Indian Institute of Technology Madras

NPTEL

National Programme on Technology Enhanced Learning

Chemical Engineering Thermodynamics
By

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Lecture 7

The p- h chart

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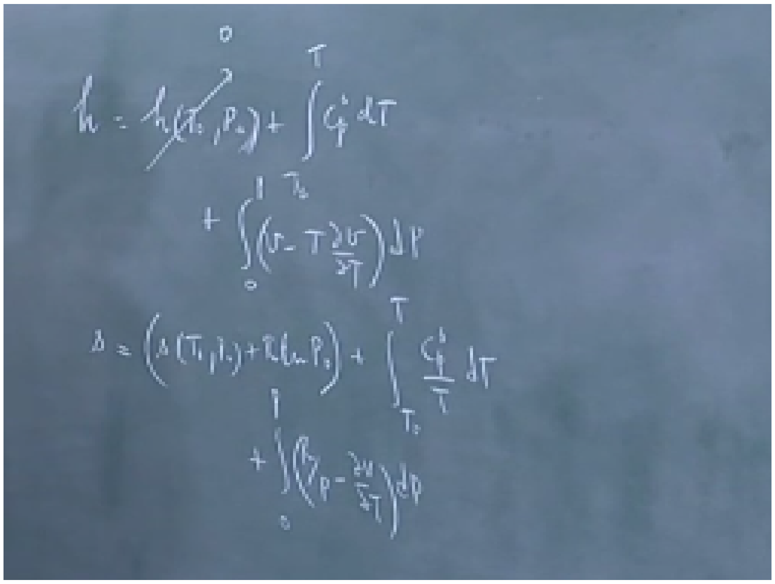

$$h = \cancel{h_0(T_0, P_0)}^{0} + \int_{T_0}^{T} c_p^{*}\, dT + \int_{0}^{P} \left(v - T\frac{\partial v}{\partial T}\right) dP$$

$$s = \left(s(T_0, P_0) + R\ln P_0\right) + \int_{T_0}^{T} \frac{c_p^{*}}{T}\, dT + \int_{0}^{P} \left(\frac{R}{P} - \frac{\partial v}{\partial T}\right) dP$$

Gain started we discussing thermodynamic properties I set this equal to 0 then entropy I have S of T_0 P_0 + sorry - so it is R/P - ∂V/ ∂T and it is a correct expression, you can check it out may be a + RL and P_0 – RL and P is that okay so these are the 2 expressions that we use and we started drawing the chart.

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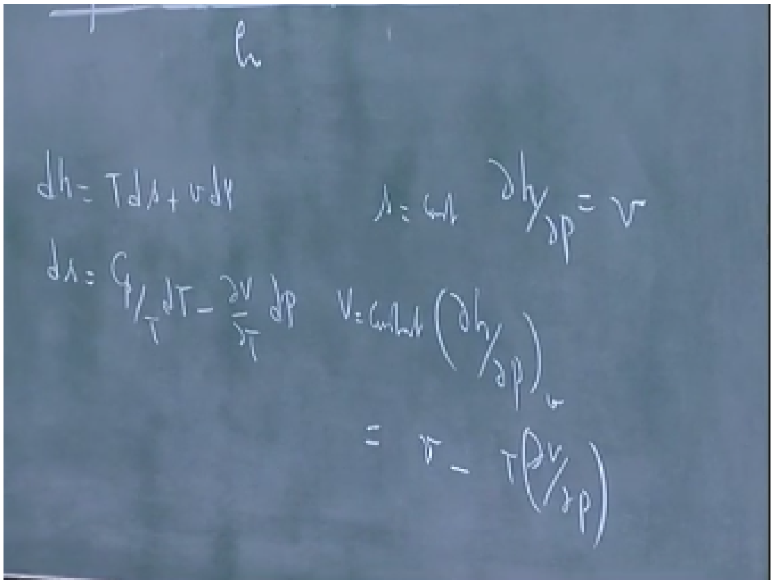

h

$dh = T\,ds + v\,dp$ $\quad s = \text{const} \quad \partial h/\partial p = v$

$ds = C_p/T\,dT - \frac{\partial v}{\partial T}\,dp \quad v = \text{constant} \left(\partial h/\partial p\right)_v$

$= v - T\left(\partial v/\partial p\right)$

If you plot enthalpy here it is usually one intensive variable on the Y axis and clearly the I say enthalpy clients are simply vertical lines and isobaric lines are like this question is what about the other line you looked at isotherms if you looked at isotherms if you look at isotherms write this has TdS + VdP dSS Cp/ TdT - ∂v with respective TdP if you look at isentropic lines for S = constant you get ∂h with respect to P remember ∂of h with respect to p is the inverse of the slope.

On this diagram this clearly = T h with respect to P at constant entropy this is sorry V okay then if you want V = constant you get ∂of h with respect to P at constant V and several ways of deriving it this is = ∂h with respect to P at constant S if you treat h is a function P and S you get dh = Tds + VdP so if you differentiating this with respect to P you get ∂h/ ∂P with respect to ∂h with respect to ∂P at constant S + this term + T ∂S/ ∂P at constant V.

This first term of course Vh with respect to P at constant S is V doing something now V + T∂S/ ∂P it is correct and to get dS S with respect to P I have to write S dT and VdP so S with respective P would be the second partial of a with respect to T and P and that is = the second partial of a with respect to T and P we get V with respect to T here is this correct so yeah at constant T.

V with respect to P is always negative and therefore this term is actually greater than ∂h/ ∂P at V we rewrite that in terms of measurable quantizes when I declared measurable quantities.

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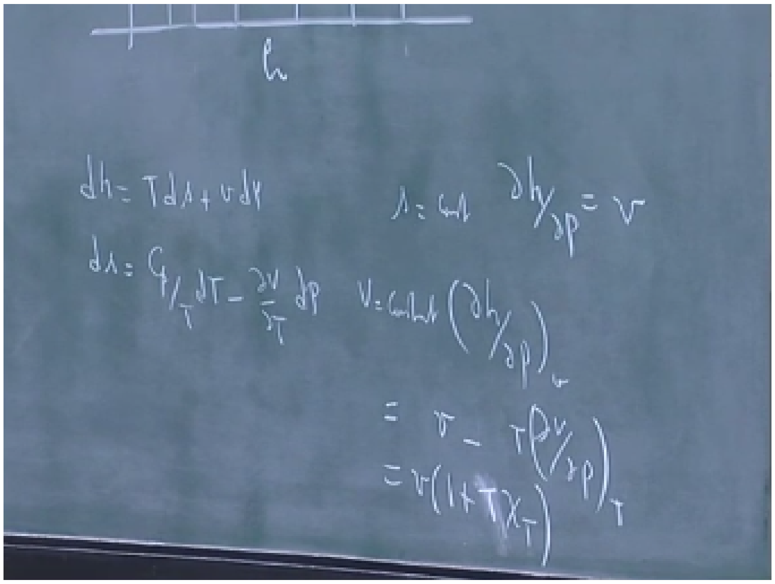

We said the caloric measurements give you Cp CV and Cσ I will discuss this later the other quantities are PV and t or will put capital T itself absolute temperature and then it is derivatives these are usually reported has 1/V ∂V/ ∂T this is the expansion coefficient and 1/ V∂V / ∂P since volume always decreases pressure increases – of it is a positive quantity so with the – this is called the constant T is called the isothermal compressibility.

And it so happens that the isothermal the isentropic compressibility are adiabatic compressibility reversible conditions this is adiabatic sometimes referred to has adiabatic should actually I should write isentropic this is of experimental importance because you can show that this is actually directly related to the velocity of sound measurements in a fluid velocity of sound they are relatively easy to measure compared to most thermodynamic properties so this an important property this is χ is a base I do not exactly remember what smith and vanes uses usually they use α for this expansion coefficient and this is β or χ.

Some book it is χ and some book so when I have ∂V with respect to P at constant temperature so this is actually simply – V times χ of T so this is = to V x 1+ χ.FT T times χFT T times χFT is dimension less actually it would have been nicer if people had defined that as the coefficient and you do not have to worry about dimensions right in practice χ FT is reported in degree K – 1 you multiply by T so most tables will give you degree K so first of all the isentropic lines when V = constant.

So let me write the slope of these lines apart from these measurable quantities the caloric measurable quantities will include enthalpy changes phases changes enthalpy changes during a phase transition it will come to that some more measurable quantities but these are fundamental once let me get back here and say the slope here.

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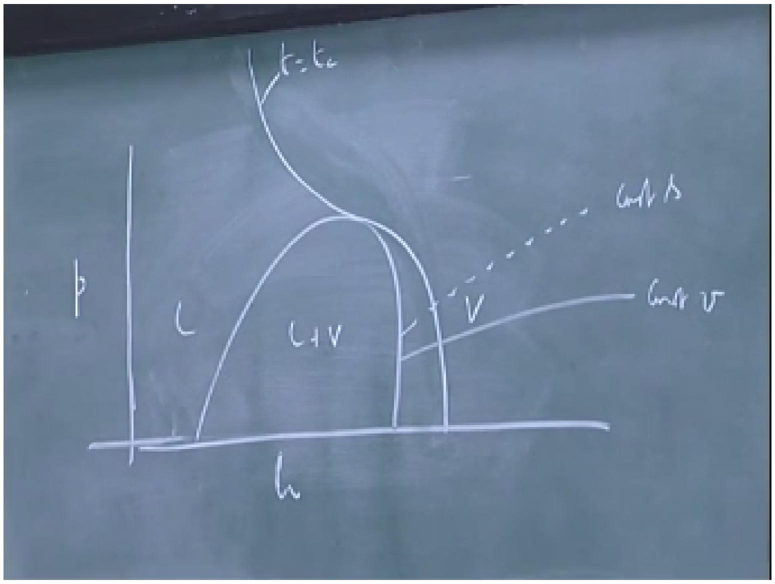

You are looking at $\partial P / \partial h$ at constant volume is simply 1/V and constant S and $\partial p / \partial h$ at constant volume is 1/v x 1+ T times χT so this slope on the p- h diagram is less than so the isentropic lines have a slope that is less than the isochoric lines so on this graph and draw this anticipation I am drawing some figures the graphs usually look like this the all thermodynamic diagrams.

Some exceptions like carbon dioxide come back to it later this is usually a liquid region a liquid + vapor region vapor region let us say I am looking at the vapor region for now, I am looking the vapor region we have already seen that isotherms would go like this or you should draw the critical isotherm and then 1 far away.

Okay this is t = tc above this is vapor actually technically this portion is called gas in this portion would be vapor between the gas and below the critical line that we would not make the distinction as far as property representation is concerned gas and vapor the equations have started the same things in but in this region this is the critical isotherm if I am looking it this region I am looking at slope of these curves.

First of all the slope here is always positive we can less the volume gets to be ∞ if you like I will write ≥ 0 in the slope here is < than this slope but it is also positive so it is always a positive slope line so one line could be like this the other line it will be of a higher slope so this is constant S lines this is constant V lines, so you get these lines isentropic lines and you got isothermals isentropic isochors then you have got the isobars which are horizontal and V. Isentropic lines which are vertical now I have essentially all the information you need.

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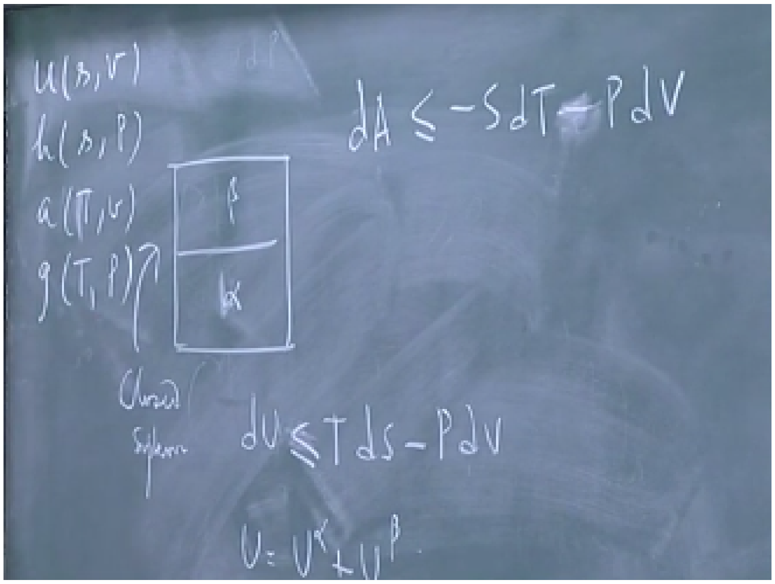

So if I am looking at work comparisons suppose I have a pure fluid I have an α phase and a β phase if I am if I write the two laws down I have TdS for a closed system PdS – PdV these equations are valid for a homogeneous phase so if I am writing a mix of two phases $U = U\alpha + U\beta$ simply the internal energy is some of the α phase internal energy + β energy.

So if I rewrite this I get dU α or I would like it actually for G it is more convened right it for G dG will be – SdT + Vd P write similarly for G also this is = dGα + dGβ I should write here is less than or equal to this is also ≤ this is – Sα dTα - S βdT β dG = this is ≤ + α dP α+Vβ dPβ we arwe actually written it for I am looking at this I am looking at the close system which is the sum of the two phases since I am looking at a close system.

I should I have started with A let me because basically what I have to do is put constrains on the system and ask when it goes equilibrium and the constrain I can put on closed system which contains two phases as you do not do any work that means I cannot be a volume change so the total volume should remain a constant if I want to impose a total volume constrain I should consider A is a natural function of T and V.

I am going to consider isothermal system with a constrain of V = constant total V so if I am considering T and P constant then dG is the natural variable, so let me come back and write this dA ≤ to – I can come to the same conclusion here but it is much nicer to do it with correct variables in we have choose a variables you may has well choose the natural once if you are doing adiabatic isothermal systems I am sorry not the adiabatic isothermal and adiabatic systems with pressure as a variable.

And you S and P has the natural variables you choose h it is the equations are simply U is a natural function of S and V h is a natural function of S and P a is a natural function of T and V and G is a natural function of T and P so we will use this as a thumb rule when ever depending on the variables depending on the constrains we have to impose in the system we will choose the independent variables.

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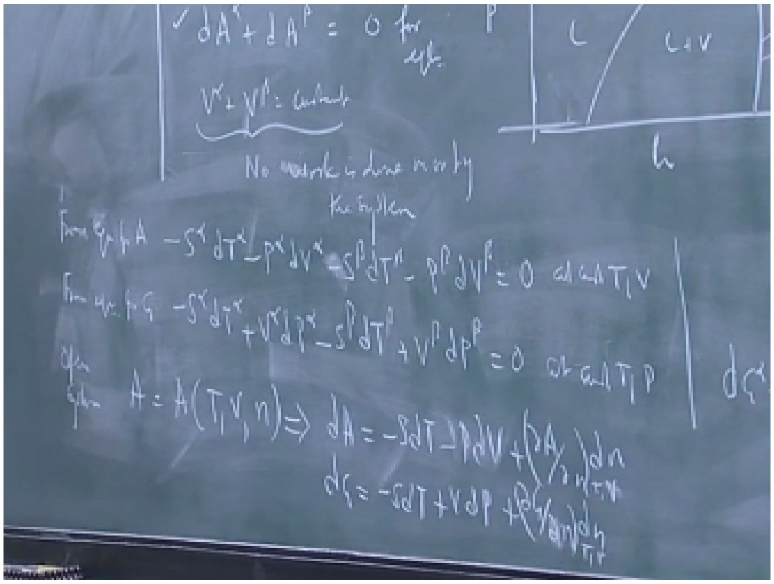

You can choose any two variables as far as pure systems are concern instantly that is purely empirical information we know from experience the given tow variables I can reproduce the state of a pure substance it is always empirical information at all levels so if I have this then I have dA α + dA β = 0 for equilibrium with V α Vβ = constant this comes from you lay the condition that no work is done on the system.

Is done on or by the questiuion itself is asked into those conditions if you keep on doing work on a system it is not going to at equilibrium so first is you stop interfering within it and then you ask when does it reach this is a closed system but if you look at a for α phase alone this can exchange molecules with the β phase so not only is the temperature and the volume of the α phase is not only at the temperature in the volume of the α phase variable the extended α phase is also variable so I should first say A an open system of constant composition A is a function of not just T and V it is also a function of a number of moles.

If I keep the number of moles constant A this is a this is specific Helmholtz free energy it is a function of T and v specific volume but if you write it for the whole system which is what we are writing here I should have written this implies dA = ∂A with respect to T which will be – S because that ∂ is take holding V and N constant if you hold it and hold N constant your talking of a system of fixed number of molecules so this is still S dT there is still a – PdV can you differentiate with respect to V you get – P + A with respect to N dN.

Now if I write the same thing for G I get dG = - SdT + VdP + G with respective N dN notice this A with respective N is holding T and V constant G with respect to N has holding T and P constant I will write that out explicitly TP this is T, P.

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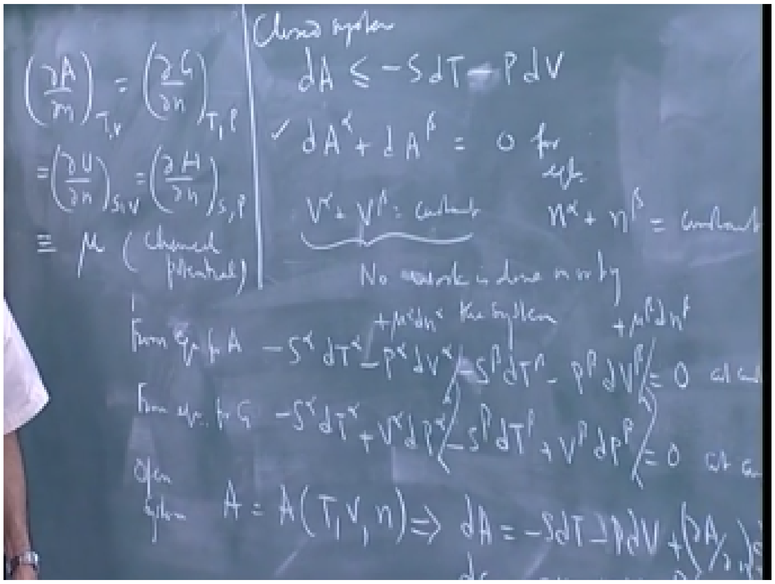

And by comparing these two you know G = A + TS so if you A + PV so if you differentiate dG + dFPV you get – SdT – PdV exactly so by this comparisons you know these two are the same ∂ way with respect to N at constant T and V = ∂G with respect to n at constant T and P the variables that you hold constant are in fact this is also = to ∂U with respect to n holding S and V constant is also equal to ∂ of H with respect to n holding S and P constant.

This is because this is a redundancy that we introduced U was the only independent quantity you introduced H A and GU and S where the independent quantities the others were introduced become combination this quantity came up again and again and for reasons that gives intuited it is called the chemical potential I will come back to it why it is called the chemical equation.

So when I write 3 lines say it is a definition so up to here I am right I need to add a term here form equation for A you get – S α dT α-PαdVα A is – S dT – PdV + μdn so I will have to add here + μ αdn α here I have to add + μβ dn β similarly here also I have add the same thing I will just put the arrow there so that term will have to be added to both those equations we have to re draw this I do not know when we are getting the full board. We have one more constrain because V α + V β is constant because the closed systems just like this is constant because on work is done.

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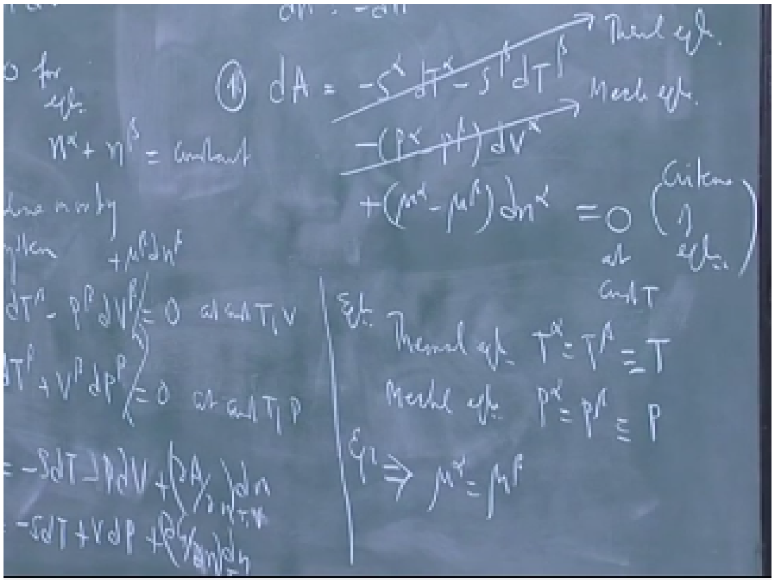

The system has a whole two phases together do nor exchange marked with the surroundings we are looking at a closed system therefore $n \alpha + n \beta$ has to be equal so in these equations $dV \alpha = -dV\beta$ $dn \alpha$ is $= -dn \beta$, so I have $dV \alpha = -dV \beta$ $dn \alpha = -dn \beta$ so I have $dA =$ for the whole system is $-S \alpha dT \alpha - S \beta dT \beta$ then $-P \alpha - P\beta$ into $dV\alpha - \mu\alpha - \mu\beta$ is $+ dn \alpha\beta$ this should be $= 0$ this is the criteria of the equilibrium.

The two laws combined will tell you dA is $\leq$ on the right hand side this is the which is $= 0$ at constant TnP at TnV at constant T that is all for a closed system it is said constant temperature because they have already held the volume constrain I have put $V \alpha V \beta =$ so at constant temperature I know A has to be minimum therefore dA as to be $= 0$ now out of these I have constant T which means then I have to specify further conditions.

When I say equilibrium I ask for 3 kinds of equilibrium and I asked for thermal equilibrium which means $T\alpha = T\beta = T$ is a it is just label it ST the two temperatures have to be equal I ask for mechanical equilibrium that means $P \alpha = P\beta = P$ some give pressure P so first I have thermal equilibrium which means temperatures have to be equal I know if temperature are not equal heat will be transferred from one to the other that is my 0^{th} law.

So also long has changes occur I cannot have equilibrium, so this term is 0 because of thermal equilibrium $T =$ constant and thermal equilibrium demands the two phases have the same temperature and I have put $T =$ constant mechanical equilibrium demands that $P \alpha = P \beta$ therefore this term is 0 I am not setting $P =$ constant all I am saying the 2 pressures have to be = the criteria of a equilibrium says dA should be 0 at constant temperature for a closed system.

I am saying of the pressures are unequal then phase will do work on the other phase it will expand till the pressures are equal and so I have to $P\alpha = P \beta$ whatever the value of P if this has to happen this implies this criteria in a equilibrium this is we call this equation 1 then implies $\mu \alpha$ should be equal to $\mu\beta$. So A is the natural variable to consider because I can build in the work functional correctly I could have done it with G equation with that.

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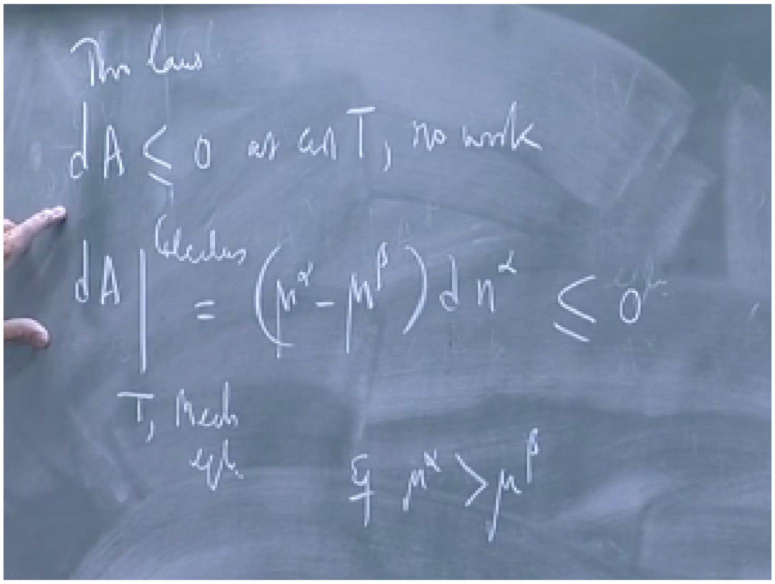

Notice that the law really says dA ≤ 0 and what you get is dA at constant temperature and conditions of mechanical equilibrium = μ α- μ β this is thermodynamics the two laws at constant temperature no work this is calculus from calculus alone you would not draw any conclusions in thermodynamics you have to always use the law at some point calculus is just going to get equal give you equalities.

So you got this result and from thermodynamics this should be ≤0 and I am saying at equilibrium it has to be equal to 0 because I have reached a minimum and if μ α ≠ μβ let us say example μ α> μ β then d n α can be of any sign if I choose dn α to be positive I change increase the number of moles in the α phase if dn α is negative I decrease the number of moles in the α phases in this I have a choose by definition as a thermodynamics I will be has be as possible and you still have to show that the law is valid.

So if you give μ α is < μ β this is positive Interviewer: ill simply choose dn α to be positive and so the energy will increase I mean I will chose sorry dn α to be negative so I can decrease the free energy further if I can decreased the free energy further I am not already in a state of equilibrium if I am currently in a state of equilibrium it should be possible for anybody to reduce the free energy of this system.

Now I let us say I am now in a state equilibrium then there must be no possible way for me decrease the free energy if this was greater than this I would simply take way moles from α phases and decrease the free energy I should not be able to do that conversely if $\mu\ \alpha$ was less than $\mu\ \beta$ I will choose $dn\ \alpha$ to positive I will add moles to the α phase and decrease the free energy again. And thermodynamics says you can never do it if your already at equilibrium therefore this conclusion that is then $dn\ \alpha < 0$ would lead to decrease in A if μ is $< \mu\ \beta$ $dn\alpha > 0$ would lead to decrease in it neither if possible if your already at equilibrium neither is expectable.

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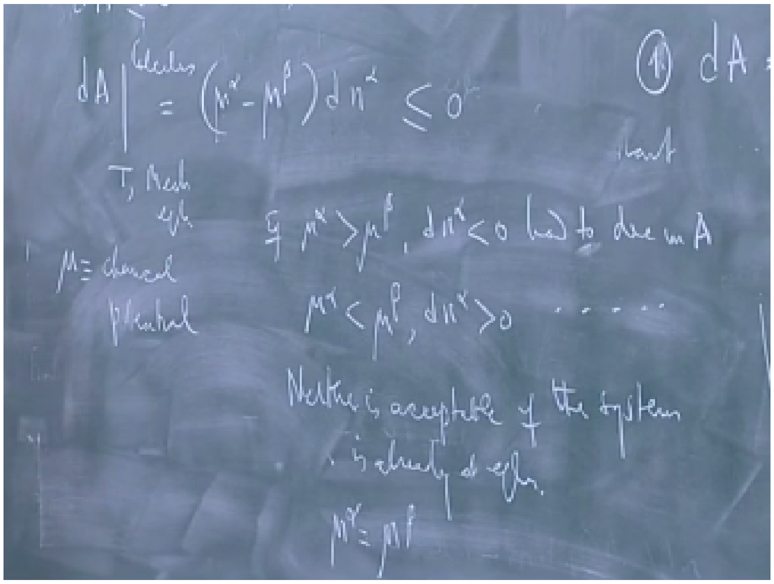

If this system is already at equilibrium so this implies $\mu\alpha = \mu\beta$ and Gibbs called that the chemical potential because if $T\ \alpha > T\ \beta$ then you have a temperature gradient and heat flows in the direction the decreasing thermal gradient similarly if $\mu\ \alpha > \mu\ \beta$ then heat moles would be transferred in the direction of decreasing $\mu\ \alpha$ so that the free energy decreases, so you call this the chemical potential probably the most important variable in chemical thermodynamics I do not know if you have read this is your reduction add up so do not prove.

When you start of a assume let us assume $\mu\alpha >$ that $\mu\beta$ then by transferring moles way from the α phase I can decrease the free energy which is upset because I am, already at equilibrium so you assume first of all that you cannot decrease the free energy then you show that if this is true then you can decrease the free energy then you could not have been at equilibrium or this is not true.

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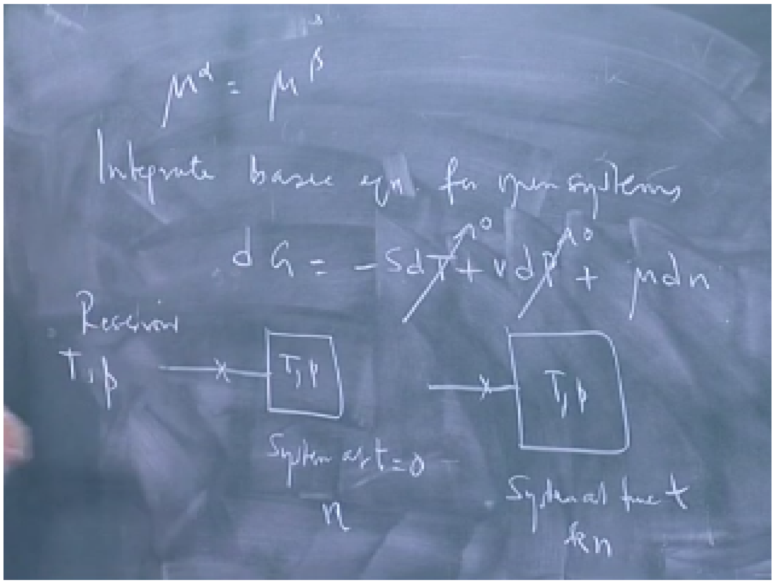

So what we have is proved that μα is = μβ then let me also integrate the basic equations and again this is very typical of thermodynamics in practical I will take this equation this is the most convent equation for most proposes you can do this with any of the equations that you have in thermodynamics so I am writing the basic equation for a open systems now I want to integrate this I am going to do something.

This is system at T = 0 T time = 0 system at time T now at time what I am going to do is am going to connect to reservoir this contains fluid at some temperature and pressure P in the reservoir I have the same fluid at the same recapture and same pressure my process is the following whole thing is a though experiment I simply take this box I add more fluid to the reservoir.

And make sure it is volume changes so that the T and P remain the same all the only difference between these states is I have n moles here I have k times n moles here. I keep the extensive variables the same so that the specific state of the system remains the same if I take one mole of the substance here one mole of the substance here the state is the same because T and P are the same.

First argument is if T and P are the same in this process for this process if take a calculation of dG this is 0 this is 0 μ by definition is partial of G with respect to n at constant T and P.

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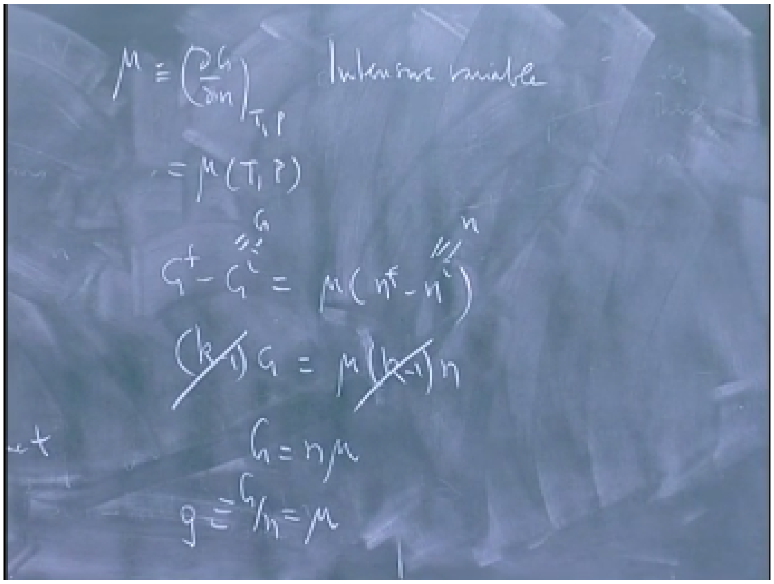

I claim this is an intensive variable because it is the property it is the partial mole properties so I am really calculating G per mole of a addition G is extensive n is extensive I am inserting the partial of G with respective n is intensive variable if it is an intensive variable it can be function only of T, P you might say this is in fundamental way and assumption and classical thermodynamics.

Might let me come back right now if μ is an intensive variable it must remain the same here as here so for this process G final – G initial is simply equal to μ times n finial – n initial this is k – 1 times G initial which is simply G μ times k – 1 times n, ni and this is the same as G μ is the notion in the initial state initial state as n moles in it is free energy Gibbs free energy is G and k need not be 1 therefore I can strike this out this is valid for all k so G is simply = n times μ.

So although we introduced a variable μ that is a partial of G with respect to n in the case of constant composition systems so are in the case of pure substances that we are now dealing with μ is simply happens to be small g this is G / n which is by definitions g is also = μ, so the specific Gibbs free energy is exactly the chemical potential. You can see the relationship with other variables because you have introduced this redundancy H is G + TS so if you are doing ∂ of H with respect to n we will get ∂ of G with respect to n which is μ + T∂S with respect to n.

And you can do the same thing with A is G + PV, so H with respect to n is μ + the quantity the only ∂ that is exactly = this specific property is the Gibbs free energy specific Gibbs energy is the chemical potential okay having said that now let me go back and look at our equations for the equilibrium so the equilibrium equation Z μ α = μ β if you have two phases you can derive the classiest equation from this + d μ α = dGL I have done that before.

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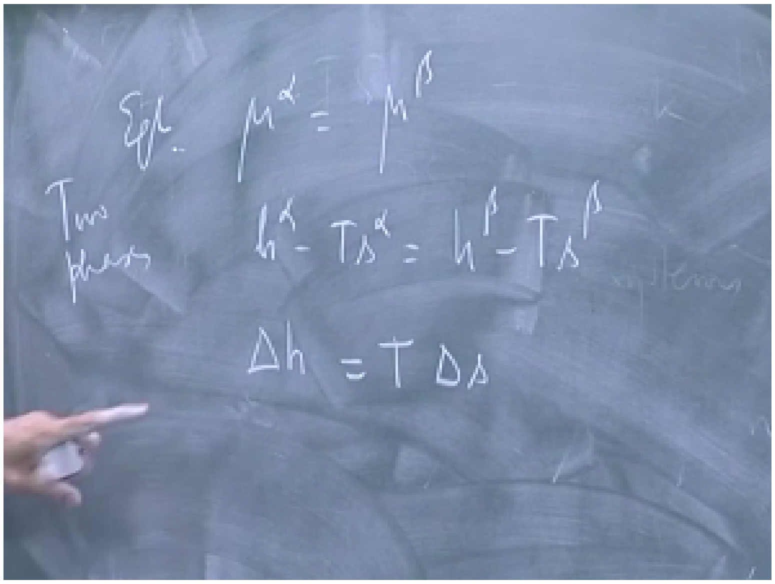

But this gives you a H α - TS α = h β – TS β hα – h β let us say is Δh = T ΔS and Δh is a measurable quantity you know that there is a latent heat which you can measure you can do this experiment so there is a positive difference in enthalpy between two phases.

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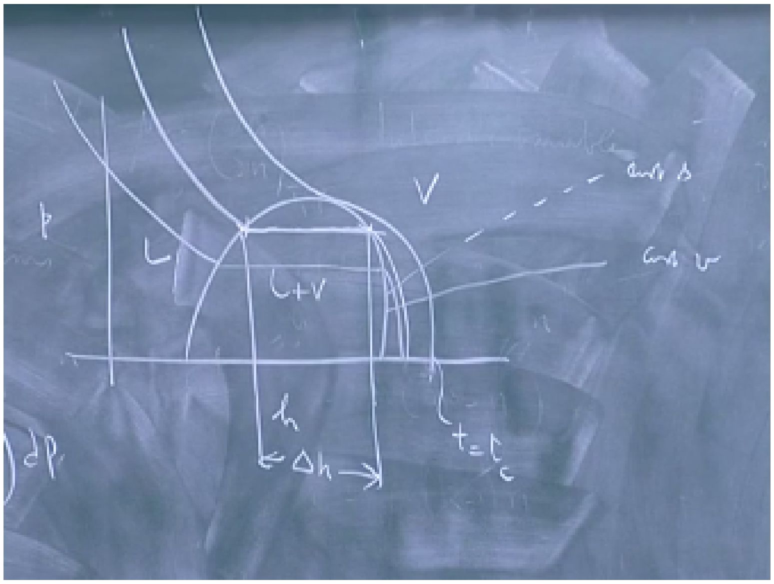

So we have done this part this is your critical isotherm this region we have seen 2 sets of curves in this is constant S this is constant V and it now if you come to if you go below the critical region the lines here are vertical as we have pointed out because it is ideal gas at low pressure you can exactly calculate this ideal gas behavioral vertical line so at constant temperature we are saying thermal equilibrium means your looking at isotherm mechanical equilibrium means you are looking at the pressure is being the same your saying the enthalpy of one phase is greater than the enthalpy of the other.

So there will be a shift here in the enthalpy this quantity is your Δh fro phase change this in case can be the α phase this can be the β phase the enthalpy is larger by conversion for vapor so you get vapor here and you get liquid here this is liquid + vapor in-between.

This Δh is a function of temperature if you go to lower temperatures you find the width experimentally you can show the width actually increases so Δh will increase has you go down and temperature we can do the calculation for that in a minute so I have done this position the isotherms here you can calculate the isotherms slopes.

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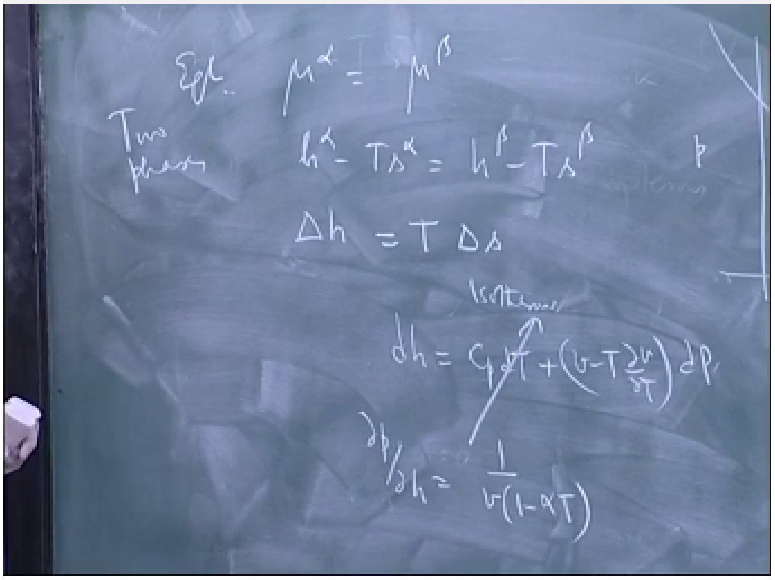

Your gain have dh = Cp dT + V - T ∂V/ ∂T to dP so at isothermals this is along isotherm this is 0 so ∂P with respect to h is simply 1/V x 1- α this is the expansion 1/V ∂V/ ∂T is a measurable quantity – αT sorry for an ideal gas αT becomes 1 and therefore you get infinite slope those lines here also the slope is reasonably steel because 1- α T becomes much small here actually 1- α T is non zero but V itself is small in the liquid region.

So it has got high pressure you get steel slopes so the isotherms are always somewhat steam so what happens is I have got these isotherm I have got the difference in the enthalpy so the isotherm will have to come to come like this it will be difference in the enthalpy then there is the other ½ so this side the vapor region this side the liquid region, what we can do I s actually calculate this whole thing and like you to computed for an van der waals fluid because in order to give you information I have to give you Cp and so I have to give you a Cp this specific heat.
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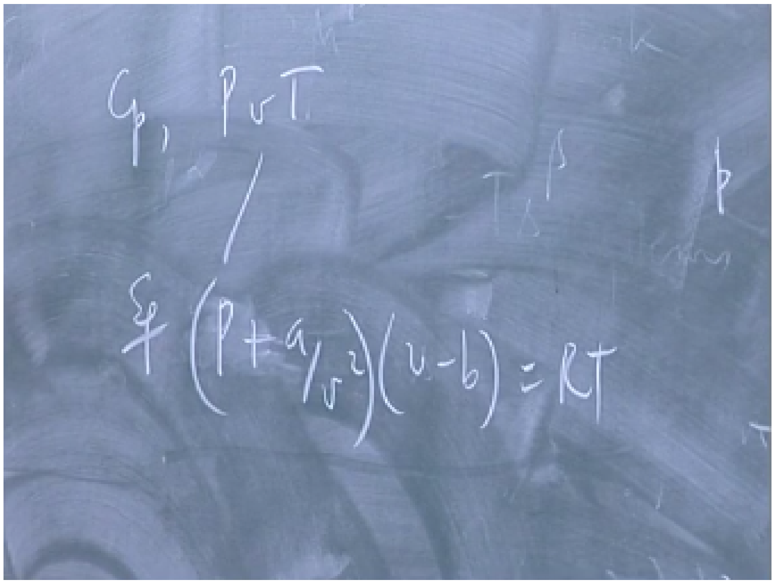

And PVT information, PvT information for example you can take the van der waals equation we said $(P+a)/v^2(v-p)=RT$, the van der waals fluid is of great importance for two reasons first it was the, the first historical equation or state that took into account attractive forces and the secondly it as non qualitative contractions you have to show that the quadratic form is positive. Iof you show that you can show what are called stability criteria, you can show we always has to decrease as pressure increases things like this which you take for granted or you take for granted that some of these coefficients are positive.

They all come from this requirement of stability, stability is not usually discussed in under graduate classes so I would not discuss it further it is only simple calculation it is putting down criteria of calculus on the second derivatives in the equations. In order to show that A is actually a minimum and not a maximum at equilibrium, so this equation has no qualitative contractions it satisfies all the thermodynamics stability criteria qualitative it does not agree with experiment but qualitatively it is one of the few equation substrate that is completely for your false, therefore it is of importance.

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