Fluid-fluid Reaction:
Kinetics and Reactor Design

Book: *Chemical Reaction Engineering*, O. Levenspiel, (Chapter 23 and 24), 3rd Edition, Wiley and Sons

Example

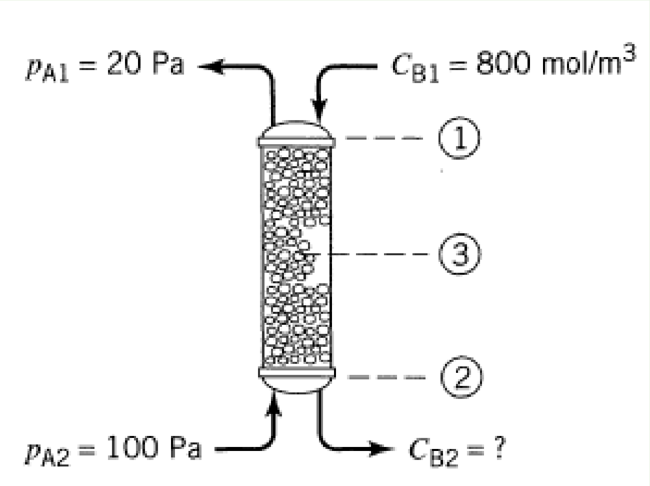
For the system described in the earlier example (concentration of impurity reduced from 0.1% to 0.02%) a reactant B having a high concentration is added to the water in the liquid phase. Concentration of B is 0.8 N (800 mol/m^3). B reacts with A very rapidly such that $k = \infty$

$$A(g \rightarrow l) + B(l) \rightarrow products(l)$$

Find the height of the tower required for counter current operations

Assume the diffusivities of A and B in water are the same $k_{AL} = k_{BL} = k_L$

The solution strategy for such problems is:
Step 1. Write the material balance and find C_{B_2} in the exit stream.
Step 2. Next it is necessary to determine which specific form of rate equation is applicable in this case
Step 3. Finally the height of the tower is calculated



Step 1. At any point in the absorption tower, $p_A - p_{A_1} = \frac{F_l \pi}{F_g C_T}(C_{B_1} - C_B)$

$$p_A - 20 = \frac{7\times10^5\times10^5}{1\times10^5\times 56000}(800 - C_B)$$

$$p_A - 20 = 10000 - 12.5\, C_B$$

$$p_A = 10020 - 12.5 C_B$$

Now, C_{B_2} is determined from $p_{A_2} = 10020 - 12.5C_{B_2}$

$C_{B_2} = \frac{10020 - p_{A_2}}{12.5} = \frac{10020 - 100}{12.5}$ = 793.6 mol/m^3

Step 2 The correct form of the rate equation has to be determined – this is a case of instantaneous reaction, therefore it is either Case A or Case B

It is necessary to find out whether $k_{Ag}p_A$ is > or < $\frac{k_{BL}C_B}{b}$

<u>At the top of the tower</u>,

$k_{Ag}ap_A$ = 0.32 x 20 = 6.4 mol/h.m^3 $\frac{k_{BL}aC_B}{b}$ = 0.1 x 800 = 80 mol/h.m^3 $k_{Ag}p_A < \frac{k_{BL}C_B}{b}$

<u>At the bottom of the tower</u>,

$k_{Ag}ap_A$ = 0.32 x 100 = 32 mol/h.m^3 $\frac{k_{BL}aC_B}{b}$ = 0.1 x 793.6 = 79.36 mol/h.m^3 $k_{Ag}p_A < \frac{k_{BL}C_B}{b}$

For both the top and bottom of the tower, $k_{Ag}p_A < \frac{k_{BL}C_B}{b}$ Hence, it is **case B**

Step 3 For case B, $(-r_A''') = (-r_A'')a = k_{Ag}ap_A = 0.32\ p_A$

$$h = \frac{\frac{F_g}{A_{cs}}}{\pi}\int_{p_{A1}}^{p_{A2}} \frac{dp_A}{(-r_A''')} = \frac{1\times10^5}{10^5}\int_{20}^{100}\frac{dp_A}{0.32\ p_A} = \frac{1}{0.32}ln\frac{100}{20} = 5.03$$

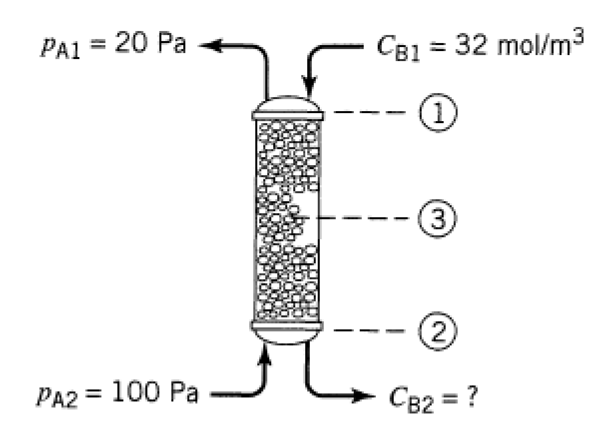
$h = 5.03$ m

Example

(i) Repeat the previous example using a feed of C_B = 32 mol/m³ instead of 800 mol/m³

(ii) In the next case use a feed of C_B = 128 mol/m³

(i) ***Step 1.*** At any point in the absorption tower, $p_A - p_{A_1} = \frac{F_l \pi}{F_g C_T}(C_{B_1} - C_B)$



$$p_A - 20 = \frac{7\times10^5\times10^5}{1\times10^5\times 56000}(32 - C_B)$$

$$p_A - 20 = 400 - 12.5\, C_B$$

$$p_A = 420 - 12.5 C_B$$

Now, $C_{B_2} = \frac{420 - p_{A_2}}{12.5} = \frac{420 - 100}{12.5}$ = 25.6 mol/m³

Step 2 Now, It is necessary to find out whether $k_{Ag}p_A$ is > or < $\frac{k_{BL}C_B}{b}$, so as to ascertain whether it is case A or case B

<u>At the top of the tower,</u>

$k_{Ag}ap_A$ = 0.32 x 20 = 6.4 mol/h.m³ $\quad \frac{k_{BL}aC_B}{b}$ = 0.1 x 32 = 3.2 mol/h.m³ $\quad k_{Ag}p_A > \frac{k_{BL}C_B}{b}$

<u>At the bottom of the tower,</u>

$k_{Ag}ap_A$ = 0.32 x 100 = 32 mol/h.m³ $\quad \frac{k_{BL}aC_B}{b}$ = 0.1 x 25.6 = 2.56 mol/h.m³ $\quad k_{Ag}p_A > \frac{k_{BL}C_B}{b}$

For both the top and bottom of the tower, $k_{Ag}p_A > \frac{k_{BL}C_B}{b}$ Hence, it is **case A**

For case A,

$$(-r_A''') = (-r_A'')a = \frac{\frac{D_{BL}}{D_{AL}}\frac{C_B}{b} + \frac{p_A}{H_A}}{\frac{1}{H_A k_{Ag} a} + \frac{1}{k_{AL} a}}$$

$$(-r_A''') = (-r_A'')a = \frac{H_A C_B + p_A}{\frac{1}{k_{Ag} a} + \frac{H_A}{k_{AL} a}}$$

$$(-r_A''') = \frac{12.5 \times \left[\frac{420 - p_A}{12.5}\right] + p_A}{\frac{1}{0.32} + \frac{12.5}{0.1}} = \frac{420}{128.125} = 3.278$$

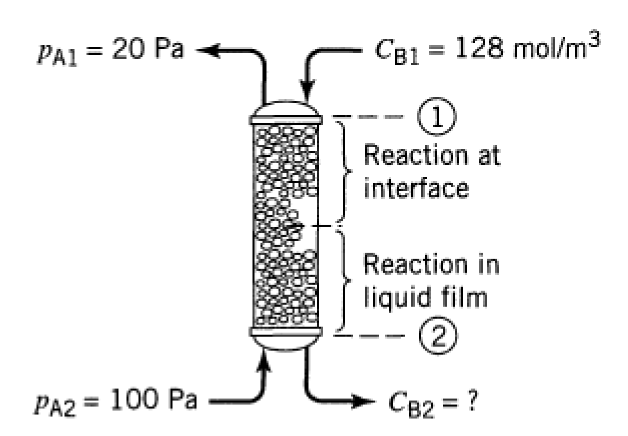
$$h = \frac{\frac{F_g}{A_{cs}}}{\pi} \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{(-r_A''')}$$

$$h = \frac{1 \times 10^5}{10^5} \int_{20}^{100} \frac{dp_A}{3.278} = \frac{1}{3.278}(100 - 20) = 24.4$$

$$h = 24.4 \text{ m}$$

(ii) In the next case use a feed of C_B = 128 mol/m³

(i) ***Step 1.*** At any point in the absorption tower, $p_A - p_{A_1} = \frac{F_l \pi}{F_g C_T}\left(C_{B_1} - C_B\right)$



$$p_A - 20 = \frac{7\times10^5\times10^5}{1\times10^5\times 56000}(128 - C_B)$$

$$p_A - 20 = 1600 - 12.5\,C_B$$

$$p_A = 1620 - 12.5C_B$$

Now, $C_{B_2} = \frac{1620 - p_{A_2}}{12.5} = \frac{1620 - 100}{12.5}$ = 121.6 mol/m³

Step 2 Now, It is necessary to find out whether $k_{Ag}p_A$ is > or < $\frac{k_{BL}C_B}{b}$, so as to ascertain whether it is case A or case B

<u>At the top of the tower</u>,

$k_{Ag}ap_A$ = 0.32 x 20 = 6.4 mol/h.m³ $\frac{k_{BL}aC_B}{b}$ = 0.1 x 128 = 12.8 mol/h.m³ $k_{Ag}p_A < \frac{k_{BL}C_B}{b}$

<u>At the bottom of the tower</u>,

$k_{Ag}ap_A$ = 0.32 x 100 = 32 mol/h.m³ $\frac{k_{BL}aC_B}{b}$ = 0.1 x 121.6 = 12.16 mol/h.m³ $k_{Ag}p_A > \frac{k_{BL}C_B}{b}$

At the **top of the tower**, $k_{Ag}p_A < \frac{k_{BL}C_B}{b}$ Hence, it is **case B**

At the **bottom of the tower**, $k_{Ag}p_A > \frac{k_{BL}C_B}{b}$ Hence, it is **case A**

It is now necessary to determine the **condition at which the transition from Case A to Case B occurs**,

$k_{Ag} a p_A = k_{BL} a C_B$

or, $0.32 \times p_A = 0.1 \times C_B$ or, $C_B = 3.2 p_A$

Putting this value in the mass balance equation, $p_A = 1620 - 12.5 C_B$ we have,

$p_{A'} = 1620 - 12.5 C_B = 1620 - 12.5(3.2 p_A)$ $\Rightarrow$ $p_{A'} = \frac{1620}{41} = 39.5$ Pa

The height of the tower is estimated considering case B from p_A = 20 Pa to p_A= 39.5 Pa and case A from p_A = 39.5 Pa to p_A= 100 Pa ,

$$h = \frac{F_g / A_{cs}}{\pi} \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{(-r_A''')}$$

$$h = \frac{F_g / A_{cs}}{\pi} \left[\int_{p_{A1}}^{p_{A'}} \frac{dp_A}{k_{Ag} a p_A} + \int_{p_{A'}}^{p_{A2}} \frac{dp_A}{\frac{H_A C_B + p_A}{\frac{1}{k_{Ag} a} + \frac{H_A}{k_{AL} a}}} \right] = \frac{10^5}{10^5} \left[\int_{20}^{39.5} \frac{dp_A}{k_{Ag} a p_A} + \int_{39.5}^{100} \frac{\left(\frac{1}{k_{Ag} a} + \frac{H_A}{k_{AL} a} \right) dp_A}{H_A C_B + p_A} \right]$$

$$h = \frac{10^5}{10^5} \left[\frac{1}{0.32} ln \frac{39.5}{20} + \int_{39.5}^{100} \frac{\left(\frac{1}{0.32} + \frac{12.5}{0.1} \right) dp_A}{12.5 \times \left[\frac{162020 - p_A}{12.5} \right] + p_A} \right] = 2.127 + \frac{128.125}{1620} (100 - 39.5)$$

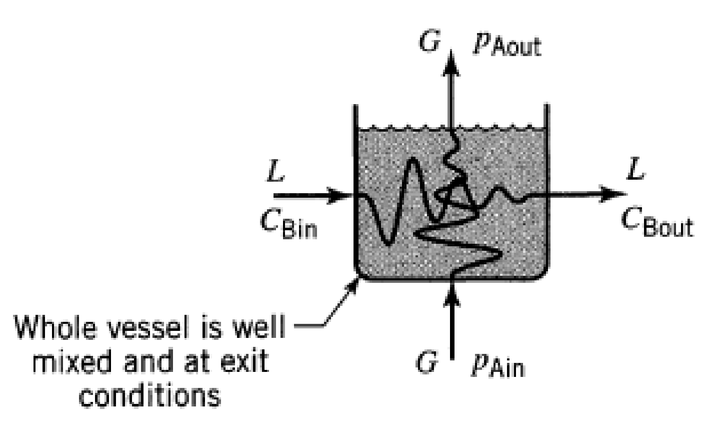
$$h = 2.127 + 4.785 = 6.91 \text{ m}$$

(4) Mixed flow gas/Mixed flow liquid – Mass Transfer + Reaction in Agitated Tank Reactor

Composition is the same everywhere in the vessel

$$(A\ lost\ by\ gas) = \frac{1}{b}(B\ lost\ by\ liquid) = (Disappearance\ of\ A\ by\ reaction)$$

$$F_g\left(Y_{A_{in}} - Y_{A_{out}}\right) = \frac{F_l}{b}\left(X_{B_{in}} - X_{B_{out}}\right) = (-r_A''')_{at\ exit\ condition}\, V_r$$



For dilute systems,

$$\frac{F_g}{\pi}\left(p_{A_{in}} - p_{A_{out}}\right) = \frac{F_l}{bC_T}\left(C_{B_{in}} - C_{B_{out}}\right) = (-r_A''')_{at\ exit\ condition}\, V_r$$

- $(-r_A''')$ is evaluated from known stream compositions and equation solved to get V_r
- If V_r is known and $C_{B_{out}}$ or $p_{A_{out}}$ is to be determined –
  - Guess $p_{A_{out}}$
  - Evaluate $C_{B_{out}}$ and then $(-r_A''')$ and V_r
  - If the V_r matches with actual V_r then calculations are stopped, otherwise a new $p_{A_{out}}$ is chosen and calculations iterated

Chemical Reaction Engineering, O. Levenspiel

Example

90% of A present in a gas stream has to be removed by absorption in water which contains reactant B

$$A(g \rightarrow l) + B(l) \rightarrow R(l) \qquad -r_A = kC_AC_B$$

This reaction is carried out in an agitated tank reactor

For gas stream, F_g = 90000 mol/h at $\pi = 10^5$ Pa $p_{A_{in}}$ = 1000 Pa $p_{A_{out}}$ = 100 Pa

Physical data: D = 3.6 x 10^{-6} m^2/h $C_U = 55556$ mol/m^3 liquid at all C_B

For liquid agitated tank, F_l = 9000 mol/h $k_{AL}a$ = 144 h^{-1} $C_{Bin} = 5556$ mol/m^3 a = 200 m^2/m^3

$k_{Ag}a$ = 0.72 mol/h.m^3.Pa f_l = 0.9

(a) What volume of contactor is needed?

(b) Where does the resistance of absorption reaction lie?

Find the above for two cases: (i) when H_A = 0 Pa.m^3/mol and k = 0 m^3/mol.h (straight mass transfer, no B in the system)

(ii) when $H_A = 10^5$ Pa.m^3/mol and k = 2.6 x 10^7 m^3/mol.h

(i) H_A = 0 Pa.m^3/mol and k = 0 m^3/mol.h

$$M_H = \frac{\sqrt{kC_BD_{AL}}}{k_{AL}} = 0 \qquad \text{and} \qquad E_i = 1 + \frac{D_{BL}}{D_{AL}}\frac{C_BH_A}{p_{Ai}} = 1 + 0 = 1$$

$$(-r_A''') = \frac{p_A}{\frac{1}{k_{Ag}a}} = \frac{100}{\frac{1}{0.72}} = 72$$

$$\frac{F_g}{\pi}\left(p_{A_{in}} - p_{A_{out}}\right) = (-r_A''')_{at\ exit\ condition}\ V_r$$

$$V_r = \frac{\frac{F_g}{\pi}\left(p_{A_{in}} - p_{A_{out}}\right)}{(-r_A''')_{at\ exit\ condition}} = \frac{\frac{90000}{100000}(1000-100)}{72} = 11.25\ \text{m}^3$$

(ii) H_A = 10^5 Pa.m^3/mol and k = 2.6 x 10^7 m^3/mol.h

$$F_g\left(Y_{A_{in}} - Y_{A_{out}}\right) = \frac{F_l}{b}\left(X_{B_{in}} - X_{B_{out}}\right)$$

$$90000\left(\frac{1000}{10^5} - \frac{100}{10^5}\right) = 9000\left(\frac{5556}{55556} - \frac{C_{B_{out}}}{55556}\right)$$

$$0.09 = 0.1 - \frac{C_{B_{out}}}{55556} \quad \Rightarrow \quad C_{B_{out}} = 555.96\ \text{mol/m}^3$$

$$M_H = \frac{\sqrt{kC_BD_{AL}}}{k_{AL}} = \frac{\sqrt{3.6\times10^{-6}\times555.96\times2.6\times10^7}}{144/200} = 316.83$$ and $$E_i = 1 + \frac{D_{BL}}{D_{AL}}\frac{C_BH_A}{p_{Ai}} = 1 + \frac{555.96\times10^5}{100} = 555961$$

Now, $E_i > 5M_H \quad (555961 > 1584.15) \quad \therefore \quad E \cong M_H$

$$-r_A''' = \frac{p_A}{\frac{1}{ak_{Ag}} + \frac{H_A}{k_{AL}aE} + \frac{H_A}{kC_Bf_L}} = \frac{100}{\frac{1}{0.72} + \frac{10^5}{144\times316.83} + \frac{10^5}{2.6\times10^7\times555.96\times0.9}} = \frac{100}{1.388 + 2.192 + 7.687\times10^{-6}} = \frac{100}{3.572} = 27.995$$

(a) $$V_r = \frac{\frac{F_g}{\pi}\left(p_{A_{in}} - p_{A_{out}}\right)}{(-r_A''')_{at\ exit\ condition}} = \frac{\frac{90000}{100000}(1000-100)}{27.995} = 28.933\ \text{m}^3$$

(b) Resistances: 38.86% in gas film $\left(\frac{1.388}{3.572} \times 100 = 38.86\%\right)$

61.37% in liquid film $\left(\frac{2.192}{3.572} \times 100 = 49.98\%\right)$

(5) Plug flow gas/Mixed flow liquid – Mass Transfer + Reaction in Bubble Tank Reactor

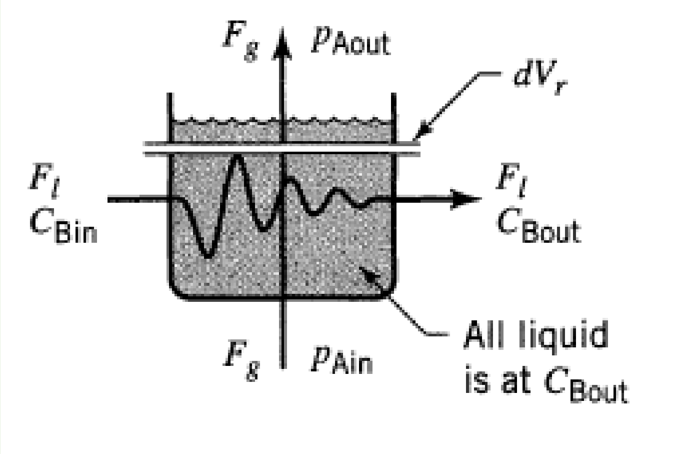
Here it is necessary to make a differential balance for the loss of A from the gas because gas is in plug flow and an overall balance for B because liquid is in mixed flow

$$(A\ lost\ by\ gas) = (Disappearance\ of\ A\ by\ reaction)$$

$$F_g dY_A = (-r_A''')|_{L\ at\ exit\ conditions}\ dV_r$$

$$(A\ lost\ by\ gas) = \frac{1}{b}(B\ lost\ by\ liquid)$$

$$F_g\left(Y_{A_{in}} - Y_{A_{out}}\right) = \frac{F_l}{b}\left(X_{B_{in}} - X_{B_{out}}\right)$$



Therefore,

$$V_r = F_g \int_{Y_{Aout}}^{Y_{Ain}} \frac{dY_A}{(-r_A'')a} \quad \text{with} \quad F_g\left(Y_{A_{in}} - Y_{A_{out}}\right) = \frac{F_l}{b}\left(X_{B_{in}} - X_{B_{out}}\right)$$

For dilute systems,

$$V_r = \frac{F_g}{\pi} \int_{p_{Aout}}^{p_{Ain}} \frac{dp_A}{(-r_A'')a} \quad \text{with} \quad \frac{F_g}{\pi}\left(p_{A_{in}} - p_{A_{out}}\right) = \frac{F_l}{bC_T}\left(C_{B_{in}} - C_{B_{out}}\right)$$

- $(-r_A'')a$ is calculated for liquid at $C_{B_{out}}$
- V_r can be calculated from above equation if outlet conditions are known
- If $C_{B_{out}}$ and $p_{A_{out}}$ are to be found in a reactor of known volume V_r , then trial and error method is required
- Guess $C_{B_{out}}$ and then find $(-r_A''')$ and V_r and match with known value

(5) Mixed flow gas/Batch uniform liquid – Absorption + Reaction in Batch Agitated Tank Reactor

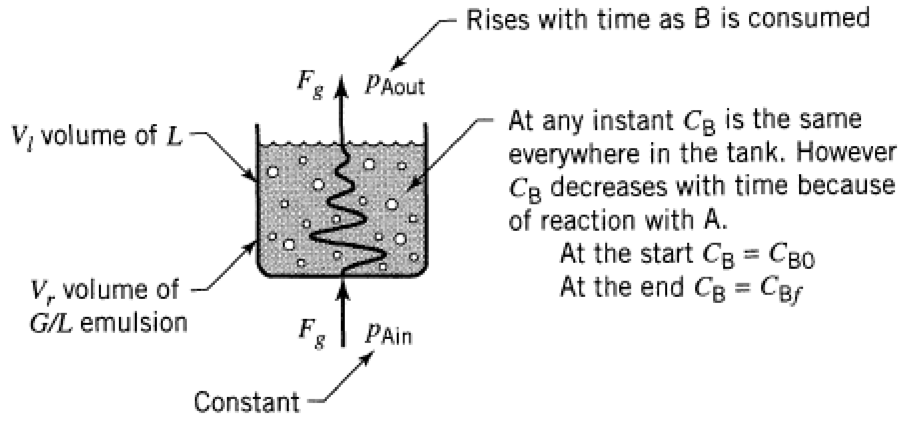
This is an **unsteady state operation**

At the start, $C_B = C_{Bo}$ and at the end $C_B = C_{Bf}$

C_B decreases with time due to reaction with A

$$(A\ lost\ by\ gas) = \begin{pmatrix} Decrease\ of\ B \\ with\ time \end{pmatrix} = \begin{pmatrix} Disappearance\ of \\ A\ or\ B\ by\ reaction \end{pmatrix}$$

$$F_g\left(Y_{A_{in}} - Y_{A_{out}}\right) = -\frac{V_l}{b}.\frac{dC_B}{dt} = (-r_A''')V_r$$



For dilute systems, $$\frac{F_g}{\pi}\left(p_{A_{in}} - p_{A_{out}}\right) = -\frac{V_l}{b}.\frac{dC_B}{dt} = (-r_A''')V_r$$

To find the time needed for a given operation,

- Choose a number of C_B values (C_{Bo}, C_{Bf} and intermediates)
- For each C_B value, guess $p_{A_{out}}$
- Calculate M_H, E_i and then E and $(-r_A''')$
- Check if $(-r_A''')V_r$ is = $\frac{F_g}{\pi}\left(\frac{p_{A_{in}}}{\pi - p_{A_{in}}} - \frac{p_{A_{out}}}{\pi - p_{A_{out}}}\right)$
- Continue till they match

- Then use the fact that

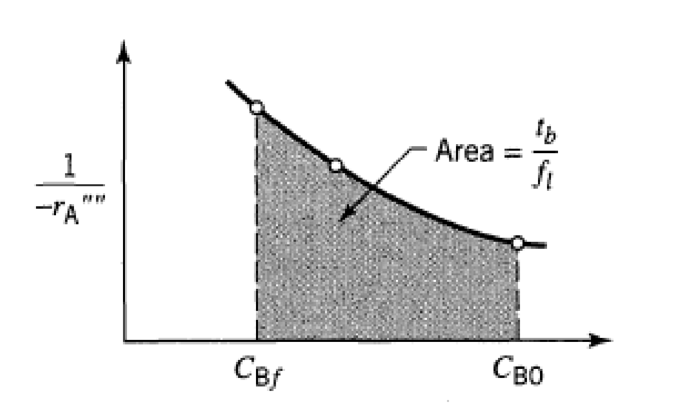
$$-\frac{V_l}{b}\cdot\frac{dC_B}{dt} = (-r_A''')V_r$$

To write

$$t = \frac{V_l/V_r}{b}\int_{C_{Bf}}^{C_{Bo}}\frac{dC_B}{(-r_A''')} = \frac{f_l}{b}\int_{C_{Bf}}^{C_{Bo}}\frac{dC_B}{(-r_A''')}$$

Minimum time needed if all A reacts ($p_{A_{out}} = 0$)

$$t_{min} = \frac{\frac{V_l}{b}(C_{Bo} - C_{Bf})}{F_g\left(\frac{p_{A_{in}}}{\pi - p_{A_{in}}}\right)}$$



Efficiency of utilization (% of entering A which reacts with B) = $\frac{t_{min}}{t}$