Indian Institute of Technology Madras

NPTEL

National Programme on Technology Enhanced Learning

Chemical Engineering Thermodynamics

by

Prof.M.S.Ananth
Department of Chemical Engineering, IIT Madras

Lecture 27

Illustrative Examples II

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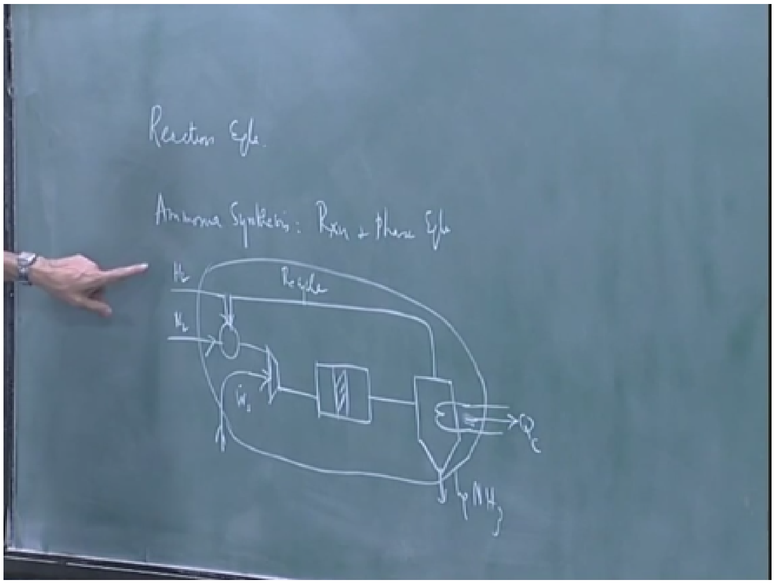

And discussing reaction equilibrium we discussing ammonia synthesis here we will discussing about the reaction and phase equilibrium and we said that we have gases coming in and mix them and we compress them goes through a hector this goes to separator and say this is the work this is my reactor I have or Q removed from here this is a condenser and there is W_S. So if you doing an overall analysis of the process first a fall let me discuss these individually, as far as the reactor is concerned we said Ky = not Ky k and I think.

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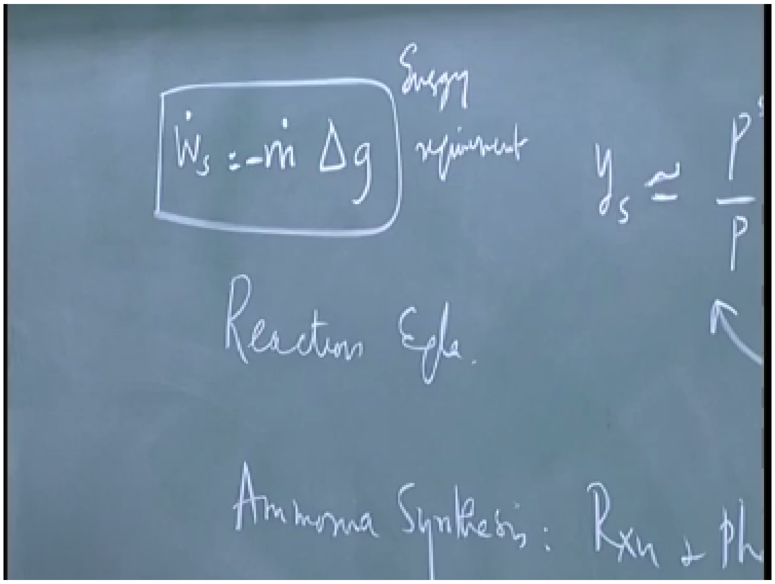

Through at the moles numbers this is we said e at equilibrium we had ½ into 1 – x this is 3 / 2 into 1- x and this x, here essentially Kn now Kn is suppose I want Ky the total moles this is 2 – x, so you had 2 – x / ½ this is 1 – x $^{p-2}$ times there is a ½ 3 is a 3/ 2 $^{3/2}$ ½ of 1 – x / 2 – x and then 3/2 into 1 – x / 2- x $^{3/2}$ this to the ½ and this ½ sorry, so this whole thing is 4/3 √3 can b erase this and writ this as 4 3√3 this is equal to this is from the definition = P times is it P or 1 /P this p $^{-1}$ it will be here so it is P.

Times Kf l ϕ and I told you when you plot this, this if you plot y ammonia which is 1 – x/2 – x this is y in the reactor this is pressure and let curve that proofs like this, and far as separator is concerned you have y separator = effectively in th P saturation for ammonia / P times exponential of V liquid – B into P – p saturation/ R^{T}, so at P saturation it becomes 1 then it comes down of course like this.

This curve us y separator actually the y separator would go exponentially up when it falls down if you taken to compared virile coefficient, so you have to do this correctly and put it in the assign I put in special assignment with additional problems this region of feasible operation, then there is p minimum and a P maximum between which the mole fraction coming out of the reactor is higher than mol fraction required in the condenser for you to produce liquid ammonia that is the rang of feasible operation.

So typical of coupling in the chemical industry where this as only reaction requirements so you can alter in order meet the technological output needs you also notice that, if I did this is always typical the problem is always simpler if you can use a larger system if I use the entire thing as a system this is my plant I get hydrogen and nitrogen and I supply ammonia that is all I care about and finally this ammonia is applied at room temperature these enter at room temperature if any heating is required I do it in between.

If I do that then you know that this is an isothermal process effectively 25^0 so S.s = m. times Δg from - so all I need is g for Δ g for this process that is I have to take the chemical potential of ammonia at 25^0 in one atmosphere subtract from it the chemical potential of these in the ratio one is 23 it I take x I take one mole there I take 13 / 2 moles and one half if I subtract the chemical potentials then i get exactly Δg you have to verify what you need to do is this is the energy .

Actually I am only interested in WS./ m. and you can take a look at the cost of energy and present TNEB rates and ask if the price of ammonia and the market corresponds to this is there will be a factor which is greater than 1, but you will find the district proportionality that is what I have starting to you what will begin separation controls most of the cost but it is a very important to process in this ammonia goes on into a urea reactor you get ammonium + carbon dioxide.

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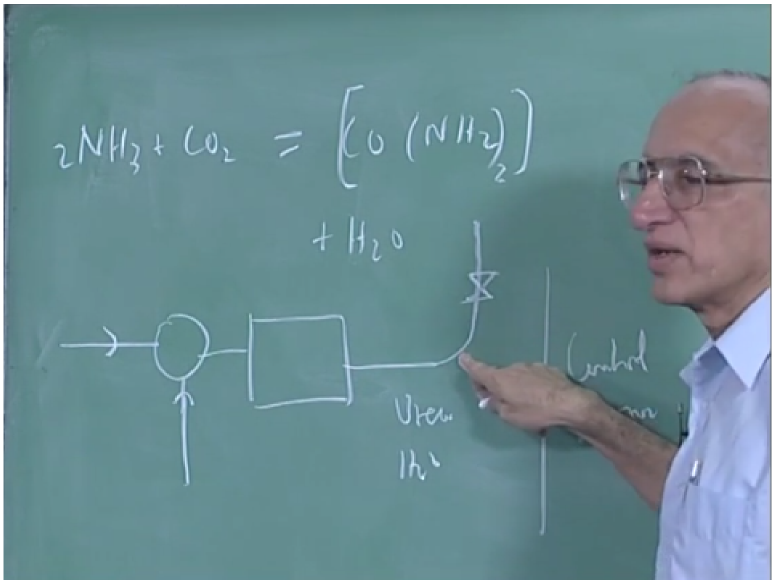

What is urea CO NH 2 twice forgotten NH_2 o CONH $_2$ and that is what I thought Co NH $_2$ twice do the balancing is one oxygen extra know to what else is extra see is okay, Oh is okay its direct synthesis it a nice to twice is there a H_2 left, so plus water if you do I do not know if you know that in the madras defender is this ammonia comes in one place and they have this reactor carbon dioxide is supplied to the reactor these two are mixed always and sent to the reactor and out of this urea comes out.

Of course H_2O there is a reactor bend and this is also done at very high pressure and turned out that the valve for this was located here in this is long ago, but 20 years ago we have a Madras fertilizers here they make this plant and they had a control room here and control rooms are not so recent I mean they have been around for many years, so this is what it is thing early 80s or so we had somebody come and talk to us there was an accident in Madras fertilizers in this hot area urea see the urea was coming out here.

And taking a bend and at this point by erosion the pipe had completely eroded then this broke urea came in it broke the glass here and about three people three scientists were killed herein the inside the control room before they could escape and nothing afterwards everything was brought under control, but it is a very elementary thing I just mentioned this after that after the create study with huge committee and all that they said the mistake lies in placing the valve here this valve should be here.

Because valves are always inspected the inside of pipelines have not inspected regularly, so when the valve corrodes it will start leaking as soon as it leaks you can fix it in this case you do not notice that this is corroded at all till suddenly the whole thing blows because this valve does not leak okay let me discuss a couple of other problems one other I wanted to discuss I brought some data's.

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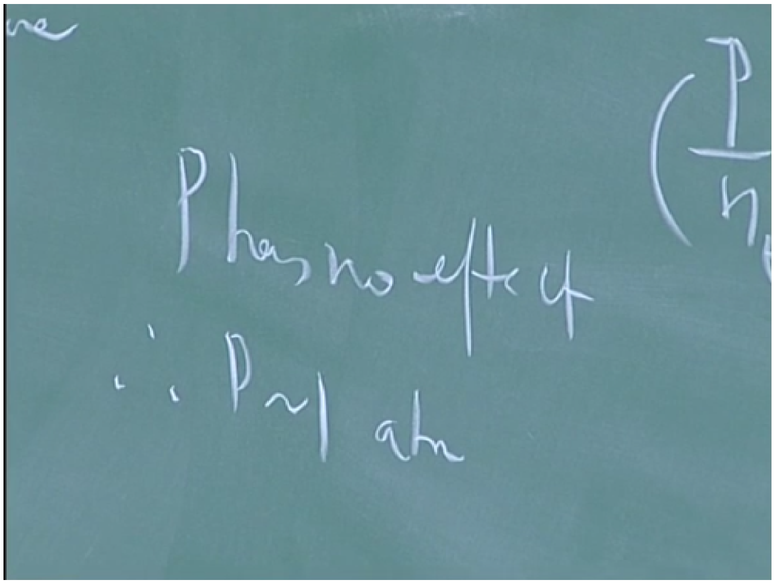

And the second is isomerization this is actually more typical it's a very simple problem this is butane to n-butane I mean n-butane types of butane then two percent HC_l this must be coming from another stream in isobutene here, they have the question is the temperature is given 300^0 what is given F, but does not matter Δg0 is known for this reaction at this condition 97.5 calories per gram mole in the reaction is n-butane to Iso butane this is just calories per gram mole not kilocalories because.

It is just an isomerization reaction so Δg ΔH are very small next problem I do not written these things wrong then the data wrong, so I have to go back and look at it okay we will just look at this problem again in this case you have all I have to do is write down here, butane is then-butane then isobutene n HCl so let us assume that I have one mole here and 0 actually it is not one mole end this thing oh, 0.9 3 moles and the point 0.5 moles initially at equilibrium I have 0.93 - x this is 0.05 + x and you can put down HCl is two or 0.02 0. 02 total moles remains.

Unchanged you have K_F is equal to exponential of - 97.5 / R_T Δgs is positive or negative you return a positive number does not matter small number, so again your K_F would be simply P, P/ np^0 and no change in number of moles, so pressure and total moles cannot affect the reaction so you cannot alter this reaction by altering inerts you know it is one form of control that you have then there is no point changing the pressure, so it will be carried out at atmospheric pressure times K_n k ϕ.

If you like since pressure does not matter nobody will bother to use high-pressures okay ϕ will be 1 and then you have only K_n, Kn is 0. 05 this is the + / 0.93 – x that is it there is no nothing else this is equal to K_F K_f, course of course is constant this is known this is 1 this is 1, so what you have to do is calculate x just add these two you get 0 point 0 5+ x / 0.98 = K_f / 1+ K_f then you have a k x calculation you have to use R and T in the right units do not mix make a measure that a trouble in reaction equilibrium is.

If you use somebody puts in point oh 8 in litter atmospheres instead of calories and your number will be so different that I cannot give you any credit for it because ultimately in engineering the order of magnitude of the number is important and in these cases, since you have never worked in the industry of no field for those numbers so you will have to be familiar with the numbers and make sure you do not make mistakes in the units normally for number numerical mistakes I do not give I do not punish you but is the which order of magnitude of you will get a – 1.

So be careful as far as that is concerned so these are the K_f is exponential of - Δ g / R_T K ϕ is 1 because pressure has no effect you would be foolish to use any high pressure right essentially P has no effect industry never uses therefore P would be approximately 1atmosphere whatever is convenient usually low pressure will be used and invariably chemical engineers and chemists are blame for all pollution thing to remember is that you are not polluting there for your own benefit you are actually minimizing the pollution that anyway would occur because if finally a plastic bucket is made only because the consumer wants.

It the question is making the plastic bucket what is the minimum pollution you will create a minute you cannot pollute the environment if you want a plastic bucket, okay let me discuss this other problems both face and reaction equilibrium problem told you about chloromethane.

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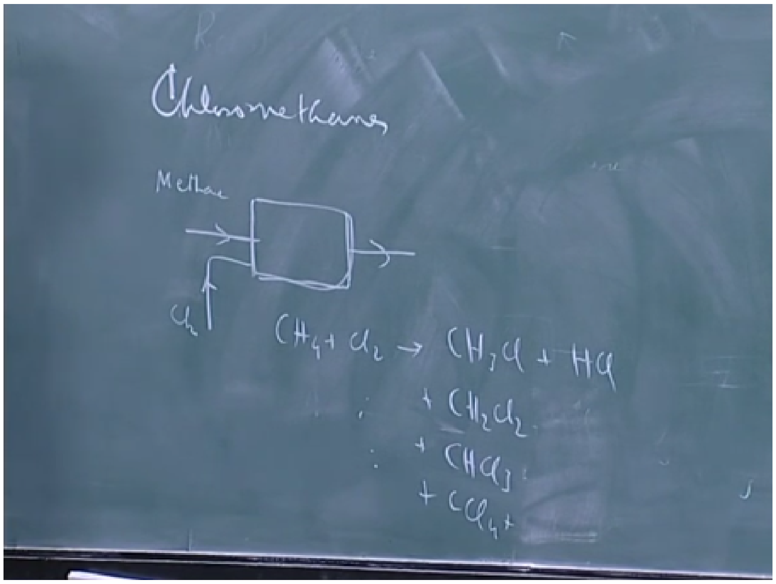

I forgot to bring the data with me this is actually a consultancy that I did many years ago quite long time, since I did consultancy what you have essentially is a reactor in which you have methane and chlorine these are not mixed pre-mixed usually because chlorine is a dangerous chemical, so you have one reactor which is all the provisions for safety so you send them in otherwise normally the ingredients of pre-mixed because chemical reaction engineering the important thing is mixing.

The product that comes out is several things you have four reactions when it is essentially corresponding to the number of chlorine atoms you can add CH_3 Cl + HCl then you can add you can add more chlorine you get CH_2 CL_2 + HCl CH CL_3 and then CCl_4 + HCl is essentially in the reaction we will just get all right take off HCL + it is a comment all, so you get all these you get all possible forms of chlorinated methane.

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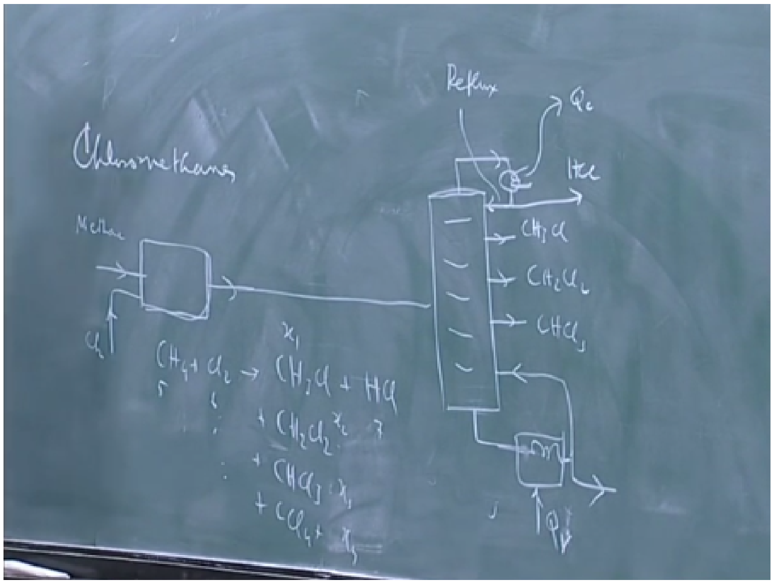

Now this whole thing is then sent to a distillation column distillation column has many trays what you do is pull out at different points a component this will be essentially CCl_4 because it is the least volatile of the compounds when I sayCCl_4 it would not be pure CCl_4 it will be99.9% and so on the other component will be present and on top of course you will get h here and then CH3 Cl suppose I need one more thing CH_2 Cl_2 and CH Cl_3 in general in all distillation columns you a certain amount of the top pressing is fed back.

What you do is actually not take out it is here like this you pass this through a condenser and part of it is taken out this product part of it is recycled, actually this is called reflux you reflects the product back and by controlling the reflux you can control the composition of the products you will do that anyway in mass transfer similarly this bottom product is also not taken notice is normally what happens is you have to supply energy somewhere, you take out energy here this is a condenser.

Then you have this is called re boiler it re boils the bottom product if you like and a part of it is taken out and the remaining goes back as vapor to the distillation column normally because the latent heat smaller latent heats of compounds are somewhat equal you will find the amount of heat taken out in the condenser in the commander heat are comparable but this is at a higher temperature they are supplying the heat here you are getting it at lower temperatures.

So there is a loss of availability it is there is a lots of energy in terms of what is available for you to do work at higher temperature the quality of heat is better than it this is actually the this part of it is fairly straightforward you do these reactions you have to assume that x1 x2 x3 let us assume x1 moles are formed x2 moles x3 and x4 you will call this one two three four call this 5 if you like this is 6 this is 7 so what you have in the product.

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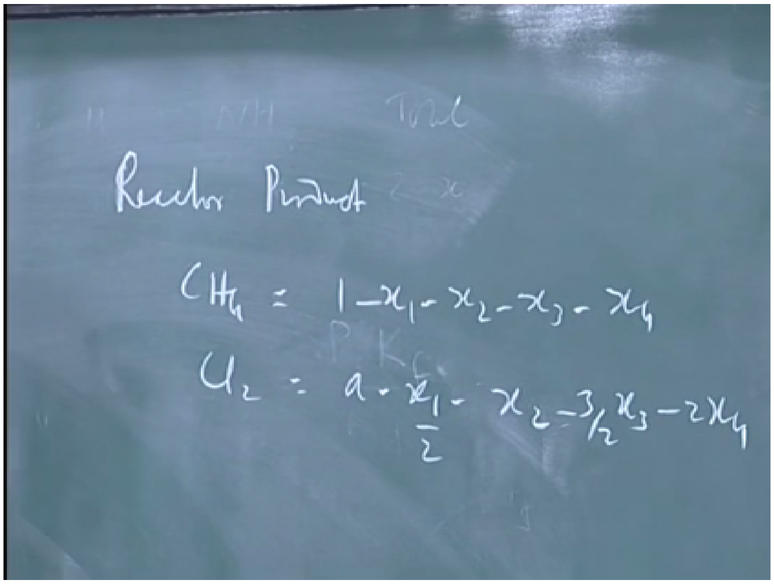

Reactor Product

$CH_4 = 1 - x_1 - x_2 - x_3 - x_4$

$Cl_2 = a - \frac{x_1}{2} - x_2 - \frac{3}{2} x_3 - 2x_4$

Reactor product which is what counts at equilibrium assume you are doing a calculation at equilibrium so you have CH_4 you will get essentially CH_4 will be let us start with one mole of this and a moles of chlorine I want to know if I can choose this a suitably, so you will get 1 – x1 – x2 – x3 – x4 that is the methane part the chlorine will be a 1 mole of chlorine will be used up here you will have two moles you step right CH_2 Cl_2 + $2HC_l$ or 3/ 2 right, so you will get – x1 – 3 / 2 x2 maybe we should write this out for every mole here you have got two moles of chlorine you step.

Now here it is half sorry a – x1 / 2 – x2 and CH Cl_3 this takes 3 / 2 moles – 3/2 x3 – 2x4 paddle no CH_3 Cl oh, then here also I must so all of them must be corrected this one is x1.

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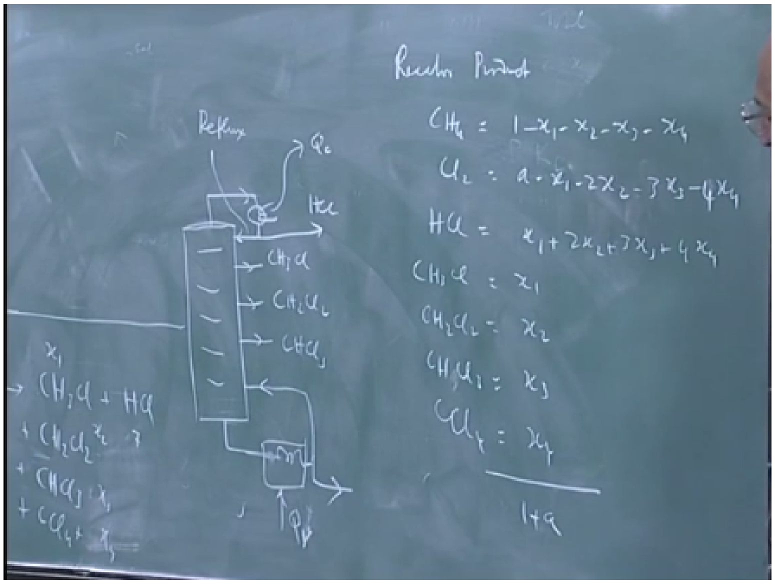

This one is what Cl_2 to HC_l so CL_2 +into 2 then next one next one will be CH Cl_3 so 3 /2 here and $3HC_l$ right, so 3 and for this I think that is all right yeah it is always best to be careful with reaction equilibrium do not get carelessly write what I wrote wait I mean if your life depended on you will spend time writing it correctly, so it is not then HCl is x1 + 2 x2 + 3x3 +4 x4 right 2 3 4 correct and then you have to write these down of course CH_3 C_l is x 1 CH $_2$ Cl_2 is x2 is CH Cl_3 = x3 CCl_4 = x4.

All are in the gas phase so you can do a summation you will get 1 + a – x1 okay all of it is balanced over into okay fine, so essentially if there is no is there if there is no change in moles in any of the reactions, so you have to write down for each of them.

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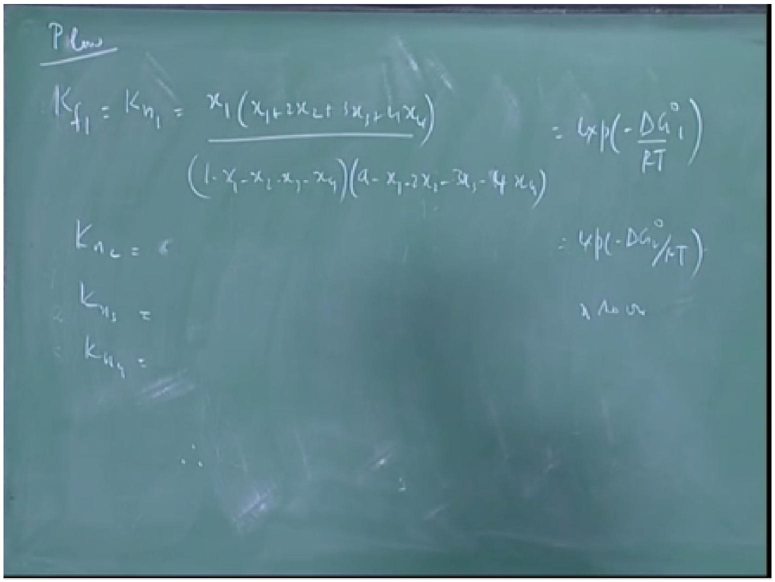

P low

$$K_{f_1} = K_{n_1} = \frac{x_1(x_1+2x_2+3x_3+4x_4)}{(1-x_1-x_2-x_3-x_4)(a-x_1-2x_2-3x_3-4x_4)} = \exp\left(-\frac{\Delta G_1^{\circ}}{RT}\right)$$

$K_{n_2} =$ $= \exp(-\Delta G_2^{\circ}/RT)$

$K_{n_3} =$ & so on

$K_{n_4} =$

k_f 1 is equal to let us assume that the pressure is low it is because none of them are affected by pressure would be foolish using any pressure we you will necessarily use a low pressure, so you our K_f of one will be essentially p by nt will be equal to Kn net k ϕ is 1 Kn times P / nT to the power change in number of moles because change in number of moles is 0 this is simply Kn, Kn oneness of the product it is x1 x HCl this is x1 + 2 x2 + 3 x + 4 x4 / you have CH_4 which is one 1 – x1 – x2 – x3 – x4 and the Cl_2 was yeah.

This is equal to of course exponential of – Δg 10 /R_T so you will simply similarly write Kn2 Kn3 and Kn4 we would not write these out in each case this will be exponential of - Δ g 2 by and say and so on, so if I give you the temperature you can essentially solve for x1, x2, x3etc. There is no effect of the total moles but you still have an effect of a on the tell me what will determine a mean what considerations will you base your two choice of this common sense that is your desirable product.

But from here you are using to raw materials simply because of mass action you will use the cheaper material in excess, so what you will do here is really use the cost of the raw material usually and also chlorine in excess is dangerous for the environment so in this case you would go with methane so you would go with the minimum chlorine requirement, so you probably use the stoichiometric amount of chlorine required but it is a useful computation to do to see how sensitive the calculations are to the ratio based one.

Coming back what you do is solve this for the reaction equilibrium and this again is coupled to this and tell you another interesting anecdote here this is chemical industry practice is full of this only thing is you have to do careful calculation the calculations a trivial in thermodynamics here you can design this distillation column, you will do this next semester and this is not a problem at all because this mixture happens to be an ideal mixture because these are very similar compounds.

These are chlorinated methane's and they all mix ideally so γ in this case in this case ϕ all your fugacity coefficients everything will come out to be one, so you are only treating the system that is you have liquid phase because you are using a distillation column you are taking out a liquid product this product isCCl_4 and they were making ccl4 you making CCl_4 of 99.99% purity Gujarat fertilizer started a new unit and they were supplying 99.9999 purity and this last two lines are important for the pharmaceutical industry.

Their purity is of great importance and you will find that if you want to go from 99.99 to 99.9999 you will the number of plates will increase tremendously that last bit of purification is what requires large number of plates you need a large number of equilibrium stages because your incremental purification is very small, manager use the general manager there and he called me and said we have this problem will you look at it so I look at looked at this problem calculate the distillation column design.

Calculate the purity that you should get they had some 74 plates in the column for 99.9 I calculated from theory to a ball you have a mass transfer book practically a worked example you can do the calculation straightway, so I did these calculations and I said the 43 plates will do you got 31 plates extra he said it cannot be then I also told them if you do have 74 plates as you tell me your purity should be 0.49s it cannot be what you are getting I told them 30 of your plates must not be working.

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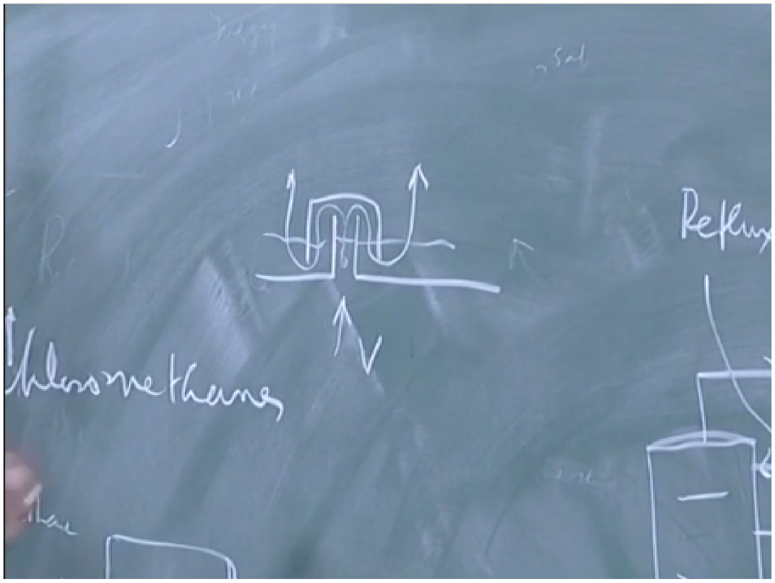

The way these works I told you what you have is every plate looks like this you have liquid and this gas vapor comes from here that is the bubble through this liquid cannot go out this way it will coat I mean the vapor will go out this way, so it bubbles through the liquid and escapes to the next this thing each of these is called a bubble cap you have a cap here, so when the when it there is a hole in the plate and the vapor comes through there is a cap preventing it so it left go out and come through the liquid but if the caps are not in place this vapor will shoot right through and you would not have contact to the liquid two days later they opened in exactly 30 plates.

They had forgotten to put this cap mistress assembled direct immediately after the war in the workers had forgotten to put that cap there but because the market requirement was only 99.99% it was working well, so they never bothered lemon interesting so there are many practical problems in operation but here what you will do is you calculate the reactor contribution this in calculation you have to first maximize your CCl_4 production because in this particular case the other products were not.

So saleable depends on the market conditions means very little demand for chloroform and most of the demand was for CCl for these two were not in demand at all, so you will try to reduce this as much as possible do the chlorination, so that you take this more x3 and x4 and x4 will be the maximum so you can play with this and ask what will alter x for most of the times you cannot control it because your a is the only variable that you had in your equations by changing a you cannot alter much, so you will be stuck with a certain fraction of CCl_4 which you have to extract.

This lecture Series Edited by
Kannan Krishnamurthy

Online Recording&
Post Production team
Subash
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Karthikeyan
Ram Kumar
Ram Ganesh
Sathiraj

Producers
K R Ravindranath
Kannan Krishnamurthy

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