BT209

Bioreaction Engineering

03/04/2023

Deign for Multiple reactions

Series reaction: i)First order followed by zero order and

ii) zero order followed by first order

iii) Two-Step Irreversible Series-Parallel Reactions

Design for multiple reaction: First order followed by zero order reaction

- First order (n_1=1) followed by zero order (n_2=0) series reaction

$$A \xrightarrow[n_1=1]{k_1} R \xrightarrow[n_2=0]{k_2} S$$

What is C_R^{max} in a batch or PFR for pure feed of A?

(CRo = Cso = 0)

Kinetics

$$-r_A = -\frac{dC_A}{dt} = k_1 C_A$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A - k_2$$

$$r_s = \frac{dC_s}{dt} = k_2$$ (upto R become non detective)

$$\boxed{\frac{C_A}{C_{A0}} = e^{-k_1 t}}$$

$$\boxed{\frac{C_R}{C_{A0}} = 1 - e^{-k_1 t} - \frac{k_2}{C_{A0}} t}$$

Cont.

For C_R^{max}

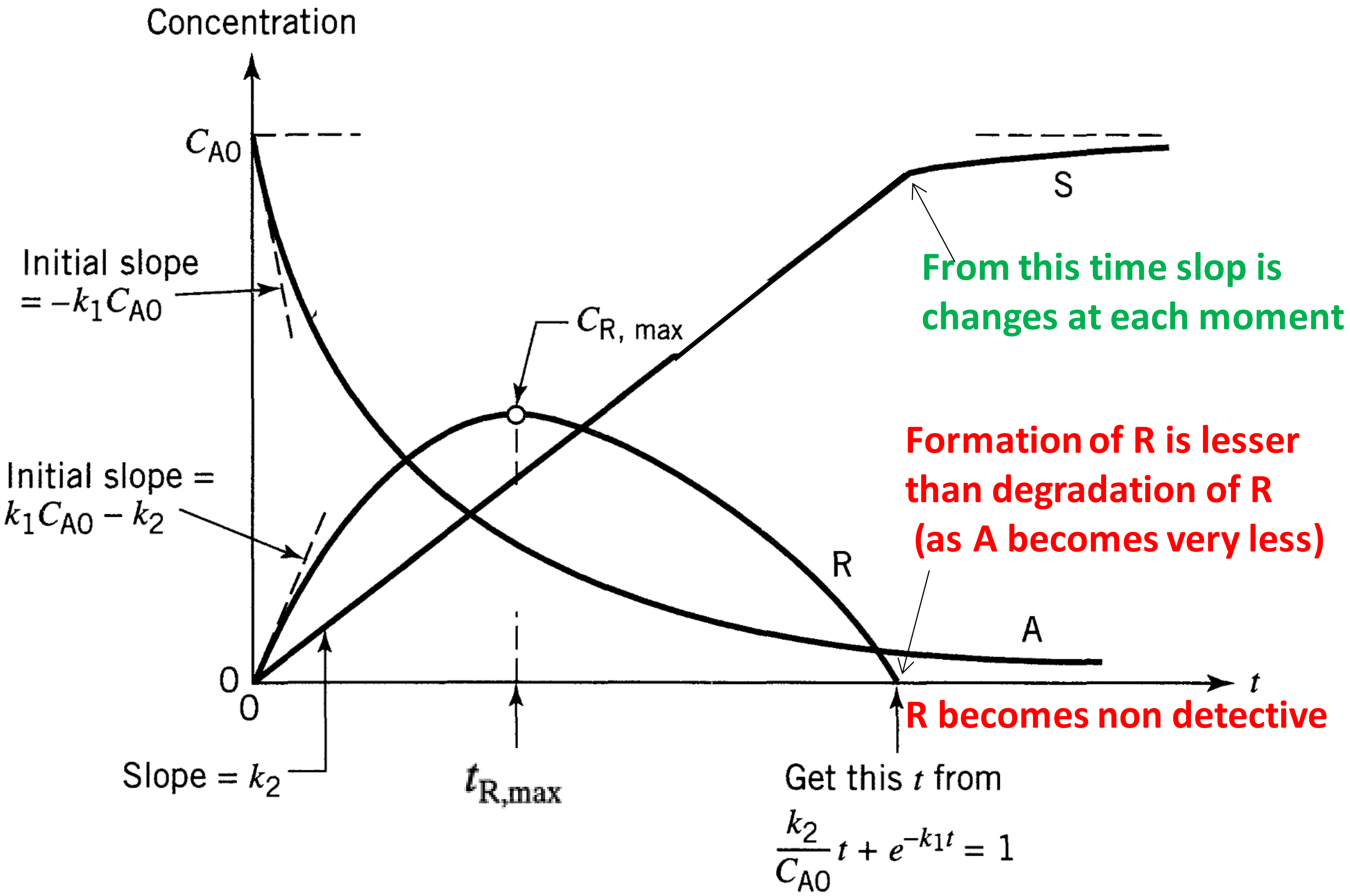
Put $dC_R/dt = 0$

Time at C_R reached maximum

$$\boxed{t_{R,max} = \frac{1}{k_1} \ln \frac{1}{K}}$$

$$\boxed{\frac{C_{R,max}}{C_{A0}} = 1 - K(1 - \ln K)}$$

$$\text{where } K = \frac{k_2/C_{A0}}{k_1}$$



Zero-order followed by First-order reaction

- Zero order (n_1=0) followed by first order (n_2=1) series reaction

$$A \xrightarrow[n_1=0]{k_1} R \xrightarrow[n_2=1]{k_2} S$$

What is C_R^{max} in a batch or PFR for pure feed of A?

(CRo = Cso = 0)

<u>Kinetics</u>

$$-r_A = -\frac{dC_A}{dt} = k_1 \qquad when\ A\ present$$

$$\left. \begin{aligned} r_R = \frac{dC_R}{dt} &= k_1 - k_2 C_R \\ &= -k_2 C_R \end{aligned} \right\} \begin{aligned} &when\ A\ present \\ &when\ A\ absent \end{aligned}$$

$$r_s = \frac{dC_s}{dt} = k_2 C_R$$

$$\left. \begin{aligned} \frac{C_A}{C_{A0}} &= 1 - \frac{k_1 t}{C_{A0}} \\ \frac{C_A}{C_{A0}} &= 0 \end{aligned} \right\} \begin{aligned} &when\ \ t < \frac{C_{A0}}{k_1} \\ &when\ \ t \geq \frac{C_{A0}}{k_1} \end{aligned}$$

Cont.

$$A \xrightarrow[n_1=0]{k_1} R \xrightarrow[n_2=1]{k_2} S$$

Kinetics

$$r_R = \frac{dC_R}{dt} = k_1 - k_2 C_R \quad \text{when } A \text{ present}$$

$$= -k_2 C_R \quad \text{when } A \text{ absent}$$

$$\text{When} \quad t < \frac{C_{A0}}{k_1} \,(\text{when } A \text{ present})$$

$$\frac{dC_R}{dt} + k_2 C_R = k_1$$

$$I.F. = e^{\int k_2 dt} = e^{k_2 t}$$

$$e^{k_2 t}\frac{dC_R}{dt} + e^{k_2 t} k_2 C_R = e^{k_2 t} k_1$$

$$I.C.:\ t = 0,\ C_R = C_{R0} = 0$$

$$C_R = \frac{k_1}{k_2} - \frac{k_1}{k_2} e^{-k_2 t}$$

$$\frac{C_R}{C_{A0}} = \frac{1}{K}\left(1 - e^{-k_2 t}\right)$$

$$\boxed{K = \frac{k_2}{k_1 / C_{A0}}}$$

Cont.

$$A \xrightarrow[n_1=0]{k_1} R \xrightarrow[n_2=1]{k_2} S$$

$$When \quad t \geq \frac{C_{A0}}{k_1} \,(\, when\; A\; absent)$$

$$\frac{dC_R}{dt} = -k_2 C_R$$

$Take:$

$$at\; t = \frac{C_{A0}}{k_1}, \qquad C_R = \frac{C_{A0}}{K}(1 - e^{-K})$$

$$at\; t = t, \qquad C_R = C_R$$

$$C_R = \frac{k_1}{k_2} e^{-k_2 t}\left(e^{-\frac{k_2 C_{A0}}{k_1}} - 1\right)$$

$$\frac{C_R}{C_{A0}} = \frac{1}{K}\left(e^{-K-k_2 t} - e^{-k_2 t}\right)$$

$$\boxed{K = \frac{k_2}{k_1/C_{A0}}}$$

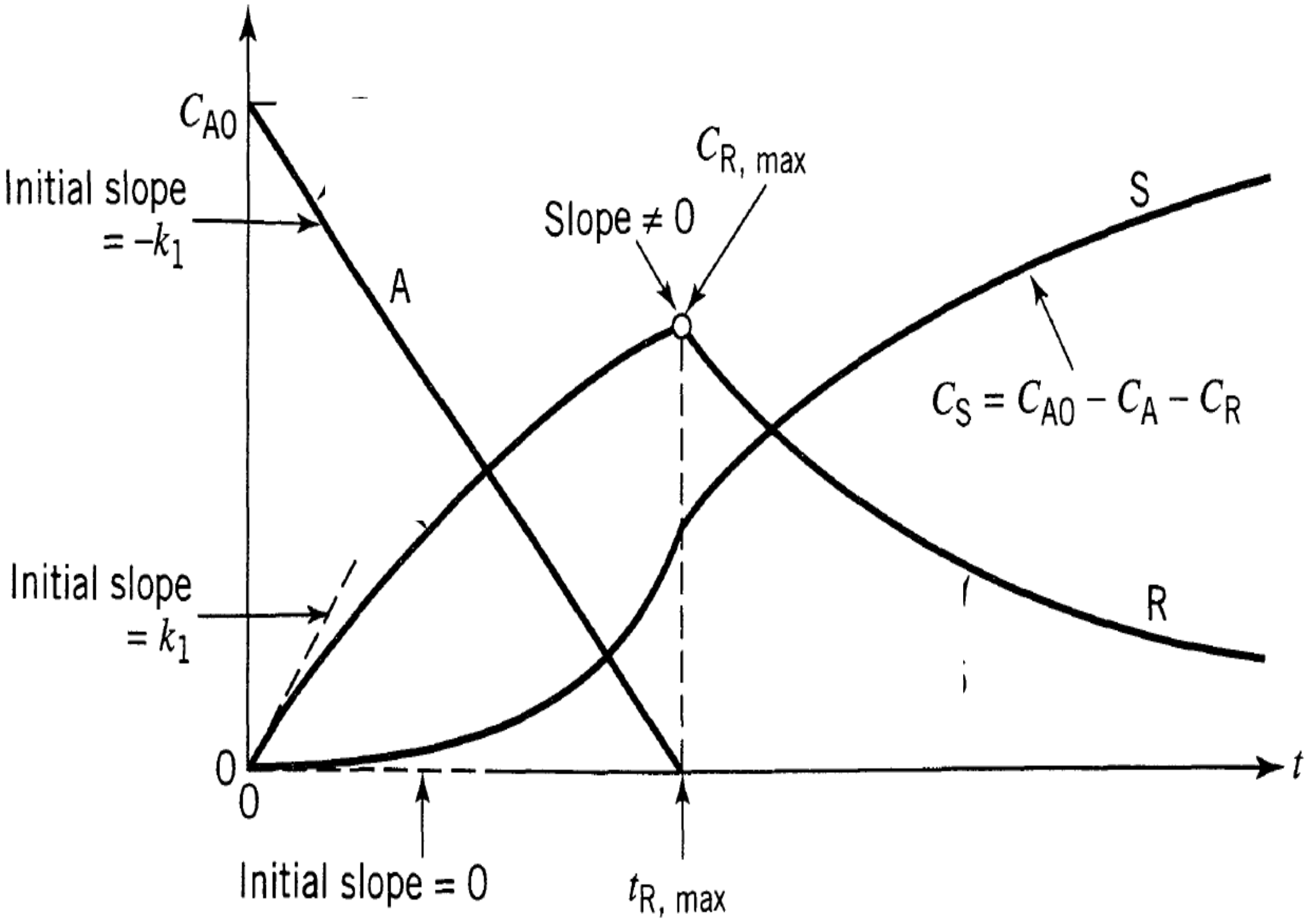
Cont.

$$A \xrightarrow[n_1=0]{k_1} R \xrightarrow[n_2=1]{k_2} S$$ (CRo = Cso = 0)

$$\boxed{\frac{C_A}{C_{A0}} = 1 - \frac{k_1 t}{C_{A0}}}$$

$$\frac{C_R}{C_{A0}} \begin{cases} = \dfrac{1}{K}\left(1 - e^{-k_2 t}\right) & t < \dfrac{C_{A0}}{k_1} \\ = \dfrac{1}{K}\left(e^{K - k_2 t} - e^{-k_2 t}\right) & t \geq \dfrac{C_{A0}}{k_1} \end{cases}$$

$$\boxed{K = \frac{k_2}{k_1 / C_{A0}}}$$



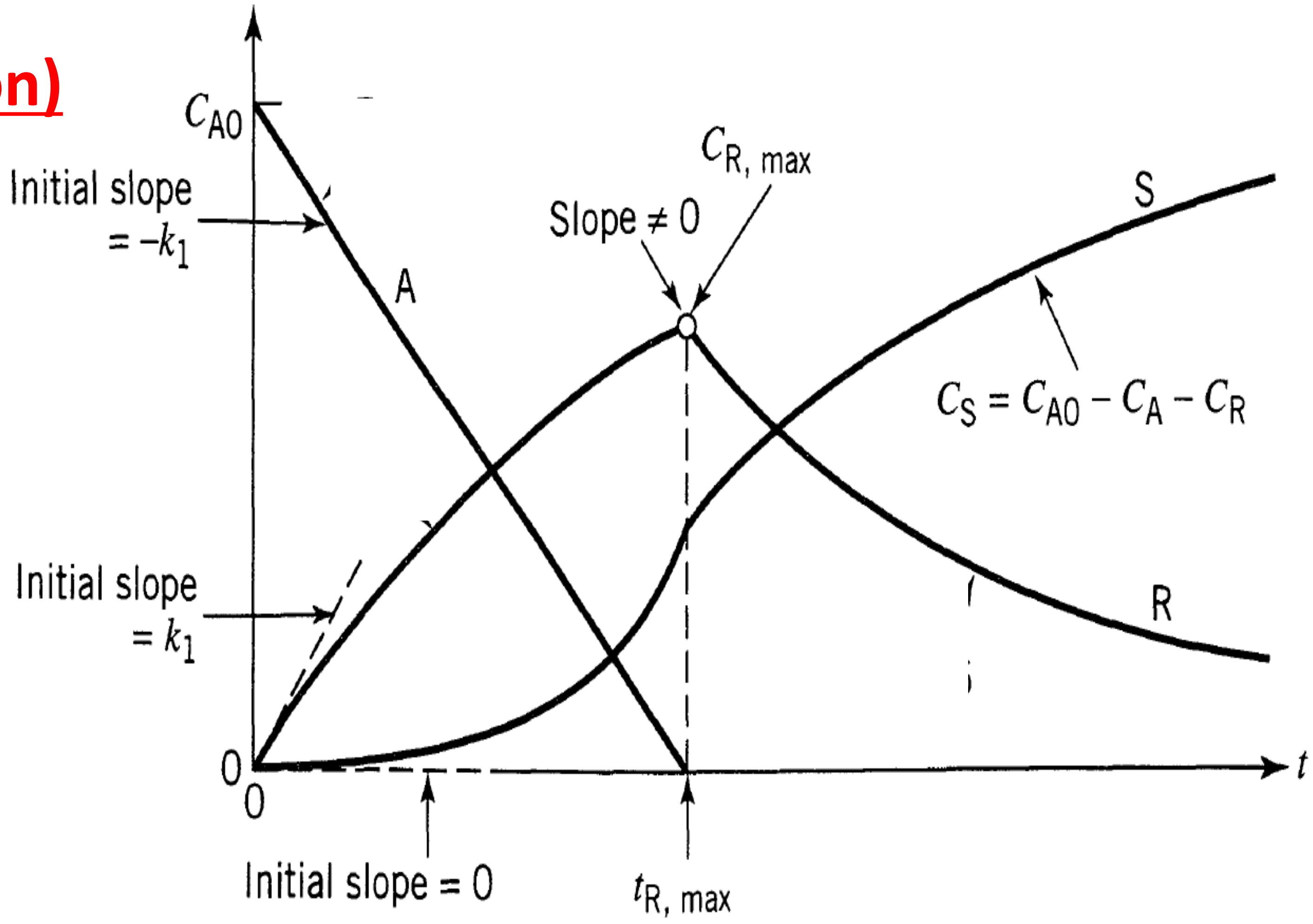
Cont.

For C_R^{max}

(Closed boundary condition)

$$t_{R,max} = \frac{C_{A0}}{k_1}$$

$$\frac{C_{R,max}}{C_{A0}} = \frac{1 - e^{-K}}{K}$$



TRY: First order followed by zero order reaction in CSTR

- First order (n_1=1) followed by zero order (n_2=0) series reaction

$$A \xrightarrow[n_1=1]{k_1} R \xrightarrow[n_2=0]{k_2} S$$

What is C_R^{max} in a CSTR for pure feed of A?

(CRo = Cso = 0)

Kinetics

$$-r_A = -\frac{dC_A}{dt} = k_1 C_A$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A - k_2$$

$$r_s = \frac{dC_s}{dt} = k_2$$ (upto R become non detective)

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \frac{X_A}{-r_A}$$

$$\frac{V}{F_{R0}} = \frac{\tau}{C_{R0}} = \frac{X_R}{r_R}$$

$$\frac{V}{F_{S0}} = \frac{\tau}{C_{S0}} = \frac{X_S}{r_S}$$

(Sign of r_R and r_S depends on what Expressions OF conversion are used)

Product distribution: Two-Step Irreversible Series-Parallel Reactions

Reactions

$$\left.\begin{aligned} A + B &\xrightarrow{k_1} R \\ R + B &\xrightarrow{k_2} S \end{aligned}\right\}$$

$$A \xrightarrow{+B} R \xrightarrow{+B} S$$

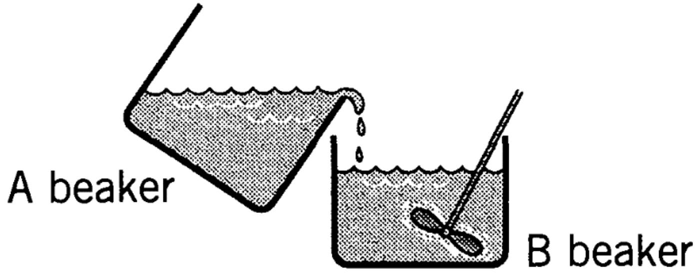
OR

$$B \xrightarrow{+A} R \qquad B \xrightarrow{+R} S$$

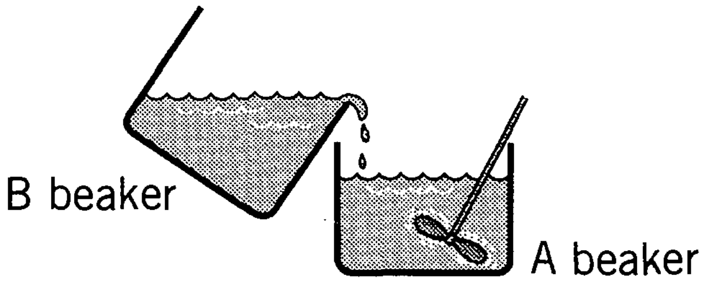
With respect to B, Parallel

Product Distribution?

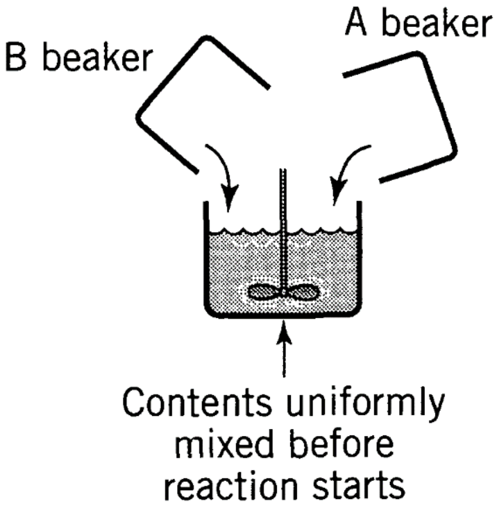
(I) Add A *Slowly to B*



(II) Add B *Slowly to A*



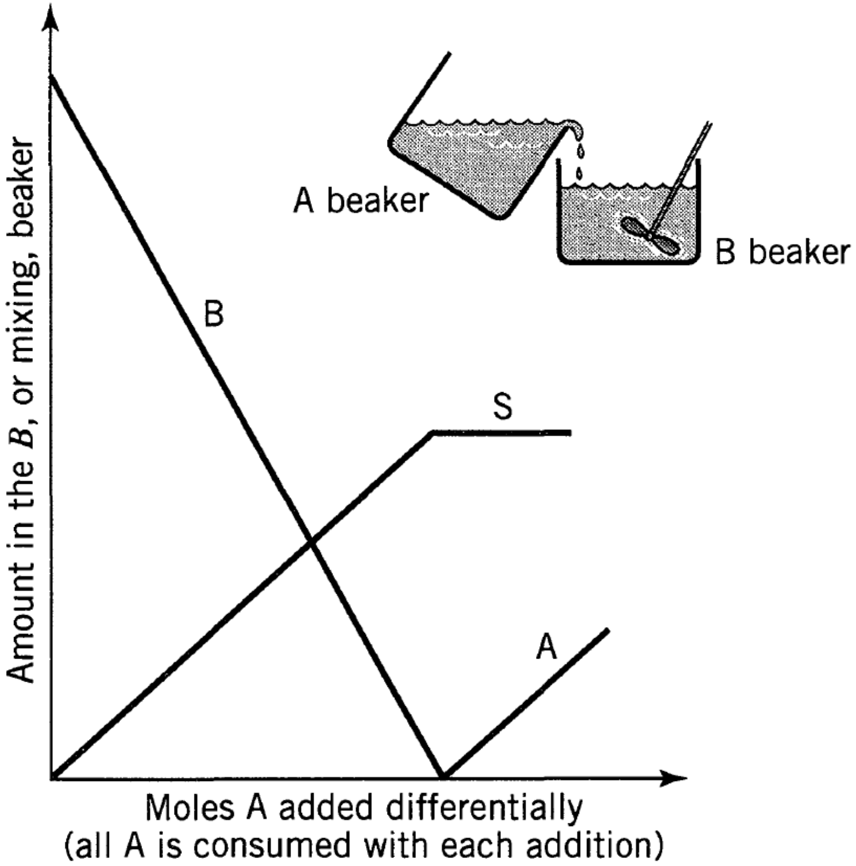
(III) Mix A and B Rapidly



Product Distribution: (I) Add A Slowly to B

- Pour A a little at a time into the beaker containing B, stirring thoroughly and making sure that all the A is used up and that the reaction stops before the next bit is added

$$\left.\begin{array}{l} A + B \xrightarrow{k_1} R \\ R + B \xrightarrow{k_2} S \end{array}\right\}$$



Product Distribution

- With each addition of A, a bit of R is produced in the beaker. But this R finds itself in an excess of B so it will react further to form S.

- The result is that at no time during the slow addition will A and R be present in any appreciable amount.

- The mixture becomes progressively richer in S and poorer in B. This continues until the beaker contains only S.

- When B is completely depleted in beaker, A will increase upon addition of A and production S will stop

Product Distribution: (III) Mix A and B mixed rapidly

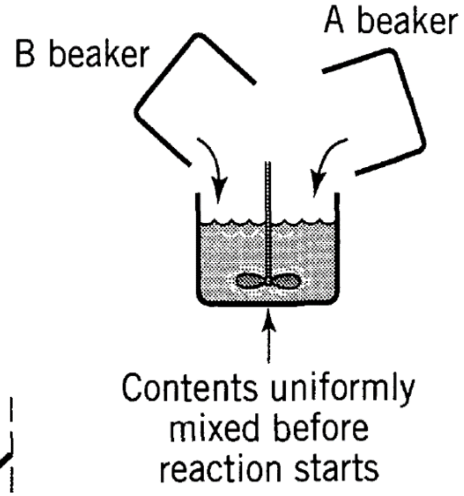
- ➢ Third alternative where the contents of the two beakers are rapidly mixed together,

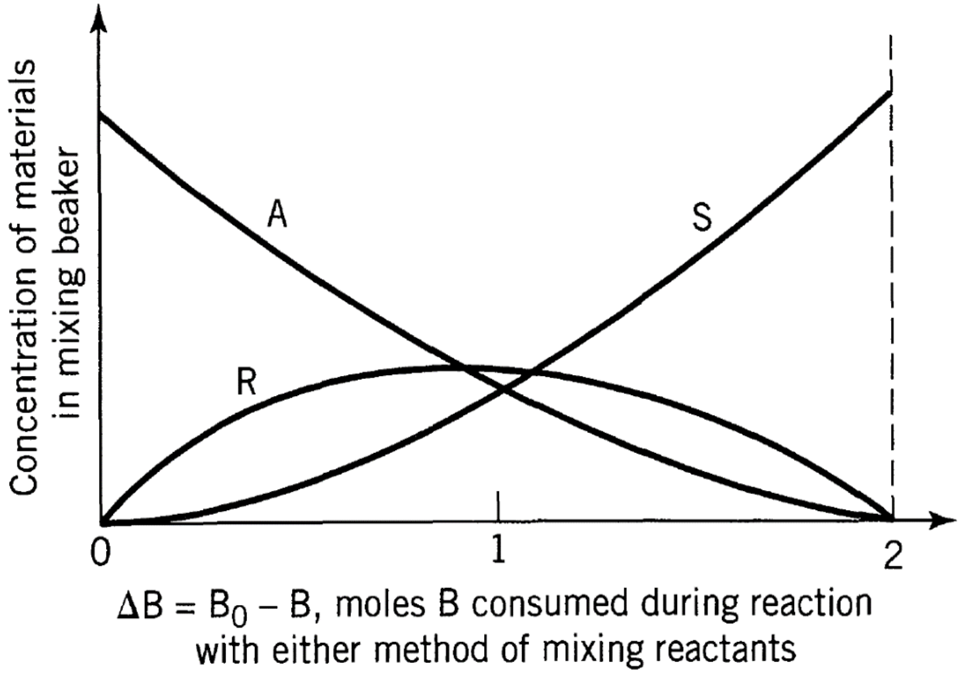
- ❑ The reaction being slow enough so that it does not proceed to any appreciable extent before the mixture becomes **uniform**.

- ❑ During the first few reaction **increments R finds itself competing with a large excess of A for B** and hence it is at a disadvantage.

- ❑ **Same type of distribution curve** as for the mixture in which type (II) B is added slowly to A.

$$\left.\begin{aligned} A + B &\xrightarrow{k_1} R \\ R + B &\xrightarrow{k_2} S \end{aligned}\right\}$$

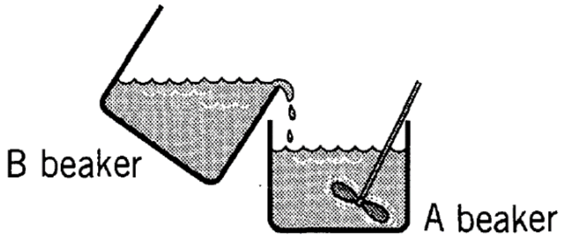




Product Distribution: (II) Add B Slowly to A

For II: Pour B a little at a time into the beaker containing A, again stirring thoroughly.

$$\left.\begin{array}{l} A + B \xrightarrow{k_1} R \\ R + B \xrightarrow{k_2} S \end{array}\right\}$$



- The first bit of B will be used up, reacting with A to form R. This R cannot react further for there is now no B present in the mixture.
- With the next addition of B, both A and R will compete with each other for the B added, and since A is in very large excess it will react with most of the B, producing even more R.
- This process will be repeated with progressive buildup of R and depletion of A until the concentration of R is high enough so that it can compete favorably with A for the B added.
- When this happens, the concentration of R reaches a maximum, then decreases. Finally, after addition of B, we end up with a solution containing only S.