Novel Separation Processes
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Lecture No. # 34
Liquid Membranes (Contd.)

Good morning everyone. So, we are discussing about the surfactant mediated sepal separation processes, and we have come to the last topic of them. We so started with the cloud conduct extraction, then we move on to mislining (( )) ultra filtration, now we are studying the liquid membranes. Now, as we have discussed in the last class, the liquid membranes the we have talked about the fundamental of liquid membrane, and how the think will over and we have look into the types of transport though will be occurring in to the liquid membrane processes.

One is the type 1 of the facilitation and type 2 facilitation. The main difference between these 2 types of facilitation process is that in type 1 facilitation, there is a chemical reactant that will be present in the internal phase. So, the solute will diffuse to the oil phase from the from the bulk phase to the oil phase, and then it will be moving to the internal phase and the internal phase will be having reactant that will immediate react to the solute, and therefore it is solute concentration for within the reactant phase will be 0.

So, it maintains the maximum concentration gradient across the in between the internal phase on the external phase. On the other hand in type 2 are facilitation, the solute will the transport of the solute will be facilitated by a complex permeation that is by a reagent present in the oil phase. So, therefore the concentration of the solute becomes 0 even in the oil phase. So, therefore, it gives the maximum concentration different between between the interface of the external phase on the membrane phase at the oil phase.

Then the solute will be transported by the complex, because of the complex does it have complex in this cannot diffuse out of the oil phase, because it does not like the aqua phase, it is hydrophobic in nature, so it will be still it will be remaining in the oil phase. And since a concentration is maximum it will moving to the internal phase at the internal phase, oil phase interface, it will release the solute as will go move in the internal phase there is concentration will be zero, because it makes it react to the reagent present in the internal phase.

So, there is the type two for facilitation. Now, what will be doing in this class we have start range of with just began the you know initial things of the modelling of the type 1 facilitation, which are moves compound in liquid emulsion membrane will do it once again and do and finished it type of modelling of this types of facilitation.

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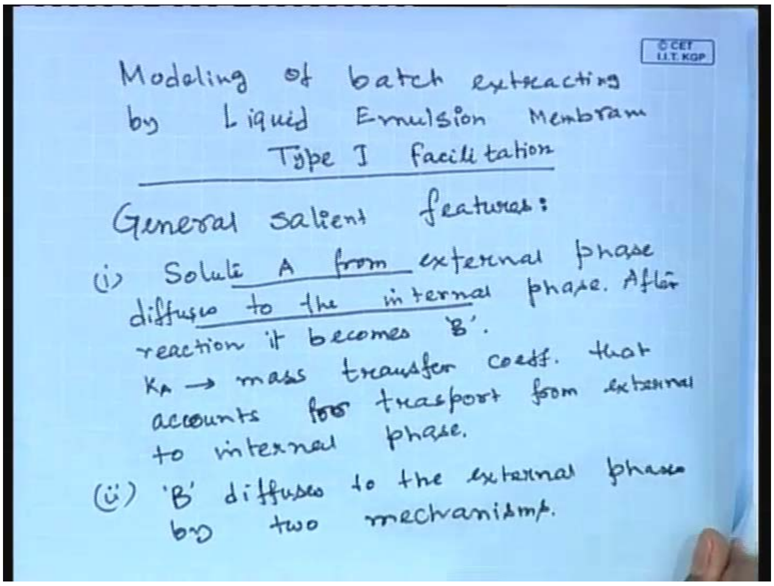

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Modeling of batch extracting
by Liquid Emulsion Membram
Type I Facilitation

General salient features:

(i) Solute A from external phase diffuses to the internal phase. After reaction it becomes 'B'.
$K_A \rightarrow$ mass transfer coeff. that accounts for trasport from external to internal phase.

(ii) 'B' diffuses to the external phase by two mechanisms.

So, will look in to the modelling of batch extraction by liquid emulsion membrane and mainly will to the talking about type 1facilitation, now will be talking about some general salient features of the type 1facilitation feature. In fact, this (( )) the features of the talking about the absolute general some of them may be, may be present in a particular system may not be present that will discuss in the tell solute A from external phase diffuses to the internal phase and there it reacts. After reaction, reaction it becomes species B, A becomes B, A does not exist.

So, it becomes B and the transport of the solute A from the external phase to the internal phase will be quantify by a mass transfer coefficient K A. So, K A is mass transfer coefficient, coefficient that accounts for transport form external to internal phase. Second point is that B diffuses to the external phase.

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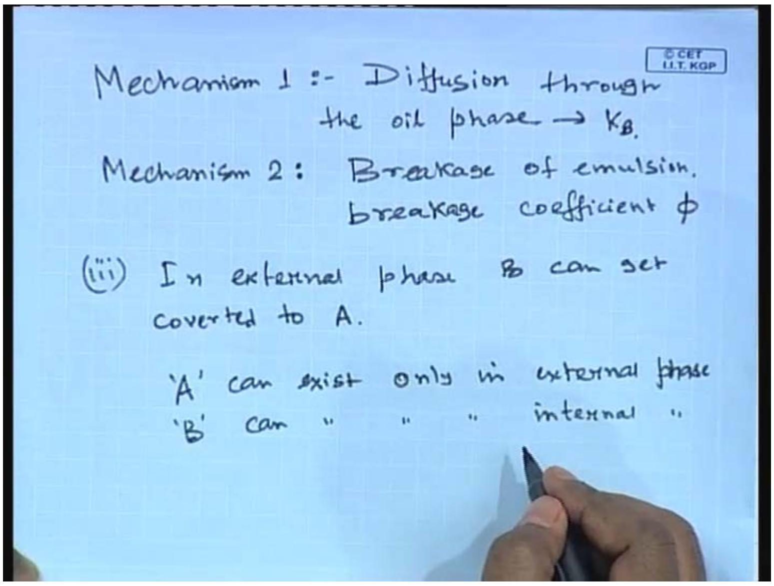

Mechanism 1 :- Diffusion through the oil phase → K_B.

Mechanism 2 : Breakage of emulsion. breakage coefficient ϕ

(iii) In external phase B can get converted to A.

'A' can exist only in external phase
'B' can " " " internal "

So, B is formed in a internal phase it diffuses to the external phase by 2 mechanisms. What are this mechanisms? The first mechanism is it diffuses through the oil phase, diffusion through the oil phase this through by A (( )) and this will be quantify by a mass transfer coefficient K B. Now, K B may be 0, K B may not be 0. If the complex that is produced that that is entirely hydrophobic ionic in nature it does not like the oil environments. So, it may not be diffusing through the oil membrane.

So, in that case K B will be equal to 0. That means, it may or may not it is most general. Second one is second mechanism is mechanism two is that the solute B, the complex that form the B it can come to the external phase, higher breakage of the membrane breakage of the emulsions breakage of the emulsions. Suppose, some the droplets or emulsion drop is the break then. Obviously, the whole thing come out in the solution and this breakage is quantify by a coefficient called breakage coefficient and this denoted by phi like the diffusion is quantify by mass transfer coefficient similarly, the breakage is quantified by breakage co efficient phi.

Third one is third solute future is in external phase, the again converse got to A. B can get converted to A, I give an example suppose, A is phenol and the internal phase will contain sodium hydroxide. So, phenol diffuses to the oil phase and membrane phase into the internal phase, it produces sodium phenolate and by some out either breakage mechanism or by the diffusion mechanism, sodium phenolate comes to the external phase. Now, if the external phase contains sulphuric acid then again sodium phenolate will react the sulphuric acid and produces the phenol once again and sodium sulphate will produce. So, therefore, it is highly possible.

So, there is the general thing now, in the external phase sodium hydroxide, sulphuric acid may be present or may not be present. So, that depends on your choice. Suppose, you are talking about acidic fluent the sulphuric acid may be present otherwise, it may not be present. If it is present it you can convert back some of the in the some of the B in to A. So, that proportional will be much less suppose, it comes to the external phase only by breakage since, the breakage amount is very less the amount of phenol producing back in the external phase will be less present of calculates, it number 1 sulphuric acid may not be present at all. So, engine will if it is present then in A external phase B can get converted into A.

So, therefore, so what, what is the conclusion about the best (( )) salient features A can exist only in external phase. A cannot exist internal phase, because it will be basically, B, A can exist only in external phase number 1and B can exist only in internal phase because if the concept some out I that through that (()) or through diffusion or by the both mechanism into the external phase B will be converted in again into A. So, B in it is form can, can present only in internal phase.

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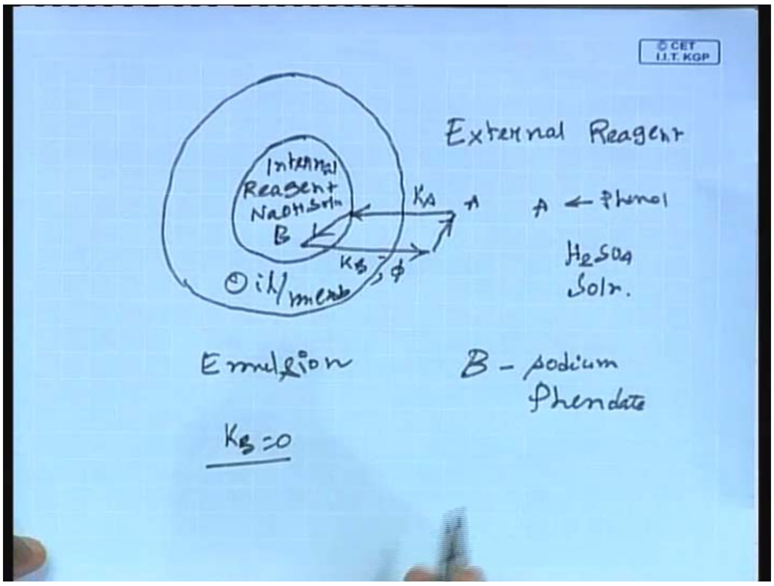

So, this is whole mechanism this can be, can be can be semantically represented as by this suppose, this is the liquid membrane this is the emulsion droplets it is basically, double emulsion one droplet is form is in side that is an internal agent another one is the external agent, and let say A is phenol it is present in the external phase and the external phase let say it is as a sulphuric acid solution and internal phase is nothing, but N a O H solution.

So, A trans into the A moves into the from, from external phase into the internal phase then immediately, it forms with sodium hydroxide sodium phenolate. So, sodium phenolate this transport is quantified by K A and this sodium phenolate, can go out either K B and some amount of breakage and then, when it comes to the external phase it immediately, react with and B. B is produce their and B is nothing, but sodium phelolate.

If A is phenol then B is sodium phenolate, phenolate and when B comes out the external phase, it again react with sulphuric acid produces phenolate that. So, this again produces A. So, this whole thing now what I am saying that K B may be equal to 0, if the species B does not like the hydrophobic environment. So, it can diffuse through the oil phase, this is the oil phase oil or membrane phase, this is the internal phase, this is the external, external phase.

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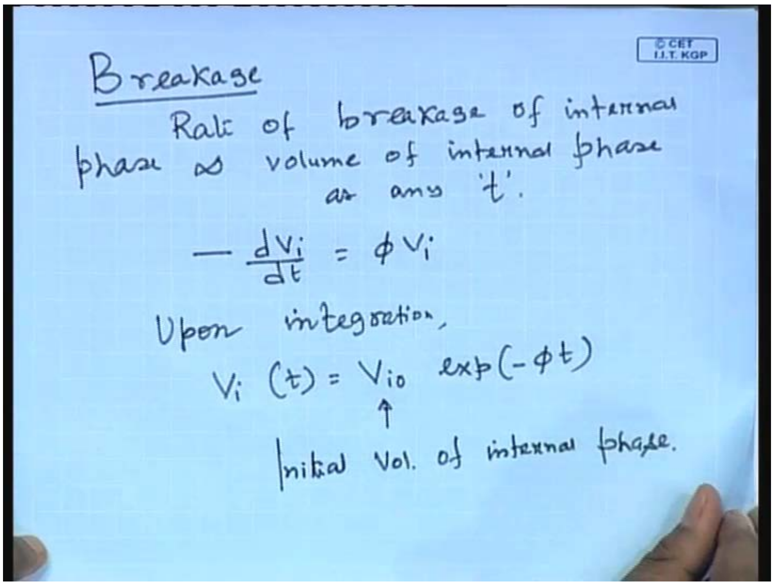

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Breakage

Rate of breakage of internal phase ∝ volume of internal phase at any 't'.

$$-\frac{dV_i}{dt} = \phi V_i$$

Upon integration,

$$V_i(t) = \underset{\substack{\uparrow \\ \text{Initial Vol. of internal phase.}}}{V_{io}} \exp(-\phi t)$$

So, the so now, we will going in to the go in to more details. Now, let us type 2 quantify breakage, breakage of the internal phase is assume to be proportional to in rate of breakage of internal phase. Breakage of internal phase is proportional to volume of internal phase at any point of time at any time t; that means, the volume becomes larger it become unstable. So, there is the more possibility of breakage. So, this is mathematical return as minus d V i dt is equal to phi times V i.

V i is the volume of the internal phase and minus d V i it is rate of decrease of the internal phase with proportional constant phi. So, you can integrate is out. So, upon integration, what you can get is that will be getting expression of volume of internal phase at any point of time V i not exponential minus phi t V i not is the initial volume of internal phase.

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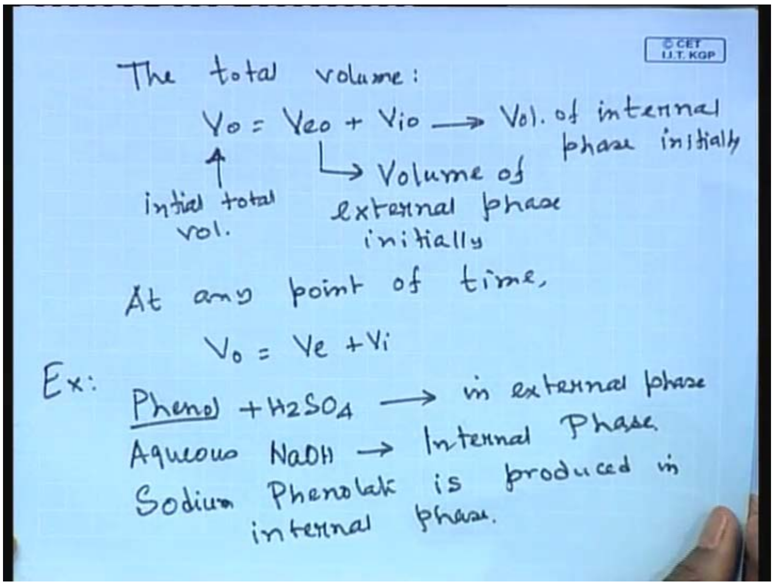

The total volume:

$V_o = V_{eo} + V_{io} \rightarrow$ Vol. of internal phase initially

$\uparrow$ intial total vol.

$\hookrightarrow$ Volume of external phase initially

At any point of time,

$V_o = V_e + V_i$

Ex:

Phenol + H_2SO_4 → in external phase

Aqueous NaOH → Internal Phase

Sodium Phenolate is produced in internal phase.

Now, the total volume of the system can be return as V naught as V e naught plus V i naught there is initially. So, this is initial total volume V e naught is the volume of the external phase initially, V i naught is the volume of internal phase initially. Now, at any point of time V naught the total volume will be same, right V naught will be is equal to V e plus V i V e is the external phase volume any point of time V i is the internal phase volume at any point of time.

Now, if you have an example of phenol plus H 2 S o 4. Now, let us look into example phenol plus H 2 S o 4 as an internal phase. As an as an external in a external phase the present in external phase and internal phase contains the aqua solution of sodium hydroxide contains the internal phase. So, what happens in a internal phase after diffusion of phenol into internal phase, it produces sodium phenolate, sodium phenolate is produced in internal phase. Now, some amount of sodium phenolate comes to the external phase where breakage. So, it does not like the oil phase it does not come out the by diffusion.

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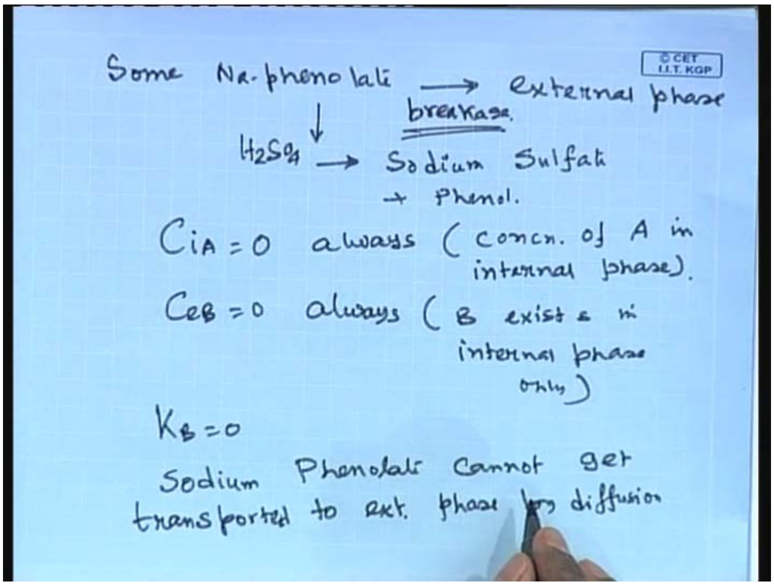

Some Na-phenolate $\xrightarrow[\text{breakage}]{}$ external phase

↓

H_2SO_4 → Sodium Sulfate

\+ Phenol.

$C_{iA} = 0$ always (concn. of A in internal phase).

$C_{eB} = 0$ always (B exists in internal phase only)

$K_B = 0$

Sodium Phenolate cannot get transported to ext. phase by diffusion

But some amount of some an sodium phenolate comes out to external phase via breakage and this then in a external phase produces react with sulphuric acid and produces sodium sulphate plus phenol again therefore, concentration of a in internal phase is always 0 will internal phase get an exist, it will just sodium phenolate. So, C i A is equal to 0 always and what is C i A concentration of A? In internal phase that simply means a exist only in external phase and concentration of B in external phase is 0 C e B is equal to 0 because whenever, the comes out in the external phase it is react the sulphuric acid; that means, B in internal phase only.

That means, that means if this mechanism prevents that sodium phenolate comes out to the external phase. The breakage only therefore, K B will be equal to 0; that means, sodium phenolate which is B cannot get transported to external phase by diffusion because it it there is the sodium phenolate being an ionic species it cannot it cannot diffuse through the oil phase that is the membrane phase. So, therefore, in that case will be will be equal to 0. Next, we get the concentration profile for the concentration proof in order to obtain the concentration profile, we have to do the material balance equations.

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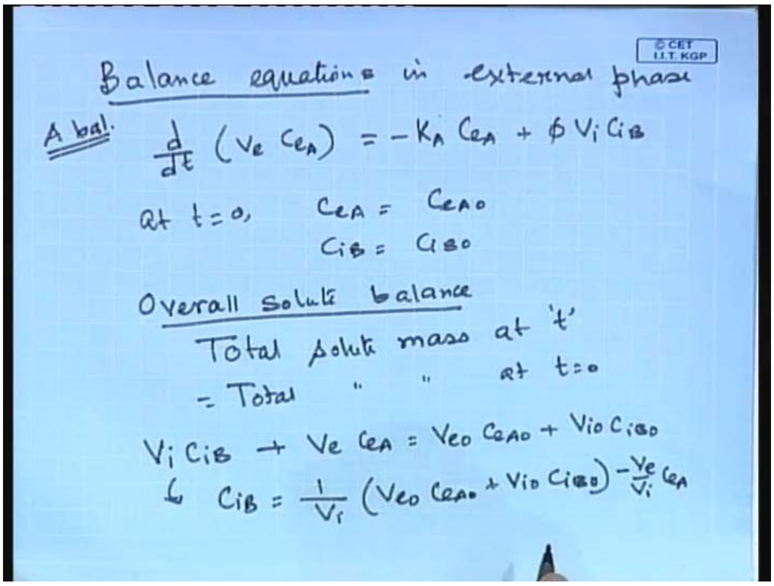

Balance equations in external phase

A bal. $$\frac{d}{dt}(V_e C_{eA}) = -K_A C_{eA} + \phi V_i C_{iB}$$

at $t=0$, $C_{eA} = C_{eA0}$

$C_{iB} = C_{iB0}$

Overall solute balance

Total solute mass at 't'

= Total " " at $t=0$

$$V_i C_{iB} + V_e C_{eA} = V_{e0} C_{eA0} + V_{i0} C_{iB0}$$

or $$C_{iB} = \frac{1}{V_i}(V_{e0} C_{eA0} + V_{i0} C_{iB0}) - \frac{V_e}{V_i} C_{eA}$$

So, balance equation you can write balance equation in external phase. If you write down the balance equation in the external phase, it will be d dt V e times C e A. So, this basically a balance mi solute balance. So, aqua rate of accumulation will be is equal to net rate in minus net rate out. So, that is that is proof for anywhere balance equation or it is say species balance or the energy balance. So, the it is momentum balance whatever. So, this will be equal to minus K A naught, K A naught you put K A. Let say K A C e A plus phi V i C i B.

So, so, some amount of a will be going into the internal phase via the mass transfer coefficient K A and some amount coming out because of the because of the breakage at time t equal to 0 C e A will be is equal to C e A naught and C i B is equal to C i B naught. Now, overall solute balance that you can, you can do so, this is the species balance equation. You can do overall solute balance, in the specific example that will have talked about phenol and sulphuric acid N a O H at time t is equal to zero that have no C i B naught because sodium phenolate was not present for the very beginning. This laminar straighten general equation in general condition. So, in the particular case C i B will be equal to 0 at time t is equal to 0 because there is no formation of phenolate there species B was not present at all at time t is equal to 0, it produce a once a will be diffusing to the internal phase.

So, overall solute balance will give you total solute mass at A at t is equal to total initial mass total solute mass at any point of time is equal to total solute mass at t is equal to 0. So, mass balance will be always maintained. So, therefore, this can be return as V i C i B plus V e C e A is equal to V e naught C e A naught plus V i naught C i B naught; that means, C i B naught may not may be 0 that is find and B will be present the only in internal phase and A will be present only in external phase.

Now, expression of species B is the an obtained you can, you can obtain the concentration of species B will be one over V i, V e naught C e A naught plus V i naught C i B naught plus minus V e by V i C e A. So, you will be getting the expression of C i B at any point of time. Now, let us talk about to to two situations in one case breakage is small. Another case breakage is loss in the breakage is generally, is small our in it is to have the small breakage. So, the two to control of breakage as well as possible to do.

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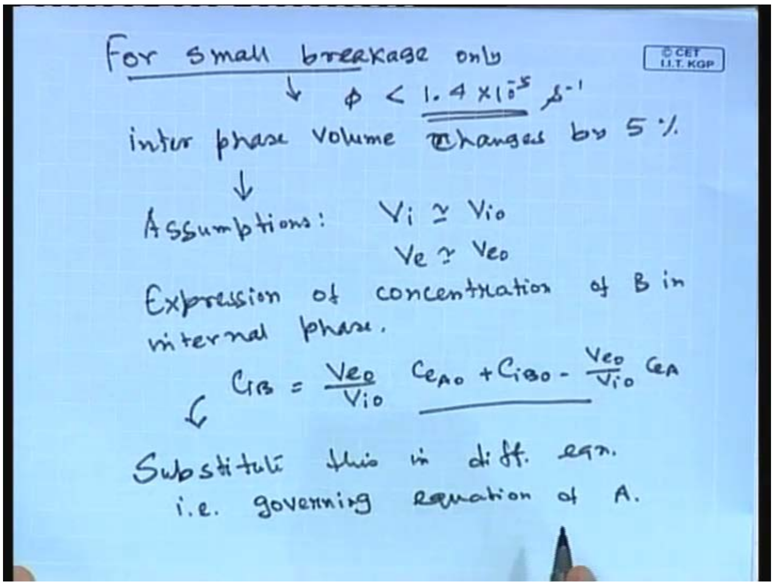

For small breakage only

$\downarrow \quad \phi < \underline{\underline{1.4 \times 10^{-5}}}\ s^{-1}$

inter phase volume changes by 5 %

$\downarrow$

Assumptions: $V_i \simeq V_{io}$

$V_e \simeq V_{eo}$

Expression of concentration of B in internal phase.

$$C_{iB} = \frac{V_{eo}}{V_{io}} C_{eAo} + \underline{C_{iBo} - \frac{V_{eo}}{V_{io}} C_{eA}}$$

Substitute this in diff. eqn.

i.e. governing equation of A.

Now, therefore talk about the for small breakage only otherwise only for the small breakage will be getting an analytical solution for larger breakage will be getting a complicated expression and we the basically, looking for small breakage only and small breakage. What do mean by in the small breakage in the large of breakage? This will be characterised by phi between less than 1.4 into 10 to the power of minus 5 second inverse. When phi is less than this value talk about the breakage will be extremely small.

So, if breakage is small the changed internal phase volume is less than 5 percent. So, can how, how this, this volume will be are reaching you are reaching this value.

So, that internal phase volume changes; that means, reduce a changes means reduces changes by 5 percent only; that means, if you put this value the the it will be 5 percent only. So, we have seen that there is a changing volume of the internal phi phase by 5 percent the changes negligibly. So, in the under the situation you can considered it can be there are two assumption is the crucial assumption, you can make the assumption which are very well be. Now, V i will be roughly equal to V i naught because there is changing volume of internal phase as well as external phase because the changes really in significant and V e will be roughly equal to V e naught. Now, under this situation you can get the expression of expression of concentration of b in internal phase as C i B is equal to V e naught divided by V i naught C e A naught plus C i B naught minus V e naught V i naught C e A fine.

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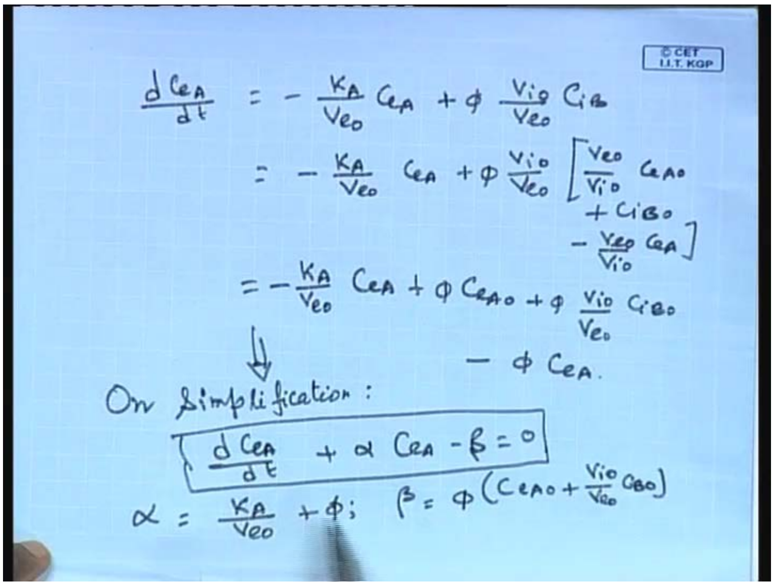

$$\frac{dC_{eA}}{dt} = -\frac{K_A}{V_{eo}} C_{eA} + \phi \frac{V_{io}}{V_{eo}} C_{iB}$$

$$= -\frac{K_A}{V_{eo}} C_{eA} + \phi \frac{V_{io}}{V_{eo}} \left[\frac{V_{eo}}{V_{io}} C_{eAo} + C_{iBo} - \frac{V_{eo}}{V_{io}} C_{eA} \right]$$

$$= -\frac{K_A}{V_{eo}} C_{eA} + \phi C_{eAo} + \phi \frac{V_{io}}{V_{eo}} C_{iBo} - \phi C_{eA}.$$

$$\Downarrow$$

On simplification :

$$\boxed{\frac{dC_{eA}}{dt} + \alpha C_{eA} - \beta = 0}$$

$$\alpha = \frac{K_A}{V_{eo}} + \phi; \quad \beta = \phi \left(C_{eAo} + \frac{V_{io}}{V_{eo}} C_{Bo} \right)$$

Now, you can, you can substitute this expression in to the governing equation of species mass balance of a substitute, this substitute this in differential equation that is the governing return of a, of a if you do that what will be getting is that d C e A dt will be minus K A divided by V e naught times C e A plus phi times V i naught divided by V e naught C i B. So, this will be minus K A V e naught C e A plus phi times V i naught divided by V e naught.

We just substitute the expression of V i v V i naught C e A naught plus C i B naught minus V e naught divided by V i naught C e A. So, finally, will be will be getting the expression minus and just opening this bracket of that will give you something that I will discussed K A minus K A divided by V e naught times c times C e A plus phi V i naught V i naught V i naught will be out, and so you will be getting phi times C e A naught plus phi times V i naught divided by V e naught C i B naught minus phi times C e A.

Now, this equation if if you see the this equation can be return in this form on simplification you can write d C e A dt plus alpha times C e A minus beta will be equal to 0 where alpha is equal to K A divided by V e naught plus phi and beta is equal to phi times C e A naught plus V i naught divided by V e naught C i B naught. So, this will be the simplify the version of the equation and all this initial values are known and K A and phi other two parameters. Now, what is this equation this is and the say this is the homogeneous, non homogeneous equation this is the non homogeneous ordinary differential equation of order one.

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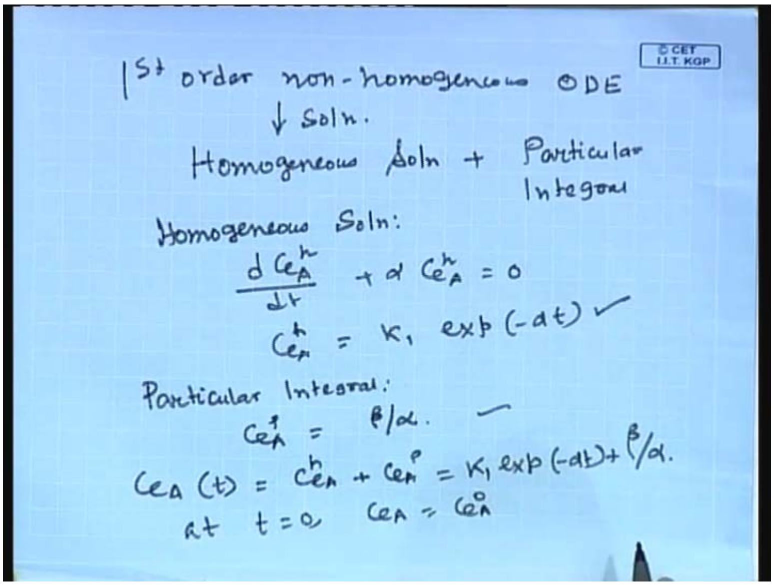

1st order non-homogeneous ODE

↓ Soln.

Homogeneous Soln + Particular Integral

Homogeneous Soln:

$$\frac{dC_{eA}^{h}}{dt} + \alpha C_{eA}^{h} = 0$$

$$C_{eA}^{h} = K_1 \exp(-\alpha t) \checkmark$$

Particular Integral:

$$C_{eA}^{p} = \beta/\alpha .$$

$$C_{eA}(t) = C_{eA}^{h} + C_{eA}^{p} = K_1 \exp(-\alpha t) + \beta/\alpha .$$

at $t = 0$ $C_{eA} = C_{eA}^{0}$

So, first order non homogenous ordinary differential equations and it will b it is solution will be constituted of two parts. One is the homogeneous part another is the particular integral right, homogeneous solution plus particular integral. Let us let us look in to the homogeneous for and the particular integral both, the homogenous solution gives d C e

A, let say h is homogeneous dt plus alpha C e homogeneous is equal to 0 and the solution is C e A homogeneous part is some constant k 1exponential minus alpha t.

The here solution of the and let us look in to the let us look in to the particular integral, the particular integral will be C e A particular in nothing, but beta by alpha how do it get it if it is a constant for if the homogeneous is constant then you have to put the whole solution their and see what is the the that constant part homogeneous, non homogeneous part. So, no homogeneous part comes out to be this. So, the total solution will be nothing, but super position linear position of the homogeneous solution of the particular integral. If you forget about how to evaluate the non homogeneous solution of partial differential order in a differential equation just look back into basic and get it first.

So, the total solution will be nothing, but a linear super position of the homogeneous part and the particular integral and this becomes C e A plus C e A, h plus C e A p and this becomes K 1 exponential minus alpha t plus beta by alpha. So, at time and the initial condition was at tis equal to 0 my C e A was is equal to C e A naught.

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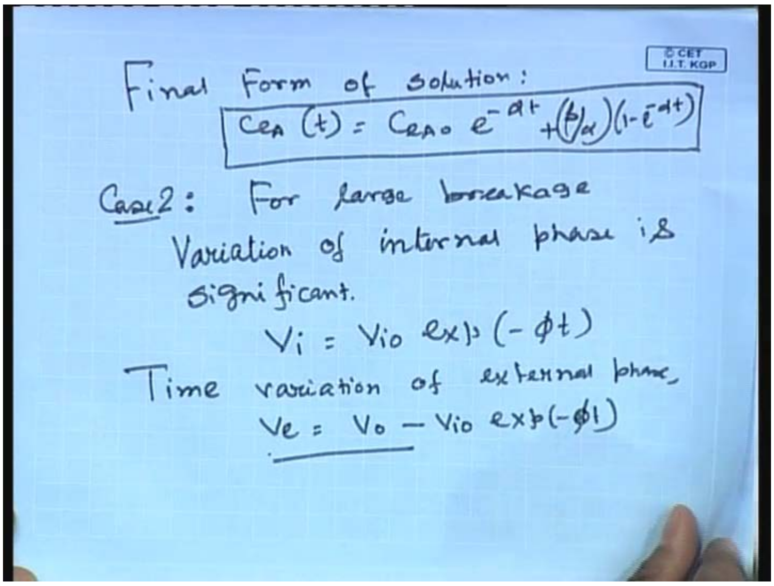

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Final Form of solution:

$$\boxed{C_{eA}(t) = C_{eA0}\, e^{-\alpha t} + (\beta/\alpha)(1 - e^{-\alpha t})}$$

Case 2: For large breakage

Variation of internal phase is significant.

$$V_i = V_{io} \exp(-\phi t)$$

Time variation of external phase

$$V_e = V_o - V_{io} \exp(-\phi t)$$

So, you can find out the it it integration constant and you can substitute their and the final of this writing the final form of the solution, the final form of the solution, solution becomes C e A at any point of time is equal to C e A naught exponential minus alpha t plus beta by alpha 1minus e to the power minus alpha t. This gives the final solution of this particular situation, when the breakage is small. Now, let us look in to the case number two where the breakage is reasonably large breakage.

And how the system will you know the solution will change. Now, in this case the variation of the internal volume becomes significant compare to the earlier phase when an it was insignificant. So, variation of internal phase is significant and what is the variation on internal phase? The variation of internal phase will be nothing, but V i is equal to V i naught exponential minus phi t that will have discussed and earlier this is the way, how the internal phase varies with as the function of time with the breakage constant phi.

So, time variation of the external phase is what? Time variation of external phase becomes V e is equal to v naught minus V i naught exponential minus alpha t alpha minus phi t right. So, we know that total volume was V e plus V i naught.

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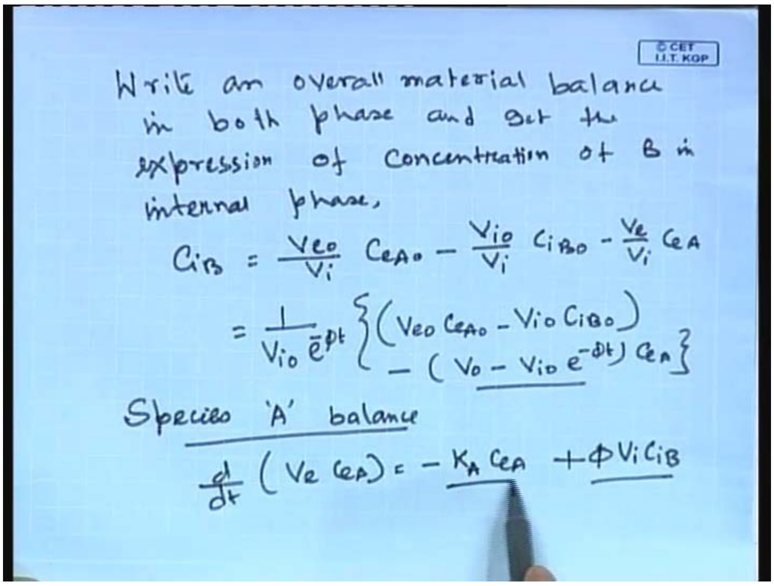

Write an overall material balance in both phase and get the expression of Concentration of B in internal phase,

$$C_{iB} = \frac{V_{eo}}{V_i} C_{eAo} - \frac{V_{io}}{V_i} C_{iBo} - \frac{V_e}{V_i} C_{eA}$$

$$= \frac{1}{V_{io}\, e^{-\phi t}} \left\{ \left(V_{eo} C_{eAo} - V_{io} C_{iBo} \right) - \left(\underline{V_o - V_{io}\, e^{-\phi t}} \right) C_{eA} \right\}$$

Species 'A' balance

$$\frac{d}{dt}\left(V_e C_{eA} \right) = - \underline{K_A C_{eA}} + \underline{\phi V_i C_{iB}}$$

So, just put the V naught is equal to V e plus V i the substitute the expression V i will be getting the variation of external phase at any volume at any point of time. Now, once you get this you can do an overall material balance and can obtain the expression of B concentration expression of concentration of B in the internal phase. Write an overall material balance in both the phase is in both phase is write whatever, you have to do done earlier exactly like that and get the expression of concentration of B in internal phase. That means, you are looking for an expression of C i B.

So, C i B becomes in the case V e naught divided by V i C e A naught minus V i naught divided by V i C i B naught minus V e divided by V i C e A. So, now, I am going to substitute the expression of V i as the function of t. So, if you do that. So, what will be getting is one over V i naught e to the power minus phi t bracket V e naught C e A naught minus V i naught C i B naught minus v naught minus V i naught e to the power minus phi t times C e A. So, what is this, this nothing, but the volume, volume of the external phase at any point of time.

Now, you do the species a balance do a species a balance and will be getting the time variation of concentration of a in the a in the external phase. So, d dt of V e C e A that is the net rate of the accumulation is equal to minus K A C e A plus phi V i C i B. So, that is the rate by huge it is coming out and there is the by huge it will be going in to going, going in to the external from the internal phase in to the external phase. Now, you just substitute the expression of C i B from here to here and the will be a function of time etcetera. So, the final expression will you give you.

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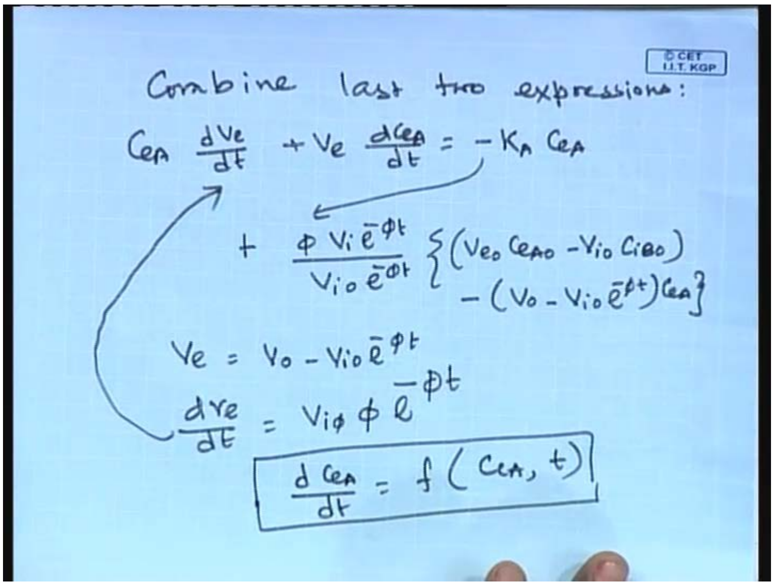

Combine last two expressions:

$$C_{eA}\frac{dV_e}{dt} + V_e\frac{dC_{eA}}{dt} = -K_A C_{eA}$$

$$+ \frac{\phi V_i e^{-\phi t}}{V_{io} e^{-\phi t}}\left\{(V_{eo} C_{eAo} - V_{io} C_{iBo}) - (V_o - V_{io} e^{-\phi t}) C_{eA}\right\}$$

$$V_e = V_o - V_{io} e^{-\phi t}$$

$$\frac{dV_e}{dt} = V_{i0}\,\phi\, e^{-\phi t}$$

$$\boxed{\frac{dC_{eA}}{dt} = f(C_{eA}, t)}$$

So, combine last two expressions. So, what will be getting is C e A d V e dt plus V e d C e A dt is equal to minus K A C e A plus we can right hand side plus phi V i e to the power of minus phi t divided by V i naught e to the power minus phi t V e naught C e A naught minus V i naught C i B naught minus v naught minus V i naught e to the power of minus phi t C e A and What is d V e dt? We know the expression of V e from the overall volume external phase volume balance V e is nothing, but V e naught minus V i naught e to the power of minus phi t.

So, you can taken find out what is the d V e dt d V e dt is nothing, but V i naught phi e to the power minus phi t correct. So, that I am going to substitute here and and you can it on other other side. So, will be getting d C e A dt as a function of you know C e A and of course, time. So, it will be getting a form of this ordinary differential equation, but the form is further we cannot have analytical solution in this particular case. And this has to be solved with the initial condition at time t is equal to 0. C e A is equal to C e A naught.

So, once. So, so it 0 basically a an ordinary differential equation it is an initial value problem and they has to be much forever using are in the cut of 4 or Euler's method or any other suitable numerical technique for solution of ordinary differential equation.

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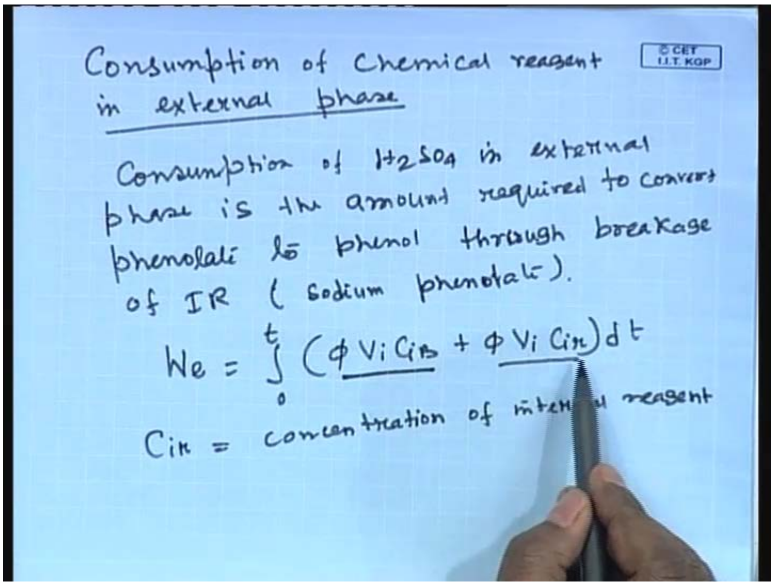

Consumption of Chemical reagent in external phase

Consumption of H_2SO_4 in external phase is the amount required to convert phenolate to phenol through breakage of IR (sodium phenolate).

$$W_e = \int_0^t (\phi \underline{V_i C_{iB}} + \phi \underline{V_i C_{ir}}) dt$$

C_{ir} = concentration of internal reagent

Next, we calculate what is the amount of consumption of chemical reagent? Consumption of chemical regent in external phase, that is quit important because this the process will be very efficient, when you will be maintain the maximum concentration difference concentration gradient that mean, the solute will be going to the internal phase react with the internal phase it is solution. It is volume become it is concentration becomes 0.

So, you can maintain the maximum concentration difference, but there is some limitation because we have the limitation of the external reagent the internal regent. So, suppose all the agent will be consumed, then the then the this process will be coming to as top almost because the concentration gradient will be decreasing and after some it will be stop.

So, it is very important to quantify the amount of chemical regent the this in that is present in the internal phase or external phase to you know. So, that. So, that thing will be going on. So, consumption of sulphuric acid the I am talking about example of phenols and sodium phenols, sulphuric acid system with the sodium hydroxide in the internal phase consumption of sulphuric acid.

In external phase is the amount required to convert phenolate to phenol through, what is the mechanism through breakage only through breakage of internal agent. That means, containing sodium phenolate, phenolate and this is this amount will be given as by this expression integral 0 to t phi V i C i B plus phi V i c i r dt. What is c i r? C i r is the concentration of internal regent. Why this come to the coming this first term will be coming since, there is the breakage.

So, breakage of phenolate to the external phase this term breakage of phenolate to the external phase and what is this term means? This term means that internal phase itself is some amount of internal phase itself is containing the sodium hydroxide, the directly come to the. So, whenever there is a breakage not only the sodium phenolate will be expression some amount of sodium hydroxide will also be present because not all sodium hydroxide is converted into phenolate. So, both of terms will be present.

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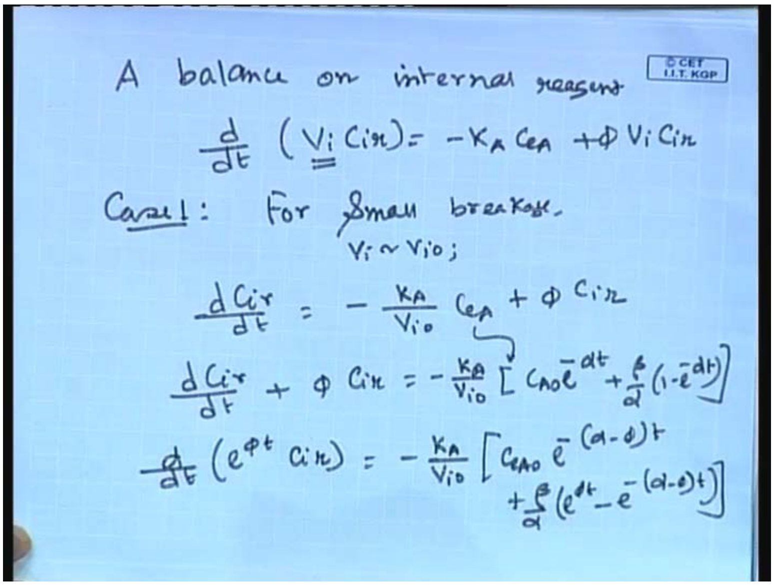

A balance on internal reagent

$$\frac{d}{dt}(\underline{\underline{V_i}}\, C_{ir}) = -K_A C_{eA} + \phi V_i C_{ir}$$

Case 1: For small breakage.

$V_i \sim V_{i0}$;

$$\frac{dC_{ir}}{dt} = -\frac{K_A}{V_{i0}} C_{eA} + \phi C_{ir}$$

$$\frac{dC_{ir}}{dt} + \phi C_{ir} = -\frac{K_A}{V_{i0}}\left[C_{A0}e^{-\alpha t} + \frac{\beta}{\alpha}(1-e^{-\alpha t})\right]$$

$$\frac{d}{dt}(e^{\phi t} C_{ir}) = -\frac{K_A}{V_{i0}}\left[C_{eA0}e^{-(\alpha-\phi)t} + \frac{\beta}{\alpha}(e^{\phi t}-e^{-(\alpha-\phi)t})\right]$$

So, this comes because of the sodium phenolate will coming into the external phase and this terms is present the sodium hydroxide. The internal agent will be coming out the because of the breakage to the external phase. Now, you can do an balance amount of internal phase internal reagent balance of on internal agent will give you this ordinary differential equation d dt of V i c i r is equal to minus K A C e A plus phi V i c i r. Now, again will be considering two cases small breakage and large breakage for small breakage we can considered V i is independent needs of time.

So, and it is equal to V i naught as the we have done earlier V i will be roughly equal to V i naught and similarly, V i equal to V i naught. So, d c i r dt will be minus K A divided by V i naught C e A plus phi times c i r. So, will be getting d c i r dt plus phi c i r is equal to minus K A V i naught times C e A and substitute the expression of C e A here that we have already known C A naught e to the power minus alpha t plus beta by alpha 1minus e to the power of minus alpha t we just substitute the solution of C e A that we have obtain earlier for the case of small breakage.

So, this becomes d dt of e to the power phi t c i r is equal to minus K A divided by V i naught C e A naught e to the power minus alpha minus phi t plus beta by alpha e to the power phi t minus e to the power of minus alpha minus phi t.

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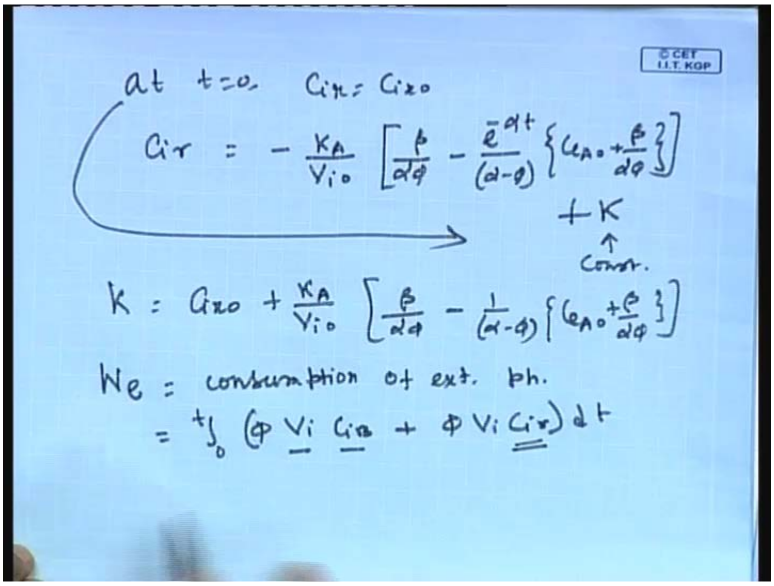

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at $t=0$, $C_{ir} = C_{ir0}$

$$C_{ir} = -\frac{K_A}{V_{i0}}\left[\frac{\beta}{\alpha\phi} - \frac{e^{-\alpha t}}{(\alpha-\phi)}\left\{C_{A0} + \frac{\beta}{\alpha\phi}\right\}\right] + \underset{\text{Const.}}{\underset{\uparrow}{K}}$$

$$K = C_{ir0} + \frac{K_A}{V_{i0}}\left[\frac{\beta}{\alpha\phi} - \frac{1}{(\alpha-\phi)}\left\{C_{A0} + \frac{\beta}{\alpha\phi}\right\}\right]$$

W_e = consumption of ext. ph.

$$= \int_0^t \left(\phi \underline{V_i}\, \underline{C_{iB}} + \phi V_i \underline{\underline{C_{ir}}}\right) dt$$

So, anyway again will be having a non homogeneous set of equation and the and type t is equal to 0 will considered c i r is equal to c i r naught. So, the integration of the earlier equation will give you c i r is equal to minus K A divided by V i naught in to beta by alpha phi minus e to the power minus alpha t over alpha minus phi C e A naught plus beta by alpha phi bracket close plus K.

This is the constant of integration, this constant about integration can be evaluated once you use the initial condition and this K transfer to be c i r naught plus K A divided by V i naught beta phi alpha phi minus whole one by alpha minus phi C e A naught plus beta divided by alpha phi. So, one can get the W e is the consumption of external phase, phase as integral 0 to t phi V i C i B plus phi V i c i r dt.

We know the expression of V i since, the it is it is small the breakage is small V i b equal to V i naught and we know, the expression of C i B earlier and right now, the derive the expression of c i r as the function of time that has to substituted here and this integral has to be evaluated numerically.

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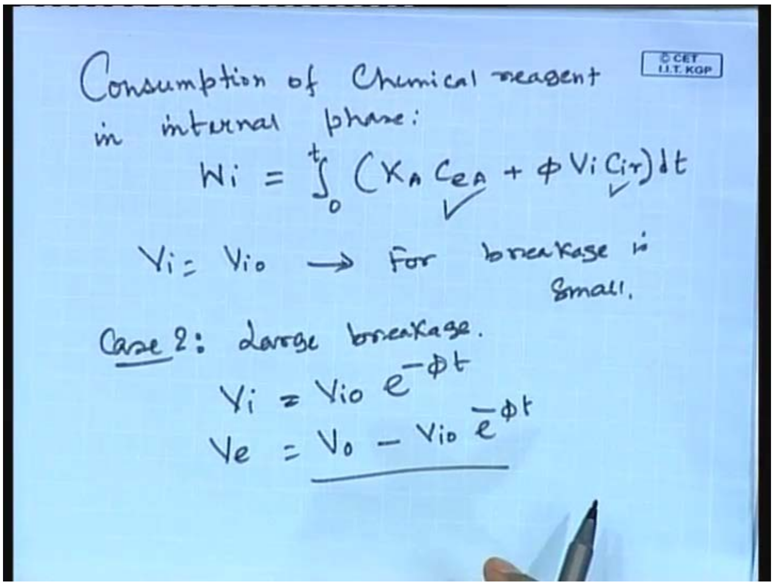

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Consumption of Chemical reagent in internal phase:

$$W_i = \int_0^t \left(K_A \underset{\checkmark}{C_{eA}} + \phi V_i \underset{\checkmark}{C_{ir}}\right) dt$$

$V_i = V_{io}$ → for breakage is small.

Case 2: Large breakage.

$$V_i = V_{io}\, e^{-\phi t}$$

$$V_e = \underline{V_0 - V_{io}\, e^{-\phi t}}$$

So, we can find out the consumption of external phase similarly, you can find out the consumption of chemical reagent it internal phase consumption of chemical reagent in internal phase can also be evaluated that mean, W i that mean, how much sodium hydroxide has been consumed to convert phenol into phenolate. So, the W i the internal phase will be integral 0 to t K A C e A plus phi V i c i r dt. We know the expression of C e A we know the expression of c i r which has derived it and V i will be equal to V i naught and we can evaluate, the amount there is consume for the of the chemical reagent in the internal phase.

And remember V i will be equal to V i naught, V i naught for breakage is small. Next, is case two when talking about large breakage in the case of large breakage. What we have to do? You have to evolve, we have to assume that the the breakage rule that V i will be reducing as the function of it is proportional to the volume. So, V I naught e to the power of minus phi t and V e will be nothing, but v naught minus V i naught e to the power minus phi t.

So, again you have to do the same balance equations that whatever, we have done earlier and substitute this here and ready to the calculation basically, it will be the exactly the same thing whatever done earlier and you will be getting an again the. So, solution will be numerically, obtained it can be analytical in nature. So, that is the roughly how will be calculating various quantities an oil will be modelling.

So, once you can you can do. So, because it was not know the value of phi and K A probably it not know this values. So, what have to do you have to do small collects experiments for a particular system and get the concentration profile. That means, you measure the concentration of the particular reagent in the external phase get the concentration profile and then and you know the numerical.

So, solution the analytical solution, so you start with the guess value of K A and phi this are the parameters and calculate concentration profile theoretically with the get set and check whether, this calculate profile match's with the experimental profile or not, if not then you read do a opt you do the reggaes the value set of the parameters values of the parameters and what how it will be done? It will be done optimizer.

So, a mains sub route has been look top with an optimizer that will automatic select the next set of parameters values and it will calculate, in the profile once again and see the some of the square is minimum or not. Now, let us look into one example of this. So, once to know the value of K A can phi for the buffer a particular system. We using a small scale experiment, then we can go for the large scale experiments in the predictive mode because this phi and K will be will be variance for the particular set of system. So, you can go for the scaling them.

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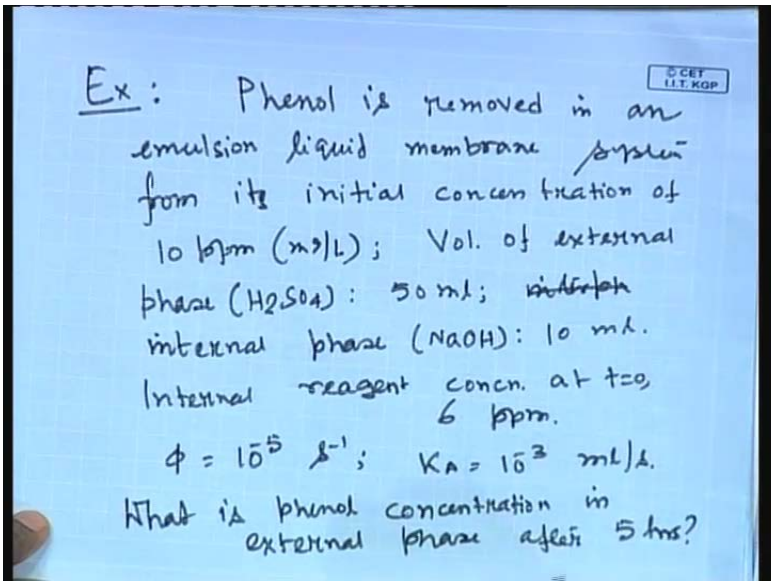

Ex: Phenol is removed in an emulsion liquid membrane system from its initial concentration of 10 ppm (mg/L); Vol. of external phase (H_2SO_4): 50 ml; internal phase (NaOH): 10 ml.

Internal reagent concn. at t=0, 6 ppm.

$\phi = 10^{-5}$ s^{-1}; $K_A = 10^{-3}$ ml/s.

What is phenol concentration in external phase after 5 hrs?

Now, we look into an example of liquid membrane phenol is removed, removed in a emulsion liquid membrane system let's say form it initial concentration of tem p p m, p p m is nothing, but milligram per litre the volume of external phase, there is sulphuric acid is 50 m l we starting with 50 m l and that of internal phase that is N a O H is 10 m l.

So, initial values are given and internal reagent concentration initially, was 6 p p m internal reagent concentration at t is equal to 0 was given as 6 p p m, 6 milligram per litre the breakage coefficient is given as 10 to the power minus 5 second inverse and K A is given as 10 to the power of minus 3 millilitre per second. So, what have to do you have to find out phenol concentration in the bulk phase; that means, in that external phase occurs 5 hours. What is phenol concentration? In external phase, which after 5 hours.

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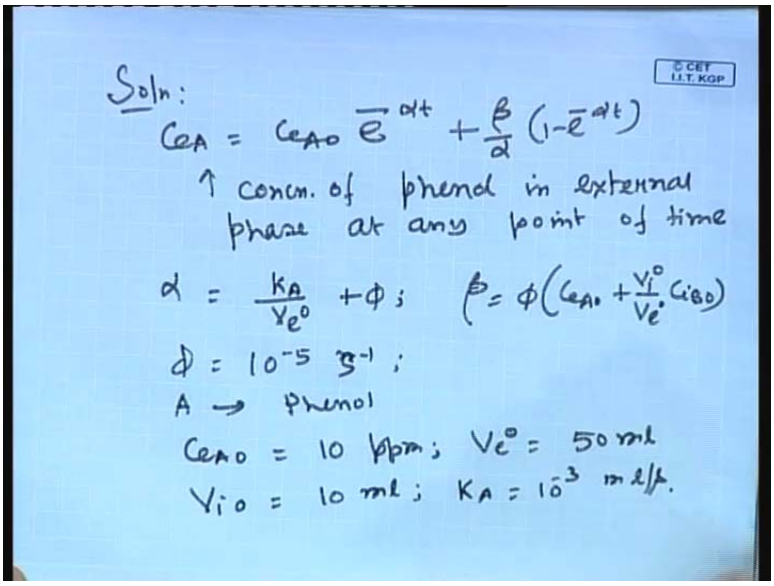

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Soln:

$$C_{eA} = C_{eA0}\, e^{-\alpha t} + \frac{\beta}{\alpha}\left(1 - e^{-\alpha t}\right)$$

↑ concn. of phenol in external phase at any point of time

$$\alpha = \frac{K_A}{V_e^0} + \phi; \quad \beta = \phi\left(C_{eA0} + \frac{V_i^0}{V_e^0} C_{iB0}\right)$$

$\phi = 10^{-5}\ s^{-1}$;

A → Phenol

$C_{eA0} = 10$ ppm; $V_e^0 = 50$ ml

$V_{i0} = 10$ ml; $K_A = 10^{-3}$ ml/s.

So, the solution is straight forward. So, you just write down the expression of C e A. C e A is the phenol concentration in the external phase at point of time C e A naught e to the power minus alpha t plus beta by alpha 1minus e to the power minus alpha t. So, this is the gives you concentration of phenol in external phase at any point of time. So, and What is alpha? Alpha is K A by V e naught plus 5 beta is equal to phi C e A naught plus V i naught by V e naught C i B naught. So, phi the breakage coefficient is given is 10 to the power of minus 5 second inverse a is phenol will denote phenol as A.

So, C e A naught the initial concentration is 10p p m, V e naught that is the volume of the external phase initial was 50 m l, V i naught is given as 10 m l K A is given as 10 to the power of minus 3 millilitre per second. So, now, we calculate various quantities.

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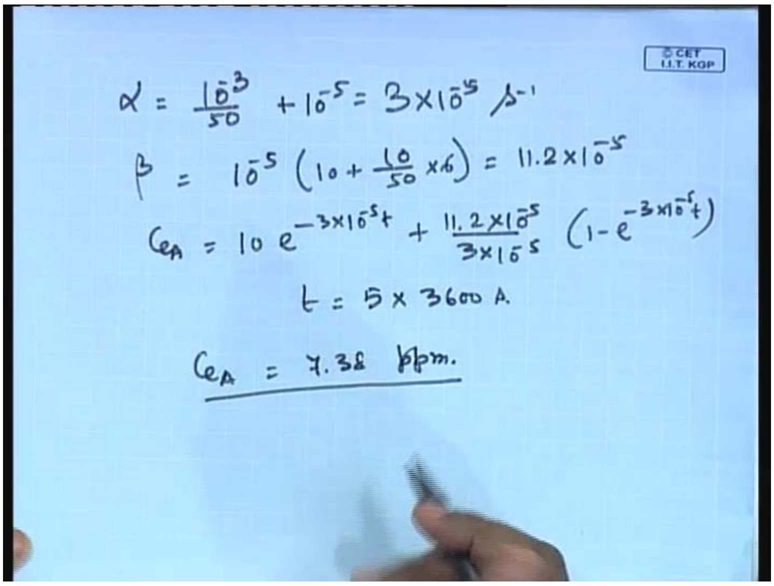

$$\alpha = \frac{10^{-3}}{50} + 10^{-5} = 3\times10^{-5}\ s^{-1}$$

$$\beta = 10^{-5}\left(10 + \frac{10}{50}\times 6\right) = 11.2\times10^{-5}$$

$$C_{eA} = 10\, e^{-3\times10^{-5}t} + \frac{11.2\times10^{-5}}{3\times10^{-5}}\left(1 - e^{-3\times10^{-5}t}\right)$$

$$t = 5\times 3600\ s.$$

$$\underline{C_{eA} = 7.38\ ppm.}$$

So, once you give already values calculate the value of alpha it is 10 to the power of minus 3 by 50 plus 10 to the power of minus 5, it transfer to be 3 into 10 to the power of minus 5 second inverse beta transfer to be 10 to the power of minus 5 into 10 plus 10 by 50 into 6. So, it is 11.2 into 10 to the power of minus 5 and C e A is given as 10 e to the power of minus 3 into 10 to the power of minus 5 times t plus 11. 2 into 10 to the power of minus 5 divided by 3 into 10 to the power of minus 5 into 1minus e to power minus 3 into 10 to the power of 5 t and we have going to find out, what is the value of t at the 5 hours. So, t is equal to 5 into 3600 second and C e A transfer to be 7.38 p p m. So, it gives some value.

So, judies solution of K A and other thing, so it it K A and b 5 will be depending on the selection k will be depend on the selection of oil phase and external phase number 1 and 5 will be depending on the the starting that you are going to have in the system. So, whether and the also the surfactant, surfactant will can give the stability of the emulsion, where the surfactant is good an for efficient enough to stabilize the surfactant. So, the breakage will be breakage will be or leakage will be minimum.

So, for define various values of you know parameters one can estimate or model this system are just given was simple calculation, but this systems are write now, much use in separation of oily separation, of oil water separation of wholes stream containing the organics containing. The inorganic it is it is extremely useful, when you are having small concentrations of metal ions for example, cadmium, zinc, arsenic and the lead so and so for.

So, this per method is also liquid membrane also used not only for the separation that to concentrate the metal ions, it can be use for the analytical purposes. What is the analytical purpose? Suppose you are having a very dilute stream of led or cadmium which is very dangerous. So, part you cannot measure it is value is concentration because lower be the concentration any instrument will be erroneous in nature it will give erroneous results. The an certain things hour the measure becomes large, when the concentration becomes lower.

So, what is done for the analytical cables? The analytical cable it to concentrate it this is the one of the method used and the cloud conduct extraction is an another method, liquid membrane is another method. In analytical chemistry to extract the concentration of the cadmium or led are the dangerous material metal ions into a face, where it is concentration becomes more. So, it can be detected much more easily, it detection or measurement becomes much more efficient. So, there is for the analytical chemistry apart from the this liquid membrane can be used for (( )) purification and the treat main purposes as well, but the point is the stability of the liquid membrane has became a problem and it is really, it is really a problem for to have a stable emulsions beyond half hour.

Even 45 minutes, 1 hour I am saying 5 hours for the particular example of 5 hour that is too large too optimalistic value generally, liquid membrane the emulsions are not stabilize to that extend. So, stability of the liquid membrane is one of the major problem that basically, hinders it is why per application industrially. So, so for so, we just we have just come to the end of the third surfactant immediate the separation processes that the liquid membrane system in the next class will move on to centrifugal separation processes. Thank you.