Indian Institute of Technology Madras

NPTEL

National Programme on Technology Enhanced Learning

Thermodynamics and the Chemical Industry

by

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Lecture 6

Properties of pure substances

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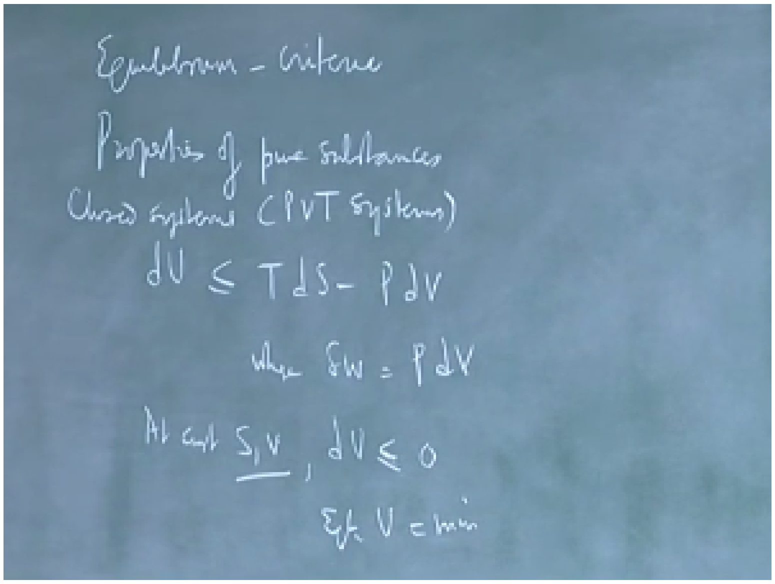

Equilibrium - Criteria

Properties of pure substances

Closed systems (PVT systems)

$dU \le TdS - PdV$

where $\delta W = PdV$

At const $\underline{S, V}$, $dU \le 0$

Eq. $U = \min$

Let us start with the same equations start with closed systems where I have taken $\delta W = PdV$ they told you in some of the newer books will be $\delta Q + \delta W$ but in that case δW will be $-PdV$ but I have taken PvT systems closed systems we say call these PvT systems which had of greatest interest in chemical engineering.

So if you write this down so you get automatically at constant S and V dU is ≤ 0 that means you can only decrease so the equilibrium criteria therefore U = minima but this constrained is important that constant S and V to internal energy has to be a minima if it reaches a minimum then you have equilibrium the reason I did not start off with equilibrium is notice that there are only two variables in a pure component system that you can hold constant so if S and V are constant.

U is automatically fix so this is not a manful criterion when it comes to pure substances when it comes to mixture it is very important criteria so only in multi - component systems with this certain will be actually used but formally I will complete this you can see similarly.

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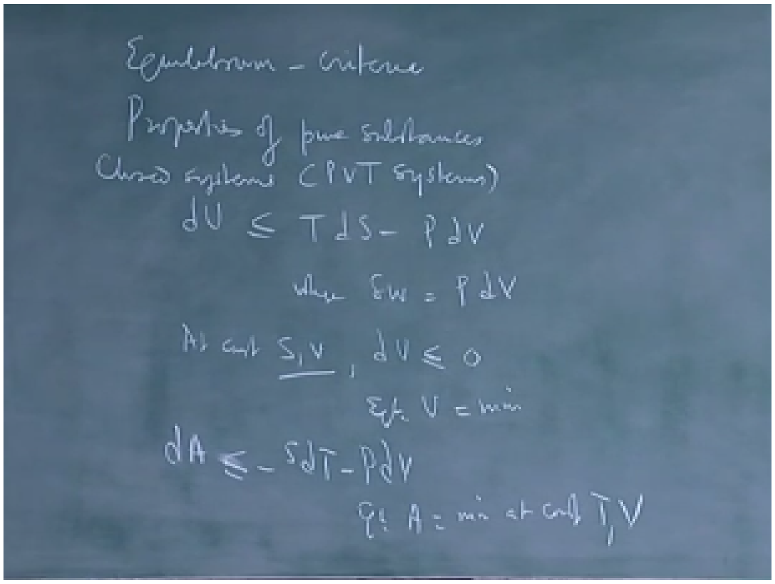

Equilibrium - criteria

Properties of pure substances

Closed systems (PVT systems)

$dU \le TdS - PdV$

where $\delta W = PdV$

At const $\underline{S, V}$, $dU \le 0$

Eq. U = min

$dA \le -SdT - PdV$

Eq: A = min at const T, V

If I now subtract if I rewrite this as dA A is U – TS, so I will have dU- TS is ≤ this – dFTS so you will get dA≤ - SdP - Pdv and consequently you get the result that A = minimum at constant T and V which is obviously a much more useful criteria of equilibrium whereas most of the chemistry experiments you will be working at constant temperature in the laboratory and at constant volume.

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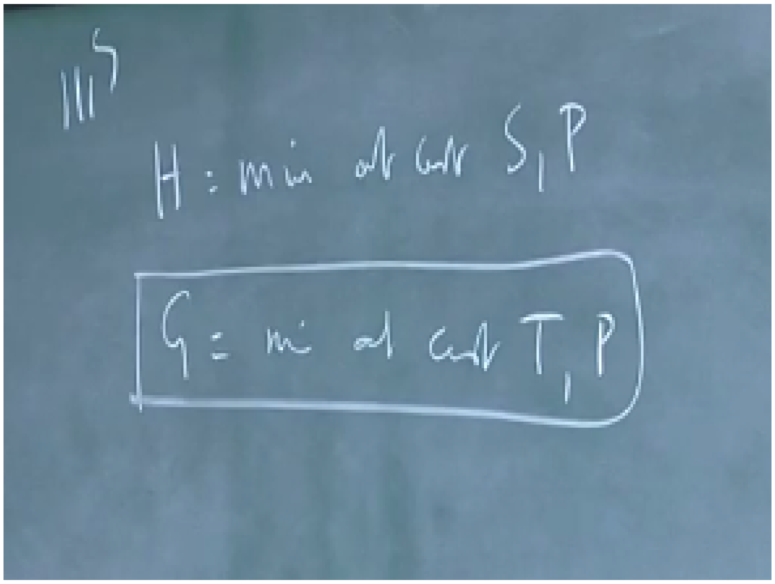

H : min at cnst S, P

G = min at cnst T, P

And for a close system again similarly H is a minimum remember H is U – PV so I subtract of dF I add U+ PV is H so I add dF PV which means I will get TdS + VdP therefore H is a minimum at constant S and P and simply say similar value and then G is a minimum at constant T and P so these two are the most important criteria of equilibrium that G being you get the same result these are all reddened expressions.

Because you know U and S are independent the rest are just combinations of variables but it just convent in calculus to everything at constant T and P it also relates directly to industrial process which are carried out constant T and P the whole process does not have to be as far as I am concern the industry is a black box something goes in at T and P come out of the same T and P so if the envelope is completely dark you know nothing about it what goes in at T and P and the other is at the same T and P then I have a process at constant T and P for which I can calculate when equilibrium is reached.

So if the product happens to be the product streams happen to be in equilibrium according to my criteria I know I cannot do better than that in the process we will do that in great deal after we do mixtures to began with I will discuss properties of pure substances we will discuss work calculations form properties.

In most systems that do work mechanical work particularly your are not dealing with mixtures then we will go on to mixtures go back to work and calculate separation work and also calculate the equilibrium criteria's.

So we will start off with properties of pure substances now so it is really there are only two sets of conclusions that you draw from thermodynamics one is about work the other is about equilibrium exactly two set of conclusions and I will show you very general forms of equilibrium expressions which you can use in any situation in fact after a while you find if you go to the literature they will simply write down the equilibrium criteria.

Write down an expression in terms of partial differential equations which after a about a month or two of familiarity you will also write down everything will always be of the same all the expressions will be in the same form except there will be a characteristic enthalpy change there will be characteristic volume change which you will be able to guess after a while simply a matter of almost a matter of familiarity but you can derive these regress.

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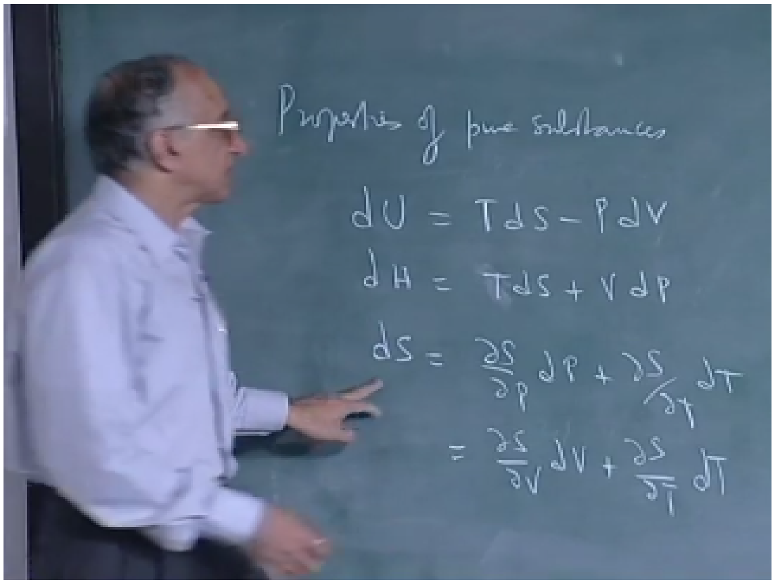

So you have dU – TdS – PdV you might say this equation is valid for a reversible process but now I am looking at changes of state from one equilibrium state to other state so I do not care what the process is and only want to know what the changes in U how the changes in US changes in SN changes in we are related now I have a choice here let me write the equations down all that in the sorry dTS + VdP so I told you I have a choice of P and T ir V and T as variables.

And I want to choose the variables I will look at this equations so I have dS I have to write an equations for S is going to be partial a ways with respect to P dP + partial of S with respect to dT it is also equal to partial of S with respect to V dV, I can use either of these criteria either of these equations for dS and then substituted back here, if you look at the enthalpy since P is already chosen as variable expression for enthalpy becomes.

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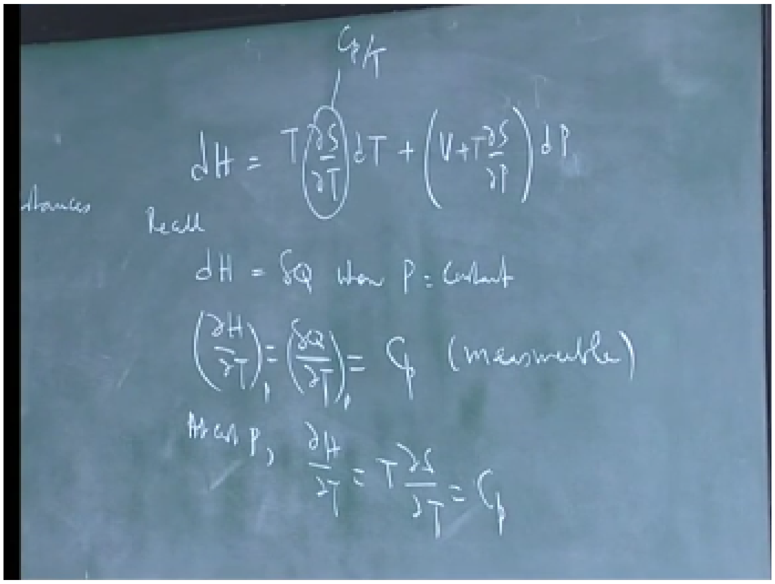

C_p/T

$$dH = T\left(\frac{\partial S}{\partial T}\right)dT + \left(V + T\frac{\partial S}{\partial P}\right)dP$$

Recall

$dH = \delta Q$ when P = constant

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\delta Q}{\partial T}\right)_p = C_p \text{ (measurable)}$$

At const P, $\frac{\partial H}{\partial T} = T\frac{\partial S}{\partial T} = C_p$

For change in enthalpy is simply T partial of S with respect to tdT + and we have tend to some variables so already familiar with I just go through it say recall dH = δQ when P = constant so when you hold one of the variables constant here, in a close system then you know the original equation is dU = δQ – δw so δQ becomes = dH and therefore this is no longer independent this is no longer dependent on the path it is independent, so I can define rates I can add heat system it is temperature change.

And I can ask what is δH / δT δQ / QT this we define as CP at constant P one of the earliest people who measured a large number of properties very accurately actually got an noble prize not for measuring properties scamarling owners I do not know if the know the name 18502 and in early 19 lived quite I think 1920 or 30 but the carmerling owners laboratory in Europe in Netherlands was a place in the 50s and 60s if an American thermodynamics is or a transport.

Okay was measuring transport properties and visited camerling owners laboratory and he was not concerned a goof scientist and sort of place of for property measurement you have to turn up there just call the coldest laboratory camerling owners himself was given the Nobel prize for liquefying helium we got one of the earliest Nobel prize in this work that sketch chart became proof very early and we will get back here, so the specific heat is define this way.

Notice this is measurable this is measurable and therefore this is measurable so the important thing about the specific heats is their measurable everything that is measurable has a special value in thermodynamics and they fit appears on the right hand side do not write and simplify the equations further actually similarly the others I can write down partial of view with respect to T at constant V this is called CV this is δV normally you would not be able to divide the heat.

Exchange by temperature in differential and data property because heat itself is dependent on the path but if you constraint the process suitably you can get functions of state changes in the functions of state an deifier you get properties another property that is important and I would not define it here is called C sub Σ which is measured along the saturation lien if you have liquid and vapor and equilibrium.

And you would change the temperature by dT keeping the vapor and liquid in equilibrium the heat that is added is measurable and then you get what is called C Σ it is a very easy measurement and therefore it is very attractive it is related to C PV we will relate it little later but right now we use this CP CV has measurable quantities so let us take this alone right now sort of the whole things is so rodent I can do it in 150 ways there is no pint doing it on those ways unless you need it.

So if this is true and notice at constant you have this equation at constant p you also have $\delta H / \delta T = T \delta S / \delta T$ at constant p this term vanish so this is = to TdS in first order differentials work like this when I differentiate the left hand side with respect to T if there is a differential here I can simply divide it by you can do algebra of first order differentials second order you cannot do the same thing, but anyway so this is equal to C_p so $\partial S/$ sorry, $\partial S/\partial T$ is simply equal to C_p so this part this is Cp/T sorry, $\partial S/\partial T$ is Cp/T then I need $\partial S/\partial P$.

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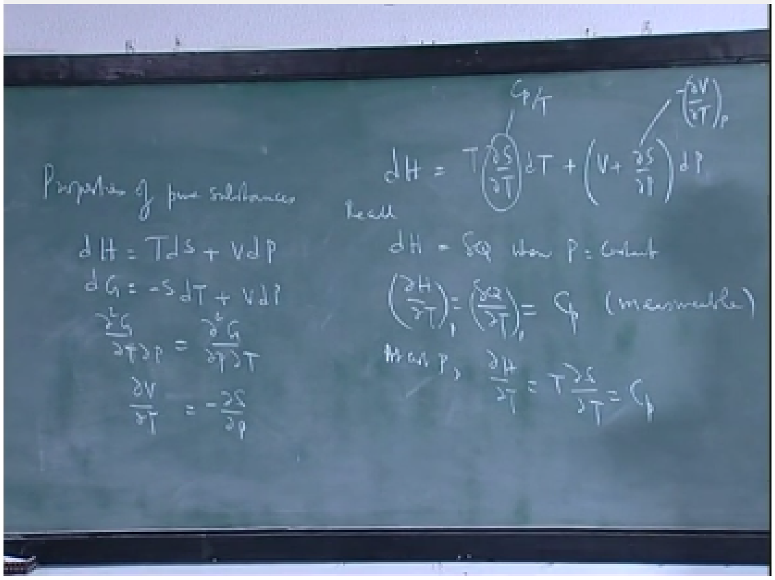

Properties of pure substances

$dH = TdS + VdP$

$dG = -SdT + VdP$

$\frac{\partial^2 G}{\partial T \partial P} = \frac{\partial^2 G}{\partial P \partial T}$

$\frac{\partial V}{\partial T} = -\frac{\partial S}{\partial P}$

$dH = T\overset{C_p/T}{\left(\frac{\partial S}{\partial T}\right)} dT + \left(V + \overset{-\left(\frac{\partial V}{\partial T}\right)_P}{\frac{\partial S}{\partial P}}\right) dP$

Recall

$dH = \delta Q$ when $P =$ Constant

$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\delta Q}{\partial T}\right)_P = C_p$ (measurable)

At const P, $\frac{\partial H}{\partial T} = T\frac{\partial S}{\partial T} = C_p$

So you know how these things are done and I have to go to S with respect to P I should get dT+, I have dG you just have to jungle these around and if you look at second partial if G is a continuous function of T and P the second partial of G with respect to T and P is the same as the second partial of P and T, this is true only if G is a smooth function I means all the derivates but be defined the first order derivative must be continuous function should be differentiable and so on.

These are generally true actually these relation, some of these relationships break down at the critical point there is a singularity at the critical point but the singularity is circular so the critical point mostly chemical engineers work for interpolation they will get 2.1° from this side of the critical point get 2.1° on the other side and then do everything by empirical interpolation the answers turn out if you write.

But the critical point itself is a very, very big point of theoretical interest right, I think there is a physics of fluids is a very prestigious journal 1963 or something edition, it was called the critical edition discuss the whole it is thicker volume only discussing the critical point if some of you are interested you should read is a paper by Fisser which is famous all about the singularity that singularity gives you a lot of information about structure but we will go off into a lot of physics.

But if you are interested, so if I do this differentiation with respect to P first I get V, so this is simply V if I do the second differentiation I get partial of V with respect to T, and here you get partial of S with respect to P so these are your famous Maxwell equations you do not have to write all of them down you got eight variables three choice of variables that is you can differentiate with respect to any two in your order, so you got you will have, you have to choose this G,T and P so 3 out of 8 variables.

So 8 see 3 possibilities and if you want to be very perverse you can do 8P3 because you even turn them upside down and so on and you will get any number of Maxwell relations. All of which is meaningless you should only derive those that you need for example, S with respect to P is not a measurable quantity but V with respect to T is therefore this becomes indirectly measurable my only aim is to get measurable quantities on the right hand side.

So I have S with respect to P I will now replace it by –V with respect to T, you notice when I do the differentiation with T P is constant so automatically P here is constant. Notice if you got V with respect to T at constant S that is not necessarily measurable but this is measurable, okay PVT are considered measurable so all the derivatives are considered measurable, so I have two equations.

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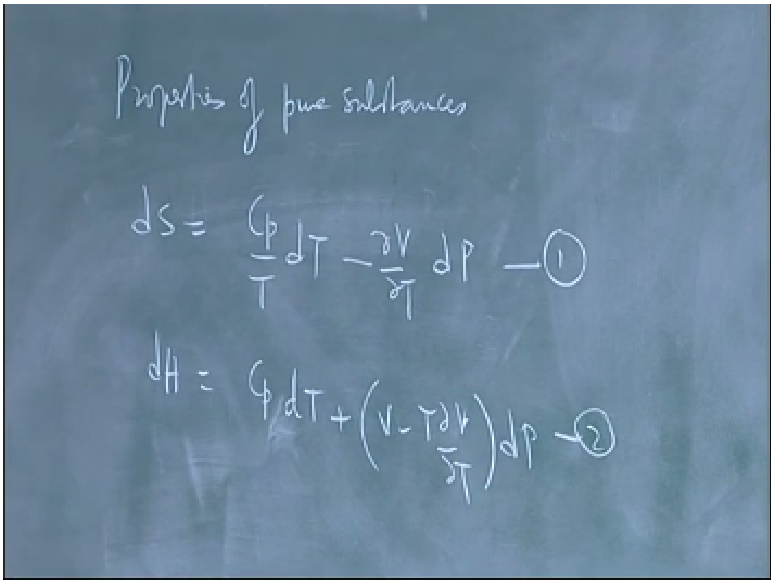

Properties of pure substances

$$dS = \frac{C_p}{T} dT - \frac{\partial V}{\partial T} dP \quad ①$$

$$dH = C_p dT + \left(V - T\frac{\partial V}{\partial T}\right) dP \quad ②$$

One is an equation for S which says dS=Cp/T dT+S with respect to P which is the same as V with respect to T dP, I would not bother to write P constant here it is sort of from the context which understood and you can go back and put it down. then dH=Cp/T I am sorry CpdT+(V-T) partial of V with respect to T dP, so these are the two equations that I have to integrate. Thus I am interested in calculating H any two variables U and S if P and T are the variables which is more convenient to calculate H and S. So this is my equation 1, this is my equation 2 I want to integrate these two equations.

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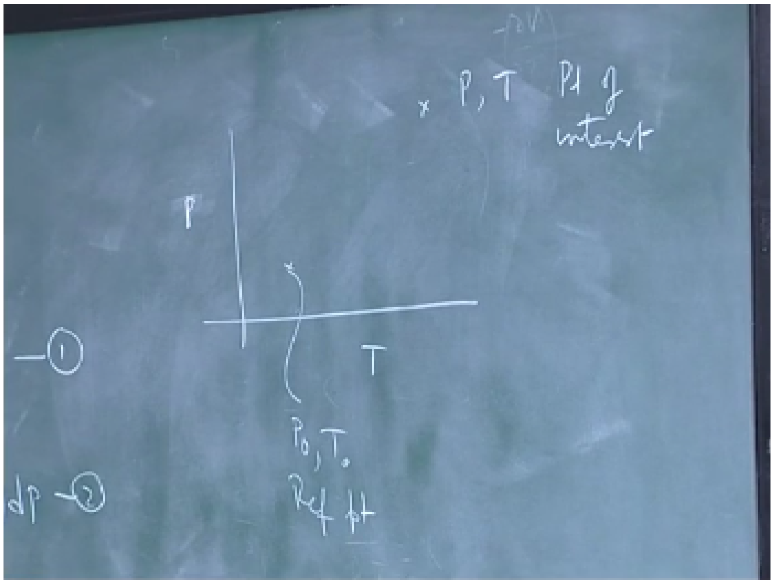

Now I have further choices it simply because there is a redundancy if let us says this P and T, I have to integrate from point 1 to point 2 I have to integrate from P1T1 to P2T2. Let us consider some reference point which will be P0T0 reference point I can choose my reference point as a please because I will integrate from P0T0 to PT and tabulated and you are not suppose to I can assign any values at P0T0 but you do not worry about that value because you will always take differences, you never take absolute values in classical integrate.

So I start from here I want to get some point PT which is I am interest, so since civilized integration requires that you do not go through some path like this you will get the same answer but if your provisos you can chose a path like that and then see how to integrate over it since we have not difficult days without being powers we will chose straight line person this diagram either this way or this way.

Anyway this is better to decide at one sign for all how you are go in to the integrations because their entirely arbitrary you must chose one that based on convenience. So let us call this path a, this is path b along we have look at what information you need in order to do the integrations.

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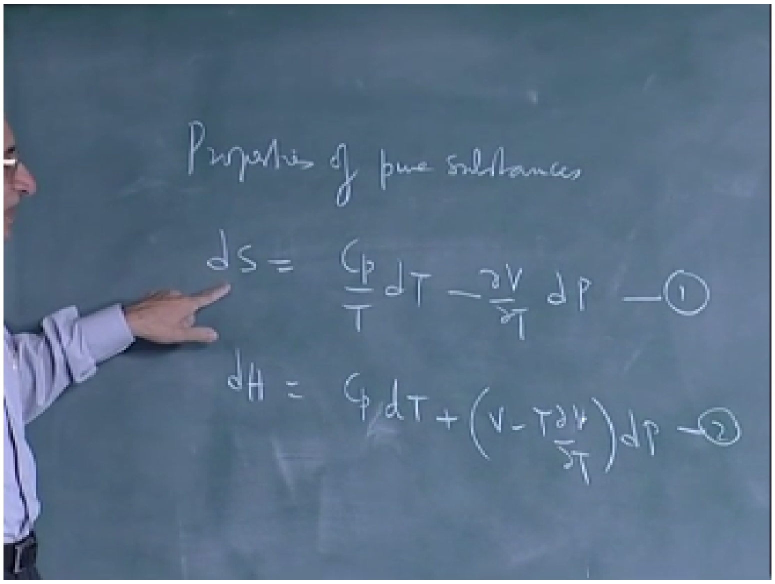

If you look at let us take a look at the enthalpy equation or given it is a very similar enter up any way enthalpy equation requires that you have CP information at constant p if I follow this path I need cp at p0 in order to get this point intermediate point because I am doing that integration at constant pressure at constant pressure if you look at this term will vanish I need only cp okay, then after I turn it is constant temperature so this term will disappear I need pvt I formation here and call it equation state at t by equation state I means measurements of pv and t and automatically all they are derivatives, this one is equation of state or pvt all our equation state are practically empirical.

You can derive them also from molecular theory but you will have to have an empirical input in terms of what they inter molecule potential is given the potential I can calculate this. So this is what I need along this path along this path you need equation state at t0 and then here I need cp information cp at p and this is where my choice of reference state comes in if I chose my p0 to be low enough I know all substances behave ideally so if I shoes this to be low enough what I need a cp at p 0 this is actually cp for an ideal gas.

If p0 is chosen sufficiently low in particular and simply chosen p0 = 0 very often you chose p0 = 1 because to 1 atmosphere gas is behave ideally but where is earlier old systems is used one psia one pound per squaring absolute. So it does not matter but nowadays the normal chats are prepared with choosing p0 = 0 very often and then t0 can be chosen at as any temperature as long as you go to sufficiently low pressure you will get the gas phase and you will get ideal behavior.

So the advantage here is that if you go back here you look at this information this is 0 for an ideal gas right you know this already, if this is 0 then h is function only of t cp becomes a function only of t if cp is a function only t we often denote the cp as cp 0 for an ideal gas it is not only a function of t.

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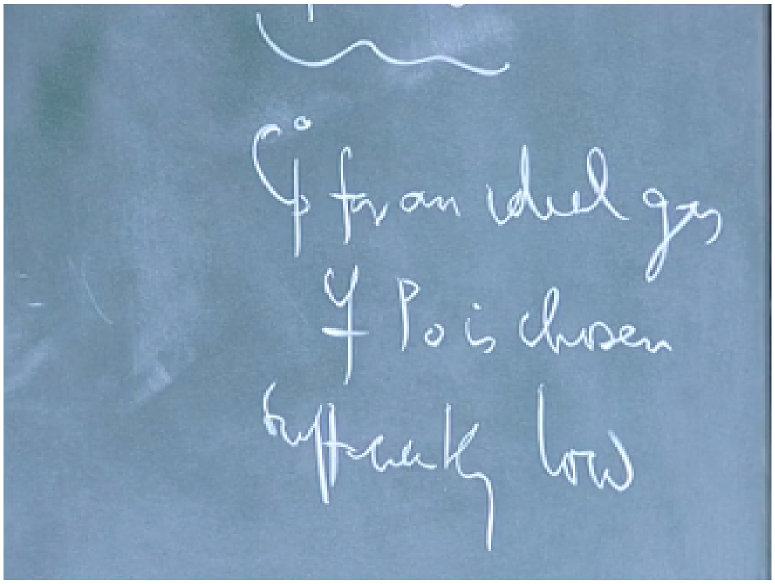

C_p^0 for an ideal gas
If P_0 is chosen
sufficiently low

You can actually calculate cp 0 from you can get it from two sources one is spectroscopic data you can measure for low pressure gases you can measure this specific heat from spectroscopic I formation you can get the values.

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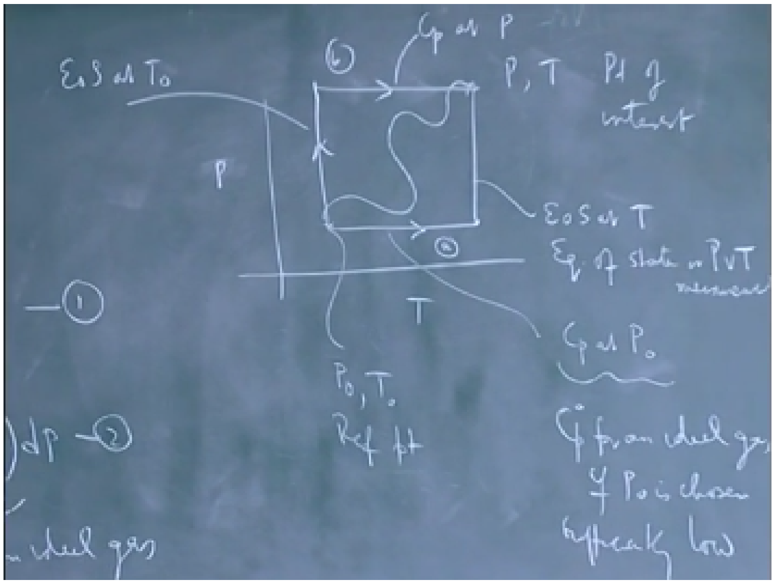

The other thing is you can actually calculated from molecular theory, so fundamentally you have two sources for cp 0 other than direct experimental measurement of cp, whereas on this side this cp is no longer a function of t alone it depends on the conditions as a gas so here I need more information then here the experimental information is the hardest to get, so you simply chose the path where less experimental information as good.

So we will always chose path a simply a matter of convenience all text books that report data all tables prepared by doing the integrations along this path because how we are complicated a molecule I can get cp 0 information, for that molecule as an ideal gas so I can always go up to the temperature of interest then I can do this integration of course this temperature will vary, so you really need data at all temperatures that is different matter here again that is also true of these lines right you can go on here you right vary this at all pressures because pressure of interest is not fixed.

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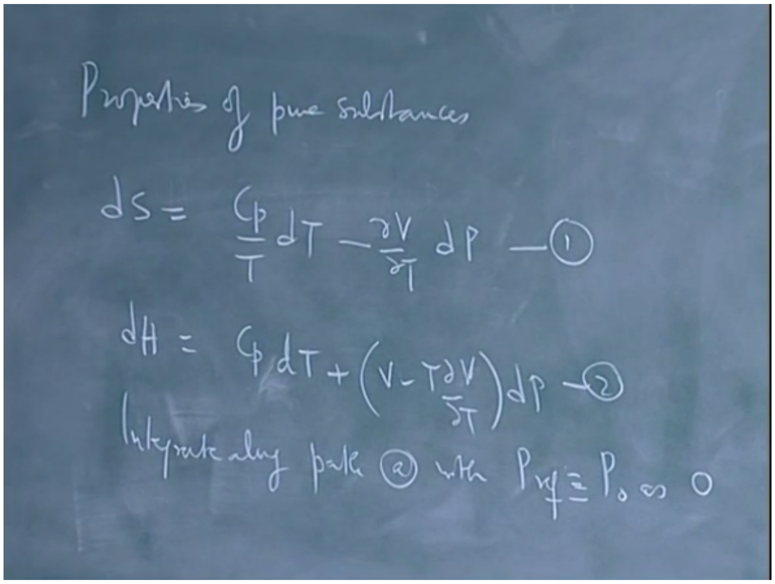

Properties of pure substances

$$dS = \frac{C_p}{T} dT - \frac{\partial V}{\partial T} dP \quad — ①$$

$$dH = C_p dT + \left(V - T\frac{\partial V}{\partial T}\right) dP \quad — ②$$

Integrate along path ⓐ with $P_{ref} \equiv P_0$ as 0

So what we will do is so will settle for integration along A path A with P reference you often write as P_0 as 0 in some books they will say one about the pressure is low enough if it is one atmosphere or one psa anything less than 1 atmosphere it is completely ideal but you have to be careful when you used to tables if one follow users one reference point the another fallow uses the other reference point we have to make the conversion.

It is prevail it is simply book-keeping so there is no point telling you 1000 time but if you make mistakes you will get -1 but anyway every number that you copy wrongly from the chart but anyway this is what we do if we do this let us look at integral of H.

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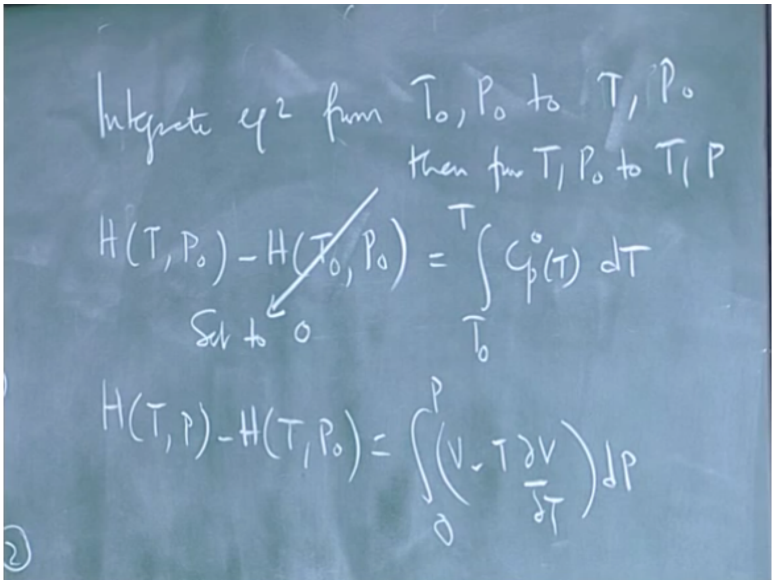

Integrate eq 2 from T_0, P_0 to T, P_0

then from T, P_0 to T, P

$$H(T,P_0) - \cancel{H(T_0,P_0)} = \int_{T_0}^{T} C_p^{\circ}(T)\, dT$$

Set to 0

$$H(T,P) - H(T,P_0) = \int_{0}^{P} \left(V - T\frac{\partial V}{\partial T}\right) dP$$

②

So I am doing this calculation H from or I will write will do equation 2 first integrate equation 2, from T_0 P_0 to T,P to agreed we did first do it at P_0 so you will get H of T, P_0 I am integrating from T0 to first I will do this as T, P_0 then T, P_0 to T,P two steps so if I am integrating this equation at constant P_0 $P=P_0$ this term will vanish I am doing this integration so simply integral C P_0 dt from T_0 to T sorry, I am doing it at constant P_0 correct.

C P0 is not constant it is a function of temperature in depth known it is assumed to be known if you want I will write C P_0 of (T) dT, then I have H of T, P- H of T,P_0 now I am integrating from P_0 to P of this term.

So what I will do here is replace P_0 by 0 because P_0 is chosen sufficiently low so the gas is ideal so $V-T\partial v/\partial T$ is 0 from 0 to P_0 so integral 0 below that so I simply replace this by 0 and then I am going to choose this to be 0 choose or set to 0 that is why you have to be careful when you go from table to table in one table T_0 P_0 is different from P_0 to T_0 from another table so if that number is different then you have to add that number that on you want to calculate the if you want to compare the data from two tables.

Likely by now people have accepted the results can usually for example T_0 is that so R as possible chosen has the triple point of this substances pure substances is the triple point which is invariant so usually chose that data so these are the some conventions but they are not always followed because the corrections strived we just have to check the table.

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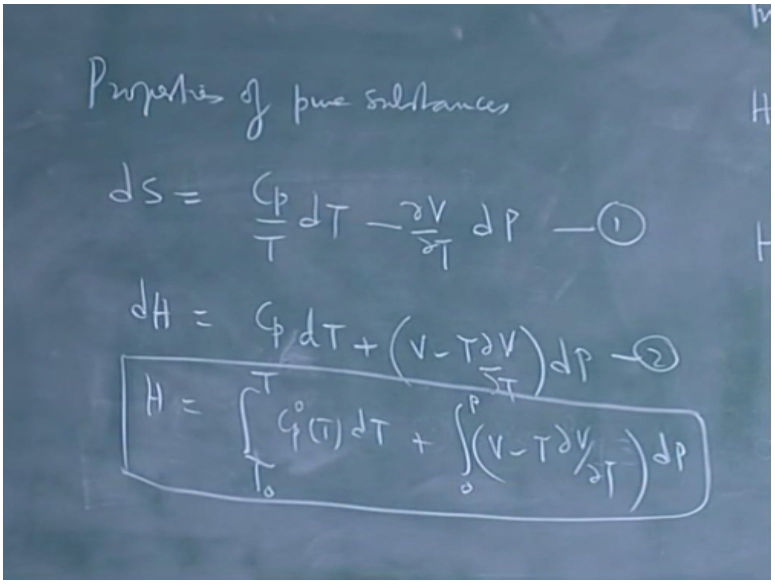

Properties of pure substances

$$dS = \frac{C_p}{T}\,dT - \frac{\partial V}{\partial T}\,dP \quad \text{— ①}$$

$$dH = C_p\,dT + \left(V - T\frac{\partial V}{\partial T}\right)dP \quad \text{— ②}$$

$$\boxed{H = \int_{T_0}^{T} C_p^{\circ}(T)\,dT + \int_{0}^{P}\left(V - T\,\partial V/\partial T\right)dP}$$

So finally you get one result the integral of this can be now written like this simply H=because it simply integral 0 to T C P_0 of T dt+ integral this is from T_0 to T_0 to P or V-T∂v/∂t so we would find any table or chart on top it will say H T_0, P_0 values will be given at 0,Pt^0 scale is equal to 0 so write on top of the table that one line will tell you what T0 P0 is it will write they will write their H at AT,0=0 those numbers represent T0 P0.

The chart also they will tell you the exactly at H=0 at this condition that is your reference condition now this is little tricky at integrate I will tell you the trivial thing is in this simply that V with respect T at low pressure will go as R/P, you have to integrate from P = 0, to P = P, r/dp will give you a log p. log p goes 0 as goes to – infinity as P goes to 0, so there is $1 - \infty$ there. So you have to work around it, the way you work around it is simply in thermodynamics is simply add r / p – r/P.

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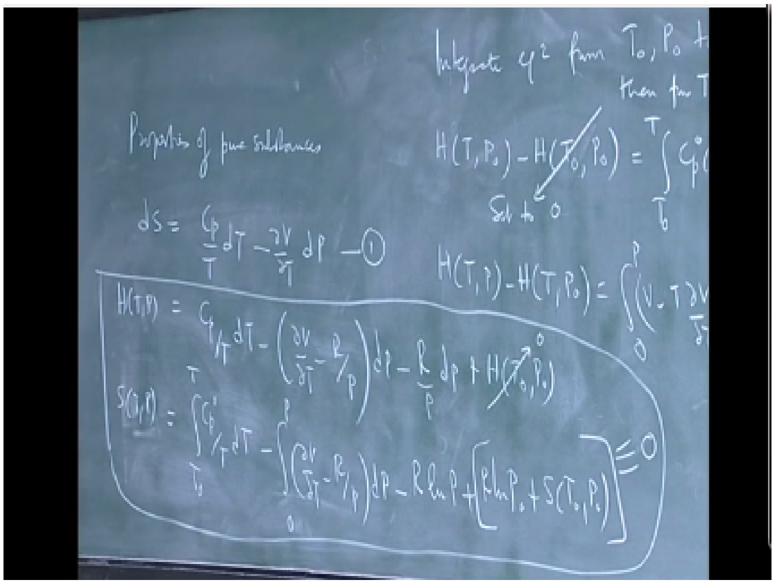

Properties of pure substances

$ds = \frac{C_p}{T} dT - \frac{\partial V}{\partial T} dP$ — ①

Integrate eq 2 from T_0, P_0 t

then for T

$H(T,P_0) - H(\cancel{T_0,P_0}) = \int_{T_0}^{T} C_p^0 ($

Set to 0

$H(T,P) - H(T,P_0) = \int_0^P \left(V - T\frac{\partial V}{\partial T}\right.$

$H(T,P) = C_p/T\, dT - \left(\frac{\partial V}{\partial T} - R/P\right) dP - \frac{R}{P} dP + H(\cancel{T_0,P_0})\overset{0}{}$

$S(T,P) = \int_{T_0}^{T} C_p^0/T\, dT - \int_0^P \left(\frac{\partial V}{\partial T} - R/P\right) dP - R\ln P + \left[R\ln P_0 + S(T_0,P_0)\right] = 0$

So you will get Cp / T and dp - ∂ v / ∂ T – R/P, d P – R/P d P. now we will do the same thing as we did there, you will get the following result S= you integrate Cp / T you simply get Cp 0/ T 0 to T and when you integrate this, you will still get the same result – P0 to P, actually P0 will remain 0 now. ∂ v / ∂ T – R/P, d P then you get this here which is – R log P + R log P + S at To, P0.

So you are integrating from T0, P0, so you will get this is S and Tp = we will start from S, T0, P0, at P0 you ∫ from T0 to T, you will get Cp/ T d T. the remaining you have to ∫ from P0 to P, as far as ∫ this is concerned replace P0 / 0 because 0 to P0 the gas is ideal, -∂ v / ∂ T – R/P, d P is 0, so that part of ∫ is 0, so I have simply added a 0 here. Then I ∫ this I get R log P – R log P0 right. I know there is a problem here because I am going to set P0 = P notice that this quantity in parenthesis, refers to entropy contribution at the reference condition.

The entire thing is at the reference condition, so instead of setting S at T0, P0 to 0, I will set this to 0, and it does not matter I calculate S difference between in entropy between 2 points and subtract of R, that same identical quantity from itself so it will cancel. If I take the limit of P0, going to 0 it will go to - ∞. So I avoid taking that limit and simply set this component = 0. This is clear, so on top of every chart there will be a chart that will give you thermo dynamics and tables, it will say h at 80 0 = 0.

S at 80 0 + R log P0 = 0, so they will not write S = 0, and does not matter because it is the same - ∞ that you are subtracting, you have to careful there are different kinds of ∞ and you cannot cancel ∞ unless they are identical ∞. According to George there are only 3 types of ∞ in fact he says he have not progress much as far as ∞ are concerned. We are at the same condition that they could count apparently only upto 3.

This is also we can count upto 3 ∞ we do not how to count for more ∞, so that is it this is basis of all charts, you have to careful if the P0 value that you take is different in 2 charts and that R log P different you have to count, if it is 0 every where it is no problem but if there is the number there and units are different than you have to careful about your choice. Normally the convention is to choose P is bars take T0 = 1.

In which case this will become 1 but 0 to1 is 0 anyway, so this can still remain 0 to P does not make any difference but this number you have to careful about when you are comparing two different charts. So this is the same chart you can blindly subtract, 99% of the time you will use the same chart, same table. So all this all that I am saying is no consequence but if you are taking data from 2 different tables please be careful.

So these are the two integrated equations, Hft is this so this is the basis of all your, if you like I will write here + hft, P0 inside this is 0.

So let us look at the chart of a substances, normally the chart that are used in you are used to PVT Diagrams but most useful thing is the pressure enthalpy diagram or the temperature entropy diagram the PS diagram is used very extensively by mechanic in it PH diagram is in many ways more useful for chemical in practice if you look at low pressure you are talking of really the ideal gas you are putting the enthalpy usually it is the choice, the choice is between one enteric variable and one extensive variable because, what you would like to do is to show how the faces differ in properties.

So if we have a liquid phase and the gas phase one of the properties will change, the pressure will remain the same for both but the enthalpy will be different and you can read the lateral heat by simply taking the enthalpy difference in the liquid and now these are prepared experimentally what I will do is draw the curves as they appear normally for more substances you get a liquid plus vapor region I will trace this regions what you do is trace isotherms, isotherms for like this is the typical element around the space this is temperature t1<tc critical temperature where is the critical temperature goes this t=tc then above the critical temperature.

Then normal qualitative diagram the one bar line may be somewhere here mostly indicated this is one atmosphere or one bar now most of charts come with the bar looking at this you can say what the lines look like on this diagram on this diagram they also have plots of constant s and then constant t I forgotten which is steam we will find out in a minute you can give qualitative arguments and find out which of them is I think V and S just on qualitative terms for example.

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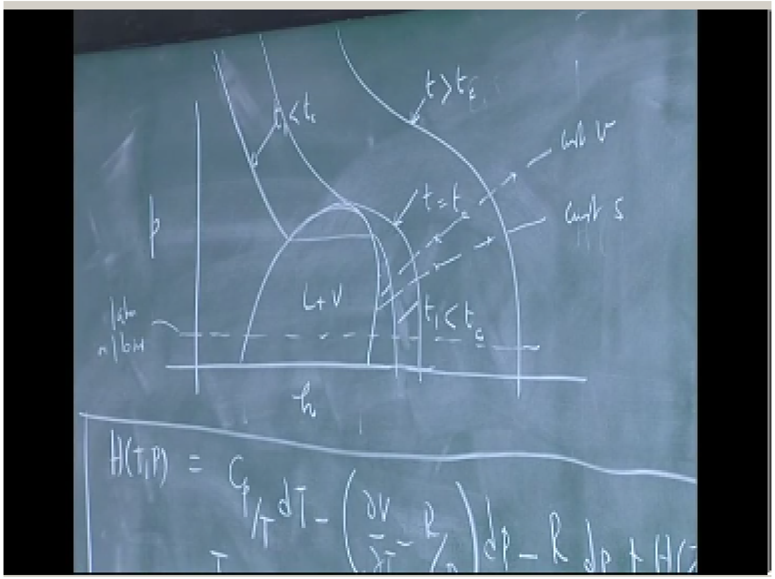

If I am looking at H and P you have I will go back to this differential equations dh=cpdt+v-trv/rt.dp you are looking at ph lines so I am always looking for ∂p/∂h to find out what the slope of the lines like easy you have to get ∂h/∂ I will do all this for unit mass so you will find in the charts they use small h in order to indicate specific enthalpy so if I do this I get partial of H with respect to p at constant t recently v-t∂v/∂t.

So if you look at isotherms at very high pressure they will have low value but, interesting thing is that low pressure ∂h/∂p is 0 or ∂p/∂h is ∞ we are looking at the inverse of the slope here so these lines have to be vertical when they come to sufficient low pressure here all these lines are vertical isotherms are vertical at low pressure now recently saying they ideal gases in the part enthalpy does not change with it pressure its function only at

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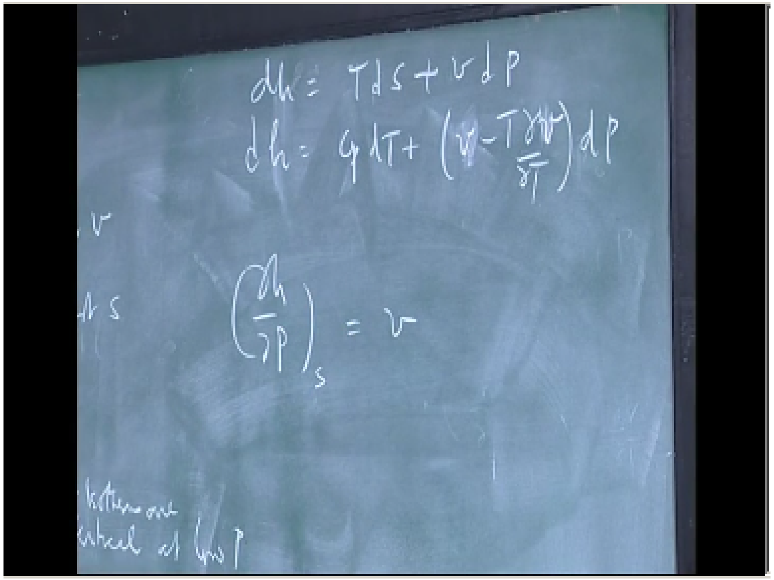

Now let us look at the is tropic and constant volume lines what I am interested in ∂h=cpdt+v-tr∂/rt.dp just write in small CP is specific for unit mass small v is for unit volume I want ∂h/∂p at constant s for that it is actually easier to go here in earlier one you get dh=tds+vdp so the constant h with respect to p at constant s will simply give me v so the isotropic lines the constant s lines have a slope =1/v by calculating ∂h/∂p this slope on this is ∂p/∂h so it is 1/Δ.

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