Indian Institute of Technology Madras

NPTEL

National Programme on Technology Enhanced Learning

Chemical Engineering Thermodynamics

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Lecture 18
Vapour Liquid Equilibria I

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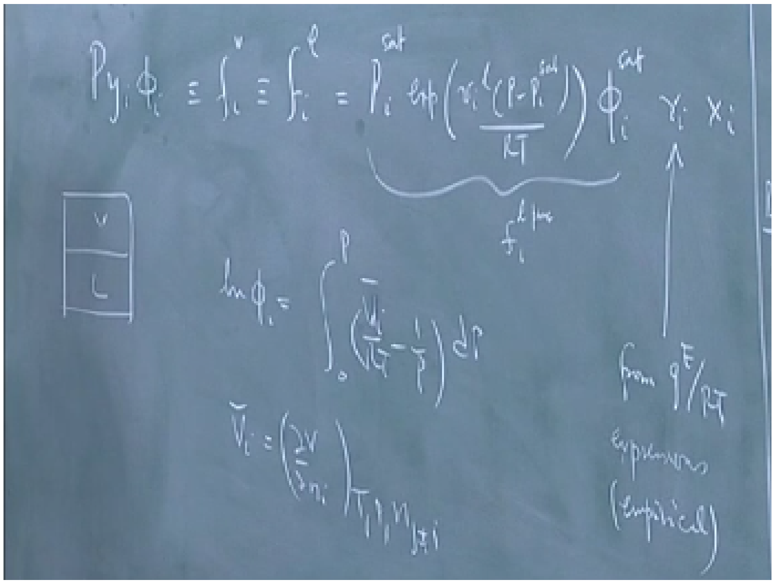

Okay we are doing vapor liquid equilibria, is the fugacity of the vapor phase is equal to fugacity of the liquid component I which is equal to this is the saturation pressure this is the pointing correction then there is non ideality correction at saturation up to this is pure, this is the fugacity of pure I so looking of each of the terms how one would compute each of these looking at the fugacity coefficient this fairly straight for this is by definition integral 0 to p and v bar is partial of with respect to ni of v.

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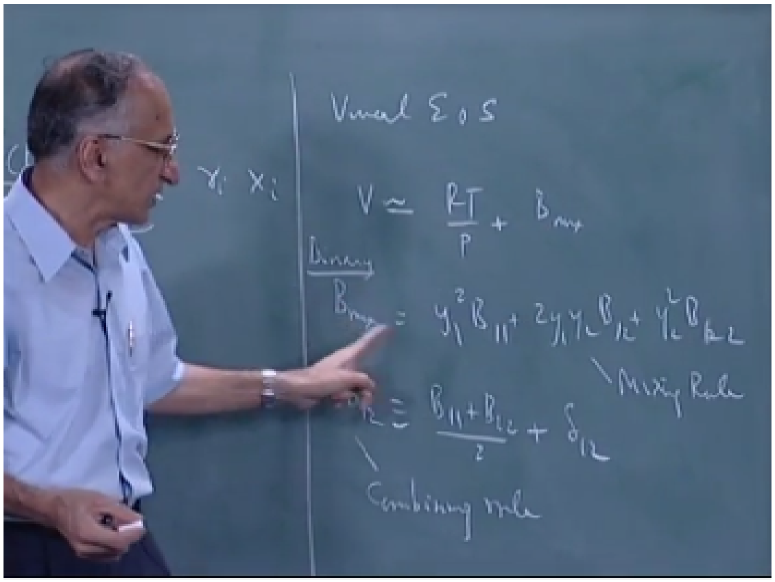

Thing we start we discussed example of the virial equation of state said v is approximately equal to discuss binary through when we had + δ 12 this is definition default option is δ 12 = 0 so this is call the mixing rule for the virial equation state is an exact role can you cannot derive this mixing rule or the combinative real rule this is the combining rule so you need twp rule imperially, this regardless of the phase the composition dependence of the chemical potential is not given uniquely by thermodynamics.

So what you are saying here is instead of the composition depends of the chemical potential I can use the composition dependence of the partial mole all volume to calculate the behavior of the chemical potential, but thermodynamics does not give you anything about the partial mole all volume either it gives you one equation less than the number of variables so you still have one degree of freedom for which you have to use empiricism, when you use the empirical rote through the equation or state you have a b mix for which if you have an educational state that is derived from molecular theory that is derive from mechanistic description then you can get an exact mixing rule otherwise the mixing rule is also empirical.

The combining rule is always empirical except in limiting cases for example b 1 2 =b11 + b22 / 2 is a limiting case where if you take very similar component of similar molecules size between methane, ethane, ethane propane it should dry you can say δ 12 = 0, otherwise this is not an exact rule this is a as for as diameters are concerned that is if you take this diameters the molecule σ 12

– σ 11+ σ 22 / 2 is exact rule in for hard fears if you use that rule be will be like a volume therefore b will be like σ q so σ q 12 = σ q11 + σ q22 / 2 that would be an exact rule for hard fears but not for real molecule.

So the various ways of deriving this but all of them are empirical ultimately only in limiting cases some are these rules are exact, so this combining rule is empirical this is this can be exact depending on the kind of equation or state you use as of now for most equation or state both are empirical, but if you do this then you can calculate φ I and therefore get the compression depends on the chemical potential then you can solve this equation

You will solve only one term which is γ I and this comes from we have already seen from gx / rt expressions these are also empirical, so as for as theory is concerned thermodynamics runs out of steam here both this, this is also empirical and what it was essentially Gibbs tells you that you will run out of steam for ever there is nobody classical they would not unmixed it that is give you an opportunity to derive a expressions for gx from without see by classical thermodynamic I mean thermodynamic that does not refer to structure of matter.

So if you go back to molecular theory you can derive expression for gx / rt youi have to make other assumptions, in all of these there is still one empirical assumptions that will be at the base of all theories of solution, for even the one large equation essentially I got this through a series of assumption again you have to make these assumptions for a and b in one large equations. So this is the route let me start with the simple example.

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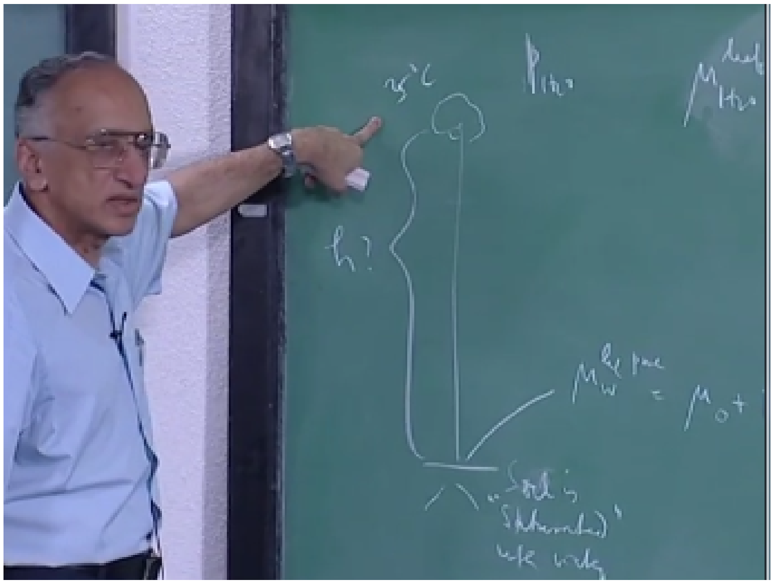

We will ask an example that has no application at all this is a tree typically now I want let us assume that unlike Madras, the soil is saturated with water what I mean is the routes are cover with water I want to know how tall this tree will grow it is an absolutely no direct use but the idea is that the thermodynamic can be use for this purpose the assumptions I make and all these assumptions are perfectly valid there is a certain partial pressure in the atmosphere.

Take Madras for example your saturation; you can calculate the value of partial pressure of h2 o in air simply from the vapor pressure water at 25^0, let us say the temperature is 25^0 at 250 c you can find out what this saturation pressure of water is right now my contention is the following that if there is a leaf here for a leaf to grow at the highest place the water has to go from here to here and this leaf the water and the leaf here will be an equilibrium with the water in the vapor in the air so I have p h2 o in the leaf = Rf h2o fugacity I will start with chemical potential.

Chemical potential of water in the leaf should be equal to μ h2 o in air, now if you have water here my let me write this out μ h2 go in air is this is a mixture so it is μ 0 + rtln py water in air this is a mixture so you also have to cocoon for non ideality, this we can take as one since pressure is p is less than one atmosphere less than or equal to one atmosphere I am talking of atmosphere equation, and growing trees inside a compress chamber.

There is water I am assuming this water here so μ water liquid pure is simply μ 0 + this is = to this μ water liquid pure is equal to μ water vapor pure which is μ 0 + rtln p saturation for water was φ saturation water plus a correction, the chemical potential is actually as along as pure substances concerned it is the Gibbs free energy perm one in gs u + ts – u + pv – ts so please remember when we wrote the first law we should not have use the internal energy which I have actually use the total energy.

So the potential normally potential energy and kinetic energy negligible so you sue the internal energy otherwise they should really be replaced by e so ion all our derivations wherever you have chemical potential equality this chemical potential should include the potential energy if the potential energy significant in this case from here to here the potential energy is significant so I will have to add that also. So the chemical potential will be this plus.

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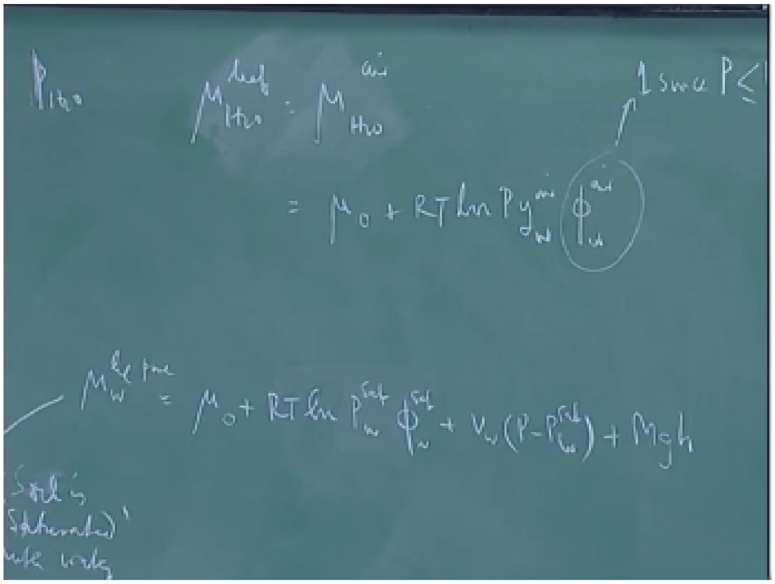

P_{H_2O}

$$\mu^{leaf}_{H_2O} = \mu^{air}_{H_2O}$$

$$= \mu_0 + RT\ln P y^{air}_{w} \phi^{air}_{w}$$

$$\mu^{leaf\ tree}_{w} = \mu_0 + RT\ln P^{sat}_{w} \phi^{sat}_{w} + V_w(P - P^{sat}_{w}) + Mgh$$

I should take in to account the height also, now this term is negligibly small I can show you that this terms is and simply say negligible I told you this is called the pointing effect.

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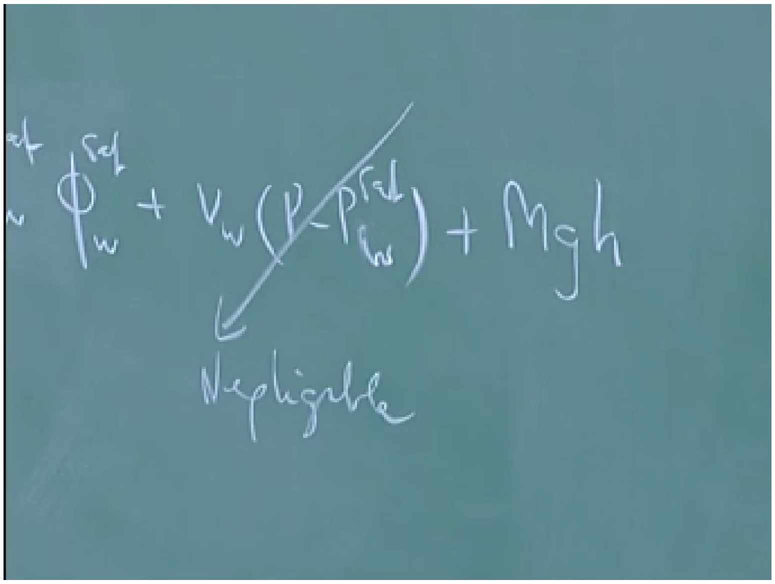

And basically all of the literature you will have books on vapor liquid equilibria at low pressures at high pressures right, the only different between those two is that at high pressures this pointing effect is important. I can make an estimate of this for you for example the pointing effect is exponential of v liquid in toi p – p saturation by rt right this v liquid for water is 18.

Let us keep this as p, p in atmospheres and r is 82 cc atmosphere this is 18Cc/ gram or so this will be 82 Cc atmospheres per gram mole into temperature is same 300^0 for typically this just making an estimate so this is 2 this about 9 approximately this is 150, so this is approximately P and atmospheres by 1350 the pointing correction which is the correction for the vapor pressure.

Because the presence of seconds of essence because the pressure is greater than the saturation pressure is significant only if exponential of this factor, exponential of P/ or P- P saturation if you like, P-P saturation, P saturation is anyway for water for example it 25^0 sets 25 millimeters of mercury certain negligibly small.

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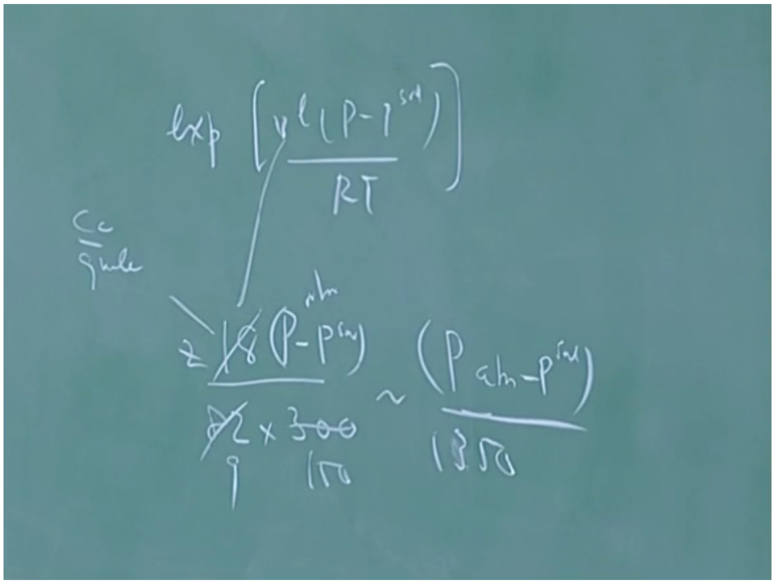

So what counts is P but y ou can see that unless P is about 50 atmospheres are higher this number is very, very small so as a thumb rule you do not worry about the pointing correction at pressure is below 25 atmospheres if you want to make accurate calculations you take into account but otherwise generally below 25 atmospheres you do not worry about the pointing correction.

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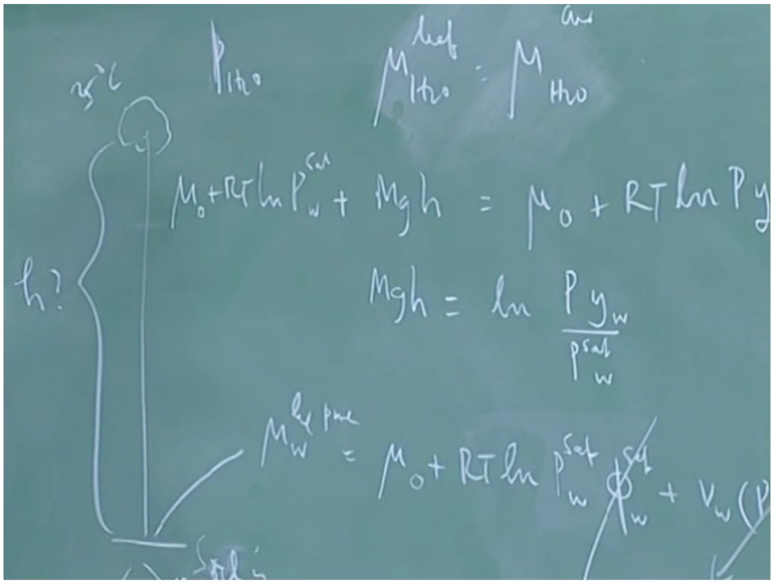

So to just to give you an idea so I do not worry about this so I am equating this is the chemical potential of liquid pure here from here to here it passes through the wings and the stem and the gets the it has to get the if there is chemical potential here this is an contact this chemical potential will also be covered by the same law except that the chemical potential is altered by the height.

So essentially what you get here is μ_o+Rtln pw is saturation I will throw this out this is 1 typically Pw saturation is about 25 millimeters right I told you so there is no figures, there is no figures of correction this can be neglected only that first Mgh so you get Mgh=logarithm of Py_w water is there by P saturation/RT there must be RT symbol by RT.

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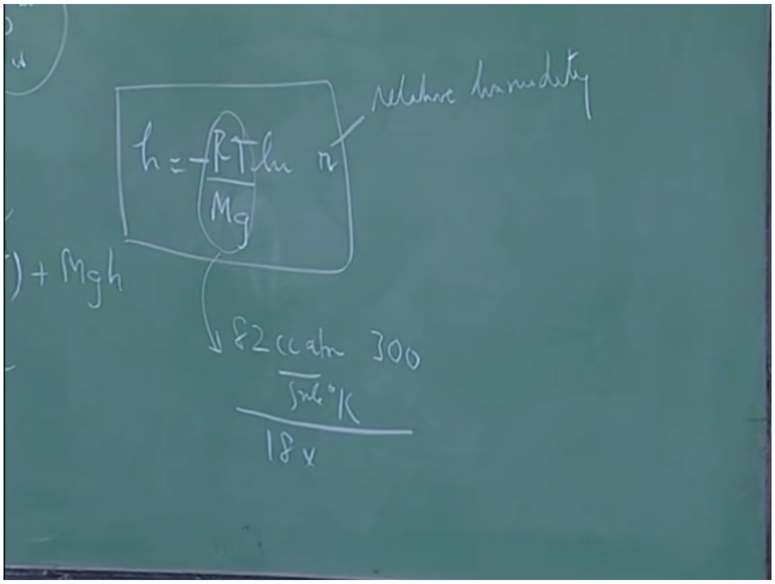

So what is the H=RT lm this is what you call essentially the relative humidity in the air the saturation pressure will represent the maximum water that it will hold and therefore you should gets the RTlm of R that this is relative humidity this is reported in the papers you know the Hindu has it every day all you have to remove read the relative humidity there by RT/Mg should have a picked up a – sign yeah this the energy here this should be a -, because this is the energy that you had , this should be –sign here.

This relative humidity is always less than 1 this is the height t9 which tree can grow and still have a water supplied from the root to the top if it grows any higher it will not have water from here without water supply the leaf would just drier to give you an idea is that what the sight is giving units here R do it in a SI units what will the value be or if I start with 82 Cc atmospheres per gram hold degree K*300 I am looking at only this factor.

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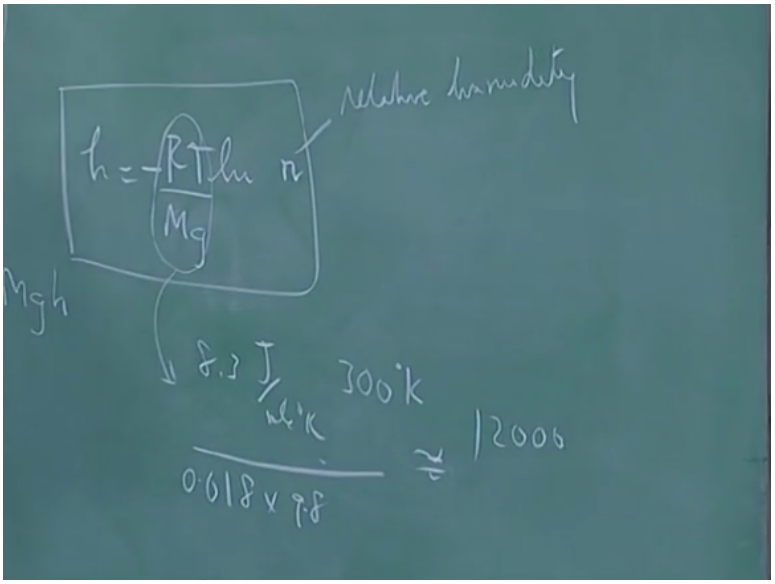

By molecular weight are 18 what is G? Sterile units see things easiest to work with Joules R will be what 8.3 Joules per mole degree K into 300 degree is K so from working with Joules this is 9.8 that correct I am making mistake anywhere, yeah this is alright this comes to .8 no, no yeah you need no, no this 18 Kg gram per mold okay. You what you want your saying is you divide by 1000. Yeah, so what is about take this is 10 this is .2 so about 40, 1200 approximately or 12000 . 02*10.2, 40*300 yeah 12000.

So you are talking about 12 kilo meters*so H is approximately -12 H in kilometers mm r, so thermodynamics juts certain limit this r will have to be the you know you have to take this value of r as close to the in the vector season possible so r can be close to 1 if it is r is 1 then this no choice no tree can grow their relative humidity will be less than 1.

But if it is less it will vary from season to season in the monsoon season for example in Madras it can be 90% humidity it will about.9 so lm is .9 is about .1 so in principle it can go to 1.2 kilometers the thing is not interesting by if the number is not so, fascinating because no tress ever goes to that height before that it gets not affect by wind or whatever but the fact that you can certain limit to the height is explore from these arguments.

All these arguments are nothing to do the trees but using those arguments you can finely certain limit on the, but lets us look at the actually what happens where you used this most chemical using it actually in distillation column most important distillation column.

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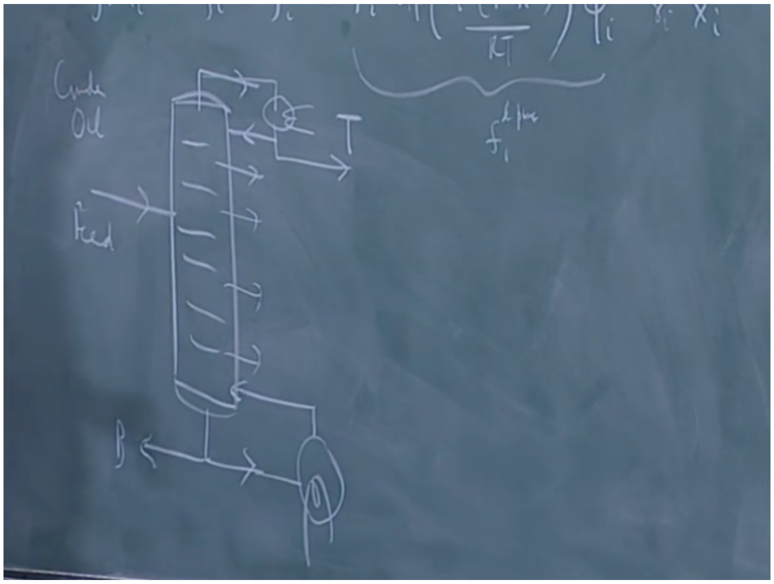

In the chemical industry till date is the oil fraction column you take crude oil distillation column actually some what looks like this not bad a picture but it does at let me you can have a series of tray I will show you what each tray looks like give you an idea then this is the feed this is the bottom product this is the top product.

A crude oil is basically mixture of components of different molecular weight and you can actually see this in the Madras Refinery I will promise that I will arrange for you go to and sleep I will talked to them what you have is crude oil coming in at some point each of these let me take 1 tray example a typical tray.

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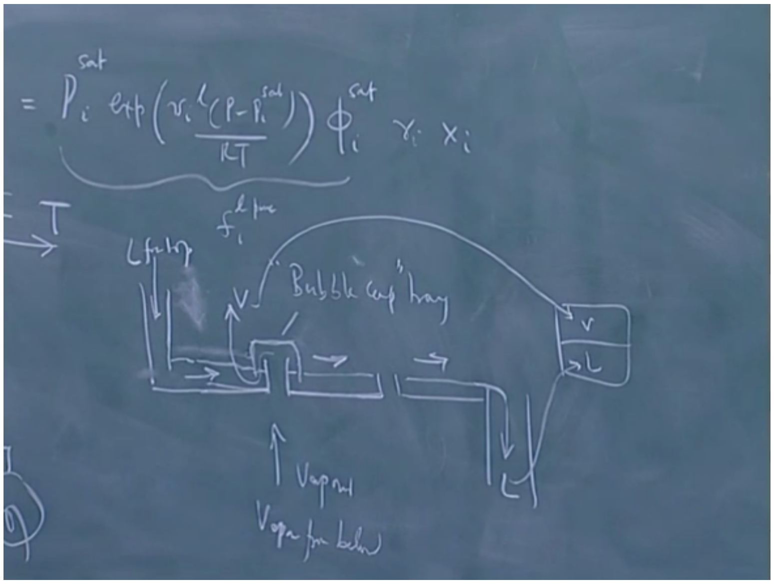

No there are much better trays but a typical tray looks like this drawing the cross section of the tray what you have is from below the vapor comes up I will find out and there is the liquid that comes from the bottom from the top, plain what this is supposed to be there is a hole in the tray through which the vapor rises.

This vapor there is a cap on top this tray is called bubble cap tray is bubble cap is the tray what happen sis there is a hole end through which the vapor rises the liquid this there is a small tube attached to the play and has the vapor rises it will have to bubble through the liquid is up to this level the vapor has to bubble through and escape like this.

As the vapor bubble through and escapes like this it has it comes to intimate contact to the liquid the contact time may be only a fraction of minute but during this time the vapor comes to equilibrium with the liquid. So this vapor that leave and at the end of the tray there is a down come up and the liquid goes through here so because the vapor and the liquid re extremely well mixed as the liquid comes from the top flows like this and finely comes to the down comes.

There is the down comer here from the previous there is the liquid coming down okay this is liquid coming down from the down comer it flows on the tray like this it goes a cross and then goes down to the next tray as a parses over the tray the vapor from blow bubbles through it these are the devices the various kinds of devices that are made in order to make sure that the gas is an intense contact to the liquid.

Typical contact time here it will be only if few seconds but during that seem it because it bubbles through in the form of small bubbles you have large area of contracts you have a sufficient contact for it come to equilibrium as for as thermodynamics is concerns this vapor and this liquid that leave or in equilibrium at one another this is from top this is the vapor from below.

The vapor coming in and the liquid coming in or not at equilibrium this is coming in from another tray this is coming down from the top tray these two are not an equilibrium but the vapor leaving and the liquid leaving or in equilibrium in practice a very nearly in equilibrium it reach about a 90% of equilibrium so you can do the calculations where finding out how much how close to the equilibrium they are so where does the thermodynamics coming my box is like this I have a liquid vapor so this is the liquid this is the vapor on top.

So the two compositions are related they are related to this equation so as I go up what happens is normally is the thumb rule if the saturation pressure is higher or if the component is more volatile then Yi is greater than Xi in the other factors that will control but qualitatively this is correct that is the saturation pressure is higher this substances is more volatile it will be more in the vapor phase than if I want two components one and two component 1 is more volatile.

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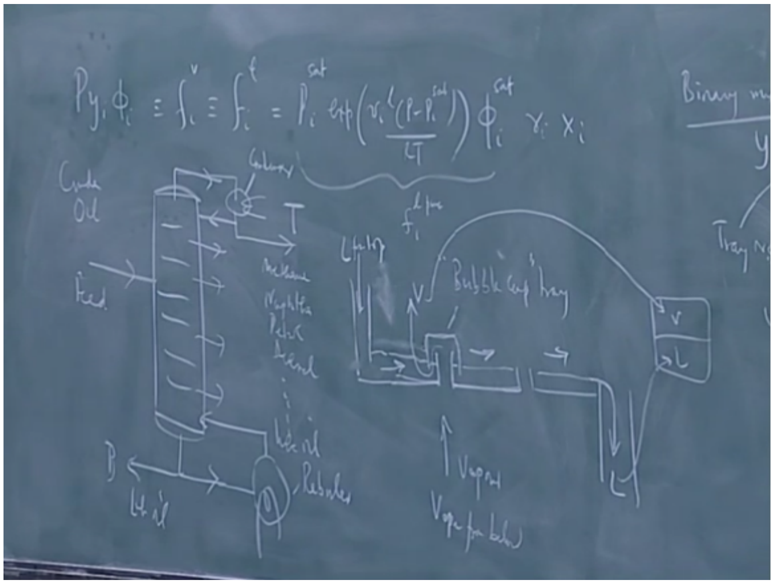

Then it will be it appears mole fraction the vapor phase will be more than the liquid phase so at every tray if Y_n is an vapor leaving the tray n, n is the tray number okay look at the binary system for a binary mixture, for a binary mixture Y_n is the in the equilibrium with X_n, X_n is the this as a composition X_n for each tray.

And you will find Y_n+1 it's measure the trays from wither up or below let me take Yn+1 is greater than Y_n ten X_n+1 is less than X_n so if I have a large number of trays I can get practically pure 1 here so if I have many components the most volatile component the lightest component will come out on top in the case of the refinery here what comes out on top is natural gas actually methane effectively lowest hydrocarbon.

If it comes out in more quantities then you can use you actually burns it there because you cannot afford to pollute the air so you will see the occasionally you get a vapor of it so far away but most of the time they burn it very effectively now they are trying to fight bit and use it as natural gas at the bottom here you get a higher and higher molecular weights at the lowest finally in a tower you will get a very high molecular weight components which go into lubricating oils.

So from methane effectively these are not exactly methane it is of that ratio it is an hydrocarbon mix with carbon to hydrogen ratio of something like 12:4 which is methane ratio this is all approximate ratios in a displaces in column you do not get into the components in an crude oil distillation column this bottom will be some lubricating oil this even this lubricating oil is liquid only because of high temperature that you maintain here.

What you this is called the reboiler what you do is send in an mix of the freed which is the crude oil this crude oil at6 the bottom is where you finally supply energy you supply in an enough energy to evaporate this crude oil also and this goes up as it goes up you can draw of streams at various points each representing level of purity for a molecular weight range.

For example the next one would be Nafta after that would be petrol then there will be a diesel and so on so you will get things like etc all the way to lube oil but even get the waxes but they would not be in the solid form in this stage the temperature will be high enough so that the wax is mold so these products you removed depending on you can change the number of trays you can tray change the point at which you draw off depending on the market if you want more diesel or more petrol.

Then you have a large number of trays at the top you will draw for lot of petrol etc and depending on that you will have to supply energy on the top the gas it is comes up it condensed and this removed or it just burnt as gas so this is the condenser this is the reboiler this is the condenser should realized that higher and higher molecular weight components will condensed.

And lower and lower molecular component will evaporate as you go up so the latten heats will balance one another so basically you do not need that much of energy in a distillation column the energy of the condensation will compensate the energy of evaporation the more volatile component will evaporate and less volatile component will condensed on each tray so this will go on and this is balanced out so you do not really need normally you do not need the detail enthalpy balance in a distillation column.

The enthalpy balance simply says that latten heats of evaporation in condensation approximately equal and that is the thumb rule in thermodynamics that the molar latten heats are approximately the same for the hydrocarbons so this is the actual column this is what you have be dealing with but what I need to design this is an input which tells me how the molecular the mole fraction of the component vapor phase is regulated to which mole fraction and the liquid phase.

This plus mass balance + necessary energy balance will solve all the equations for you will be able to get exact because when you do the mass balance you will have the liquid coming in from the previous tray about for the feed tray there will be a special treatment because this is another stream that being added for every between two tray if you are taking out stream that tray will lead us special treatment.

The only input you need is this and this input will be given to you in the form of graph as far as distillation column mass transfer course concerned so you will think you did not use the thermodynamics etc this input comes from thermodynamics you calculate this curve from thermodynamics so in practice what you need to do is do this calculation practice the vapor phase corrections and the pointing corrections are not so important the most important correction from γi.

If there is the non ideality largest, largest non ideality correction is from the liquid phase that is the most important part of it so we will look at for example liquid phase non ideality in practice I have given an problem in order to find out if you understand everything I am ask you to calculate may give you a problem at two atmospheres and still ask you to correct calculate the pointing correction just to find out if you know how to calculate not much well.

But in actual practice for anything below 10 atmospheres or even 20 atmospheres the pointing correction is neglected this is neglected saturation I notice also that so very often this ratio is 1 even an individual non ideality or not 1 so you can often through away the corrections for figures to coefficients.

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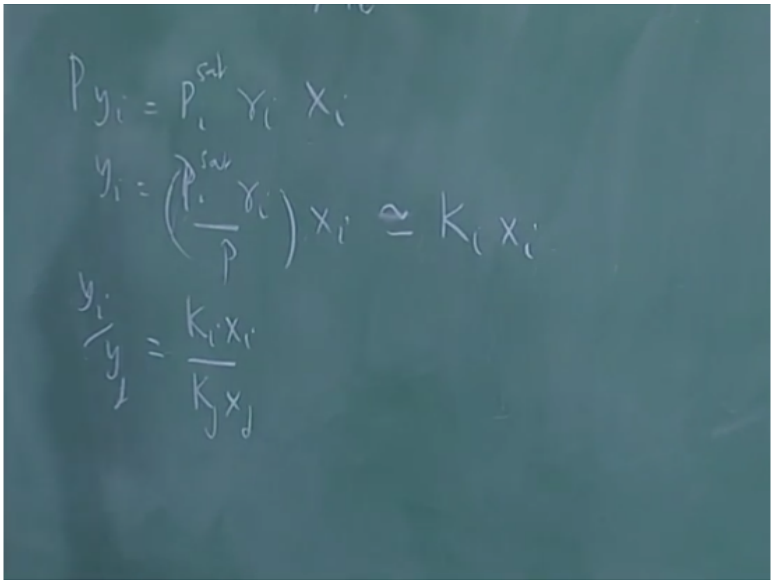

$$P y_i = P_i^{sat} \gamma_i x_i$$

$$y_i = \left(\frac{P_i^{sat} \gamma_i}{P}\right) x_i \simeq K_i x_i$$

$$\frac{y_i}{y_j} = \frac{K_i x_i}{K_j x_j}$$

So most of the time you used I will say at low pressures pointing correction is approximately 1 and you take Øi/ Øi saturation as pproximately1 so the equation boils down to Pyi and into the treatments you write it as Ki*Xi is Pi saturation γi/P this actually function of compensation strictly speaking but in classical treatments n chemical engineering their views Yi=Ki*Xi more importantly Yi/Yj by this stroken is equal to.

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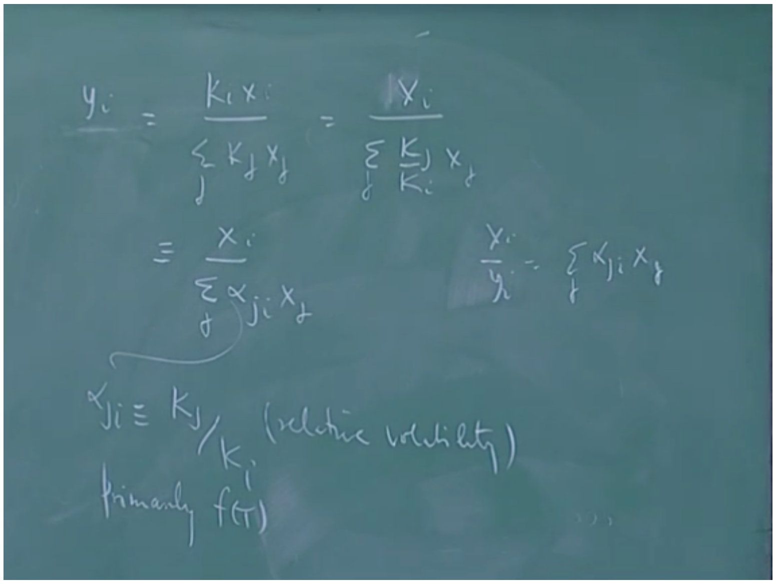

$$y_i = \frac{K_i x_i}{\sum_j K_j x_j} = \frac{x_i}{\sum_j \frac{K_j}{K_i} x_j}$$

$$= \frac{x_i}{\sum_j \alpha_{ji} x_j}$$

$$\frac{x_i}{y_i} = \sum_j \alpha_{ji} x_j$$

$\alpha_{ji} \equiv K_j / K_i$ (relative volatility)

primarily $f(T)$

In order to get Yi now simply have to do Ki, Xi because some over Yi Yj is 1 so some over this has to be equal to 1 this is equal to Xi some over by Kj/Ki *Xj this αji is defines as Kj/Ki this Ki is called essentially this is called volatility this determines how volatile component I is in Kj/Ki is called relative volatility.

It is an rather important engineering quantity because it is much more constant ki, so Ki is actually function compensation dependent quantity and it can be very quite a lot but usually ki/Kj is approximately constant at given temperature so this is primarily a function of temperature in typical distillation column you can go from something like 600 degrees here it is about 100 degrees here in centigrade.

It is part of very wide range of temperatures so very often what they will do is to same the lower half you use 1αIj and in upper half you use other αj because it varies with temperature α is vary widely so it convenient divide intersection in constant α over each section but this gives you a representation of equilibrium very nicely for example if you have Yi /Xi or Xi/Yi.

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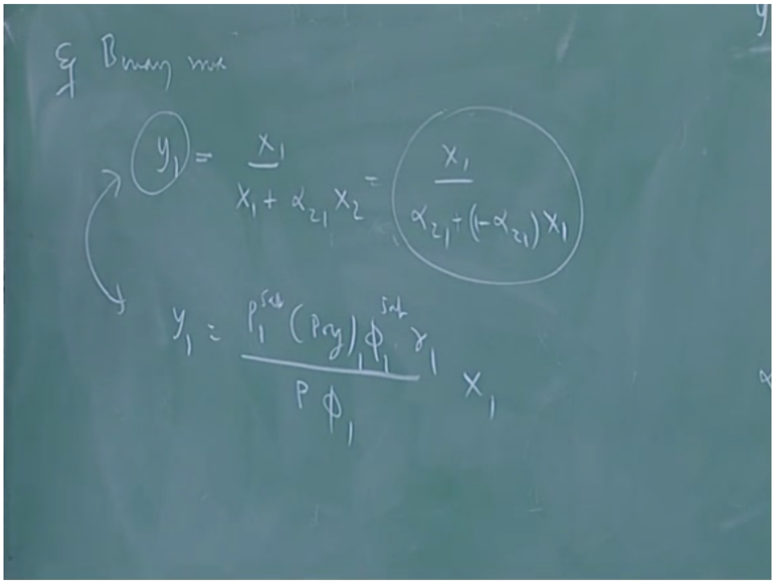

So instead of giving you γv data instead of giving you an expression for gx is which you calculate γ I can give you data on K which makes life very simple or data on α example binary mix you get Y_1=X_1/1+αIi is 1 really α_{21} X_2 not this is X_1+, so very simply the relationship between Y_1 and X_1 this is 1- X_1 of course.

So this is the relationship between Y and X this also gives you the relationship between Y and X you can then therefore calculate expression for α in terms γif you had an binary this would simply means Y_1=P_1 saturation all if that etc pointing correction for 1 if you what saturation γ1P_1*X_1 so you have to compare these two you get the some connection between α1 this expression and γ1/.

So α can be related to γ so yesterday we discussed lot of problems that I have give you vapor liquid equilibrium and one of the most one interesting way one of the question says how do you get these values γ values you get it through the equations but how do you get parameters in these equations and look at some examples of gx.

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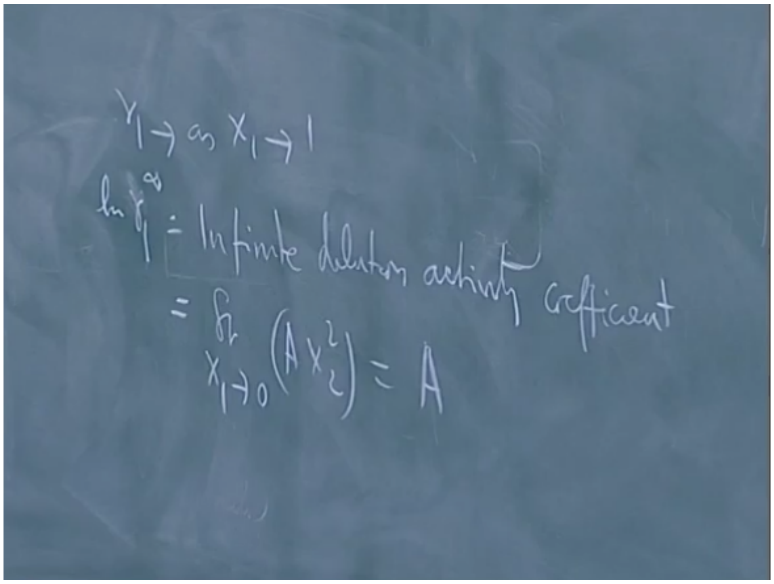

I have gx/RT then $\log\gamma_1$ for example already seen this for example you have A, X_1 and X_2 this is AX_2^2 now we know that γ_1 goes to 1 as X_1 goes to 1 and S $\gamma 1\infty$is called infinite dilution activity coefficient some over ∞ is limit as X1 goes to 0 of AX_2^2 through this simply A, so if you can measure non ideality at very low compensation to X1 and you get this coefficient here in log $\gamma_1\infty$, log $\gamma_1\infty$ is simply A.

So this infinite dilution activity coefficients are often the way in which data are reported that is if you have different correlating equations these constants I have to give you data on these constants for you to do predictions because if you know the gs's expression along with theses constants for particular system then you can calculate γ and you can solve this set of equations.

So in order to solve this set of equations I had to give you vapor phase non ideality which means I have to give you an equation state or tell you the pressure is low so you through away all the fees and make them 1 so I will give method of calculating this I have to give the liquid volume so that you can calculate pointing correction if necessary and then you have to calculate γ to calculate γ I have to give you gx's.

The way in which gx's data is given is often your told that it is some equation and to get the constants I mean give you I can give you values of or the constants or simply give you limiting activity coefficients so with that actually the vapor liquid equilibrium treatment is over all I have to do is give you large number of problems in discuss individual problems in particular interest or if the other way of getting these through measurements some assume troops will discuss this in next class I will discuss getting constants in these equations using data from isotropic mixtures.

If this systems has isotropic okay really that covers vapor liquid equilibrium in case of liquid mixtures where all the components are solvents will still have to discuss the case where one of the components in the liquid is actually solute in which case you cannot get this P_i saturation you will not P_i saturation you will get some other reference value you cannot go to the liquid state okay I will stop there.

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