Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
Department of Chemical Engineering
Indian Institute of Technology Kharagpur
Lecture 09
Thermodynamic Network

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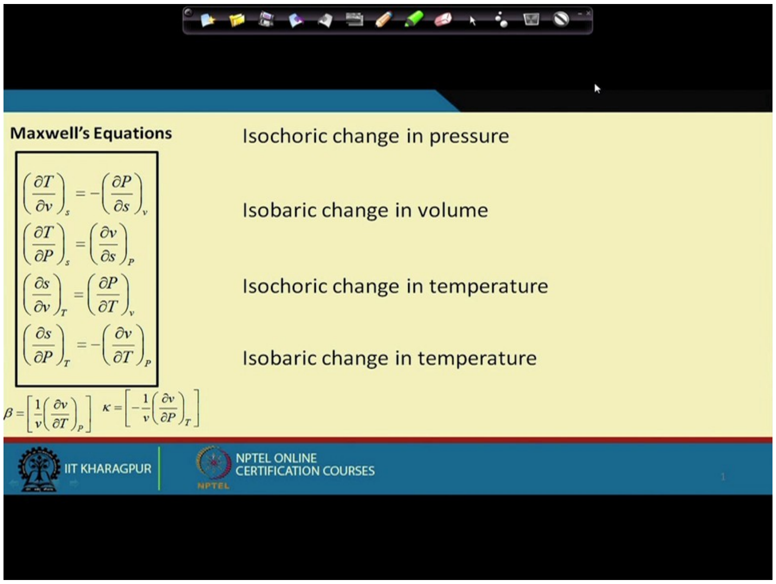

Maxwell's Equations

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v$$ Isochoric change in pressure

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$$ Isobaric change in volume

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$ Isochoric change in temperature

$$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$$ Isobaric change in temperature

$$\beta = \left[\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P\right] \quad \kappa = \left[-\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T\right]$$

Hello everybody, so in the last class while discussing the properties of the thermodynamics potentials we came across or rather we developed a set of Maxwell's equations which I have written down on or which have been written down here for your convenience. Now if you observe this particular set of Maxwell's equations you will find that these equations they actually relate the change in entropy with the change in pressure change in volume.

So in other words this basically relates the changes in entropy with changes in pressure volume and we will also see how they are related to the changes in temperature? And from here we are going to derive the changes of enthalpy, internal energy etc with changes of pressure volume etc and this is as an endeavor to relate the measurable and the non-measurable properties. So that we can estimate the non-measurable properties simply by measurement of the measurable properties.

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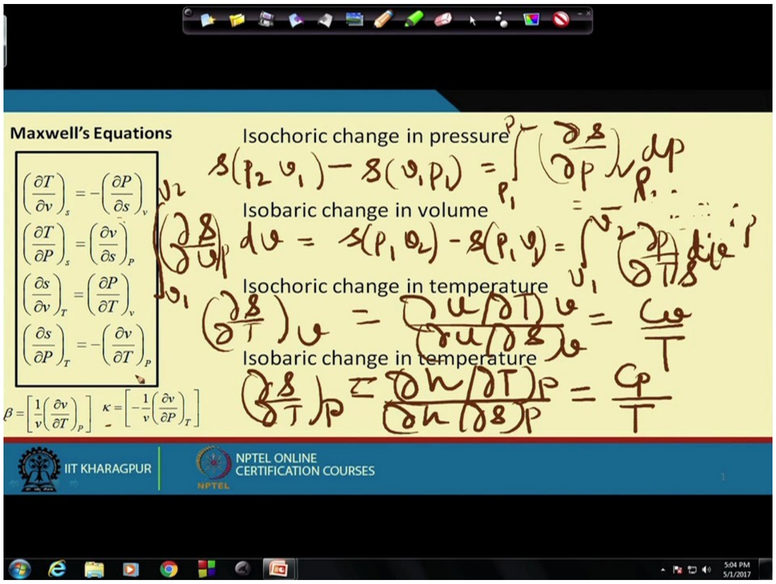

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$$\beta = \left[\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P\right] \quad \kappa = \left[-\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T\right]$$

Isochoric change in pressure

$$s(P_2 v_1) - s(v_1 P_1) = \int_{P_1}^{P_2} \left(\frac{\partial s}{\partial P}\right)_v dP$$

Isobaric change in volume

$$\int_{v_1}^{v_2} \left(\frac{\partial s}{\partial v}\right)_P dv = s(P_1 v_2) - s(P_1 v_1) = \int_{v_1}^{v_2} \left(\frac{\partial P}{\partial T}\right)_s dv$$

Isochoric change in temperature

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{(\partial u/\partial T)_v}{(\partial u/\partial s)_v} = \frac{c_v}{T}$$

Isobaric change in temperature

$$\left(\frac{\partial s}{\partial T}\right)_P = \frac{(\partial h/\partial T)_P}{(\partial h/\partial s)_P} = \frac{c_P}{T}$$

Now among the measurable properties the common ones as we all know they are pressure, volume, temperature out of which pressure and temperature are most easily measured and most easily controlled along with that we also know that beta and Kappa these 2 the coefficient of isothermal compressibility and the coefficient of thermal expansivity these 2 can also be measured. Now let us see how we can play with these set of Maxwell's equation in order to find out say the change of entropy the isochoric change of entropy with pressure.

What does isochoric change in entropy means? It basically means del s del p at constant v, right? Now if you observe then this is related to, if you see the first Maxwell's equation this will be equal to del v del t at constant s, so therefore we can write it down as say for instance s from some particular initial state say P2v1 to say v1P1 this will be equal to del s del p at constant v integral of say from P1 to P2 dP which can also be written down as minus integral P1 to P2 del v del T at constant s dp, right?

In the same way suppose I tell you to find out the isobaric change in entropy with volume, what does this signify? This basically refers to del s del v at constant p, right? So therefore we would like to find out integral of this as a function of volume that means it is from v1 to v2 this is dv, okay. So therefore this is equal to s say P1v2 minus s P1v1 which will be equal to if we relate it we find that in this particular case their relevant Maxwell's equation is the second Maxwell's equation, isn't it?

We find out that the second Maxwell's equation which del s del v at constant P with del P del T at constant S. So therefore this will be equal to integral v1 to v2 del P del T at constant s dV, right? In the same way suppose I would like to find out the isochoric change in temperature, what does that mean? That means del s del T at constant v. Now can you tell me in what way can I find this particular quantity out?

Can I not write this quantity as del u del T at constant v divided by del u del s at constant v? What is del u del T at constant v? We have already discussed the specific heat capacity as constant volume and constant temperature, what is del u del s at constant v? remember the differential equation du equals to Tds minus PdV from there we find del u del s at constant v is nothing but equal to the absolute temperature, right?

Same way if you want to find out del s del T at constant p we can simply write it down as del h del T at constant P divided by del h del s at constant P all these things they come from the cyclic rules again we know del h del T at constant P is nothing but equal to del q del T at constant P which was equal to Cp and this term again from the original dh equals to Tds plus VdP we get this is equals to T. So therefore we find that in this particular way we have been able to relate the change in entropy with change in pressure with change in volume with change in temperature at constant volume the change in temperature at constant pressure.

Now before I proceed I would like to remind you that when we were discussing the Maxwell's equation or the evolution of Maxwell's equation from the thermodynamic potentials we had derived the equation in terms of total quantities and I had used all sorts of capital alphabets in order to denote vt sorry v, s, g, a, u and h. Now as I told you that all of these are extensive properties and the same relationships which hold for total properties are also applicable for molar properties or for specific properties at this moment we are going to deal with molar properties and therefore since we are dealing with molar properties I have written all this Maxwell's equations in terms of lower case alphabets meaning that I have been relating the change in molar entropy with the change in molar volume, pressure and temperature.

It's important for you to remember that the same equations that I have derived here can be derived for total quantities as well the important thing to remember is if you are dealing with total quantities all the quantities here should be total, if you are dealing with molar quantities all the quantities written down is molar that is the only thing that we need to remember. Well, now suppose we go for the?

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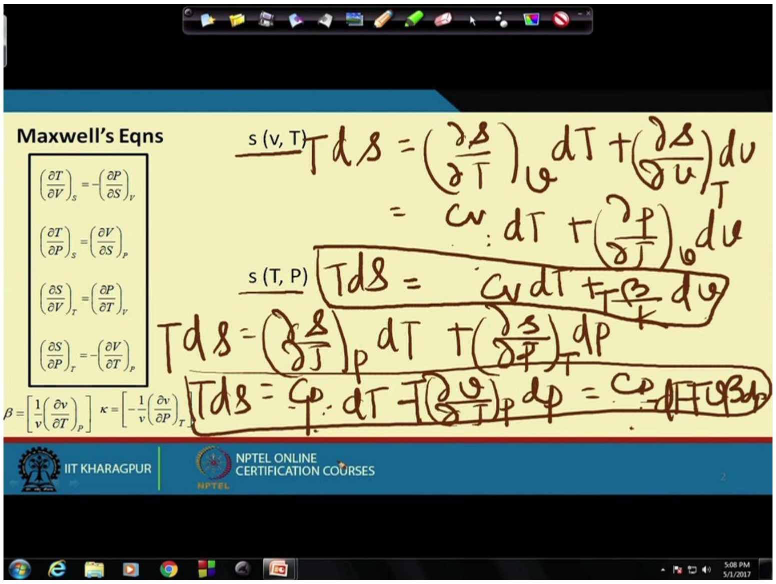

Maxwell's Eqns

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$$\beta = \left[\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P\right] \quad \kappa = \left[-\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T\right]$$

s (v, T)

$$Tds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$$

$$= C_v\, dT + T\left(\frac{\partial P}{\partial T}\right)_v dv$$

s (T, P)

$$\boxed{Tds = C_v\, dT + T\frac{\beta}{\kappa}\, dv}$$

$$Tds = \left(\frac{\partial s}{\partial T}\right)_P dT + T\left(\frac{\partial s}{\partial P}\right)_T dP$$

$$\boxed{Tds = C_p\, dT - T\left(\frac{\partial v}{\partial T}\right)_P dp = C_p\, dT - Tv\beta\, dp}$$

Suppose in this particular case, now let us see once we have derived or rather once we have discussed how entropy changes with pressure, volume, temperature etc then we should be in a position to derive that Tds equation which are known or in other words we should be able to derive entropy as a function of volume and temperature and entropy as a function of pressure and temperature.

Let us see how we go about doing this, for in order to derive this in terms of volume and temperature we just need to write this as ds equals to as a function of temperature and volume, so this is del s del T at constant vdT plus del s del v at constant T dv in the last slide I have already derived this as nothing but equal to Cv by T dT plus del p del T at constant vdv the Maxwell's equation have been written on the side so that you can refer to them and find out the way I have derived.

This can also be written down in terms of beta and Kappa in that particular case this becomes CvdT plus beta by Kappa dv, right? And using the and if in case you would like to find entropy in terms of temperature and volume then in this particular case again we write it down in terms of temperature and pressure, sorry I think I have mentioned volume it was pressure. So I can write it down in terms of temperature and pressure and in this particular case this becomes CP by

T dT minus del v del T at constant pdp which can also be written down as Cp by T dT minus v beta dp, right?

Now usually what we do is, these particular equations they are written in the form of Tds for our convenience, right? And we usually write them down as Tds equals to CpdT minus T of this or in other words here also we would like to write it down as CpdT T of this, right? Here also suppose I would like to express it in terms of your Tds equations then in that case the equation can be written down as it can be written down in the form of Tds equals to CvdT plus T of beta by k Kappa, now these 2 equation they not only show us how s varies with temperature pressure and volume temperature but they can also be used for finding out a large number of other things as well.

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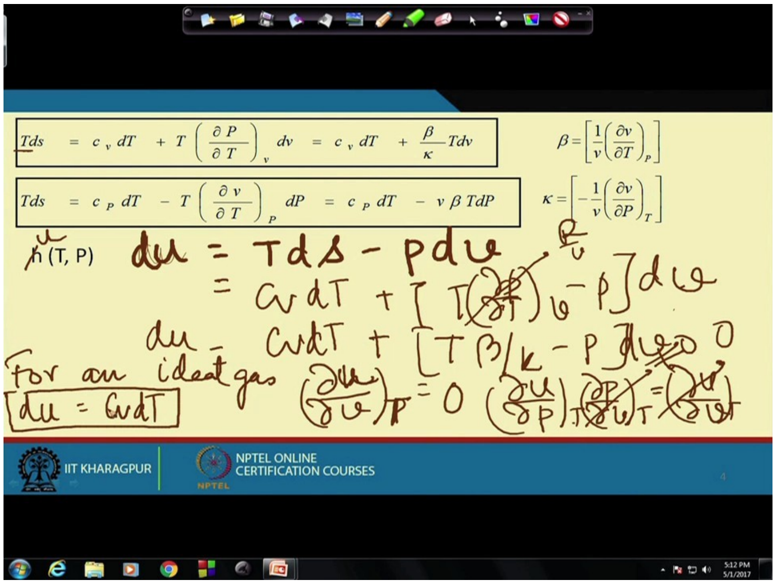

$$\boxed{Tds = c_v\,dT + T\left(\frac{\partial P}{\partial T}\right)_v dv = c_v\,dT + \frac{\beta}{\kappa}T\,dv}$$

$$\beta = \left[\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P\right]$$

$$\boxed{Tds = c_P\,dT - T\left(\frac{\partial v}{\partial T}\right)_P dP = c_P\,dT - v\beta T\,dP}$$

$$\kappa = \left[-\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T\right]$$

$\overset{u}{\cancel{h}}(T, P)$

$$du = Tds - pdv$$

$$= C_v dT + \left[T\overset{\beta/\kappa}{\cancel{\left(\frac{\partial P}{\partial T}\right)_v}} - p\right]dv$$

$$du = C_v dT + \left[T\beta/\kappa - P\right]\cancel{dv} \rightarrow 0$$

For an ideal gas $\left(\frac{\partial u}{\partial v}\right)_P = 0$ $\quad \left(\frac{\partial u}{\partial P}\right)_T \cancel{\left(\frac{\partial P}{\partial v}\right)_T} = \cancel{\left(\frac{\partial u}{\partial v}\right)_T}$

$$\boxed{du = C_v dT}$$

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For example suppose we would like to find out u as a function of T and v, how to proceed in this particular case? We already know the basic equation, what is the basic equation that we know? We know that du I would just like to make the pen a little thicker, so that is it is easier for you to see. We already know du that is equal to Tds minus pdv, this we know. And from the first Tds equation which I have written down, from this particular Tds equation can I not substitute this particular Tds and write it down as CvdT plus T del P del T at constant v minus p dp, right?

Or in other words I can also write it down in the terms of beta kappa etc. I can also write it down as CvdT plus T beta by Kappa minus P sorry this is dv I made a mistake this is going to be dv, right? So therefore by using the 2 Tds equations the first Tds equation I could actually express u as a function of CvdT in this particular equation, okay.

Now from here let us see some very interesting result that we get, say for example for an ideal gas what do we get? For an ideal gas, what is del h? Suppose from here sorry not del h what is del u del v at constant p? We know for an ideal gas Pv equals to RT for one mole since we are dealing with molar properties, so therefore in this particular case if you substitute del p del T at constant v then for an ideal gas this particular term it becomes R by v. So RT by v is nothing but equal to P. So therefore what do we find? The internal energy dependence on volume for an ideal gas it disappears off and we find that del u del v at constant T that is that becomes equal to 0, right?

And I would like to remind you that when we were dealing with the first and second laws under that condition I had told you that for an ideal gas du equals to CvdT. You had assumed that what I was telling was correct I could not prove that at that time. Now I show you from Maxwell's equation why for an ideal gas del u del v at constant T equals to 0. Same in the similar way suppose I would like to find del u del P at constant T.

How to find this particular term out? We know from the cyclic relationships del u del p at constant T del P del v at constant T that will be equal to del u del v at constant T isn't it? From the cyclic relationships we have already proved that this is equal to 0. We know that this term is not equal to 0. So therefore what does it imply? It implies del u del p at constant T will be equal to 0, right? So therefore we have not only deduced du in terms of CvdT but we have also shown that for an ideal gas u is independent of pressure and volume it is just a function of temperature and nothing else which is a very well-known equation.

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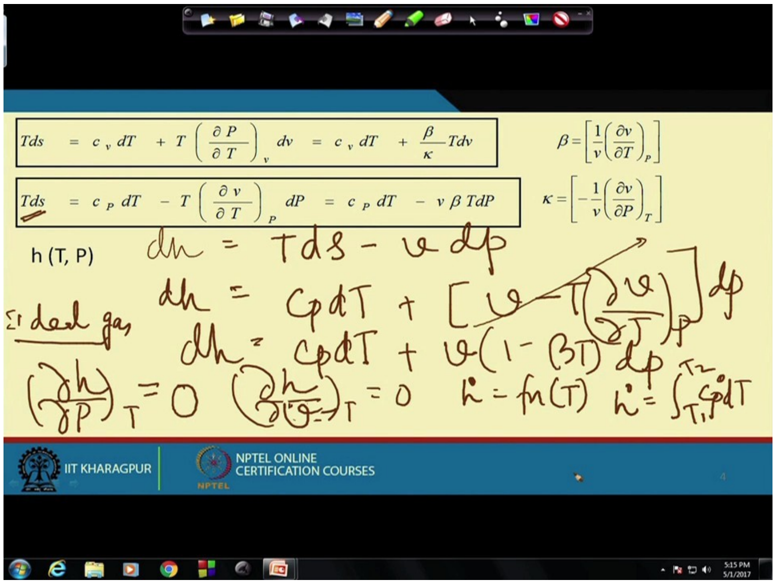

$$Tds = c_v\,dT + T\left(\frac{\partial P}{\partial T}\right)_v dv = c_v\,dT + \frac{\beta}{\kappa}Tdv$$

$$\beta = \left[\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P\right]$$

$$Tds = c_P\,dT - T\left(\frac{\partial v}{\partial T}\right)_P dP = c_P\,dT - v\beta TdP$$

$$\kappa = \left[-\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T\right]$$

h (T, P)

$$dh = Tds - v\,dp$$

Ideal gas

$$dh = C_p dT + \left[\cancel{v - T\left(\frac{\partial v}{\partial T}\right)_p}\right]dp$$

$$dh = C_p dT + v(1 - \beta T)\,dp$$

$$\left(\frac{\partial h}{\partial P}\right)_T = 0 \quad \left(\frac{\partial h}{\partial v}\right)_T = 0 \quad h^{\circ} = fn(T) \quad h^{\circ} = \int_{T_1}^{T_2} C_p^{\circ} dT$$

In the same way suppose I would like to derive the equation for, in the same way if I would like to derive the equation for h(T,P) right? In that particular case what do we get for h T,P suppose I in the same way in this particular case I would again like to remember that sorry dh equals to again from the Tds equation, Tds minus vdp, right? Again I substitute the second Tds equation here the same way that I had done and then from there once I substitute what do I get?

I get dh is nothing but equal to CpdT plus v minus T, delv del T at constant P dp or in other words this can also be in terms of beta kappa etc. We can write it down as CpdT plus V into 1 minus beta T into dp, right? So therefore and this particular equation is particularly important because for most of the practical applications we come across enthalpy changes of physical as well as chemical processes. In this case also suppose I try to find out del h del p at constant T for an ideal gas what do I get?

Suppose I do it for an ideal gas, so the for an ideal gas let me find out del v del T at constant p what is del v del T at constant p for an ideal gas? It is nothing but equal to R by P. So therefore RT by P for one mole of the gas is nothing but the molar value therefore this whole term cancels out if you are dealing with ideal gas which shows us that del h del P at constant T for an ideal gas is 0. Just the way we have proceeded for internal energy we can show in this particular case del h del v at constant T will also be equal to 0.

I will just write it down properly, so this is also equal to 0. So therefore for an ideal gas what do we know? h it is a function of temperature only h ideal we denote ideal gases with a subscript 0. So therefore from here we can write h0 is nothing but equal to T1 to T2 Cp 0 dT. At this juncture I would just like to remind you once more something which I had mentioned in the last class something about nomenclatures. By this time you must already have been aware of the fact that we are dealing with a large number of properties and if we do not denote the properties consistently we might get lost in it.

So therefore again I would like to remind the consistent nomenclatures that we are going to follow in this class all the total properties the total energy, the total entropy, the total enthalpy etc all of them will be denoted by capital letters and all molar quantities will be denoted by lowercase letters and you must have noticed from the beginning of the class I am just using lowercase letters just to emphasize upon you that I am dealing with molar properties only but at the same time it is important for you to remember that the same equations that I am deriving will be applicable for total properties as well.

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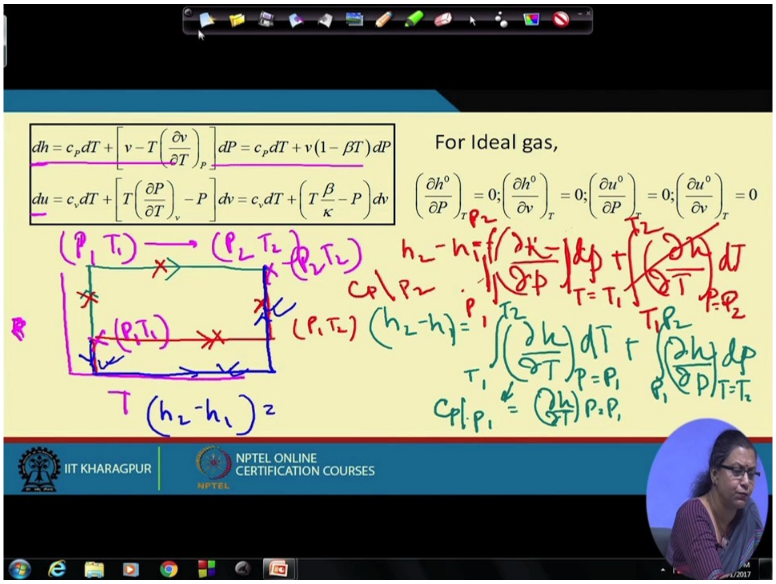

$$dh = c_p dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dP = c_p dT + v(1-\beta T)\,dP$$

$$du = c_v dT + \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] dv = c_v dT + \left(T\frac{\beta}{\kappa} - P\right) dv$$

For Ideal gas,

$$\left(\frac{\partial h^0}{\partial P}\right)_T = 0; \left(\frac{\partial h^0}{\partial v}\right)_T = 0; \left(\frac{\partial u^0}{\partial P}\right)_T = 0; \left(\frac{\partial u^0}{\partial v}\right)_T = 0$$

$$h_2 - h_1 = \int_{P_1}^{P_2}\left(\frac{\partial h}{\partial P}\right)_{T=T_1} dP + \int_{T_1}^{T_2}\left(\frac{\partial h}{\partial T}\right)_{P=P_2} dT$$

$C_p|_{P_2}$

$$(h_2 - h_1) = \int_{T_1}^{T_2}\left(\frac{\partial h}{\partial T}\right)_{P=P_1} dT + \int_{P_1}^{P_2}\left(\frac{\partial h}{\partial P}\right)_{T=T_2} dP$$

$$C_p|_{P_1} = \left(\frac{\partial h}{\partial T}\right)_{P=P_1}$$

Now I have introduced one more additional nomenclature, what is it? Whenever I am dealing with ideal gases I am just putting superscript 0 just to differentiate that these properties refer to ideal gases in contrast to any particular real gas or any particular real substance, right? Now so by this particular time we have already come across we have deduced the 2 Tds equations from the 2 Tds equations we have also derived the equations for dh and du.

And we have also derived or rather we have also shown that both enthalpy and internal energy for an ideal gas both of them they are unique functions of temperature and both of them are independent of pressure as well as of volume, right? Now before I proceed further I would like to ask one particular question to you, we have this particular equation, at this juncture I would like to remind you that for most of the situations we will be dealing with changes in enthalpy and entropy as we come across changes of these quantities in practical applications.

So primarily I will be dealing with dh, ds quantities but it is important for you to keep in mind that you can proceed similarly for du as well, right? Suppose I have some particular gas at a pressure a P1 and a temperature T1. I would like to take it to another state with pressure P2 temperature T2, now how do I propose to proceed? Suppose I would like to plot the changes on a P-T curve, right? So here what do I have? I have one particular gas at P1 T1, right?

I would like to take it to P2 T2 state, what are the different ways by which I can perform this particular process? One is I can perform an isobaric process initially, okay where I go from P1

T1 to P1 T2 and then I follow an isothermal process. This I can indefinitely do for this particular process initially I have performed, the initial process was isobaric, so for this particular process I can write this down as del h del P dp this has to evaluated at T equals to T1 this integration will be from P1 to P2 plus del h del T at dT this is at constant pressure, this is at P equals to P2 and this integration is going to be from T1 to T2.

This is one particular thing that I can do, what have I done for this particular part? Initially I have performed an isothermal compression from P1 to P2 at temperature T1 and then I have performed an isobaric heating from T1 to T2 at pressure P2, right? On the contrary there is one other thing that I can in this particular case. I can first perform the isothermal process and then I can perform the isobaric process very well. Since at both these points I am dealing with properties which are dependent on the initial and final states as you already know so hardly it should matter in this case.

For this particular case what is my h2 minus h1 equals to? In this particular case initially I am going to write T1 to T2 del h del T at constant P equals to P1 into dT plus integral P1 to P2 del h del P at constant T equals to T2 dp, right? So therefore I can either perform it by this process or I perform it by this process, normally it should hardly matter, okay but let us see from the practical point of view which particular process we should be or rather we should be opting for.

Now tell me what is del h del T at P equals to P1? This should be something like this should refer to Cp at P1 which should be equal to del h del T at P equals to P1 and for this particular case what do I need? For this particular case I need Cp, I need information on Cp at P2 and in order to find these 2 properties, what do I need? I just need if you would recollect I simply need the PVT behavior of the gases and this I need for sorry I have made a mistake in this particular case this is not here, for this case I will be needing this one is equal to Cp at P2 sorry.

So therefore we find, in order to find this particular integration and this particular integration for these 2 integrations I just need the PVT behavior of gases, right? I need to find out how h varies with P at T1, for this case I need to find out how h varies with P at T2, right? But from the practical point of view we know that Cp data are available for ideal gases only, Cp data are not available for or rather they are much rarer and much less accurate for higher pressures, right?

So therefore usually at low pressure Cp data are available. So therefore from practical considerations we would neither prefer this particular process nor we would prefer this particular process, from practical considerations what are we going to prefer? We are going to prefer I will select a separate colour for your convenience. We shall be preferring, we would like to come down to pressure P equals to 0 when at P equals to 0 we would like to perform the change in temperature and then from here we would like to go to P2 T2.

So the process which we would prefer in this particular case, that particular process is we would prefer to undergo an isothermal expansion of the gas from P1 T1 to P equals to 0. At this P equals to 0 where the gas behaves as an ideal gas we would like to bring about the change in temperature and then once the change in temperature is affected at the low-pressure then from this P equals to 0 we would like to go to P2 T2, right?

So this is the practical path which we are going to adopt. We neither adopt this path nor we adopt this path also normally just we would have felt that it hardly matters we can take up any path but normally but under practical considerations we would prefer this path. So for this path suppose I would like to write h2 minus h1 for this particular path equals to, let us see what should be the h2 minus h1 for this particular path?

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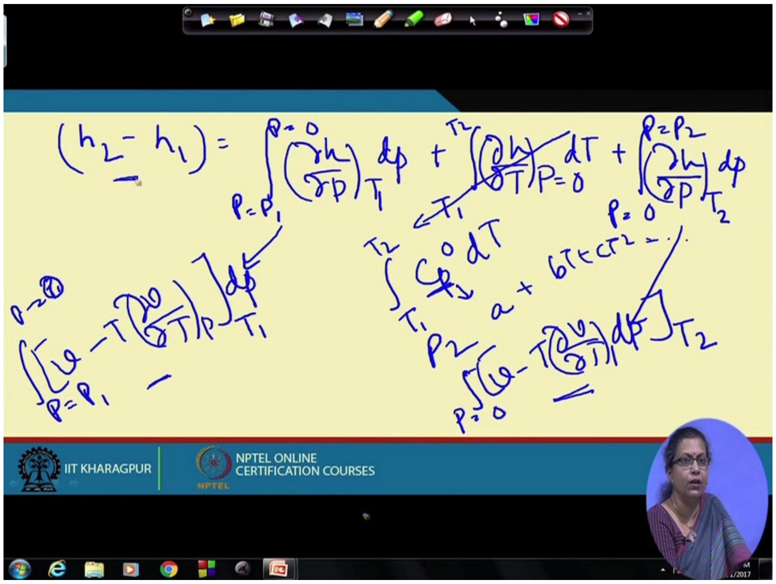

$$(h_2 - h_1) = \int_{P=P_1}^{P=0} \left(\frac{\partial h}{\partial p}\right)_{T_1} dp + \int_{T_1}^{T_2} \left(\frac{\partial h}{\partial T}\right)_{P=0} dT + \int_{P=0}^{P=P_2} \left(\frac{\partial h}{\partial p}\right)_{T_2} dp$$

$$\int_{P=P_1}^{P\to 0} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right]_{T_1} dp$$

$$\int_{T_1}^{T_2} C_p^0 \, dT \qquad a + bT + cT^2 + \ldots$$

$$\int_{P=0}^{P_2} \left[v - T\left(\frac{\partial v}{\partial T}\right) dp\right]_{T_2}$$

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For this particular path it is going to be the h2 minus h1 expression that should be equal to it should comprise of an isothermal expansion. So it is P equals to P1 to P equals to 0, this del h del p at constant T dp plus at this particular pressure at this p equals to 0 we would like to perform del h del T at constant P from T1 to T2 at P equals to 0 dT plus from P equals to 0 to P equals to P2 we would like to perform del h del P at constant T dp, isn't it?

So therefore this would be at T2, this would be at T1 and we know the value of this now, this is nothing but equal to integral T1 T2 Cp 0 dT and we all of us know that Cp is a unit function of dT, normally Cp 0 is given by a plus bT plus c(t) square plus so on and so forth. So therefore we can find out Cp 0 as a function of T and you can use that data for due to which we had devised the roundabout path in bringing about the change of this state from P1 T1 to P2 T2.

So now if I complete this particular equation, so what do I get? I find that this will be equal to this amount this is nothing but equals to v minus T del v del T at constant P this whole thing integral P equals to P1 to P equals to P almost 0 dp and this particular path that also comprises to the same term del v del T a constant p dp but in this case this is from p equals to 0 to p equals to Pt this here we have supposed to evaluate it at T2, here we are supposed to evaluate it at T1, right?

So therefore for this particular case what we have done actually? This particular case we have devised a path in order to use Cp0 and other than the data on Cp0 we find that we just need data on the PVT Behavior of gases which tell us how volume is going to vary with temperature at the constant pressure. Once we have an idea regarding the PVT Behavior of the gases we are able to calculate these 2 terms and we can find out h2 minus h1 for any change of state from any initial state T1 P1 to any final state T2 P2. We will continue with our discussions in the next class on this particular thermodynamic estimation of properties, have a good day.