Indian Institute of Technology Madras

NPTEL

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Chemical Engineering Thermodynamics
by

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Lecture 24

Liquid-liquid equilibria
Reaction Equilibria

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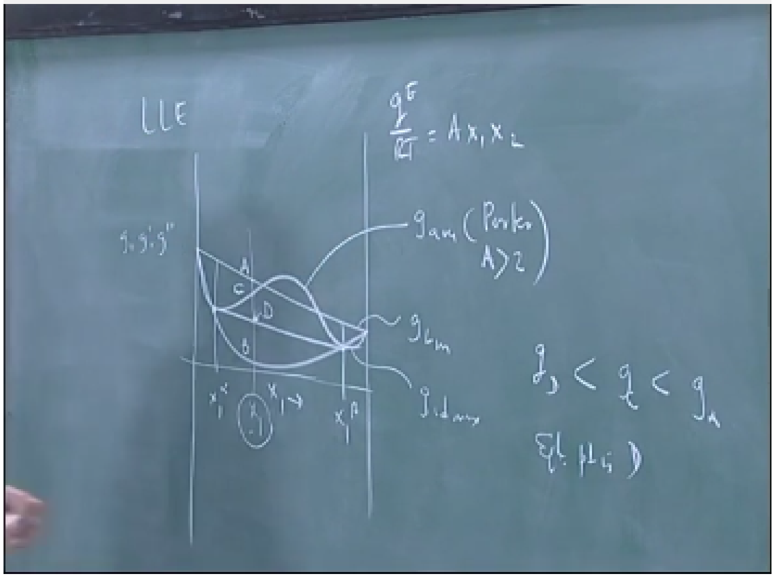

Liquid phase equilibria, liquid-liquid equilibria we said you could have this is g before mixing here the ideal mixture we envisaged a case where we after mixing and I have gxx. So we pointed out that if you this is let us say x_1^α this x1 I take a mixture of 1 and 2 with of composition x1 then the such a mixture before mixing has this Gibbs free energy if it formed an ideal mixture of 1 and 2 it would have this free energy at B, if I accepted Porters model it would have hypothetically this free energy at C.

But if I take these two points the lowest points in the free energy curve and draw a common tangent you get this point D that it is a geometric exercise to show that there exists a common tangent. But if you have a mixture of composition x1 one phase of composition x1α another phase of composition x1β and you have a mixture of these the free energy would then be at D. Now this ideal mixing does not count because this is the, this only hypothetical case if they mix ideally then there are miscible in all proportions.

So A,B,C are the ones that count and D has the lowest free energy so you will have to say gD<gC<gA therefore the equilibrium point is D. So you then have is α and β this is x1α, this is x1β.

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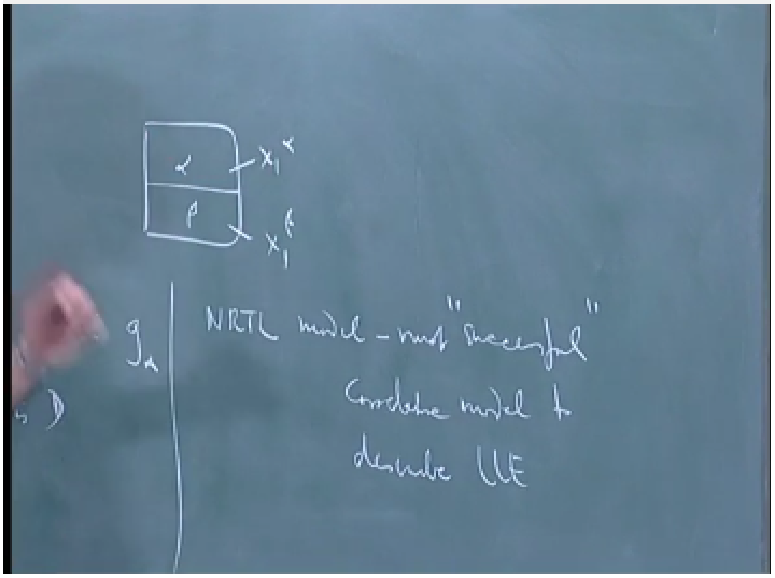

And the extent of the two phases the amount of α phase present and the amount of β phase present is going to depend on the mass balance what you start with. So if you have these two compositions as I said for example in the case of ethyl acetated in water this is not a good model for ethyl acetate water you will have to actually use a more complicated model and the most successful liquid-liquid equilibrium model is the NRTL model. I said the algebra gets a little out of hand so I would not do the so might say the most describe LLE so as far as this course is concerned I will put out a table of gxx I forgot do that I do not know if it is already there I told Krishnamoorthy to put up a table did you see the website is there a table of gxx, you have to look at the course website and I will ask Krishnamoothy to put it up there.

He will need to know those models specifically for each system what I would do is in the normally in the exams you specify exactly what model to use, so what I will do is simply give you a problem there are suggestions on the base and passed experiences as to what models you use for what cases, for example alcohol, hydrocarbon systems it would be either Wilson or Van Laar.

So like this there are regular suggestions for many kinds of systems and these are tabulated in wall as there is no unique answer but you will have take the probable model and work with it, soon we I think the next and all the assignments are in but I will give, I will put in some variations for it these assignments are same as last year's assignments.

So what I will do is simply put in some variations to emphasis only a few models about 10 models you have to really know and other than that unless you doing research you do not need to know more than that. What I want to do is I want still simply stop with this at this stage that is you got this these two at equilibrium this is what you have to first do for water ethyl acetate in the problem.

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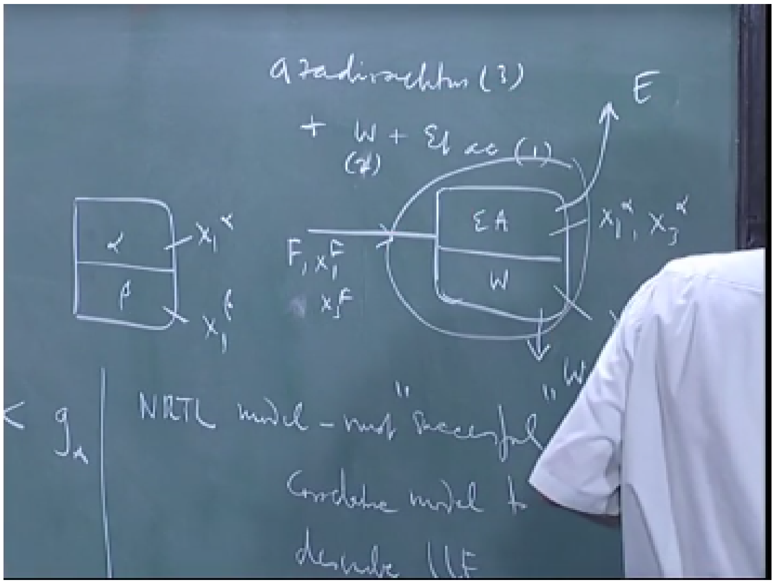

As it is acting +water +ethyl acetate you will have these two you will then have a turnery system I have a water layer and ethyl acetate layer and water rich layer and ethyl rich layer and you are interested in this case and it is solve you this is let us this is 3, this is 1 actually this is 1 this is 2 by normal convention you put the most volatile compound as 1 in the less volatile as 2 and then 3, so this will be x1 this is ethyl acetate rich layer this is x1β which is less than x1α, actually it will be much less and then you will also have x3α and x3β.

So what you have is system in which you form these two phases and then you pull out the ethyl acetate phase and the water phase separately you allow it a settle you draw of the water phase and ethyl acetate phase. So if you draw a mass balance around this if this is the feed with composition x1F and x3F and all I have to do is write a mass balance around these three this will be extract layer E and this is say the water layer.

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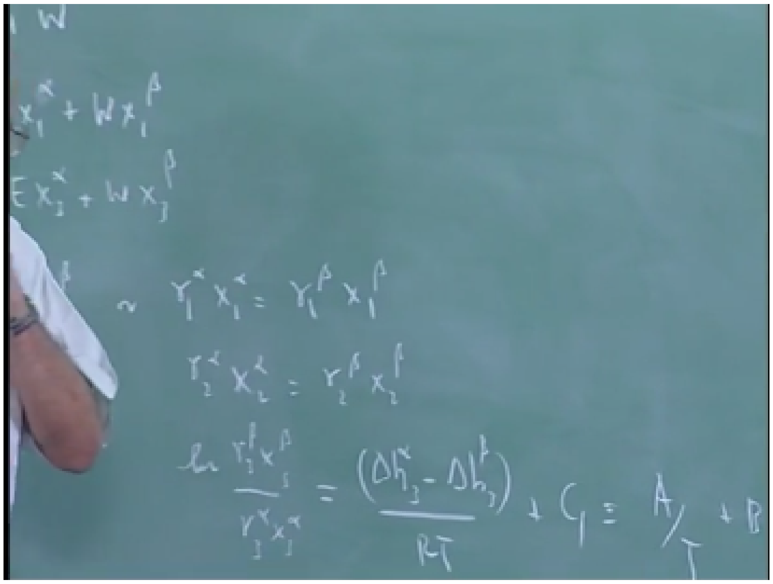

So you will get F=E+W then Fx1F actually the layers are α okay, does not matter E is I have mark as x1α+Wx1β and then I have a balance on aZ reactant on Fx3F, β, and then I have chemical potential of 1 in the α phase same as chemical would potential of 2, because I am talking a small amount of aZ reactant in the equilibrium will not be affected it will be affected some extent these numbers will change.

But broadly speaking you will have two layers with an ethyl acetate rich layer and a water rich layer exactly like this in the final compositions will be closed to these except you have to account for aZ reactant in presents. Essentially you will have these equations μ1, 1 and 2 are actually solvent like substances so you have γ1α x1α=γ1β x1β this will be again γ2α x2α=α2β x2β here we have a slightly different expression we had log as a γ3x3β/γ3αx3α.

Remember we had this in terms of the heat of solution this would be the difference in the heats of solution in the α phase and the β phase because μ3 would be μ3*+RTlnγx and μ3*/T you will divide by T and differentiate with respect to T, so you will get –H3* where RT^2 if you treat the difference between $\bar{H}$3∞ in the α phase and the β phase difference between these two as constant you can integrate this, so you will get essentially Δh this will produce a minus sign so this till be Δhα phase-Δh3 in the β phase/RT this is a constant plus some constant C1.

It is you write the chemical potential module for this, models for the solute remember these two are solvents this is solute, the solute will have you in three stat so you divide by T and differentiate with respect to T you will get $\bar{h}$3 and you would recognize that when you rearrange the equation that $\bar{h}3$ actually refers to is independ should be independ of composition so you will go to the limit as 3 goes to 0s you will get an infinitely dilute solution in these cases when I say α phase in a phase that contains x1α of ethyl acetate. In the β phase is water ethyl acetate mixture with composition x1β.

As long as a solution and dilute you can take this binary equilibrium as giving you the compositions so the two solvents if you like effective solvents as far as calculation of Δh3 is concerned. In practice what you do is just treat this is another constant so this will be of the form A/T+B you just treated as some constant. So what you will need is data at two points and you will have to solve these equations normally because it is a very dilute solution as x3 goes to 0 you have γ3 going to 1. So γ3β/γ3α will be taken as 1, so you will have x3β x3α so you have a total of variables are x1α, x3α you do not have to list.

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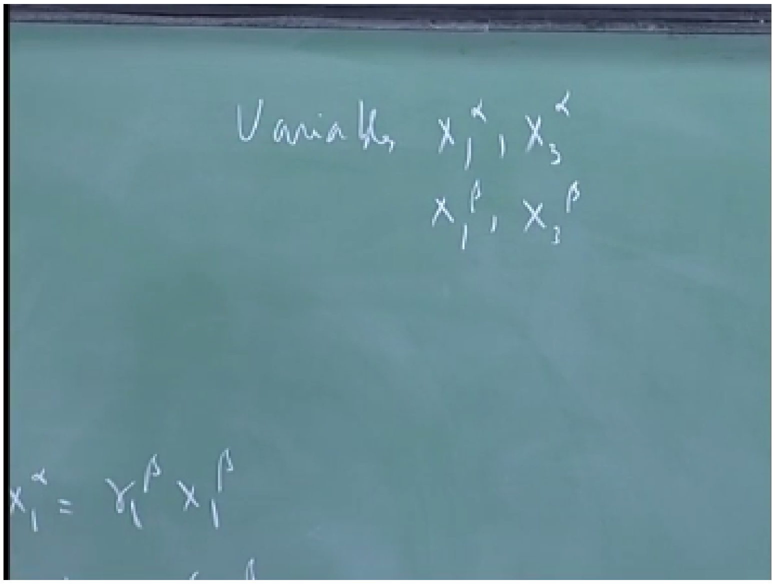

Variables x_1^α, x_3^α

x_1^β, x_3^β

$x_1^\alpha = \gamma_1^\beta x_1^\beta$

Then x1β and x3β I do not list x2 these are the four variables they have to solve. Let us first do the degrees of freedom.

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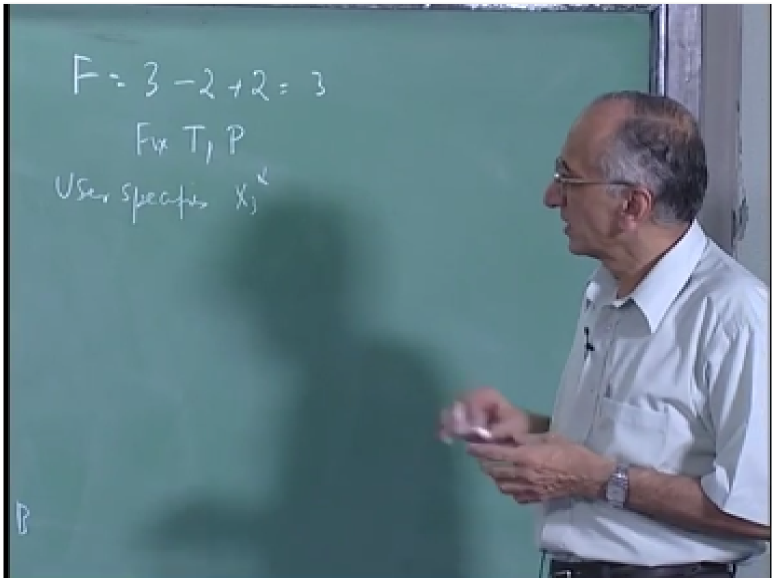

Degrees of freedom will be in this case you have water ethyl acetate and as direct 3 components 2 phases + 2 so you have 3 degrees of freedom. Of which you fix T and P if so one degree of freedom left that means if you specify x1 for example if I want the final concentration you know I do a separate analysis I take the ethyl acetate with the SR direct in it and I will do analysis at what concentration will it is an economical recover aZ reactant in or how much does in cost.

So I fix x3α for example as an objective, if I fix that the whole system becomes invariant everything can be calculated about the equilibrium. So this is really a specific designers specification the user will say I want aZ reactant in, in ethyl acetate at essence if you concentration, so I will say normally user specifies this is also user specified but user specifies x3α in particular. This is as far as the thermodynamics is concerned and then you have the mass balances here.

The thermodynamic gives you x1α, x1β, x3α, x3β these are known to you the feed composition is known, but this is also under control because the feed comes from what you do is add this feed you also add actually this feed comes from let me may be I will be raise this complete the picture, you should really do this problem with in NRTL calculation.
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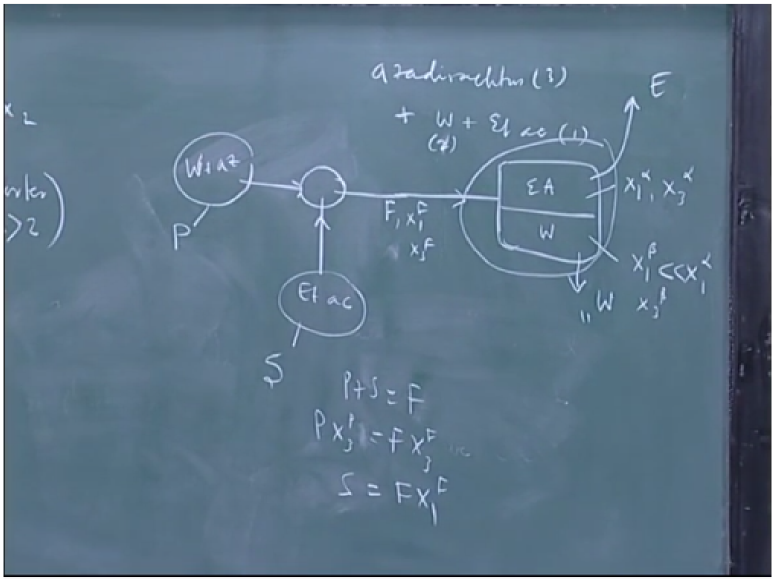

This is water plus aZ reactant this is ethyl acetate, this is what comes from the extraction unit so what you have as neem seeds which are ground extracted with water that water contains as a reactant plus other component normally you in this analysis we are ignoring the other components if you do an actual exact calculation you have to analyze then you see get all the components in it that will dissolvent in water then give a multi component analysis. But you have this you add a certain amount of ethyl acetate.

Now the ratio of this, this to this we will call this primary feed and this is you have already used E this is solvent addition S, so this P+S is also equal to SF then Px3p=Fx3F and if you like Px2 or I do not have to do the balance on 2 I am doing 1 and 3 all the time, so S=Fx1. So what you have control over is this ratio of P to S, so you must use this P to S so that you get the right F here which leads to finally this x3.

So look at what is specified this is specified all the rest are under your control here T and P are specified that is all, but once that is specified the equilibrium gives you these values so these are calculated from these three equations you need experimental data on A and B that is you should have made the measurements at two temperatures son that you get A and B these are available so once these are available you can therefore calculate out of this you can calculate all these quantities. If these quantities are known I will just tick them these are known from phase equilibrium.

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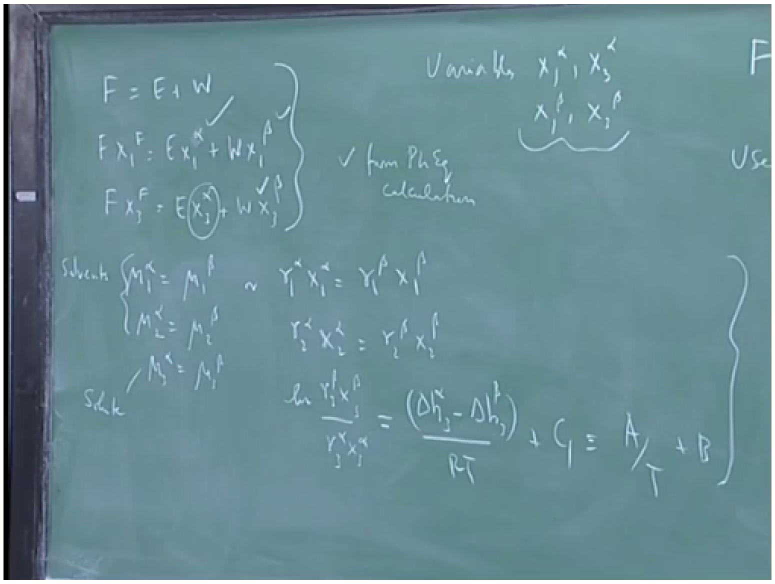

Look at the totality of the problem and this is actually a simplified problem it just looks complex but the principles are trivial, it looks complex because along with as a reactant you have at lesat12 other are come in, and you have to first make sure that none of those other 11 components other than as a reactant you know it kills the plants because you are finally getting a pesticide you are getting a bio-pesticide that is friendly. Suppose you isolate some other component turns out to be deadly to the plant that you are growing then your bio-pesticide instead of killing the pesticides killing the original plant that was designed to protect.

So you have to first do a spectral analysis of those compounds may sure they not are ethyl if they are then you will have to another, have another extraction unit remove those or you must know the concentrations below which they are not need. So you have to those components into account when you write your models you would not write just three you will write balances for the remaining 11, but simply more detail calculation because all of these independently are known solubility's of each of these are known in the form A/T+B.

For many, many compounds you have this data in fact it is that data based called diekema I think Professor Kannan has a limited diversion of it this is computer in design package called Aspin which comes as the thermodynamics package. In the thermodynamics package there is a lot of data in it diekema is very, very expensive for the university it is meaningless to buy it all though it is a little cheaper for the university then for the industry if you buy it you can get exact numbers but since we do not earn money out of it there is no point buying it, if you buy it you must buy it with industry support.

We probably will get industry support and we can buy it because it is cheaper for us and we can use it but if you but it at cheaper rate you cannot use it for consultancy that is the rule. But the point is anyway such data is available so if you just put in the compounds it will give you A and B for example, it will give you the it may not give you to you in that form it may give you in the form lnx2 in β alone.

It is in the β phase in the presence of a certain amount of water and certain amount of ethyl acetate, what is the variation of solubility with temperature. Similarly lnx3α alone will be given you are simply taking a ratio in this problem so these are known A, B are known it will be in the form of two constants one for the α phase one for the β phase, sometimes you have to put it together you have solubility in solvent A, solubility in solvent B and you have two interpolations between these two.

But all that the program will do there are default options that, so basically once you have all this data you simply calculate the equilibrium and you go back here. So given this x3 you can calculate to what should be x1F and x3F and you can modify those by changing the ratio of P to S so it just works backwards, so you start from the other end where the users specifies what the final product you want is and then work at this, quite very often in these cases it will be a solid product that they want, we want as a reactant. In which case the ethyl acetate will be evaporated and send back to the use here, so the whole process at chemical plant actually looks very, very confusing.

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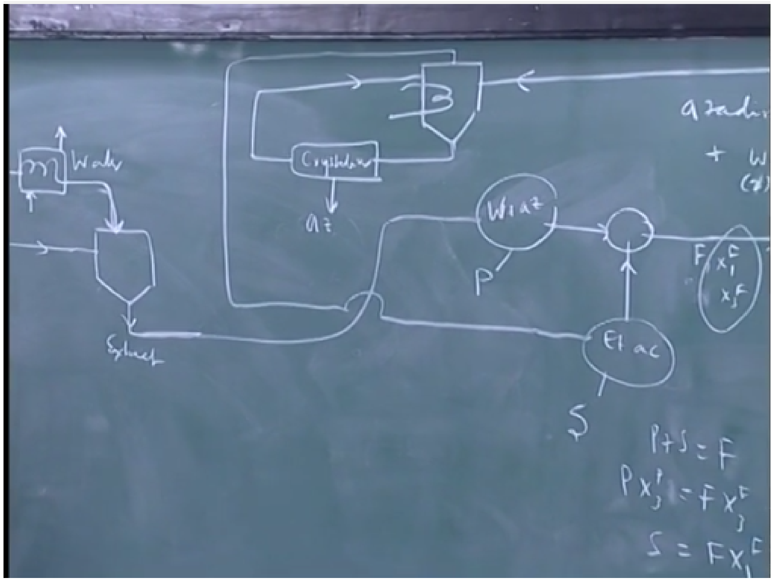

So as I told you the first thing is some you use they usually a ball mill of some kind so these are neem seeds and even here there will be picking there will be a whole lot of labor picking of other things because you do not get neem seeds as such, so you get at the lot of garbage and then you have to select the neem seeds you put it in a ball mill and then you pass it through after it is ground the powder comes out.

Then what you do is add some kind of a solvent in this case water and if necessary the water will pass through a heater depending on what temperature you choose to use, you have so you take out the extract here this extract contains this is your water plus as a reactant and then you add ethyl acetate go through a phase separator take this out this would contain the primary ethyl acetate so this will go here it will go to an evaporator and you will take out AZ reactant.

Evaporator then it will go through a crystallizer and in that, from the crystallizer you take out AZ reactant and this solvent will go back to evaporator these lines that go back and forth this vapour this will be ethyl acetate that is removed that will go back here you have recycle this, if you go to a chemical plant this Chennai petroleum corporation it is things that strikes you first is that are chemical plant consists of pipe line occasionally connected to units solution okay. So I will do is I want to in order to complicate your life a life more I want to discuss a bit of reaction equilibria.

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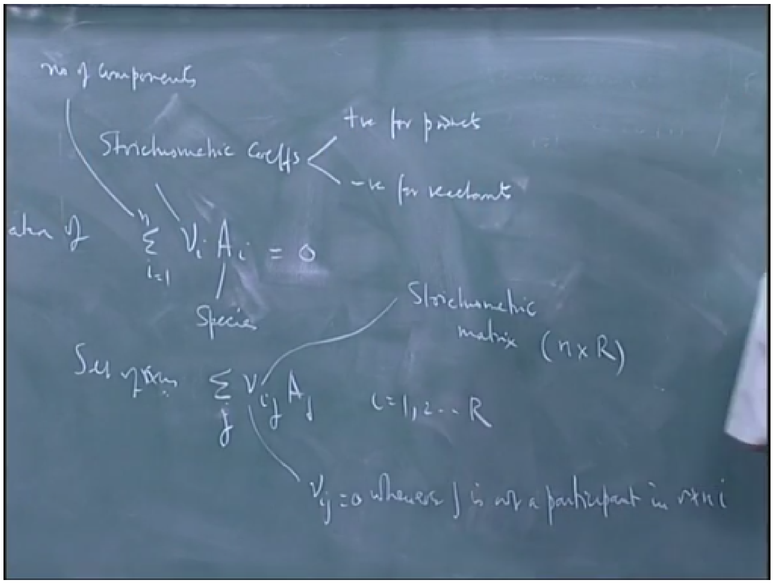

Reaction equilibria what you do is generally the, you have a general representation of a reaction you need to there is υiAi=0, υi stoichiometric coefficients Ai are species this is not a mathematical equation it is a representation simply symbolic, the stoichiometric coefficients by convention are positive for products and negative for reactants and you know by experimental evidence that all the υis you also know from atomic theory know the υ1s are always rational numbers, certain number of moles of one species will react with certain number of moles of another species these are integral numbers so you can present υis as rational now.

If I have a set of reactions I write this as ∑iυij ∑j for i-1,2…. up to R reactions I put down the same species I take all the species in the system and write the set of reactions in this form υij forms what is called the stoichiometric matrix, if there are n components it is nxR matrix this is i= 1 to n, n is number of components. In this representation what we do is to say υij=0 whenever j is not a participant in reaction i.

One typical system we worked for say long ago, if you look at the blast furnace for example for making iron you have essentially iron or lime and coke these are the things that are added the coke is actually burnt and the exothermicity of carbon going to carbon dioxide makes up for the endothermicity of iron ore being reduced to iron it is like a packed bed reactor but you have to actually write about 14 balances of 14 reactions.

There are many minor components which play an important role in iron making. So I will have for example 14 species participating typically but υij will be 0 for many of them for example

Fe2O3+carbon monoxide giving you FeO + carbon dioxide I can balance this reaction only four components in word out of 14 for 10 of them will be 0 so you will essentially get a matrix stoichiometric matrix which is often described as sparse that means many entries are zeros.

But you will get a matrix so this is the representation, now question is what is the mathematical equation that describes the equilibrium of such reactions, I want to know what the final equilibrium is in the case of the blast furnace I have two layers as well I have a phase equilibrium come reaction equilibrium problem I have molten iron and slag on top the slag has the calcium oxide essentially as a base but calcium magnesium oxide and there is the molten iron as well and both of these have a distribution of components and all the way have 14 components.

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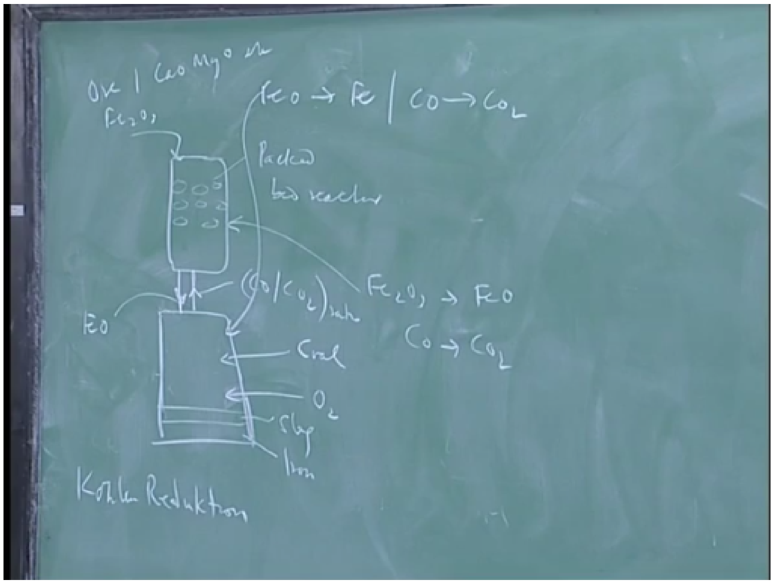

The care process consists of two parts and tell you why it is also interesting because it has to this is more or less like a packed bed reactor I will tell you what it contains, what you have is iron ore coming in and then you have actually you drop carbon particles from some height these are burnt and then you have oxygen this is coal. What happens is coal and oxygen burn of course to give you a carbon dioxide the exhaust emission that you have two layers this is the iron layer and this is the slag layer.

As the iron ore particles are actually fed from the top here form of pellets and as the over falls it starts off as Fe2O3 so you go to FeO and in this reactor you go from FeO to iron the reductant is always carbon monoxide it is in gaseous form it mixes with this thing it is everywhere when this happens you have FeO going to Co2 you have to balance these reactions out, then you have condition alright.

Now this gas that goes here is also has a CO2 CO2 ratio and you can control the temperature here simply by the amount of coal you burn per unit of over added, you can vary this so you will get this reactor has been this is essentially iron oxide actually I should not put iron ore, iron ore will go here actually I forgot June 2015 years since we did this, this is Fe2O3 sorry, yeah, this is a Fe2O3 this is ore I have got this backwards this reaction occurs here this, reaction FeO goes in this, this goes here what you get here is FeO from the packed that the reactor Fe2 O3, FeO and then FeO gets reduced here and you get iron at the bottom and of course you have slag because iron ore contains an addition it contains CaOMgO etcetera.

If you do not have enough for the slag formation then from the linings it picks up the magnesium that is what happened they did not have enough magnesium and calcium the thing I picked up the magnesium from the fabric. The blast furnace because of air using air the velocities of e are very high and because of that you cannot use iron ore fines I do not know if you have been to a steel plant you must take a look at the blast furnace it is an absolutely optimized chemical reactor it is very hard to see anything but the size will impress you.

When the air goes up it will take away these particles so you have to have iron particles of a certain size and when you grind or two particles are suitable for a blast furnace you also get fines so if you go to a place like any place where there is a steel plant Pillayar or Kala whatever it is you would see mountains of iron dust so in order to use the iron ore fines you cannot use the blast furnace you have to use some process like this where the air velocity is much less because you're using oxygen.

So one fifth the velocity you will get effectively so it would not carry away the fines so these fines iron ore fines and poor quality coal which is what we have in plenty we can use only in alternative process to the blast furnace they do not replace the blast furnace you have the main blast furnace and then you use additional you make additional iron using these processes. In the coal and reduction process an excellent process where you have to part control.

In the Ingrid process one reactor in which both of these occurred and it was called Ingrid because the heating was by induction in addition to coal burning in that there was an induction coil around which did part of the heating. But this is a much better process in turns out in this process they did not have the lining problem because they had made sure that there was enough magnesium in the input it was quite a simple correction. But if you do this calculation all you have to do is I list out the 14 reactions and you can try doing the calculation the major problem is only doing a numerical calculation with these numbers some of these numbers are very small in doing the calculation with that as a problem. But the thermodynamics itself is trivial and you have to keep all components in because finally you have to make sure that one component does not interfere with the other.

And for this there is a lot of data because the iron ore industry is a very old industry metallurgist I understand the blast furnace very well so they have studied all the reactions associated with it. One of the important things remember in metallurgy is the temperature is so high the reactions are very fast so your equilibrium calculations are even more valid, because the rates are very fast they reach equilibrium very quickly. So many, many metallurgical systems can be designed exactly using thermodynamic data.

Whereas in chemical practice you often have to take the rate of reaction into account it does not reach equilibrium, so coming back to this, this is what I am trying to analyze so I have got some j will be i will go from 1 to 14 typically or even more so you need a good numerical analysis program but not analyze this what do I have to do I have to first recognize that stoichiometric plays an important role.

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