Indian Institute of Technology Madras

NPTEL

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Chemical Engineering Thermodynamics

by

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Lecture 23

An industrial example

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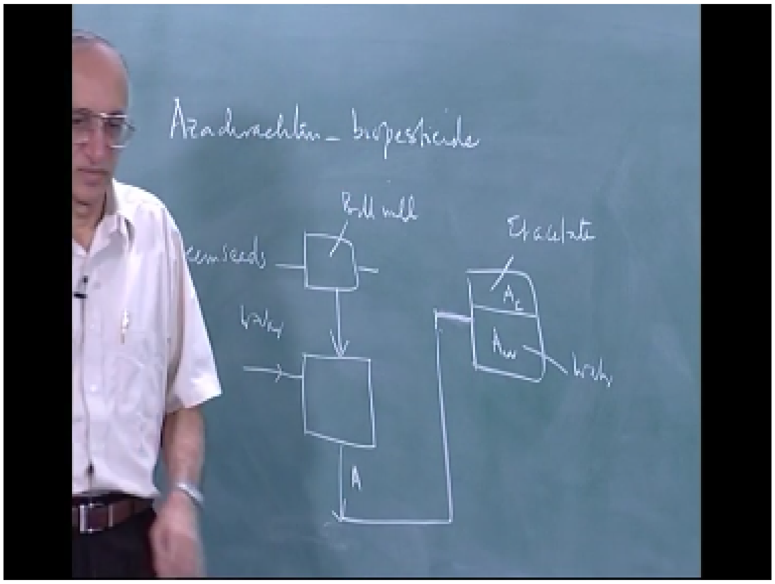

I will give you an example of manufacture of component called an azade reaction actually a bio pesticide I do not know if AD parry mixture it been talked about you know, it is big contravenes about neam the lot of theses neem seeds are been powered and used as fertilizer in this country but suddenly this company is come along and they want to in fact they panted and said hereafter use by farmers in India they will pay.

This is one of the few battles that we actually won I think it is doctor marshal car CSI dietary general whose pure headed this attack and finally there is a class here that says the traditional wisdom cannot be patted if patted you cannot charge the guys who had the traditional wisdom in the first place but, we have a lot of such a cases but this is a bio pesticide taken out of neem seed it is actually long ago there was a consultancy project that came but the way the industry developed this is simply by empirically doing it in the lab and scaling it up.

And so on but they do not do the fundamentals what I wanted to in fact, they came to me and told these are the fundamental measurement that are required so, I will trace that that will give you an ideals where we used our basic liberal information what you do is actually you take your neem seeds this is bio pesticide theses the whole area of bio pesticides became important after they discovered in the USA that the golden eagle eggs where breaking because of DDT content in the shell you are using DDT very widely as a pesticide it is sort of went through the chain.

And finally somewhere along the, I think the rabbits ate it and the golden eagle ate the rabbit so on finally DDT pests so the level of DDT got so high that the shell of the egg broke very easily therefore a number of golden eggs decreases this is the study by a environmental group but finally they decided these pesticides have more harmful effects than short term benefit so they were looking were bio pesticides one of the bio pesticides that is used that is recommended strongly is called as hazard direction no idea about it is structure and things like that but the way it is made what you do is to take neem seeds.

And you grain them this is some ball mill some mill of some kind it comes under your unit mechanical operations if you still have a course we have a course called mechanical operations you have a course you do sixe deduction particles ball mills and broad mills and things like that you do not have a description you have it in the curriculum I forget whether you have it or not anyway this powder is taken typically what they do is process could be batch or this thing you add water and you take out the extract the water dissolves the large number of components including hazard directly.

And describe the process then what you have is the liquid, liquid extractor this is water this is ethanol sulphate hazard direction is basically a non polar component is a thumb rule non polar components are more soluble in organic solvents then polar solvents like water so you take a liquid, liquid extraction you have distribution of hazard direction.

Let us say the component that I am interested in is A is the hazard direction so you have A in both phases AW and AE ethane acetate in both this extract is taken out then in some kind of heater the methyl acetate is evaporated out in the hazard direction is connected as you increase the temperature the- what you really do is you get to a point where the ethane gets evaporated in lease behind in more.

And more concentrated solution of hazard direction finally the hazard direction separated the broadly the process that they use water extraction use regardless of the fact that the solubility of hazard direction water is very low but water is about only 10000 times cheaper than ethyl acetate so you can use 1000 times the amount of water and extract the compound first along with that while come some and desirable components then what you do is choose a solvent in which the distribution coefficient that is the solvability of hazard direction in ethane acetate divided by the solubility in water is very high.

So with the small amou8nt of ethane acetate you can get a large amount of hazard direction and one of the problem is that if they had they develop the processing industry is just capable of and there is a monitory drive it is just a capable of getting a process through effect they will develop a process faster than you know because they will keep asking fundamental questions one of the questions that you have is what is the distribution coefficient what is the solubility in water because this almost can be a furcated solution so thermodynamics quantities have been interest of what is solubility of hazard direction in water and off course how does it vary with temperature.

Because the variation with temperature will determine where you going to have a boiler that heats the water up brings the water at some temperature normally pressure affects in negotiable in the condense phase normally it is pressure is not is you can ask a another question here about ball mill also you can ask is there an optimal a various intimation of ball mill you can ask how many ball should you have inside it? What should be the size and what is the rotation speed? These are very poorly understood.

So it will lot of fit enclose by empirical correlation in chemical engineering one of the things that is very still not well understood is simply mixing second is grinding the energy required broadly speaking the energy required is wise for creation of surface area instantly in thermodynamics courses we write $du=tds-pdv+\sigma dA$ where σ is the surface energy for unit area so you have to add this term 99% to the application this is very small but if you are looking at something like a ball mill where energy is created this is negotiable this is the significant part.

So unit where area created if you have very small particle the surface area for unit volume increase the dramatically therefore you have to pay more penalties but this kind of thing is already you should make this de because you should include potential kinetic energies you should include forces and their conjugate but this is a mechanical operation and then you have this extraction with water normally these are done counter current you know water goes in and comes out.

And that is the this thing which is collected but, this is one question the second question is what is the distribution coefficient for hazard direction between water and solvent equation is the what is the best solvent and there are 100 construction for the best solvent ideally if thermodynamics progress to a point where you stand it fully you should be able to sit at a computer and choose the best solvent some extend you can do that now a data available is very extensive and you can do that to a large extend eventually you will put ethyl acetate water hazard direction you will not put ethyl acetate put in water and hazard direction and what is say.

And say what is should be the next other solvent for the next step and go through all these you hit the idiot box on the head you actually move the mouse around and click this solvent so you do not even have to be very educative effect as been take as lot of these flow sheets everything is marked there so you click design dilation column and design this state you just have to meet and know how to read the output but let me come back here as far as thermodynamics is continued still have to supply this data or even in aspect there is a thermodynamics package which is where you need to so all I have to do is

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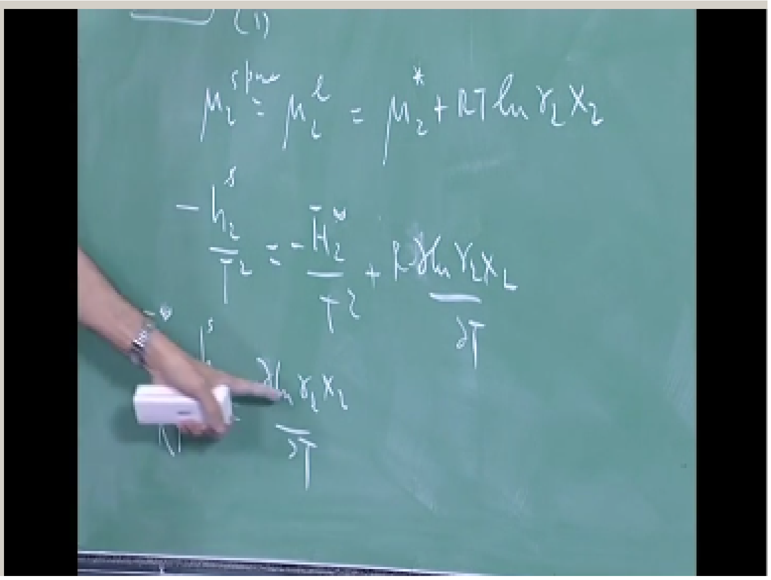

If I call this to which is water this two water plus hazard direction this is component one this is component two so I said $\mu2$ is solid=$\mu2$ this is I just leave this as pure it has to be written as $\mu2$ liquid hazard direction is a solid so you will write this as $\mu2^*$ and as I told you, you do this whenever you do you have a * you cannot get a way in equation thumb rule divided by t differentiate with respect to t so you get $-h_2/t^2 = h_2/t^2 + r\gamma 2x2/\partial t$ so you integrate this equation if you know this value or if you know that h2 is solid h2 * will become ∞ because you know you can go to infinite delusion.

So this is ∞ because when you divide by t and differentiate with this respect to t first of all when you divide by t this term is independent of composition so the left hand side should also be independent of composition so you can go to the limit as composition goes to zero so h2* is same as h2*∞ same as the partial molar enthalpy and ∞ dilution this is the measurable quantitative so if you can have data for this by t^2 $rp2\gamma 2/\partial t$ even if you do not have this data you can treat this as a constant and fit the data you need an expression for $\gamma 2$ so $\log\gamma 2$ in this case.
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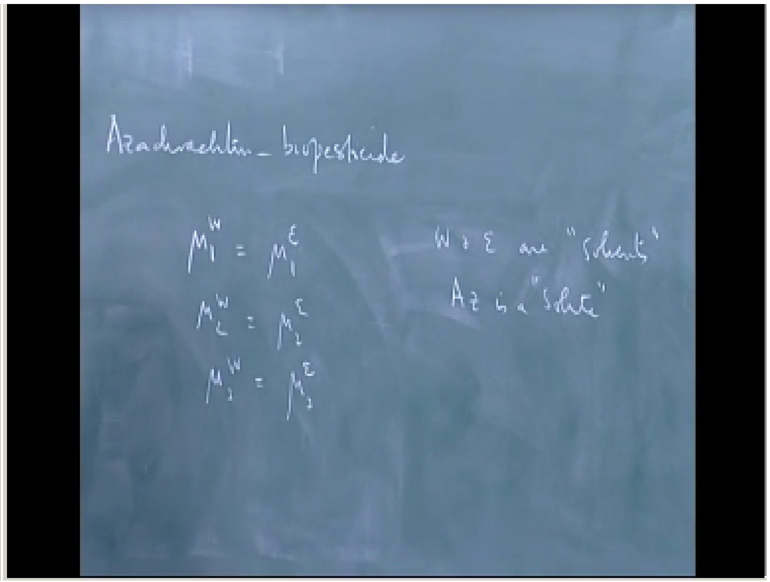

Azadirachtin – biopesticide

$\mu_1^W = \mu_1^E$

$\mu_2^W = \mu_2^E$

$\mu_3^W = \mu_3^E$

W & E are "solvents"

Az is a "solute"

Hazard directive self is a non polar solvent and the polarity of water does not affect it enough for you to worry about these theory you can write this as $Ax1^2$ I will say example so you get log a which is the constant function of temperature and $x1^2$ this logarithm is $ax1^2$ then you have logx2 so you can integrate this equation with some data on solubility that is you have to have measured solubility of hazard directive here apparently did not have this data x we had to do some measurement to get this data this is trivial or you do get some hazard direction put it on a beaker of water maintain that water at some temperature and wait for ∞ time and must have rate ideally you should wait ∞ time normally you wait a hour.

And then, it comes to reasonable equilibrium then you make a story but we having done this so you get these constants and therefore you can get x2 so you can get x2 as a function of temperature from these equations and some data have to give you bit of data and seen if I have the data in a case I cannot give you the industrial data because there but I will see if I just take a look see if this data I will give you the data then you can fit you treat this as one constant the other constant is this is approximately constant because you treating with water the temperature range that you are talking about is going to be something like 30 to 80% centigrade much wider in absolute term this is small range of temperature.

Now 300 to 350 degree scale we are talking about the small range in temperature so you can treat this as constant this is one constant b that is the constant am so you will fit to constant and you will be able to get it expression for x2 as a function from this equations so that you do and then you can ask later in an optimization program you have to work this also you have a θ theorem you have to supply some q for this is at room temperature this is at some desired process temperature you have to ask what is an optimal value for t? normally what will happen is in any industry they will have a boiler they will have some waste heat so it is convenient to pipe that waste heat and do the heating anyway.

So that energy caused may not be for them may not be a explicit caused in industry those have local variations if you have to set up a boiler it may not be worth it but any way this is one part of it the other part of it is the distribution coefficient at again what you do is to ask what happens if there is water plus hazard direction this is component one this is component two this is ethyl acetate this is component three plus hazard direction which is component in practice actually you will get some ethyl acetate here plus water here the solubility of ethyl acetate in water and solubility of water in ethyl acetate.

So they were worried about recovery of ethyl acetate as well so you have now essentially equations like this new one water $\mu1$ ethyl acetate this is the ethyl acetate layer this is water layer one is for water $\mu2w=\mu2e$, $\mu3w=\mu3e$ where two layers and you are asking for equilibrium between them one is water you will find these solution as sufficiently dilute so you must remember that this is these two are solvents in the water layer actually in both layers I can say ethyl acetate in this case in both layers water.

And ethyl acetate are solvents and hazard direct ant is solute as far as we have consent this is the solvent of solute depending on the phase on which it is at temperature and pressure so at this temperature and pressure that they are using these two are liquid and ethyl acetate states of liquids so you can use these solvent models for them so in both phases here you will simply write $\mu1+rt\gamma1x1w$ means w phase.

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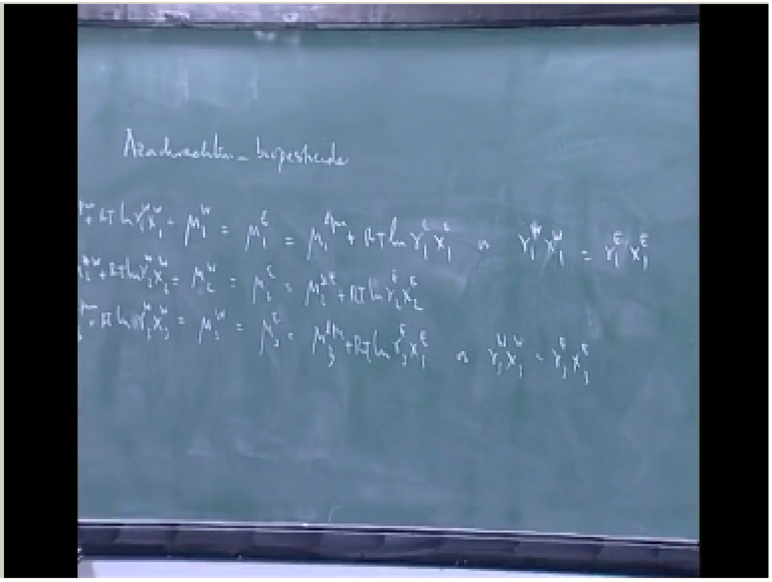

This will be equal to μ1+Rtln $r1^{e}x1^{e}$ so for solvents this μ1 liquid will cancel on both sides because this is the chemical potential of pure water at temperature and pressure of solution at temperature of the at temperature and solution is the same here so this element is simply cancel and all you have is γ1x1=γ1x1 notice the water phase will have nominally more than 90% it will be water so where x1w is slightly to be almost 0.9 or higher.

So it is because γ1 is much higher in the ethyl acetate phase if you are able to get this kind of distribution then if you look at this μ2w again this two is water two is solvent you have a small problem here you have to write μ2*w+Rtlnγ2x2=μ2*e+Rtlnγ2x2 for the last one which is again a solvent this can be rewritten very simple.

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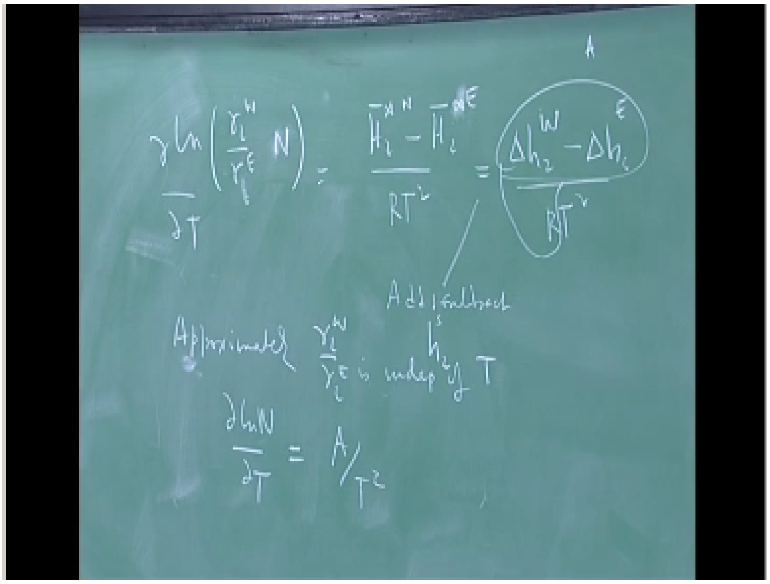

$$\frac{\partial \ln\left(\frac{\gamma_1^W}{\gamma_1^E} N\right)}{\partial T} = \frac{\bar{H}_1^{W} - \bar{H}_1^{E}}{RT^2} = \frac{\Delta h_2^W - \Delta h_2^E}{RT^2}$$

Approximately $\frac{\gamma_1^W}{\gamma_1^E}$ is indep of T

h_2^s

$$\frac{\partial \ln N}{\partial T} = A/T^2$$

So what you really have in the liquid, liquid extraction system is some amount of water as I told you plus hazard direction plus ethyl acetate this is the water phase this is the ethyl acetate phase this again as same as like water plus hazard direction plus ethyl acetate if you doing a batch process for example it is simply the amount of you can vary the amount of water in the amount of ethyl acetate so that is the another control variable you have so you have to worry about the amount of water phase you have for unit of ethyl acetate phase.

Because what you will get is an input to the system that essentially as input as then you take two outputs the water layer and you separate these two this is done by gravity all you have is you have to be careful not to disturb the interface and pull out the water phase with ethyl acetate phase but what you do is a mass balance of hazard direction that comes in equal to the hazard direction that greaves in the two phase so you will have three mass balance equation so water ethyl acetate and hazard direction you have to combine them with these three and then solve you can vary the amount of ratio of ethyl acetate to water that you take in the beginning that extend to the phases that is the control variable you can therefore control.

But, you have to solve these three equations call this one, two and three whether with there is a mass balance equations you can write them down is a mass coming in and a mass to leave you are assuming that you are giving enough time in the system for equilibration to occur again if you mix this system well and allow you to settle when it usually comes to equilibrium very quickly so these are mere equilibrium process many of these process they come under I think they will thought under mass transfer one the other course is about processor in which you do not reach equilibrium in the first set of processes thermodynamics is very important.

Because the equilibrium calculation is what tells you how much you will be what will be the composition these two will be in equilibrium this is what co0mes from your previous extraction it is water with hazard directive because it is actually the actual process is complicated by the fact that part two hazard direction you have many other solvent neem seed does not double with just hazard direction usually has about 12, 13 components so you have to write all the components and the balance is and solve this equations together in order to worry about whether those components effect the activity coefficient of hazard directives so you will have a multi compound expression already you have three component so you write a multi component expression.

So in actual practice I will not give you the in an under graduate course one does not give you the details but I think one assignment I will improved three component system so I have to do one calculation to get a feedback the calculation is too complicated for you to do in a exam suppose this is not about exam knowing how to do the calculation so basically this is the only equation you have to worry about really so you look at log $\gamma2x2/\gamma2x2$ this $\log\gamma2x2-\log\gamma2=\mu2^*-\mu2^*w/RT$ what you are really interested in is $x2w/x2e$ this is the distribution coefficient n of hazard direction in water phase in the hazard x2 ethyl acetate is much higher in the solubility ethyl acetate is much higher.

So you actually excep0t n in this case will be written much less than 1 so actually in a sense using water phase to do the extraction is averse but the two advantage of using water one is a expensive you can use a lot of it as a directive second is it tends to take out the other non polar compounds in smaller quantity if you use ethyl acetate the bulk of the seed memes heat when ground consists of inorganic matter all of it will be extracted into ethyl acetate if you use it directly then you let us upper eight the components in with elastic layer this way as a direct incomes out more dominant it.

So happens a deserter and solubility in water is low but it is higher than the solubility of the other organic components in the museum so it is an advantage to use water first so what you do again here is to differentiate if you differentiate you will get partial of log I leave this $\gamma2 / \gamma 2$ e into n into 1 by n is it x 2 w now into n with respect to t is equal to this is h 2 bar ∞ in the water phase -

h 2 bar ∞ in the ethyl acetate face by RT^2 it is to bar ∞ in eat elastic face if I differentiate this I told you these things are independent of composition.

Therefore I can replace h2*/h2 bar ∞and again h2bar ∞ in me now if I subtract this solid enthalpy of as a direct andh2 solid from both I will essentially get Δ H for Δ H too if you like in the water phase minus Δ H 2 in the ϕ straight face by RT square it is add in subtracth2 solid pure if I write small edge to it is pure so this is essentially.

The heat of solution of water this is the heat of solution I mean heat the solution of as a directing in water the other one is Z direct in mini realistic this data is available and usually this is a constant so you can treat this as a constant μ 2is not constant that is why you cannot do this stunt here the Δ h is more constant than the chemical potential itself so you do this and once you have this data you have to integrate this normally the solutions in water and ethyl acetate are both sufficiently dilute for you to treat γ 2 in this case in these two they would not be the ratio will not be one ratio will be constant so γ 2 w γ/2 e very often in the process is treated as a constant so you get one more constant to the fitting or if you differentiate this logγ2 w byγ2 e you can neglect that so effectively.

And say approximately this is what is used for correlating data you get Δ log M by ΔT that isγ2 W/ γ 2 e is not won the advantage of having e-trailer status that it is the activity coefficient is Δ state is much lower so you get higher solubility but this ratio is independent of temperature approximately independent of temperature I will say γ 2 m w by γ 2 e is independent of T in the range that you are talking about therefore you get Δ log n by Δ log e this will be some constant you get is equal to a by t square take this along with the are then you get log n =- ab y T + B so you do two experiments in the at two different temperatures you can get both your concentration be you have to measure this distribution you have to do this you keep this in the lab.

And measure the concentrations both phases in the actual process I told you this could be ninety percent of it of this vessel could be filled with water ten percent will be the ethyl acetate face or you can vary this and you can ask what is an optimum so essentially this is where thermodynamics is involved in a process in this process you will simply ask what is the right temperature to use what temperature should are used so that I get an advantage is distribution coefficient you solve all these all this can be solved directly on our computers I mean doing it by hand is a pain but you can do it straighten fact the best way to do it as far as industry is concerned is to use a spreadsheet.

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