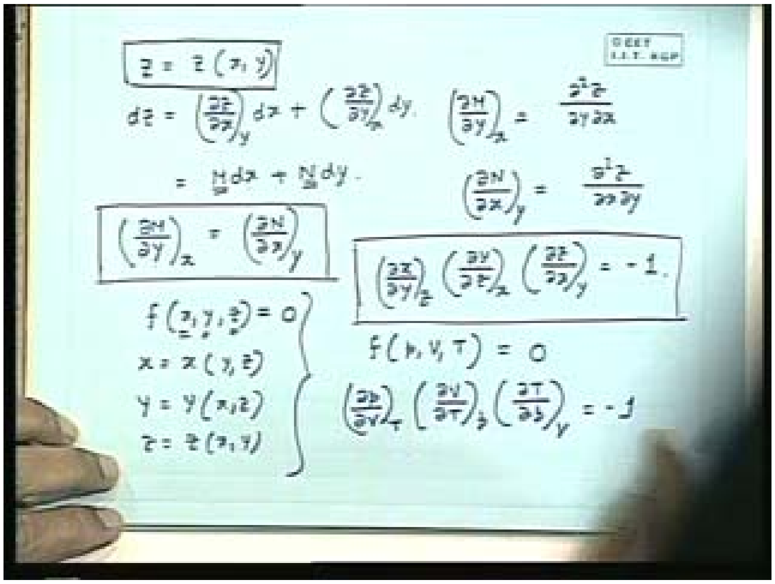

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$$\boxed{z = z(x, y)}$$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \qquad \left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial y \partial x}$$

$$= M dx + N dy \qquad \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial x \partial y}$$

$$\boxed{\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y}$$

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1.}$$

$$\left.\begin{array}{l} f(x, y, z) = 0 \\ x = x(y, z) \\ y = y(x, z) \\ z = z(x, y) \end{array}\right\}$$

$$f(p, V, T) = 0$$

$$\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V = -1$$

I use this cyclic equation, del p divided by del V at constant T into del V divided by del T at constant p; that means, del T divided by del V at constant p is del V divided by del T at constant p. This will be cancelled. So, we see that del T divided by del p at constant V is this is cancelled. del V divided by del p will go there; that means, minus1 by del V divided by del p.

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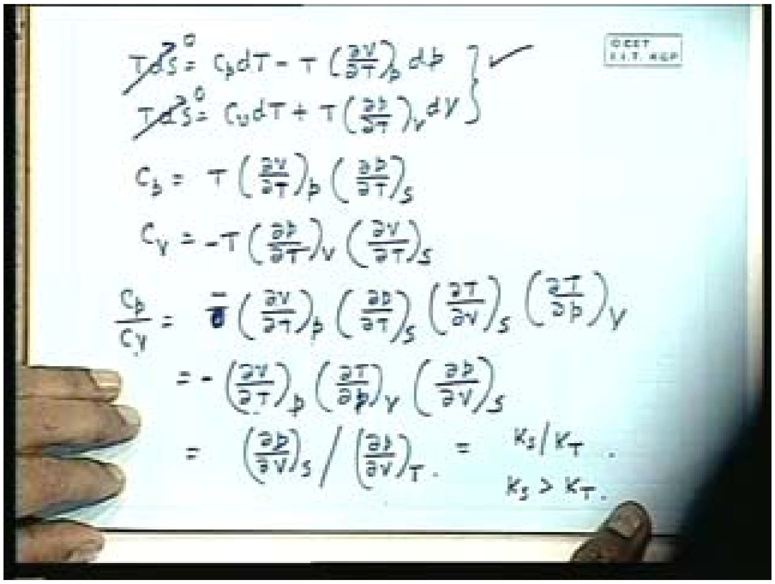

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$$\left.\begin{array}{l} T \cancel{dS}^{0} = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_p dp \\ T \cancel{dS}^{0} = C_v dT + T\left(\frac{\partial p}{\partial T}\right)_V dV \end{array}\right\} \checkmark$$

$$C_p = T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_S$$

$$C_V = -T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_S$$

$$\frac{C_p}{C_V} = -\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_S \left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial T}{\partial p}\right)_V$$

$$= -\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V \left(\frac{\partial p}{\partial V}\right)_S$$

$$= \left(\frac{\partial p}{\partial V}\right)_S \Big/ \left(\frac{\partial p}{\partial V}\right)_T. = K_S / K_T.$$

$$K_S > K_T.$$

This becomes del p divided by del V at constant s divided by del p divided by del V at constant T. So this minus sign will go because this del V divided by del T, del V divided by del T at p and del V divided by del T at constant p, this will be minus1 by this. So, this comes here. So, I am replacing del T divided by del p at constant V from this cyclic equation.

So, this becomes equal to… as I have defined earlier that the isentropic compressibility by isothermal compressibility. Since c_p is greater than c_v, this will be greater than 1 which proves that isentropic compressibility is greater than the isothermal compressibility.

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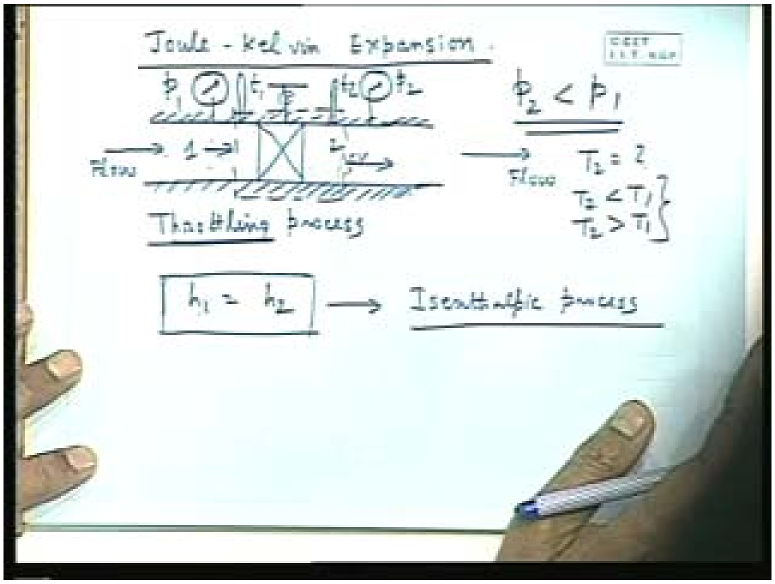

Now, I will start a very important aspect of thermodynamics is Joule-Kelvin expansion.

What is Joule Kelvin expansion? So far, we have discussed about the property relations. These are nothing but the mathematical relations, some algebraic things without any thermodynamic concept much of any thermodynamic concept.

Now, what is Joule minus Kelvin expansion which is very important or Joule minus Kelvin effect?

Let us consider that a fluid is while passing through a tube is being restricted to flow by a valve. What is this physically? Let this tube and these valves are all insulated.

We know the different types of valves are inserted in a pipe, the basic functions of the valve is to control the flow that is known to everybody even who does not have any much qualifications are not gone through engineering studies they know that. If there is a flow of fluid, so if we have to regulate the flow in the down stream direction, we have a valve which gives a restricted passage. If the valve is completely closed then the passage is completely closed and the flow cannot come here. So, this becomes a static condition; the flow comes here, strikes here and exerts a pressure. There will be no flow here.

As we gradually open, the valve allows the flow to take place that means to restricted passage, the flow starts taking place. Now, in such a condition of a partial opening or partial closer of the valve, when the fluid comes through this and flow through the valve some at steady state, some flow is maintain. Then we know that pressure across this valve is dropped; that means there is a certain drop or decrease of pressure across the valve.

If one keeps a pressure gauge here, let this section is p_1 and also keeps the temperature t_1 and keep a temperature $t_{2.}$ This is the state two and keeps a pressure gauge $p_{2.}$ So, if we place pressure and temperature measuring instruments at off stream, further off stream from the valve. So, that is where this stream is undisturbed. Again, this downstream location will be at somewhere when again there will be no disturbance from the valve.

At a certain distance from here where again the steady state is there, same flow is flowing through this, but there is a decrease in the pressure $p_{1.}$ p_2 is always less than $p_{1.}$ This process is known as Throttling process.

This is a colloquial term in engineering term used in soft floor. That fluid is throttle means the flow is throttle so that there is a large difference of pressure. The fluid flows through this special difference. So, flow rate is automatically reduced to take care of the frictional pressure down. So, this pressure is dropped because of the friction in the form. Entire thing is adiabatic that is insulted.

Now, try to understand the physics of this process. Why the pressure is being reduced? Because of the fact that there is the frictional dissipation, pressured energy is being converted into intermolecular energy.

So, basically, this is an irreversible process. But what will be $T_{2?}$ Will it be less than T_1 or will it be greater than T_1? Now the answer to this question is, T_2 may be less than $T_{1,}$ may be greater than T_1 depending upon the situations which will be discussed.

That is because there are two countering effects taking place in changing the temperature from initial to the final state. When there is a change in the pressure, because of the friction, some of the pressure energy, the part of the mechanical energy is being dissipated into intermolecular energy or heat. Therefore, the fluid temperature or the system temperature should increase. But at the same time, when the pressure is decreased depending upon its equation of state, its temperature will also decrease. Because of a decrease in pressure, the temperature will decrease. So, temperature will decrease because of a decrease in pressure.

Following its equation of state, we do not know, what is extend or decrease in temperature that depends upon the typical equation of state.

At the same time, because of some fraction of the pressure energy is a part of mechanical energy being converted in an intermolecular energy temperature should increase. So, these two countering effects decide that which one will dominate over the other, so that there will be either an increase or a decrease in temperature. Under usual conditions, our common practice is that whenever we throttle a fluid so that its pressure is being reduced to allow it to flow through a restricted passage. Usually temperature also drops, but it is not always the case.

Now, let us analyze this case by taking a control volume like this. Now tell me, what is this process actually? This is an irreversible process. We can write, always the first law of thermodynamics or the conservation of energy for any process, reversible and irreversible process. If I write this in steady flow energy equations, at one and two, flow is going out. For this control volume, what can we write? Now, steady flow energy equations we can write for unit mass basics. We can simply write h_1 is h_2. Why? Because v_1 is v_2. Because the flow rate is same, the cross sectional area is same.

So, if we recall the complete energy equations, h_1 is h_2 is the outcome of the energy equations. The applications of this steady flow energy equations for this case because the change in kinetic energy is 0, change in potential energy is 0. So, simply h_1 is h_2. There is no other energy interaction; neither heat nor work. Therefore, this throttling process is an isenthalpic process, where the entropy of the process remains same.

[Conversion between Student and Professor minus Not audible ((00:54:37 min))]

Enthalpy of the process remains the same, but one very important thing is that this process is an irreversible process and not a reversible process. So, the initial and final enthalpy remains the same. This process ensures the initial and final enthalpy to remain same and it is an irreversible process.

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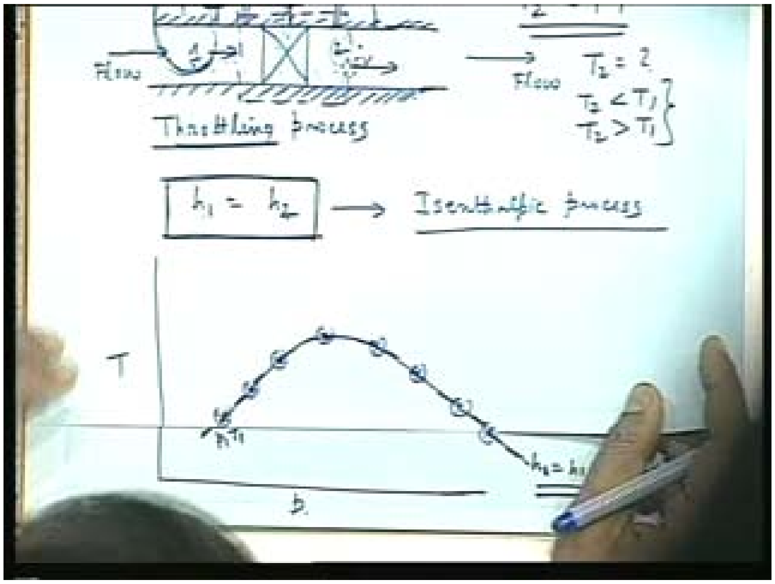

Now, if I draw this process in Tp curve but immediately we must ask Sir, how can you draw a process in a thermodynamic coordinate plane if the process is an irreversible one? So, I cannot draw this process. Therefore the question does not come but what I can draw in TP plane that if I go on varying these inlet condition p_1, t_1 at different values.

No sorry, if I i am not going sorry, I am extremely sorry. If I keep this p_1 t_1 fixed, but if I go on varying the position of the valve if I throttle to different pressures and temperatures, that means starting from full with close position, if I go on slowly opening the valve that means at different valve settings, creating different restricted passage areas which means that if I throttle to different pressure and temperature, you will see that throttling pressure and temperature will be different.

For keeping the same initial condition, if I throttle at different valve settings so that I get different pressures and temperatures, I can tell that since the basic energy equation for this process is h_1 is h_2, all the values of enthalpy corresponding to different pressures and temperatures will correspond to the enthalpy at 1 which is kept fixed. That means I can generate the different state points with varying p and T, but with the same enthalpy by doing so. We can draw a curve which is nothing but the locus of same enthalpy and the curve will look like that. If I do so, the curve will look like that.

This is an experimental fact. What is this curve? Let this point is p_1T_1 and this is h_2 is equal to h_1 constant. By doing these experiments, I can plot different points on pT diagram and this can be joined by a dotted line, because this does not show a thermodynamic process; rather this shows a curve of same enthalpy; locus of equal enthalpy point. That means I can generate number of pairs of p and T points whose enthalpy equals to the enthalpy h_1 which is the enthalpy corresponding to the initial state p_1 and T_1.

If we generate this way, a number of pairs of points with p and T having the same enthalpy and we can draw the locus of a constant enthalpy in Tp plane. This will increase first, have a maximum and then it will decrease. So, this way, we can generate a family of such curves if we now change this initial condition p_1 and $T_{1.}$

If we change now initial condition $p_{1,}$ T_1 that means we are going to a different enthalpy. Again, at that same initial condition p_1 and t_1 set to a different enthalpy, we can throttle to different pressures and temperature, and generate again differentiates of p and T values corresponding to these initial enthalpy. This way, we can generate a family of curves which represent the constant enthalpy in Tp plane.

This we will discuss in the next class because time is up for today’s class

Joule-Kelvin expansion, we will again discuss in the next class.

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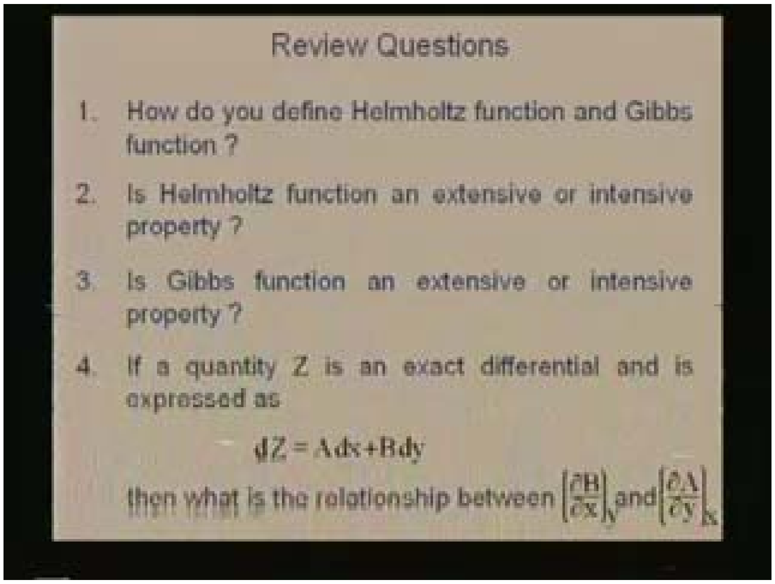

Review Questions

1. How do you define Helmholtz function and Gibbs function ?
2. Is Helmholtz function an extensive or intensive property ?
3. Is Gibbs function an extensive or intensive property ?
4. If a quantity Z is an exact differential and is expressed as

$$dZ = Adx + Bdy$$

then what is the relationship between $\left(\frac{\partial B}{\partial x}\right)_y$ and $\left(\frac{\partial A}{\partial y}\right)_x$

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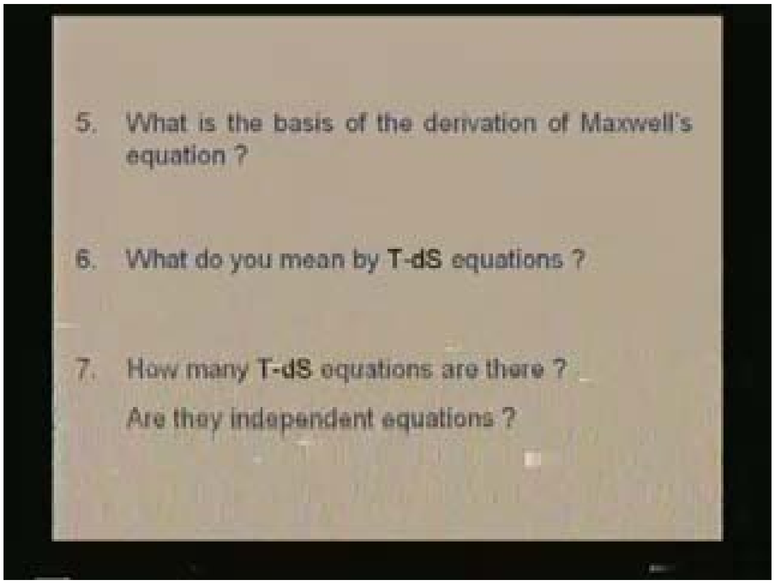

5. What is the basis of the derivation of Maxwell’s equation ?
6. What do you mean by **T-dS** equations ?
7. How many **T-dS** equations are there ?

   Are they independent equations ?

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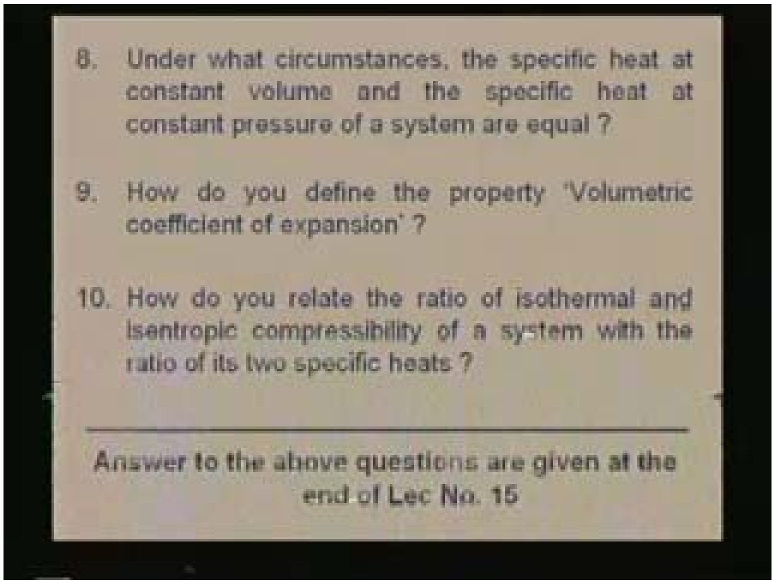

8. Under what circumstances, the specific heat at constant volume and the specific heat at constant pressure of a system are equal ?

9. How do you define the property 'Volumetric coefficient of expansion' ?

10. How do you relate the ratio of isothermal and isentropic compressibility of a system with the ratio of its two specific heats ?

Answer to the above questions are given at the end of Lec No. 15

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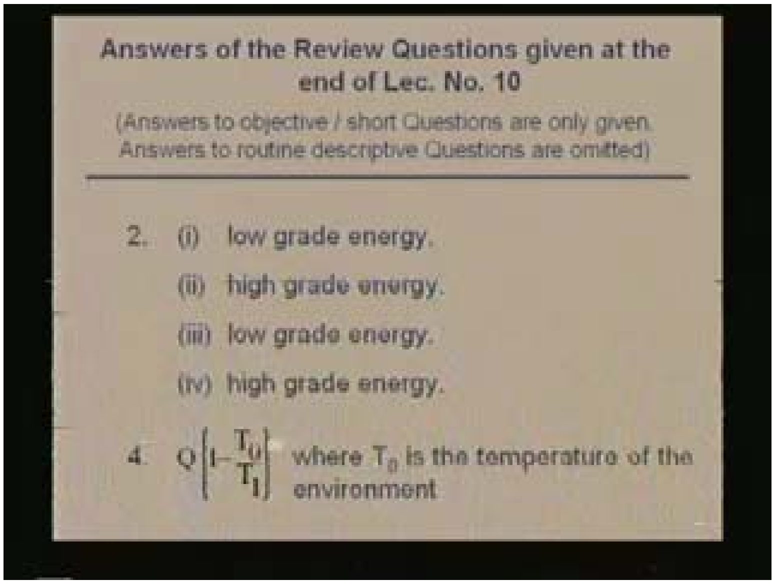

Answers of the Review Questions given at the end of Lec. No. 10

(Answers to objective / short Questions are only given. Answers to routine descriptive Questions are omitted)

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2. (i) low grade energy.
   (ii) high grade energy.
   (iii) low grade energy.
   (iv) high grade energy.

4. $Q\left[1-\frac{T_0}{T_1}\right]$ where T_0 is the temperature of the environment

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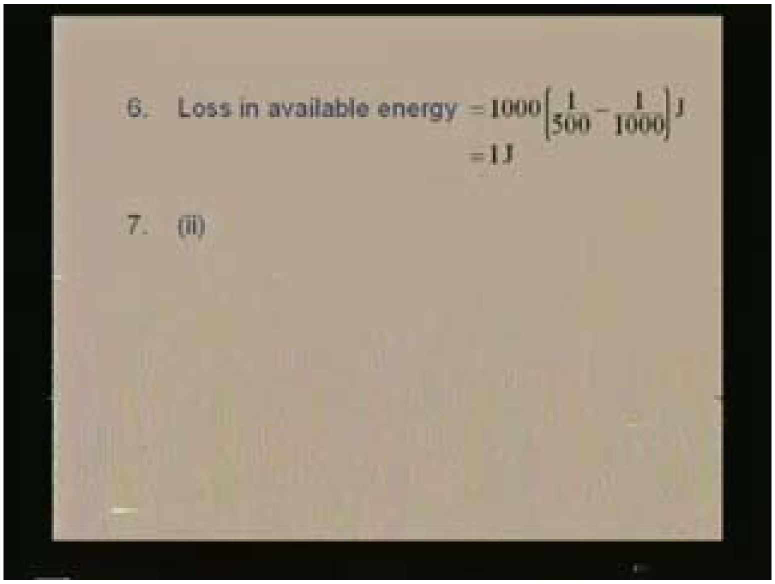

6. Loss in available energy $= 1000\left[\frac{1}{500} - \frac{1}{1000}\right] \text{J}$

$= 1 \text{J}$

7. (ii)