Indian Institute of Technology Madras

NPTEL

National Programme on Technology Enhanced Learning

CHEMICAL ENGINEERING
THERMODYNAMICS

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Lecture 19
Vapour-Liquid Equilibria 1

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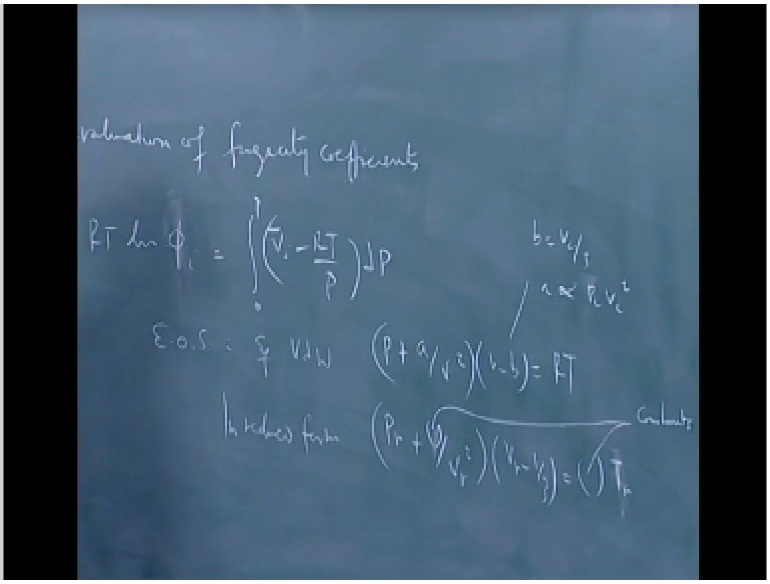

valuation of fugacity coefficients

$RT \ln \phi_i = \int_0^P \left(\bar{V}_i - \frac{RT}{P}\right) dP$

$b = v_c/3$

$a \propto P_c v_c^2$

E.O.S. : eg VdW $(P + a/v^2)(v - b) = RT$

In reduced form $\left(P_r + \frac{(\ )}{v_r^2}\right)(v_r - 1/3) = (\ )\,T_r$ Constants

Hence we have to discuss evaluation of rapacity coefficient, formula is very simple the equation of state we have already seen the equation of state for example Vander's we have seen it show the corresponding statements of first of all $p+a/v^2.v-b$ you can reduce form we have p reduce is equal to some constant I forget the constant there okay some constant remember we wrote the cubic equation in the equate them showed that is you can see b is vc/3 and a is r aαpvc^2 so I think there is a constant here also not necessarily one there are two constant.

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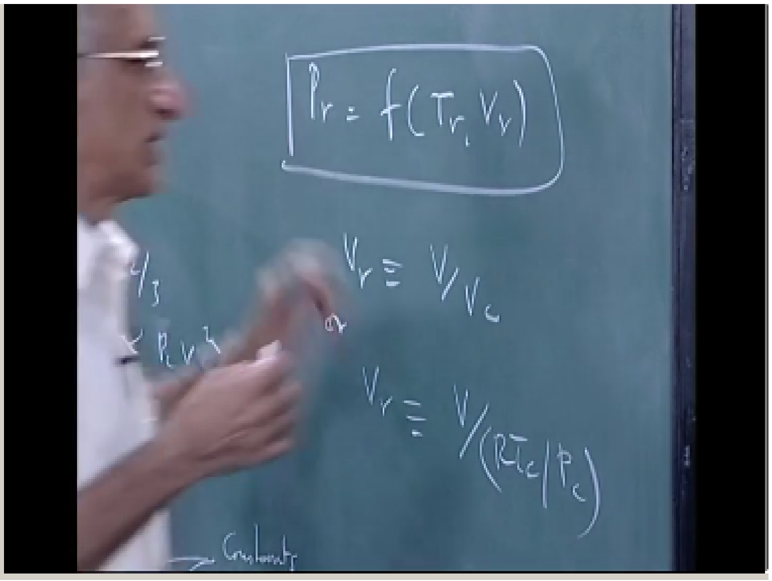

But the point about the venders principle was that pr=f(tr,vr) in general you should know the vc is very, very difficult to measure critical volume so very often vr is defined v/vc but vr can also be taken as vr=v/(rtc/pc) we will say r either of them, either in some correlations you non dimensional the volume using Tc and pc rather than using an idealist critical volume if you like the ideal gas really does not have a critical there is no conversation but, one of these is used but basically you get this equation this is the equation the fundamental equation for corresponding states what it states is that at the same Tr and Er.

The reduced pressure is same for all substances so universal it is an equation the corresponding state it means for every t and v of reference substance there is a t and v of the actual substance for which the T reduce and V reduce are the same under those conditions p/pc is the same for both substances so it is sufficient in principle to measure the data for say are going easy to measure and you make all the measurement for put the equation as state the empirical measurements in this form and then you can use it for any other substance provided you measure PC, PV.

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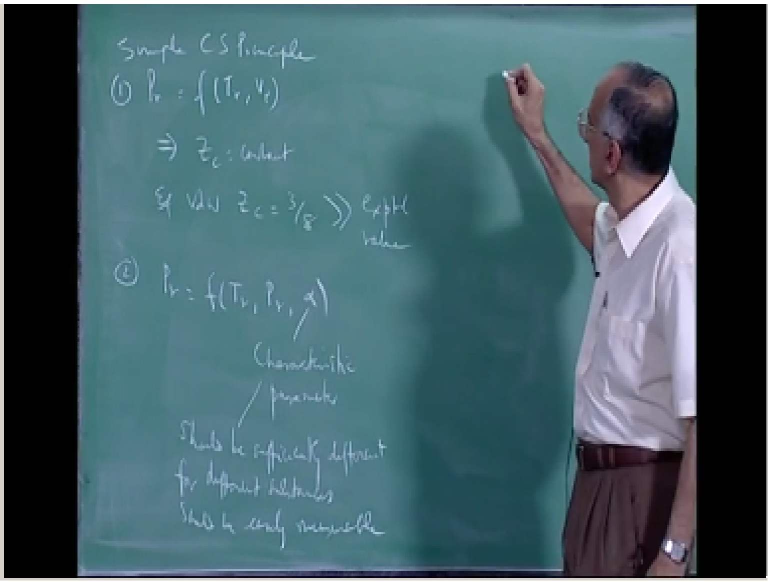

So really it is the matter of reducing one is universal isolation second is reducing experimental data but, more universally this implies some function of TR and VR implies the ZC is constant in the case of Vander's ZC comes out to be 3/8 so for example zc=3/8>>experimental value, is actually vary in more like a between 0.2 and 0.35 wide variation ZC values and typically for many substances I think for the inner gases about 0.27, so croton, neuron, all these can be correlated very well methane then you start having departures so what people suggested was as this is first corresponding states.

This is called the simple corresponding states principle all other corresponding state principle simply add more parameters to this so you write PR=f(tr,pr,α) where α is some character tics parameter essentially this character tics parameter should have ideally it should be distinguee for disguised substances if substances behave differently and α should be correspondingly different it should be easily measurable so only two requirements should be sufficiently different for different substances and should be measurable easily measurable.

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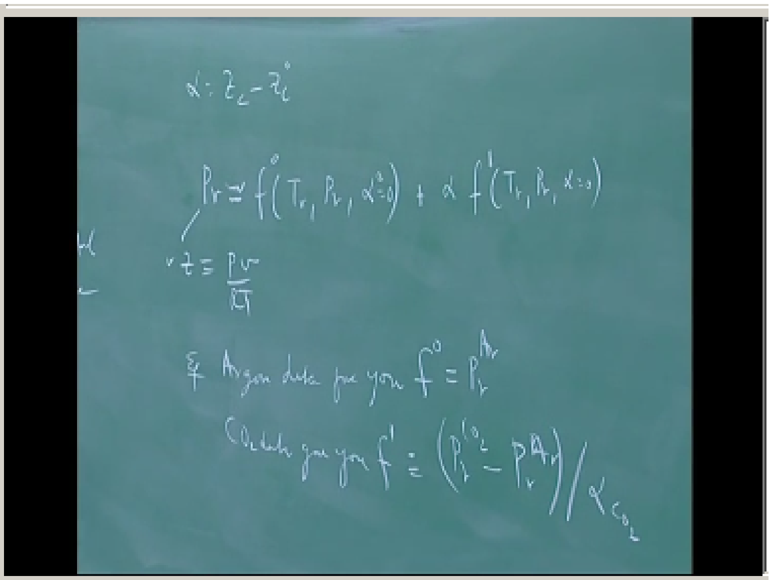

Historically first one that was tried was α=zc itself actually it is taken as zc-zc0 because for simple inner substances zc0 is the critical compressibility factors say for argon for inner gas methane and so on if you take this difference as the parameters and it becomes very convenient you can then do if you do this, you can then write pr=f you can expand this in Taylor expansion pr=f(tr,pr,α)+the value of α, actually α0 is 0 so you make a Taylor series expansion you can write tr=0 actually normally it is rather than PR you write z itself the compressibility factor which is dimensionless.

So rz, zc is the critical compressibility factor z is the compressibility factor z is pv/rt zc is the value at the critical part I is just a 3rd parameter it should be different because you would like to use a reason for using a Taylor series expansion is the following if I now measure for organ then α=0 this term will disappear I get enough information from just argon measurements.

Then let us say I do a measurement for carbon-dioxide for which I know α then carbon dioxide will give me f0 plus the whole thing of which this is known so from the left hand side measurements for carbon dioxide I can calculate f1 this is actually partial of f with respect to α at α=0 but I do not have to look at it that way just a function of Pr.
And I can get it from experimental data once I get for argon and carbon- dioxide I simply use f0,f1 universally and find α for every new substance I have to measure now tc,pc, vc and α if I measure 4 quantities I have got the complete equation of state for any substance because I have already made measurements for argon this comes from example you do argon data give you f0 then carbon-dioxide data give you f1=pr for carbon-dioxide if you write pr for argon remember

pr for argon is exactly this f0 is pr for argon if I take this difference and divide by α co2 I get f1 I do have to measure pr is the function of Fr Tr.

And I keep saying pr here this should be Vr sorry I got Vr in the left hand side which is the more convenient way of doing it just to measure z as a function of pr and Tr we need two variables on the right hand side, left hand side should be a dimensional less part so in principle it is sufficient for me to measure carbon, carbon- oxide data and argon data and measure four quantities for each substances TC,PC,VC and α now this has be done for example in great details by hug hen disconcertion is a book by how hug hen Watson.

And regards more of historical interest it is a good book the three volume book of chemical engineering I think volume 1 you use in schiometric in your course right so there are two other books where second book is on thermodynamics it contains extensive calculations using this once I have an equation state I can measure I can calculate p all I have to do I lot of algebra I have to find v at every p and T differentiated with respect to N I in a mixture and do this have to do the same thing for a mixture, for mixture α will be we will have a suitable combing root every parameter they appear in the base in the equation state we will combing rule right if you do this first the first thing that you do is do this for pure substances then for pure substances off course.

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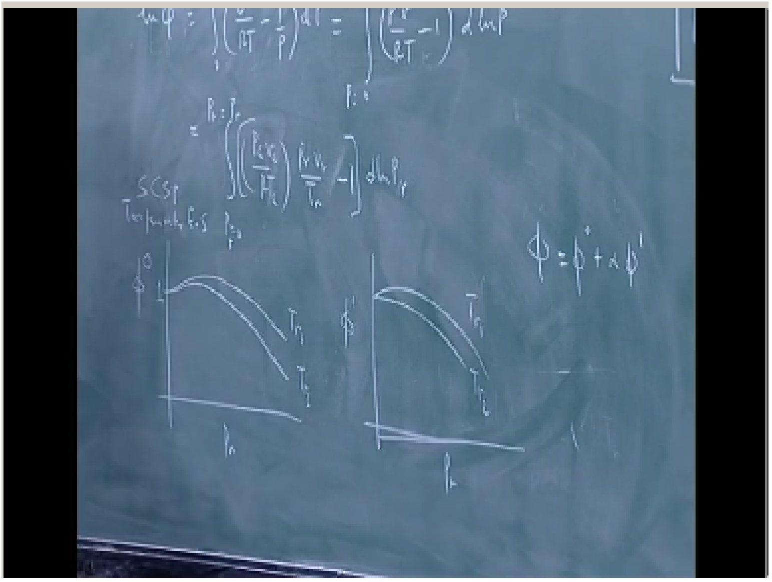

This is for pure substances 0 to p v/rt-1/p.dp v reduced by t reduced have to multiple this, this is do then I have a pc inside then I have pv/rt-1.dlp is same as this p=0 to p pcvc/rtc.pc./tr-1.dpr therefore the limits will become pr=0 if it is a two parameter equation of state like the Vander this is known this only 3/8 so I can do this calculation once and for all I can give the plots of the tables in the book and you can just use the all you have to find is what p/pc you can then plot for various values of pr it will always go to 1 in the limit does p goes to 0 that is called like this, this is for different pr.

This is the simple corresponding states principle sc, sp right for two parameter equation substances if there are only two parameter then zc is the constant the two parameter can be determined in terms of pc,vc and tc then you can have a universal plot I think this is given to you if you have a second parameter here α then you will get a ϕ0 and a ϕ1 so you get two plots you can otherwise have let us call this ϕ0 to indicate that it is for substances that are described completely by two parameters equation state typically this would be obtained from argon data r methane, argon.

And so on and there will be a second parameter you will plot ϕ1 which corresponds to f1 there against pr for various values of pr I do not remember what the curve looks like you get a series of graph you will get ϕ0 ϕ=ϕ0+αϕ1so the easiest way is to do this simply take the ϕo graph take your p, and v of the substance divided bt tcpv for reduced quadrants at a given pr you go and correct pr and read the value of ϕo similarly read the value of ϕ1 and do this calculation so all I need is one table that gives me tc, pc, vc and α now there are many, many parameters α that have been used.

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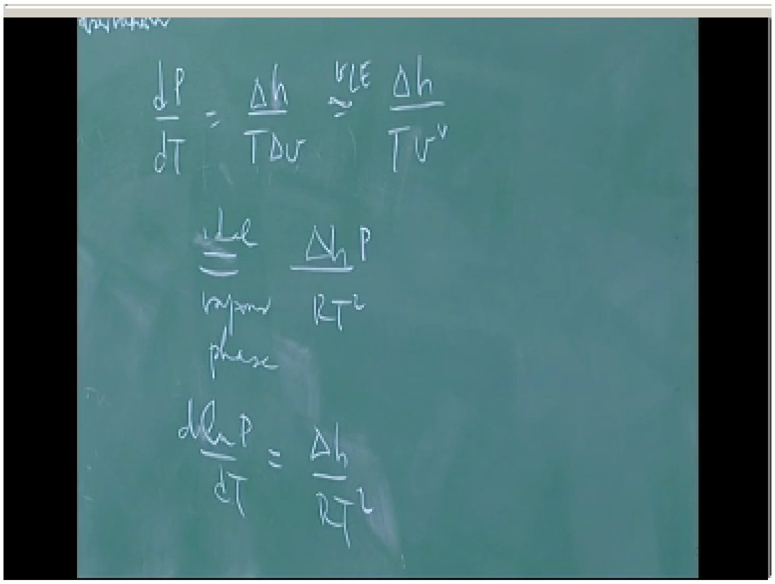

$$\frac{dP}{dT} = \frac{\Delta h}{T\Delta v} \overset{VLE}{\approx} \frac{\Delta h}{Tv^v}$$

$$\underset{\text{vapour phase}}{\overset{\text{ideal}}{=}} \frac{\Delta h\,P}{RT^2}$$

$$\frac{d\ln P}{dT} = \frac{\Delta h}{RT^2}$$

But the most successful one is called pictures ascetic factor picture introduced a centric factor on the phase on if it is I am using how 1 would come up with something like this it is the definition of an centric factor it is an argument actually it came from this you know that if you plot log of the vapor pressure v saturation versus 1/t it is well know that you will get a state line as a temperature increases you move this way and the pressure increases you will get a straight line like this.

This is experimental observation it is also a consequents of using a classic vapor on equation and the ideal vapor phase you have dp/dt=Δh/tΔv for vapor liquid equilibrium this is approximately equal to Δh/tv and this is equal to an ideal gas this is Δh/rt^2/p so you get d log p/dt=Δh/rt^2 and if Δh is constant this is along the saturation curve when vapor and liquid are in equilibrium so log p plotted against 1/t should give you a straight line for given Δh if Δh is constant in actual practice Δ is an vary with a temperature the variation is very small this is been known experimentally.

And if you do this by in reduced quadrant that is if you plot log pr saturation this is 1/tr so you will get a straight line and tr=0.7 is approximately the normal boiling point and you get a straight line for all for simple gases typically inner gases again methane spherical molecules you get nice statement it turns out at tr=0.7 this point here this value I am plotting now log$_{10}$ for convents just numbers pr saturation at pr=0.7 pr saturation is approximately 0.1 this is an experimental observation for simple substances I am sorry I will take this back not normal point.

This is close to the normal boiling point okay I take this back tr=0.7 is close to normal boiling point but it is not exactly at tr=0.7 pr saturation is equal 0.1 for inner gases so $\log_{10}$ pr -1 then it will be 0 so make it approximately 0 for inner gases for all other substances ω is different from 1 it is very many character tics first data is readily available this is pr saturation you take saturation pressure vapor pressure of the substance of pr=0.7 then you get ω is readily is measurable and it varies between 0 and 0.4 approximately which is very nice for Taylors series expansion.

Because you are doing a Taylor series expansion if ω is the parameter if ω <1 then you have guarantees of conversion as Taylor series expansion so it should be small that is a another criteria that people came up with if α is very large then you get large you cannot do a Taylor series expansion conveniently and thirdly ω it is measure of a centric nature of the inter molecular force it is the inter molecular force effectively it is like you take two molecules in model them like spheres and then you have to have a center of mass for each and center of force for each because you have to know what the line of interactions.

And if the centers of force is set as mass of coincident the molecule is said to be centric a centre of force not been centered located with center of mass a centric if you like so what is actually discovered is that ω for example for carbon-dioxide is almost 0.38 get the exact value it is quite large so what is happened is ω this is very useful correlations this is the most popular correlation so you write +ω in effect it is the only 3 parameter correlated that you have to know it is widely used for gases and it gives you excellent correlation this combined with rule that is if you are dealing with mixtures Lewis and ran dell rule tells you that vi=vi therefore ϕi=ϕi is given by this most find 90% of treatment gas phase non ideality uses this rule.

And therefore you have to calculate only almost invariably calculated as 0there is a variation of this in the literacy this words called a test lee Keble equation this is been very successful state uses ω exactly like this what it does is makes the equation of state inter positive because ω is 0 for inner gases and some almost 0.4 for carbon-dioxide all other gas behave in a intermediate fashion so you use an interpolative equation of state which essentially gets all the data for any substance between that of argon and carbon-dioxide.

So lee Keble equation state essentially has a detailed equation of state but it also calculates exactly like this ɸ0 andɸ1 are calculated for the lee Keble's equation this is been done for several equations of state in particular for lee kepler equation of state I will give you that it is given I think in Wales in detailed there are also much more complicated equations all I want to say about equations of state and calculations of figures.

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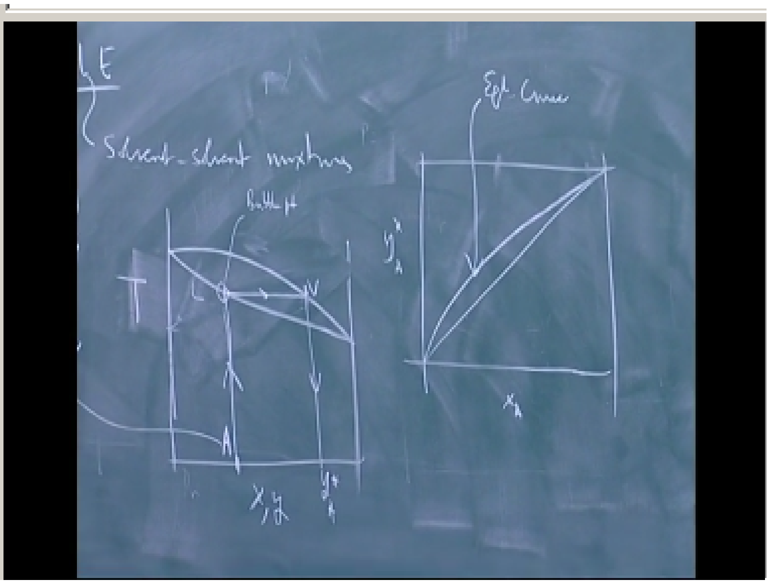

We will just look at vapor liquid equilibrium of various forms in this case when I am talking about liquid I am taking about solvent, solvent case so if you have solvent solid pictures you are either talking about solidity of a gas or a solubility of a solid so I will discuss those topics separately now if you look at solvent solid mixtures the final diagrams are plotted like this let us look at binary if you plot for example isobaric data t is often plotted like this all you do is take experimental data you take a mixture liquid mixture this can be x or y I will take a liquid mixture of this composition.

Let us say 0.1 it is a liquid mixture of composition xh some sufficient load temperature I increase the temperature to some point and at this point you begin to have vapor formation and the vapour that comes out as this composition I should have plotted the other way around this is normal let me explain why normally if you have a binary you choose this x and y so that the more x composition refers to the more volatile component so that the vapor is usually in the liquid form this is the liquid this is the vapor so this liquid is in equilibrium with this vapor here vapor line is on top.

So the composition y is larger than the composition x so I boil this liquid at this point the first bubble of vapory forms in this point is called the bubble point if it was the pure substance it will be only 1 point at which the vapor and liquid will be at equilibrium but I am talking about the mixture this point is called the bubble point so this is the composition why in equilibrium with so this will be Ya* the * indicates that equilibrium with XA if you plot this ya* was you can do this every liquid composition if you plot ya verus xa we just plot this is the 45° line it could get for us curve like this you could get something like.

This is your equilibrium curve if instantly conversely if you have started with complete vapor of this composition let us say this point is B if you have started with vapor of this composition and you have reduced the temperature your are tool advanced and pressure all this is done at concept pressure you would have come to this point at which the first proper liquid will form this is called the dew point after the fact the due forms from here.

Early in the morning when the temperature drop, very early and not convert may be 1o clock, 2oclock so two points characterize mixture the dew point at the double point I have vapor you have talk about the dew point if you have these is one of concern and chemically hearing and pumping for example, if are pumping the liquid and you do not while vapor form producing a rotary device.

And if the vapor forms the captured bubble breaks on the break encases erosion if you do not want to completely liquid you do not want it to be vapor so will have to make sure the temperature does not go about this point as long you keep the temperature below this point you won't have any vapor forms similarly if you having using a device for the vapor and you do not want liquid drops when you will make sure the temperature.

Which is above this point so that you do not have so determine a liquid dew point and double point will determine the operation temperature or for example, the pressure this is the temperature diagram.

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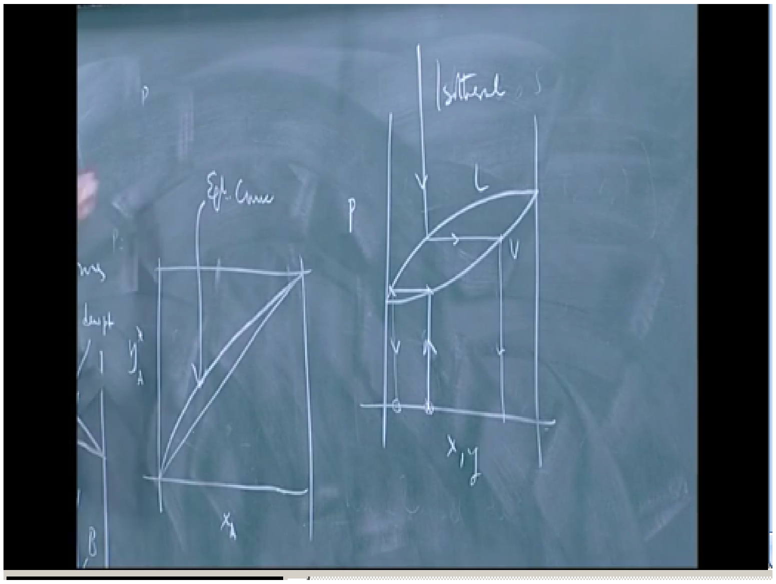

If you did the isothermal will calculations anodic and this is the important in this isoclinic because most industrial column operate advance in pressure very large fractions atmosphere insulations the other cases isothermal will operation if have plot P verses X,Y and discussed this way you get curved that way concentrate temperature if you go from this point and increase the pressure.

At some point you have conversations have this is the liquid, this is the vapor so this is the liquid in equilibrium to this wave and if you have start with the liquid for example and come down reduce the pressure handily will be vapor formations of this composition may this in quite simple because this diagram can take for 1000 shapes, for example there are an mixture where the Y does not always lie above I think plot either if in this form.

At concept pressure are you cannot when they you are binary system I have establish that, let me establish degrees of figure.

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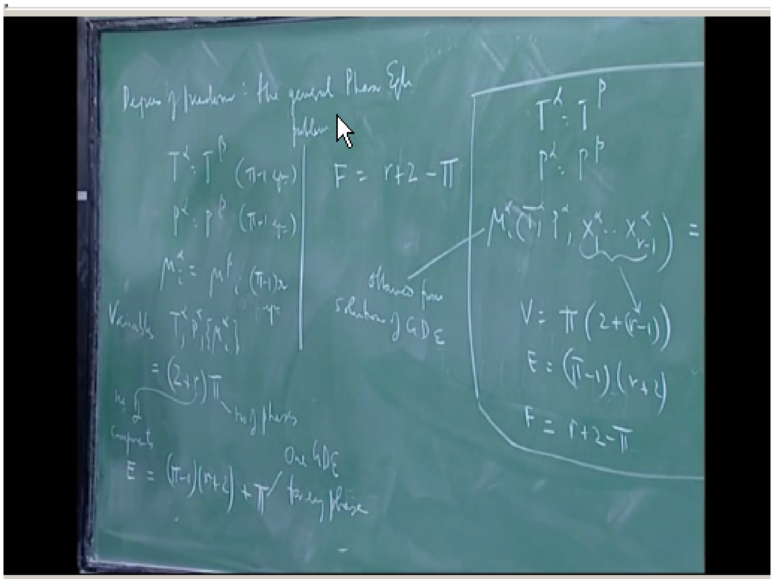

The basic equilibrium problem simply Tα=Tβ Pα=Pβ considered tell you Mα=Mβ are Mi=Mi inside the general basic equilibrium problem so what are the variables many this in the problem on T,P Miα above we set it is actually 2 Tα,Pα Miα so (2+r) components α is the number phrases into π phrases this is number of phrases this is number of components .So the number of variables is simply=2+r =π .

What is the number of equations this is I fix α ,β can run from 1,2 π-1 so this is π-1 equations this is also π-1 equations this is again π-1 for each component =r equations so the number of equations recently (π-1) (r+2) so the number degrees is the freedom is simply the number of variables – the number of equations r+2 is something wrong okay, this is alright =I got some (r+2) what is wrong.

And some more concerns is this all the number of equations I claim the one more set of equations like I been talking about nothing but those equations and X specify K a phrase is like and talking about chemical potential what downs the composition depends the chemical potential that it gives the double equation name so this is one equation for every phrase so I have +π which is 1 GD equations foe every phrase.

So you get –π that is if you treat the chemical potentials as independent variables so you are talking about r intensive variables so this each phrase but each of those r components is given by human equation so you have take this in take on so you get you are famous r+2-π you can neither do this r simply write set of equations Miα =Miβ you put a model for a chemical potential that is you solve the equations.

Which have we do it we assume a model for G axis derive expressions Mi interms x1,x2,xr-1 and write this equations has if and an equation governing r-1 composition variables not r chemical potentials that ids the other alternative STRπ Tβ Pα =Pβ Miα which is the function (Tα,Pα,X1α,xr-1α)=Miβ(Tβ,Pβ,X1β,XR-1β) so the number of variables is π again itb is π-the number of variables is π variables π phrases.

Each phrase as 2 +r-1 now the variables are not Mi but these now you already sloved Gibson equation because you have got composition depends this is the pained from the Gibson equation each phrase for example, if you have writing the vapor phrase you will write in terms of figurate effusions you will calculate figurate effusions from an equation of state so it is automatically satisfies the Gibson equations because figurants corrosions where obtained from Vi, bar Vi bar is pentagram.

So those satisfies the Gibson equations in the liquid phrase you may use the excess phrase model so these are given I have given you this expression yhas a function of compositions so only this many variables now the equations are exactly have we written on π-1r+2 so you take v-e you will still get the same equations F is simply =r+2 –π because πx r +2-πxrπ-xr 2 exactly r+2 mean you have a π –π.

Actually this is the way we solved the problem and these are the obtained from solutions of the Gibson's equations how you solved in detail for the vapor phrase you do not solved the Gibson equations is simply go to the equations state get Bi bar, get B for the liquid phrase you go to the x- so in a sense this information's is really empirical expert that most cases the number components ,and the number of frailly obvious so it is a very good rule it is an extract rule but you do not know r and π exactly all the time and therefore F is not shown. So coming back here we will discussing binary two phrase equilibrium so you have here r =2 and π=2 so the number of degrees a freedom is 2-2+2 =2 degrees of freedom.

So if you fix temperature are pressure when the only freedom you have either with liquid compositions, vapor composition so I fixed temperature and liquid composition everything else is fixed or if I fixed for example pressure in this case I fixed the pressure and I fixed the liquid composition automatically T is determined so number of degrees the freedom is you have to look at carefully that we tell you what measuremetially to make.

Here for example every often we can measure the X, Y perversely called one measurement more than is required that you measured P also your two measurement more than usually π so you can actually used this data is verified to Gibson equations now then start the actually forties ,by forties they started believing it then they said verifying the internal consisting require mental data when the data do not satisfies Gibson equations.

You will tell him not the data is not right send it back to fellow asking the measure it again then now it just used if you do not measure the additional data because such a new session assume the Gibson equations will valid so let me get back here so in the principle of all separation process use to taken X if you let us do the isobaric this example when isolation column you take a several composition X and you find the vapor.

When you have the series that actual way the physical column setup you won't recognizes that normally what you do is take has T is still in the laboratory concept pressure and increase heated with the two complete equilibrium you measure this composition so you do it when the laboratory actual practices dissolution column by the what you haven the why you need is good mixing between the liquid and vapor and you get the equilibrium so actual dissolution column.

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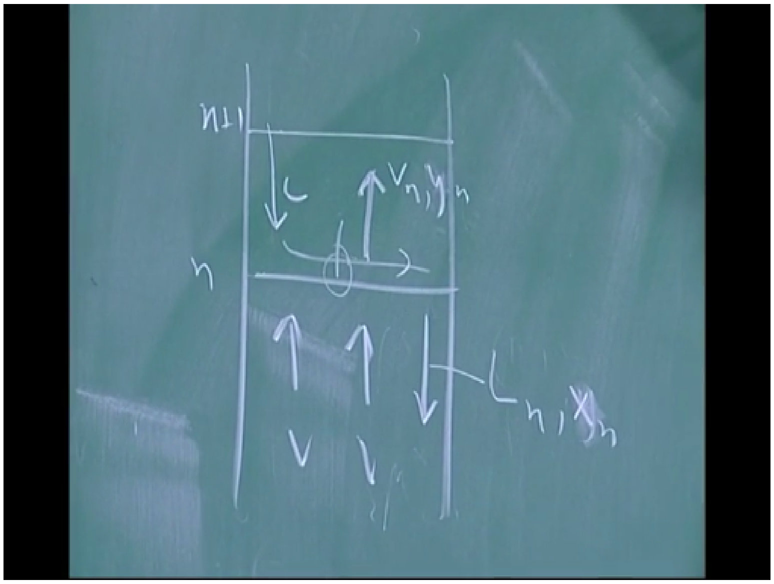

Last term looks like this n+1 n prime in the liquid from the n+ 1 straight comes down here c and the vapor comes alover the place this liquid flows out this way then flows down this thing this vapor coming up bubbles through and it makes sure that there is good cobntact between the liquid nad vapor when the vapor leaving here nad this liquid this Ln this is vapor leaving ,this is the liquid leaving these two are equilibrium.

The composition of this Yn binary system this Xn Vn what if this is the N liquid this equilibrium vapor which is much richer in component one in the first component so as you group you will get the vapor that contains more and more sorry, this is Yn this is Xn this you go up you get vapor richer and richer and in more potential component and finally at the top sufficient number of trace you will get your component.

If it a binary you will get compare component one so component two at the back that is all you do in binary desolation if it is a multi-component desolation very often strutted like a binary the most volute component will be treated with one component all the rest should be one together is recurrent second component and you can do all the treatment all the way down that you come.

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