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 26

Illustrative examples I

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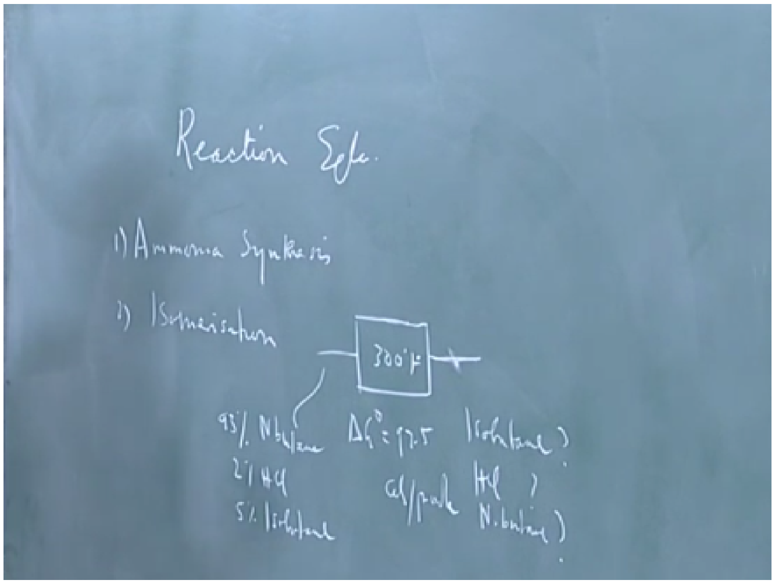

Bases things okay we will discuss reaction equilibrium I brought some data just illustrative examples I will give you 2, 3 these are part of your 1 is the classical problem is ammonia synthesizes 2nd problem isomerization front I should probably bring you some data from a consultancy I did long ago yes chloromethane kemplast the sun mark kemplast group as a huge chloromethane factory.

We discuss it is chlorination of methane's you get all the 4 compounds up to CCL4, very funny actually it was long ago this is the problem is still a mean the same kind of problems arise again even now I will discuss it let me here you have N butene going to isobutene never so clear in actual industry this for example this is some data 93% is input gases 93%, 2% HCL, 5% isobutene.

It is there is a little isobutene in the input itself question is what you get here isobutene is the major thing that you are looking at HCL and normal butane you want to find out what the mix you will get is the temperature is given 300^0 F and Δ g0 is given okay then taken another 3 problems I will put on.

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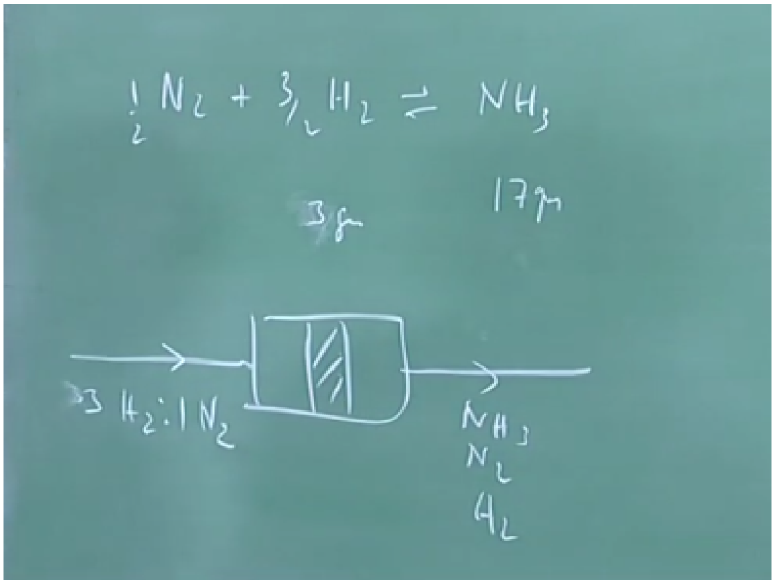

All these are fairly straight forward this is benzene + hydrogen giving you C_6H_{12} this is cyclohexane, it is a hydrocarbon mix okay but look at the process incidentally the reason this is so expensive is because hydrogen is not a raw material that is available right it is always avail in the form hydrocarbons which have to split you have to produce hydrogen various ways in the cost of producing hydrogen turns out to be very high now if you have this you usually a catalyst usually the ratio is in this ratio of 3 of hydrogen to 1 of nitrogen.

That is the ratio here so you have ammonia nitrogen and hydrogen incidentally this is als0 coupled to a phase equilibrium problem so I may as well discuss it in a couple fashion. If you actually look at the process you have nitrogen and hydrogen coming in maybe I should draw a mixture here only a symbol.

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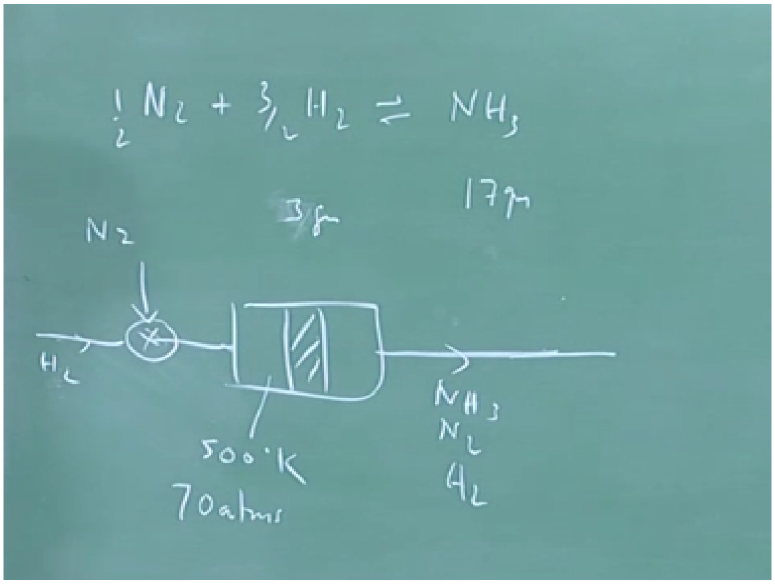

In the ratio 1: appropriate ratio this is a mixing unit we would send it in this is a reactor this is catalyst you get this typically if you we are going to do the calculation you will get about 10% ammonia production and only 10% of the raw material be of nitrogen, hydrogen will be converted to ammonia this ammonia will have to be condensed typically the temperature here I think I have the temperature for the data here.

This is 500^0k the original process was 450^0 C you have improved the catalyst therefore they can get the same rates at lower temperature remember that catalyst is not going to give you different equilibrium okay the equilibrium conversations will be the same at a given temperature but you will get the rates will be different, so you have 500^0k typically the pressure is 70 atmosphere that means these gases I should have put in a compressor here so that sorry.

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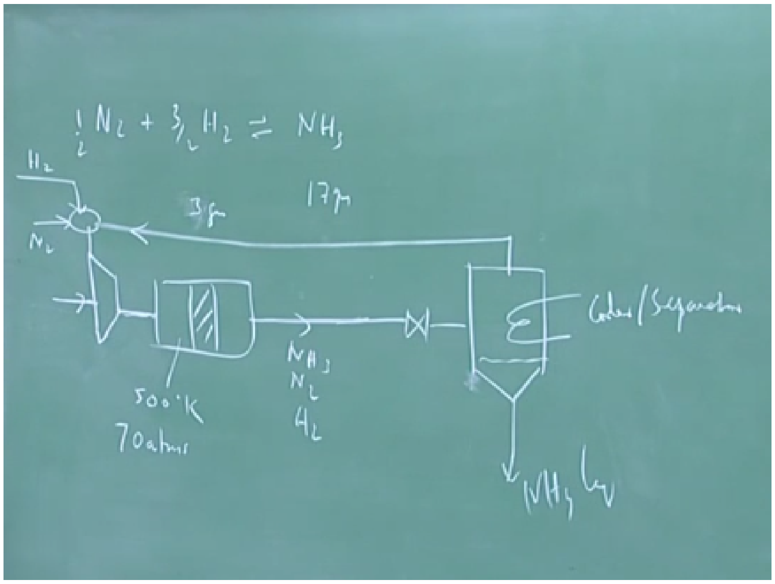

So you put in work in a feet to this comes from a mixture this is nitrogen and hydrogen they compressed insentient here you have a throttle volve you have a separator normally you have a cooler or a coolant cooler comes separator what this does is condense out the ammonia this is liquid ammonia and then the gaseous the part of it is condenser remaining gaseous most of it already a lot nitrogen and hydrogen here these will have to be recycled.

This liquid ammonia simply because it room temperature ammonia happens to a liquid and it is very convenient to separate it out this way because this liquid the rest are gases you can separate them out so what I need is the following in the actual process I have to calculate reaction equilibrium here I have to calculate phase equilibrium since you have already done the phase equilibrium, let us look at the phase equilibrium.

The solubility of hydrogen and oxygen hydrogen and nitrogen in liquid ammonia is negligible so we will treat ammonia has pure phase.

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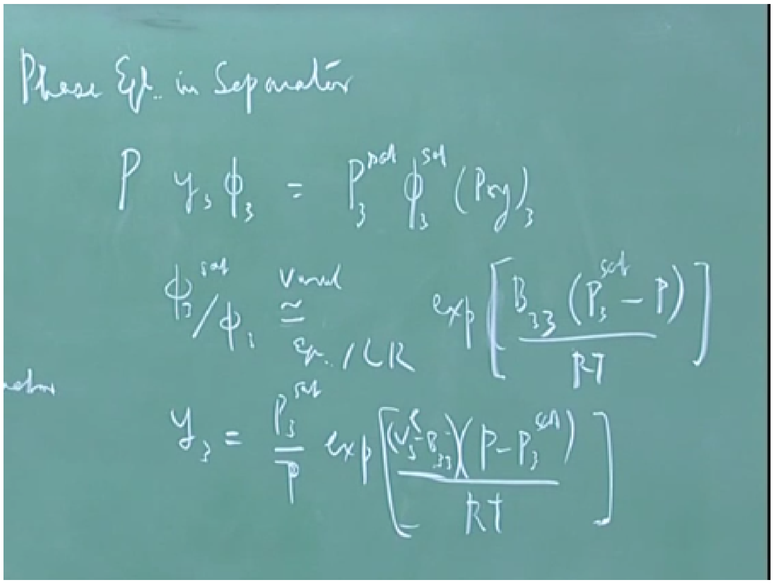

Phase Eq. in Separator

$$P\, y_3 \phi_3 = P_3^{sat} \phi_3^{sat} (Poy)_3$$

$$\phi_3^{sat}/\phi_3 \underset{\text{Eq. / LR}}{\overset{\text{Varial}}{\simeq}} \exp\left[\frac{B_{33}(P_3^{sat}-P)}{RT}\right]$$

$$y_3 = \frac{P_3^{sat}}{P} \exp\left[\frac{(V_3^L - B_{33})(P-P_3^{sat})}{RT}\right]$$

So we will look at phase equilibrium in separator I am looking at ammonia alone let us say nitrogen is component 1 hydrogen is component 2 ammonia is three so I have Py_3 times ϕ_3 this P is the pressure in the separator we will mark it Pl because it is a low pressure there is a high pressure part just for or some other symbols Ps for separator P subscript S okay P separator = you will get P_3 saturation ϕ_3 saturation pointing correction for component 3 $\gamma 3$ there is no γ 3 sorry.

That is all because the liquid is pure so γ is 1 your pure liquid phase so this should be = to this so what is Y_3 = what we will do is for the purposes of this calculation we will take ϕ_3 / ϕ_3 saturation by ϕ_3 is approximately 1 you can do this calculation right anyway I will just take this right now so if you look at Y_3 Y_3 is simply P_3 saturation / P in the separator I think I will forget this subscript.

So dame nascence to carry this subscript just keep it has P this by this into exponential of V_3 or I will write I will also write an expression for this sorry let me write this at terms of varial equations we will use varial equation we will use Lewis and Randall rule. Lewis and Randall rule is a good assumption that means ϕ_3 in the mixture is a same has ϕ_3 in the pure state.

So in the gas phase I have hydrogen, nitrogen and ammonia ϕ_3 for ammonia is a the same as if I use the varial equation this is simply exponential of B, B is the second varial coefficient for ammonia because it represents pair interactions you put 2 subscripts in the second varial coefficient we will write B_{33} ϕ saturation will be P_3 saturation by RT/ ϕ_3 so – P / RT this sis ϕ_3 saturation by ϕ_3 the pointing correction is V_3 liquid into P- P_3 saturation / RT.

Y_3 is P_3 saturation by P this is the pointing corrections then I must add this, this is B_{33} x P_3 saturation – P this is P - P_3 saturation so it will simply be V3 liquid – B_{33} incidentally this phase equilibrium problem arise in many situations I will tell you see here I have taken I will give you an example let me plot this first and then we will describe the physics of it.

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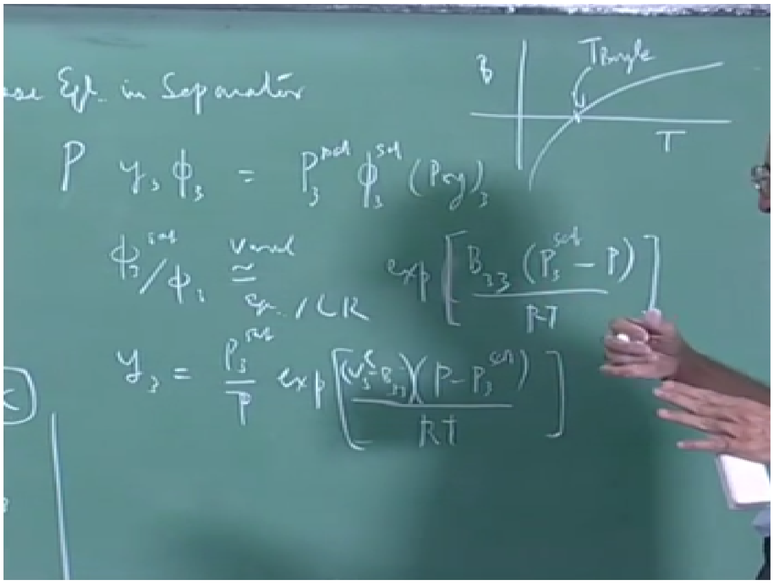

se Eq. in Separation

$$P\, y_3 \phi_3 = P_3^{sat} \phi_3^{sat} (P_{oy})_3$$

$$\phi_3^{sat}/\phi_3 \overset{virial}{\simeq} \exp\left[\frac{B_{33}(P_3^{sat}-P)}{RT}\right]$$

eq./LR

$$y_3 = \frac{P_3^{sat}}{P} \exp\left[\frac{(v_3^L - B_{33})(P-P_3^{sat})}{RT}\right]$$

At a given temperature incidentally there is some common scene conditions the coolant you can use in large amounts is only water in water at room temperature because this water will be we put on of a cooling tower it will come down a cooling tower it will cool by evaporation so you will get water at what is called the wet blub temperature little lower than the room temperature, so typically 80^0 F you can take in say 30^0 C so if you take about 30^0 C the maximum temperature to which you can cool this tower will be about 35.

You have to give difference so 35% will be the practical temperature here, so this will at this whole graph will be at say 35^0 C this is fixed I fix the temperature and I ask how does the composition vary with pressure has the remember some things V3 liquid is positive number B_{33} is the second varial coefficient which is a function of temperature this can be plotted from experimental data if you plot B verses T you get a curve that looks like this typically up to what is called the boiled temperature at which the varial coefficient is 0 second varial coefficient exactly 0 this is called T Bayle after the famous scientist Bayle below T Bayle B is always negative.

And T Bayle is fairly high for most substances it is well about the normal boiling point, so this is it is little usually below the critical point but above the boiling point but this very high so B_{33} is generally negative the idea being this is the first correction to ideal gas behavior ideal gas behavior tell you PV = RT then next correction is P= RT/ V I am sorry I should write it this way.

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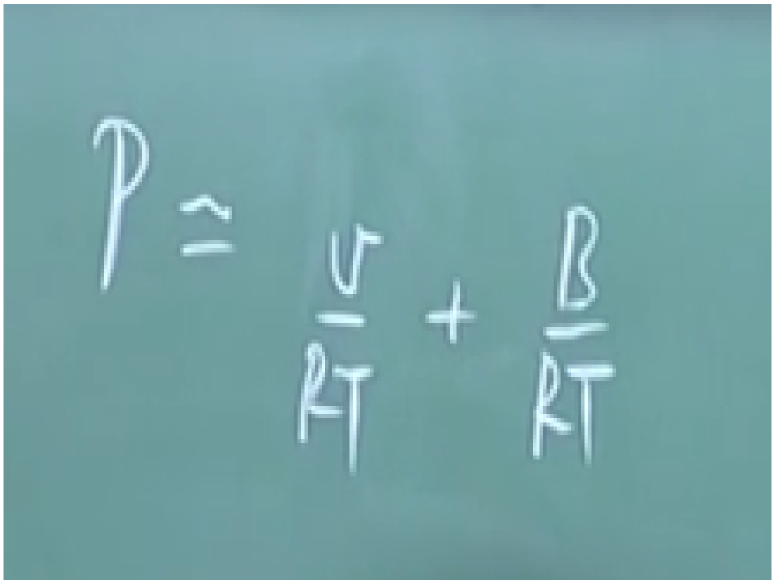

$$P \simeq \frac{v}{RT} + \frac{B}{RT}$$

If P = you writing at as RT/ V + B/V now B / V x RT this is okay PV / RT = 1+B/V right so if I do this approximation you just what B/ RT is it into B yeah right thanks this is V/ RT getting it all backwards.

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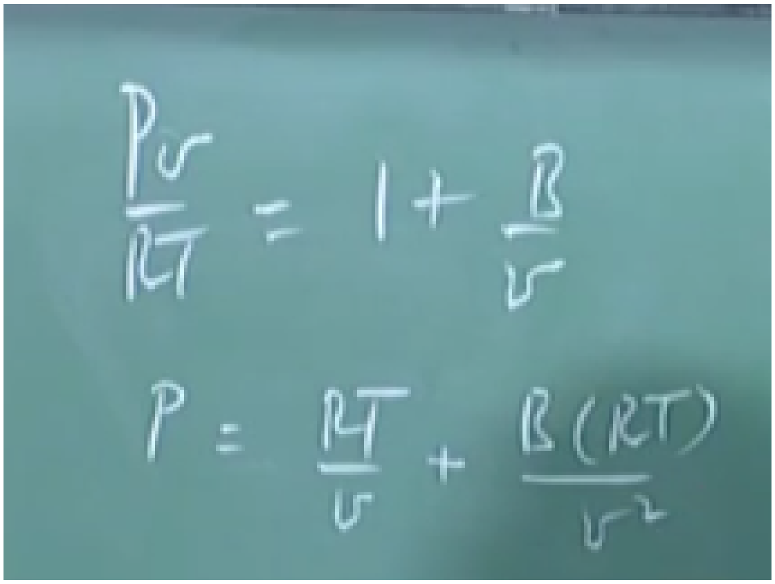

$$\frac{Pv}{RT} = 1 + \frac{B}{v}$$

$$P = \frac{RT}{v} + \frac{B(RT)}{v^2}$$

I will write it out in now I could make sets with new states B/ V so the pressure itself or take a this is RT/ V which is ideal gas pressure + B x RT/ V^2 this is the pressure that you would have if it was an ideal gas if there a retroactive forces the pressure would be less because the number of molecules that pull the molecules at collide against the wall is proportional to 1/ V the number of molecules that are pulled away from the wall is also proportional to 1/V.

So there is a correction due to attractive forces proportional to 1/ V^2 because it is a correction that reduces the pressure B must be negative. So unless you are taking of very high temperatures at very high temperatures this becomes positive because you are getting into let me explain why that happens also.

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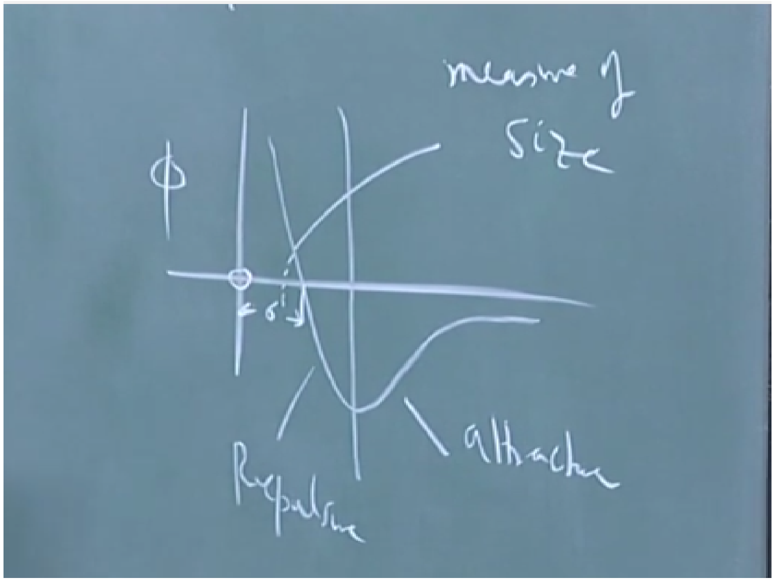

If you look at the potential energy between two molecules do not have a size this is your potential energy the derivative of this with a – sign by convention is the force so here this region is repulsive this region is attractive so the thumb rule is of you have a molecule at the center and you have another molecule moving towards it the force is attractive up to this point and then it gets repulsive.

This distance σ is taken as a measure of size it beyond that the force becomes so steep so repulsive that is unlikely the molecules mole but actually what is meant by size if I take a second molecule in a particular kinetic energy it will keep coming towards this till the kinetic energy gets converted to poetical energy when these two are equal it will stop and then it will go back so where it is stops depends on the temperature depends on it is initial kinetic energy.

So the higher the temperature the smaller the size of molecule appears to so effective these sizes will get smaller and smaller so what your taking about is if you are talking about collisions against the wall if the number of molecules if these if the temperature gets very high then and the density gets high you get a number of molecules within the repulsive range, so the pressure will actual begin to increase in a real gas compared to an ideal gas.

When the repulsive force is dominate you get a increase in pressure when the attractive force is dominative you get decrease in pressure so P will generally be negative and then it will turn positive as you go to high temperatures. So I am telling you this because in bulker the applications of such nature that is your talking about the solubility of or in this case you are talking about the mole fraction in the gas phase.

At which you get condensation in this particular case, so the mole this is the mole fraction at which condensation occurs if you want liquid ammonia you must have a minimum of Y_3 of this beyond this excess over the will condense as a liquid that is how you take out a product now if you look at this mole fraction V- B_{33} is positive so v – B_{33} / RT we will call it α.

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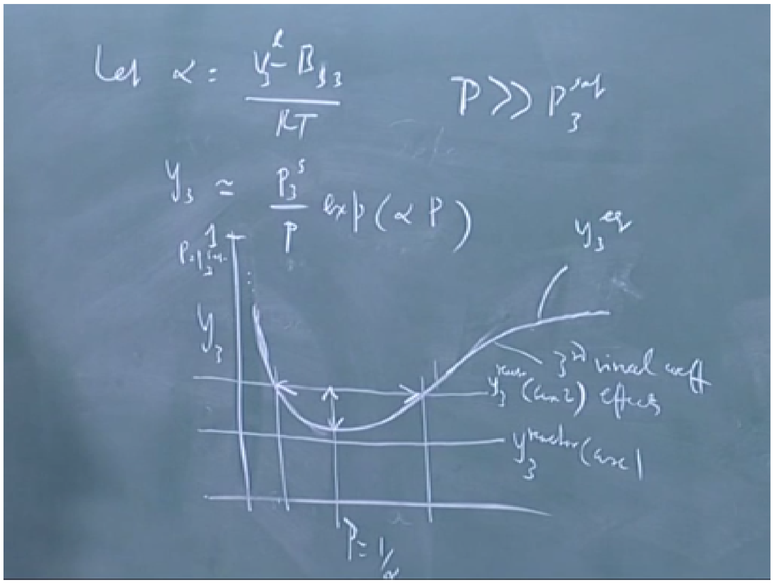

In the form of that expression is essentially $Y_3 = P_3^S$ / P P is let us say P > than P saturation okay at room temperature this saturation pressure of ammonia will be below 1 at atmosphere and your looking at pressure is here that a quite large, so you get an exponential increase in pressure and a fall in pressure due to this 1/ P factor clearly this is going to have initially when P = P saturation there is no this is P – P saturation.

At very low pressures this effectively Y_3 is 1if I plot it will be at 1 here and then it will fall off because of this P then it will increase because of this e $^{\alpha}$ P finally it will go to infinity it will go very high α is generally small RT is very large V_3 – B_{33}/ RT is small in this point you can verify the minimum will occur when this times the differential of this = this times the differential of this so P = 1/ α VDU = UDV denominator.

That is how we mugged it because U/ V you differentiate U/ V you get V^2 VDU – UDV you mug it differentially at least my daughter mugged it has nominator denominator and all that I do not know how you okay this goes to actually this is sort of point it up here this pressure already is much later greater than saturation pressure and that you have gab this will be 1 at P = P saturation/.

So it comes down here it comes to so you have this curve now when will I get condensation in that this is the equilibrium curve actually this is curve is not quite correct because as you go to vey high pressures I have to take the 3rd varial coefficient into account and all these corrections are the second varial correction over corrects for attractive forces so then it will decrease so the actual curve if you plot the actual curve it look this it will turn around sort of flatten out at some point here the 3rd varial coefficient is important.

You have to add 3rd varial coefficient effect up to this somewhere here 2nd varial coefficient will do so we will get a linear portion $e^{\alpha}P$ power then you will get another P^2term $e^{\alpha}P$ 3rd virial equation coefficient times P^2/ T so the varial equation actual curve will turn like this but the principle is like this supposing you want condensation here you want to take out ammonia here if this is actual y3 at equilibrium this is the equilibrium curve you are getting ammonia out of the reactor supposing the mole fraction of ammonia from the reactor is here.

Supposing the mole fraction y3 reactor is here then you can get no condensation at all right supposing Y_3 reactor is here this is case 1 then this is Y_3 reactor case 2 then if the mole fraction in the reactor is greater than Y_3 equilibrium then the liquid will condense right unless I have more ammonia than the equilibrium demands I will not get condensation so if Y_3 actual is this line anywhere in this region I will get condensation.
So if I want to remove liquid ammonia as a product Y_3 from the reactor should be higher than the equilibrium value then at equilibrium you will reach the equilibrium value the balance of ammonia will condense out condense out in the liquid phase this clear so for example if I am operating at some pressure here for example a $P= 1/\alpha$ this much of ammonia will have to condense out till the composition actually reaches Y_3 equilibrium same problem arises here in our liquid faction unit.

It s a slightly different problem if you are liquefying air you have carbon dioxide as an impurity and the way you do liquefaction of air you bring it to a lower temperature and do a Joule Thomson right when you do a joule-Thomson expansion you get cooling but you know the Joule Thomson coefficient can be positive or negative it reread it go goes into the cooling region only below a certain temperature we can work that out.

So what they do is say at 130^0 K they will pass it through a needle wall throttle it from high pressure to low pressure this causes cooling when you throttle it through a needle valve in the needle valve you are worried about I have a needle valve this is the air liquefaction problem the problem is the same thermodynamically I have here air plus carbon dioxide and I throttle it through this one this needle valve I do not know if you have seen a needle valve but really what it says it is just got a pinhole through which the whole thing goes up.

Now in this case carbon dioxide goes directly from gas phase to solid if a solid carbon dioxide forms it will plug this needle wall so what is the thermodynamic problem solid carbon dioxide vapor phase air plus carbon dioxide I have the same identical thermodynamics problem this is CO_2 forget that it is only a speck this is the air plus CO_2 I am asking what is the mole fraction of carbon dioxide at which solid carbon dioxide will form.

Identical formula and get the same curve this will be why carbon dioxide versus pressure α will be different no α will be B carbon dioxide - B carbon dioxide carbon dioxide by RT I can do the same calculation and get the same result here my worry is that this carbon dioxide should not solidify if it solidifies it will block my needle work we actually had an accident cap 30 years ago in our liquefaction plant they had a small explosion I mean this is known they were careless what you normally do is the.

Here this instead of reactor I will have Y carbon dioxide in the ambient which will be typically 10^{-2} mole fractions or 10^{-3} mole fraction this air is bubbled through mono ethanolamine solution so here before it gets here they will bubble it through actually it is not the same this is Emmy this is here plus CO_2 of course it is bubbled through so the CO_2 composition here will be $y = 10^{-4}$.

So it will be below this curve the same curve you will get below the curve you'll get ambient carbon dioxide there will be no solidification you have to make sure that the composition of a carbon dioxide and air is below this lowest point at any given temperature then you are safe at a higher point you will have solidification here you want solidification you want liquefaction so you are looking at this range here if the mole fraction is here for carbon dioxide you will operate either below this pressure or above this pressure on either side the phase equilibrium curve lies above the ambient composition so you would not have any liquefaction condensation.

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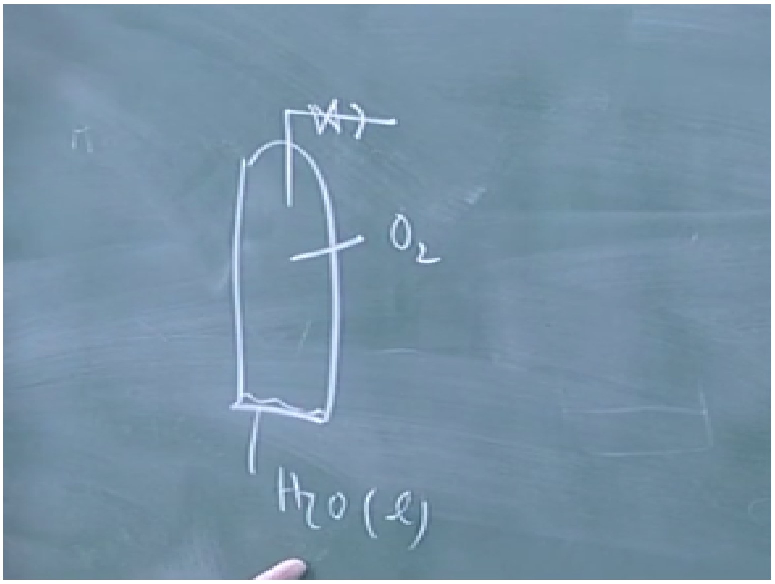

The same problem arises in another context you have if you look at oxygen this is oxygen in cylinders this oxygen or a static oxygen all of them make oxygen by finally bubbling it through a liquid solution to remove other impurities so this oxygen is said to be packed when it is wet that is it is bubbled through water in the final stage so it will have some water vapor so typically in the cylinder you will have h_2o liquid at the bottom you do not see it these cylinders come at very high pressure.

There will be a small layer of water can even be few drops and it can be a one millimeter thick layer and when you pump this oxygen out this oxygen will carry water with it but our wafer with it the amount of water vapor that the oxygen carries is given by the same formula liquid phase vapor phase contains oxygen plus water vapor how much water vapor Y_3 is equal to same equation.

Now in some experiments water is very detrimental to the catalyst so you have some organic chemistry experiments where they are using this oxygen in oxidation they want this oxygen to contain water less than 10^{-5} they will give you a pre specification they will say tolerance for water is 10^{-5} mole fraction if that is true what you need to do is operate at a pressure where this Y_3 is below that value of course this has this lowest value has to be 10^{-}otherwise you cannot reach that value.

So you will choose a pressure here such that the phase equilibrium value is lower than the required value that is here the design specification is the other way wrong I tell you this limit I draw the limit Term Y_3 that I can tolerate for the water to be below that value I have to operate again between these pressures so same problem will just appear in different ways in all these cases the thermodynamic diagram is simply α β 2 phases and then you equate chemical potential.

So let me get back here in this phase equilibrium problem I have already plotted I want Y reactor to be certainly above this minimum if it is below the minimum I cannot get any product out of the plant so what I need this is my specification this is design specification that is Y_3 greater than Y_3 minimum Y_3 minimum is here.

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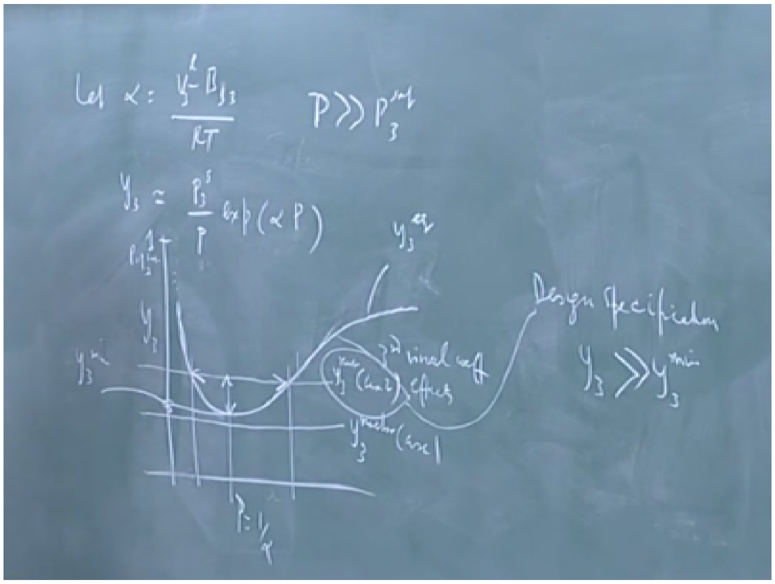

In order to be sure you do not get ammonia in sports say much greater than Y_3minimum so if Y_3 minimum is 0.03 you will probably ask for 0.1 one so you need 10% so that is a specification then you have to ask what are the conditions in the reactor here that will give me that concentration in the outlet now let me tell you another thing suppose I reduce the pressure too much here or even if I reduce the pressure when I send this back I have to compress it again.

So I will need a compressor here so you will need more work input normally this is avoided by operating the separator at the same pressure as the reactor you have to work out the economics of it whether it is worth putting a compressor here or not but if it is at the same pressure so this pressure is fixed from this consideration the temperature is fixed so simply solving a phase equilibrium problem asking what is the ammonia you can get what is Y_3 equilibrium.

So essentially the pressure may be fixed at some point here this is P reactor you can choose the P reactor but it is also equal to P separator so you choose this pressure so that Y reactor is greater than Y in the separator and how do I calculate Y reactor I got to this equation.

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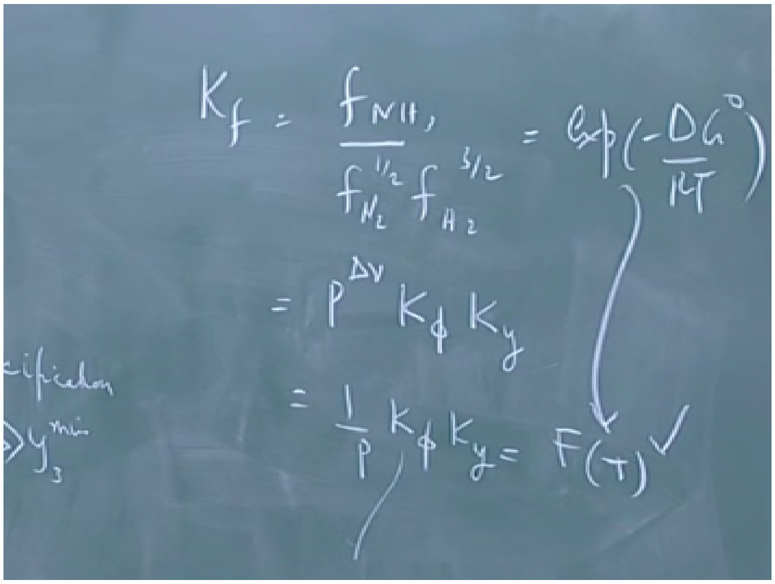

$$K_f = \frac{f_{NH_3}}{f_{N_2}^{1/2} f_{H_2}^{3/2}} = \exp\left(-\frac{\Delta G^0}{RT}\right)$$

$$= P^{\Delta\nu} K_\phi K_y$$

$$= \frac{1}{P} K_\phi K_y = F(T) \checkmark$$

I have Kf = fNH3 / F $N^{1/2}$ $fH2^{3/2}$ this is equal to exponential of - Δg0 be careful about taking Δg0 data because sometimes the data is given for 2 moles of ammonia then this will be twice this will be ½ of what the data is in the tables you must write it for one mole of ammonia otherwise you write the reaction with for two moles and write this as f NH^3 3 times the trouble about reaction equilibrium is that if you make mistakes even silly mistakes your numbers will be so different that everything is an exponential.

So instead of exponential of - 2 you may get exponential of -4 huge difference between -2 - 200 power so this is the same as if P to the power the change in number of moles actually you recall that this P to the power was sum over ν_{ij} for that particular reaction and sum over for reaction I mean sum over ν_{ij} just sum or the species is called Δ ν so the change in the number of moles Δ ν for I^{th} reaction so you will get P to the power Δν times KP x KY so in this case Δ ν is 1 -this thing so this is – 1.

K ϕ is a function of T and P normally for gas phase reactions we replace ϕ by ϕ PR do Lewis and Randall rule, so you take ϕ for the pure substances but you would not ϕ ammonia in the mixture you will take ϕ ammonia and the pure in this case has been studied very extensively in an old paper in Newton and Dodge Dodgers a chemical engineer so this is equal to of course this is known exponential this is F of T this is known at a given temperature so you solve this equation K_y for y you solve it for Y ammonia.

Let us look at the degrees of freedom in this case or let us write out that expression to see what it looked lik3.

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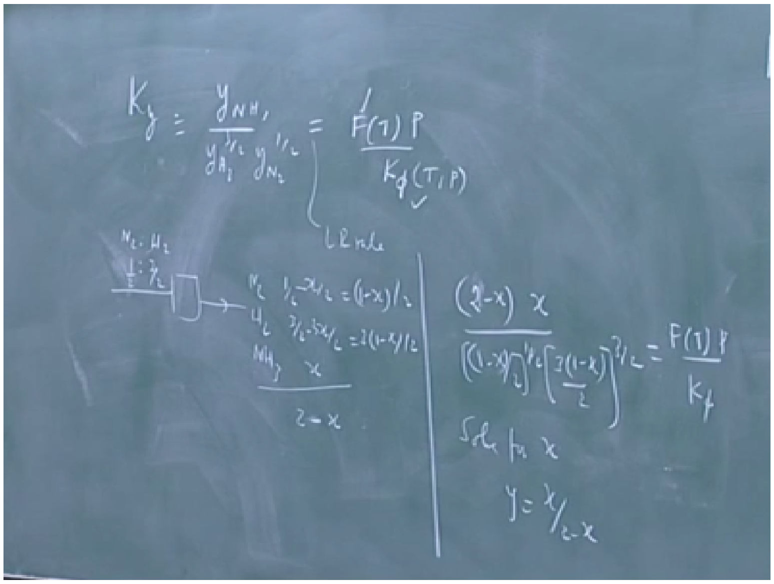

K_y is y ammonia by hydrogen to the power 3 /2 nitrogen to the power ½ this is a definition this is equal to some function of T which is known times pressure by K ϕ is a function of T and P because you are using Lewis and Randall if you use Lewis and Randall rule fie becomes ϕ pure so it is no longer a function of composition these are known functions this is known actually I start off maybe I should write this in terms of n.

So we will start off with 1 : 3 of nitrogen to hydrogen then I have nitrogen hydrogen and ammonia, so if X moles are formed ammonia will be X hydrogen nitrogen would be 1 - X /2 this is 3 /2- X / 2 or 3 - X / 2 all right this is ½ - 2 this is you start with ½ and 3 / 2 moles so your total moles is 2 - just 2 now 3 / 3X / 2 so this is 1 - X / 2 this is 3 times 1 - X / 2 so this is 2 –X.

So you can solve in terms of X so you will get essentially 1 - 2 – X into ammonia which is X /1 - X /2$^{1/2}$ x 3 x 1 -X / 2$^{3/2}$ = fT x P/ K ϕ so you will solve for x and therefore solve for frac mole fraction ammonia X /2 – X in case you can see the way the reactions are written down this looks like a complex algebraic expression X will increase if P increases and this said KP is a weak function of pressure basically it will increase if P if the right-hand side will increase if P increases and if P increases X will increase because it is X by something into 1 - X more ammonia is produced so it will increase so if you look at the graph here I just erase this graph.

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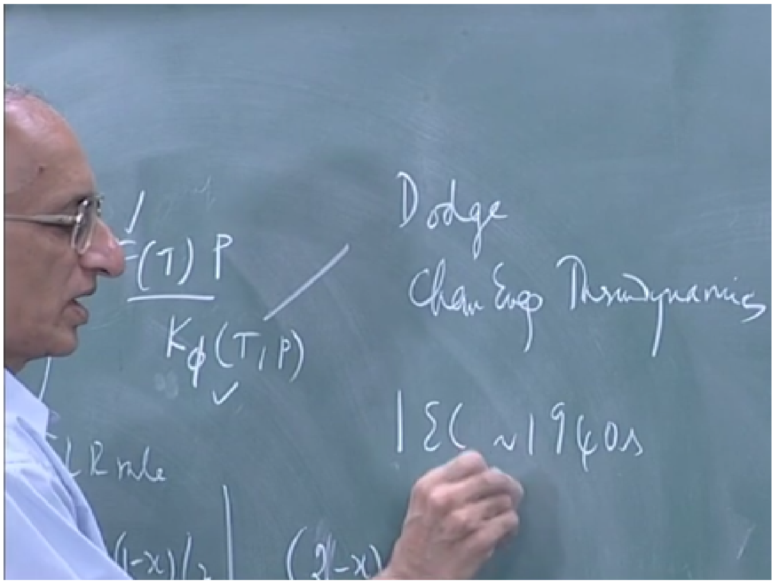

This is phase equilibrium the reaction equilibrium curve will go something like this it is the pressure increases so this range this is a reaction equilibrium this is phase equilibrium so only when the reaction equilibrium produces ammonia more than is required for condensation you can get a product ammonia out of the react so this is the range of feasible operation range of thermodynamically feasible operation.

I think dodge uses the notation γ for ϕ but you can get this K γ data K ϕ data from this book by dodge chemical engineering thermodynamics the original reference is INDC sometime in the 1940s it is available in our library it is called Industrial Engineering chemistry it is still one of the good journals in chemical engineering it is by Newton and dodge.

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