Potpourri of Multiple Reactions

Chapter 8

This chapter considers all sorts of reactions where the product formed may react further.

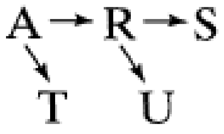
Here are some examples

$$A \rightarrow R \rightarrow S \rightarrow T$$

Series

$$\begin{aligned} A + B &\rightarrow R \\ R + B &\rightarrow S \\ S + B &\rightarrow T \end{aligned}$$

Series parallel, or consecutive-competitive



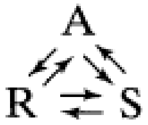
Denbigh system

$$A \rightleftarrows R \rightarrow S$$

Reversible and irreversible

$$A \rightleftarrows R \rightleftarrows S$$

Reversible



Reversible network

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

IRREVERSIBLE FIRST-ORDER REACTIONS IN SERIES

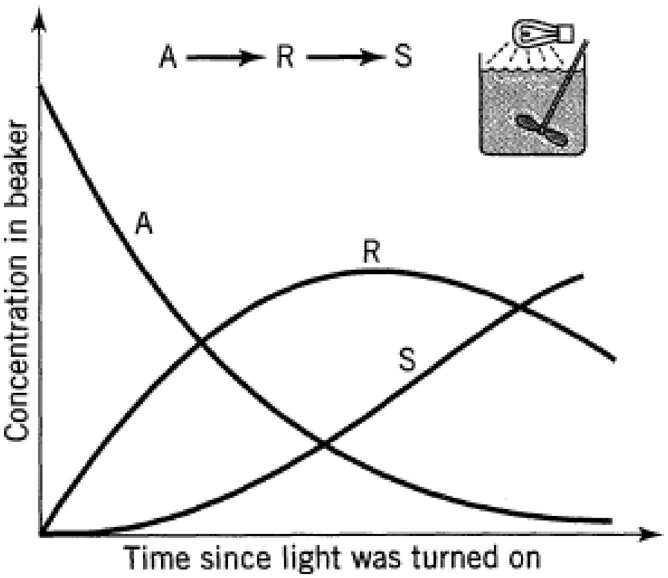
$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

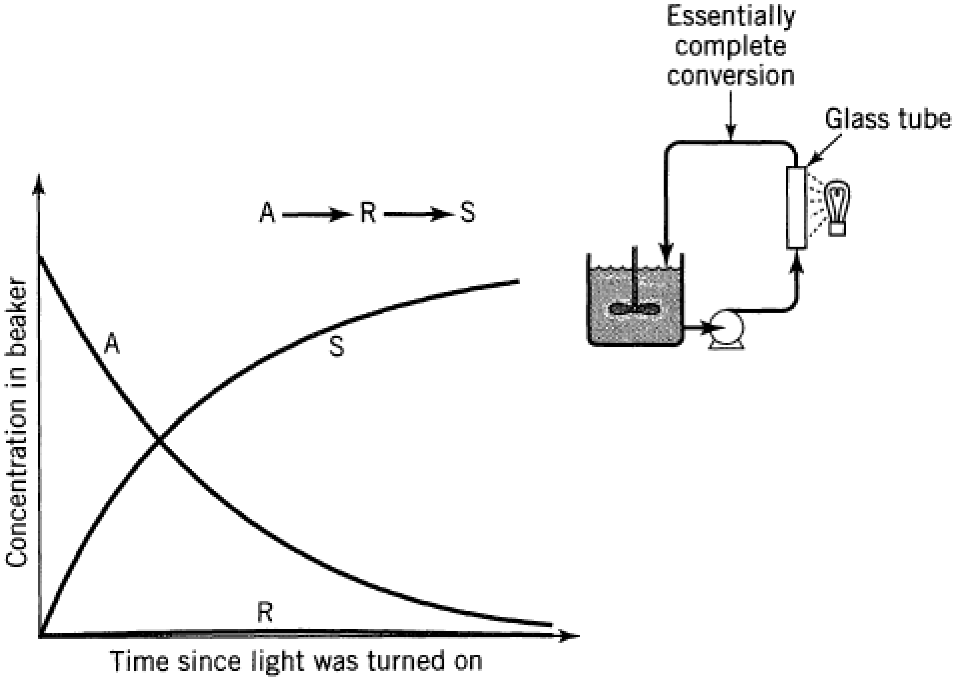
$$r_A = -k_1 C_A$$

$$r_R = k_1 C_A - k_2 C_R$$

$$r_S = k_2 C_R$$

Concentration-time curves if the contents of the beaker are irradiated uniformly.





Qualitative Discussion About Product Distribution

- Consider the following two ways of treating a beaker containing A:
- First, the contents are uniformly irradiated;
- second, a small stream is continuously withdrawn from the beaker, irradiated, and returned to the beaker;
- the rate of absorption of radiant energy is the same in the two cases.
- During this process A disappears and products are formed.
- Is the product distribution of R and S different in the two beakers.

Case 2

- If the flow rate is not too high, that the fluid being irradiated reacts essentially to completion.
- In this case, then, A is removed and S is returned to the beaker. So, as time passes the concentration of A slowly decreases in the beaker, S rises, while R is absent.
- These two methods of reacting the contents of the beaker yield different product distributions and represent the two extremes in possible operations.
- One with a maximum possible formation of R and the other with a minimum, or no formation, of R.
- As the intermediate is frequently the desired reaction product, this rule allows us to evaluate the effectiveness of various reactor systems

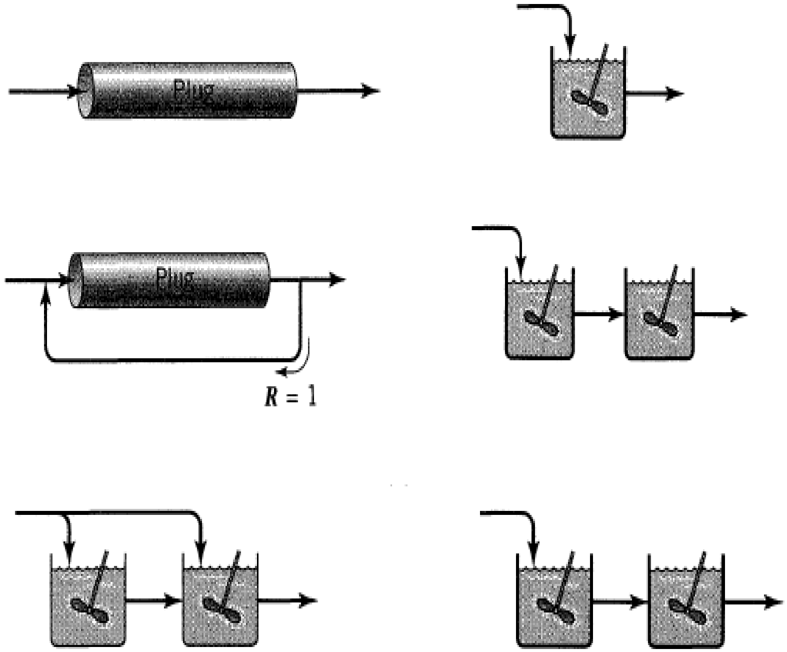
Homogeneous Vs different composition mixing

- For example, plug flow and batch operations should both give a maximum R yield because here there is no mixing of fluid streams of different compositions (Homogeneous mixture).
- On the other hand, the mixed reactor should not give as high a yield of R as possible because a fresh stream of pure A is being mixed continually with an already reacted fluid in the reactor (different composition mixing).
- In mixed flow there is always fresh feed mixed with mixture/ solution
- We then give a quantitative treatment which will verify these qualitative findings.

FAVORABLE CONTACTING PATTERNS

For any set of irreversible reactions in series:

Which contacting pattern, when properly operated, can give a higher concentration of any intermediate, the contacting pattern on the left or the one on the right?



- The left pattern is better; in fact it is the best possible flow scheme.
- the left is closer to plug flow for both first- and for second-order reactions. So we generalize this to any positive order reaction.
- The right pattern is better because it is closer to plug flow.

Turbulent flow has less intermixing of fluids (homogeneus) of different ages, less bypassing; hence, the right scheme is better.

Quantitative Treatment, Plug Flow or Batch Reactor

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

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

$$\frac{C_{R,\max}}{C_{A0}} = \left(\frac{k_1}{k_2}\right)^{k_2/(k_2-k_1)}$$

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

$$\tau_{p,\text{opt}} = \frac{1}{k_{\text{log mean}}} = \frac{\ln(k_2/k_1)}{k_2 - k_1}$$

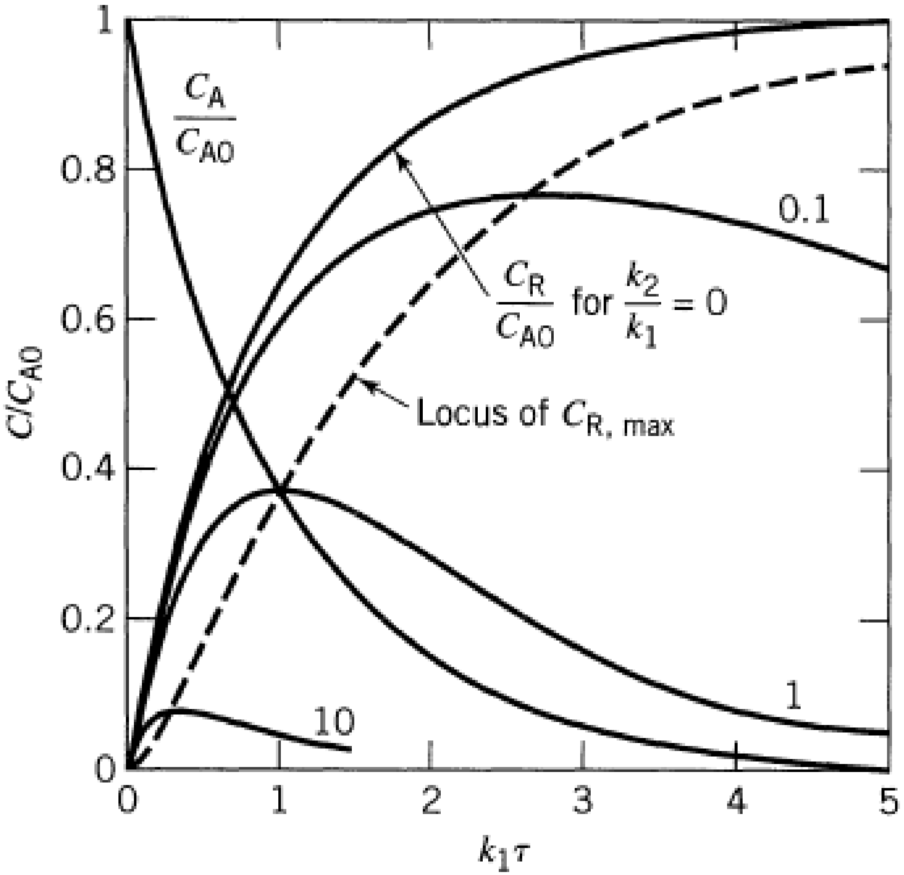
$$C_S = C_{A0} - C_A - C_R$$

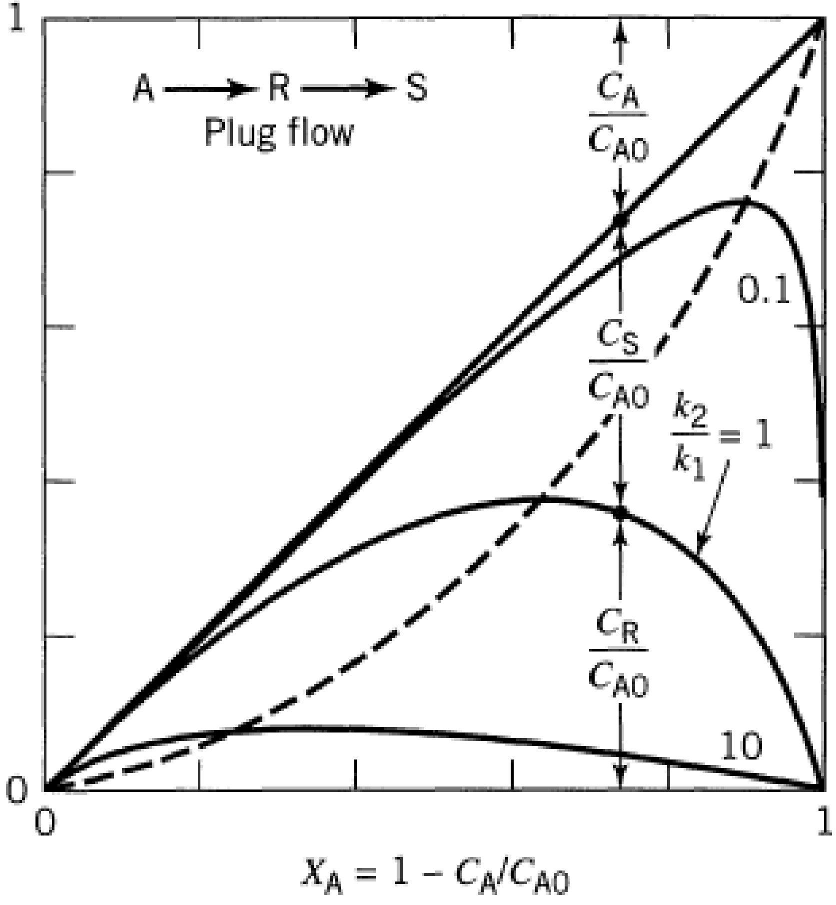
This is also the point at which the rate of formation of S is most rapid.

C_R prepared for various k_2/k_1 values

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S, \quad C_{R0} = C_{S0} = 0$$

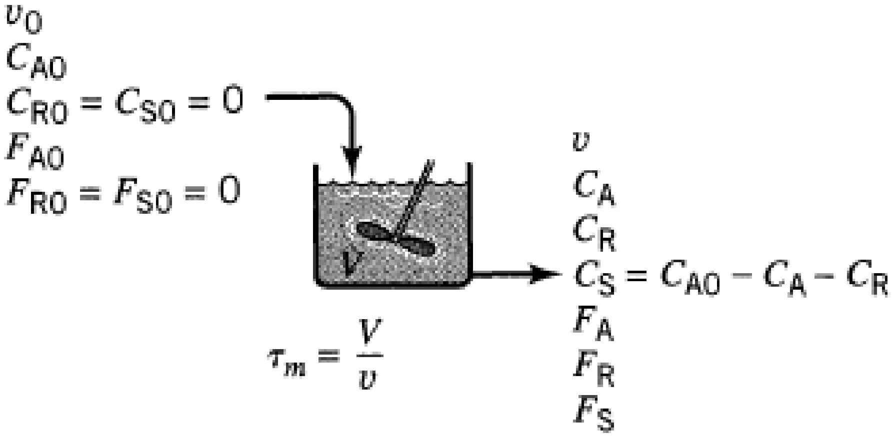
Plug flow reactor





Quantitative Treatment
Mixed Flow Reactor

The derivation will be limited to a feed which contains no reaction product R or S



By the steady-state material balance we obtain for any component

input = output + disappearance by reaction

$$F_{A0} = F_A + (-r_A)V$$

$$vC_{A0} = vC_A + k_1 C_A V$$

$$\frac{V}{v} = \tau_m = \bar{t}$$

$$\frac{C_A}{C_{A0}} = \frac{1}{1 + k_1 \tau_m}$$

For component R the material balance,

$$vC_{R0} = vC_R + (-r_R)V$$

$$0 = vC_R + (-k_1 C_A + k_2 C_R)V$$

$$\frac{C_R}{C_{A0}} = \frac{k_1 \tau_m}{(1 + k_1 \tau_m)(1 + k_2 \tau_m)}$$

$$C_A + C_R + C_S = C_{A0} = \text{constant}$$

$$\frac{C_S}{C_{A0}} = \frac{k_1 k_2 \tau_m^2}{(1 + k_1 \tau_m)(1 + k_2 \tau_m)}$$

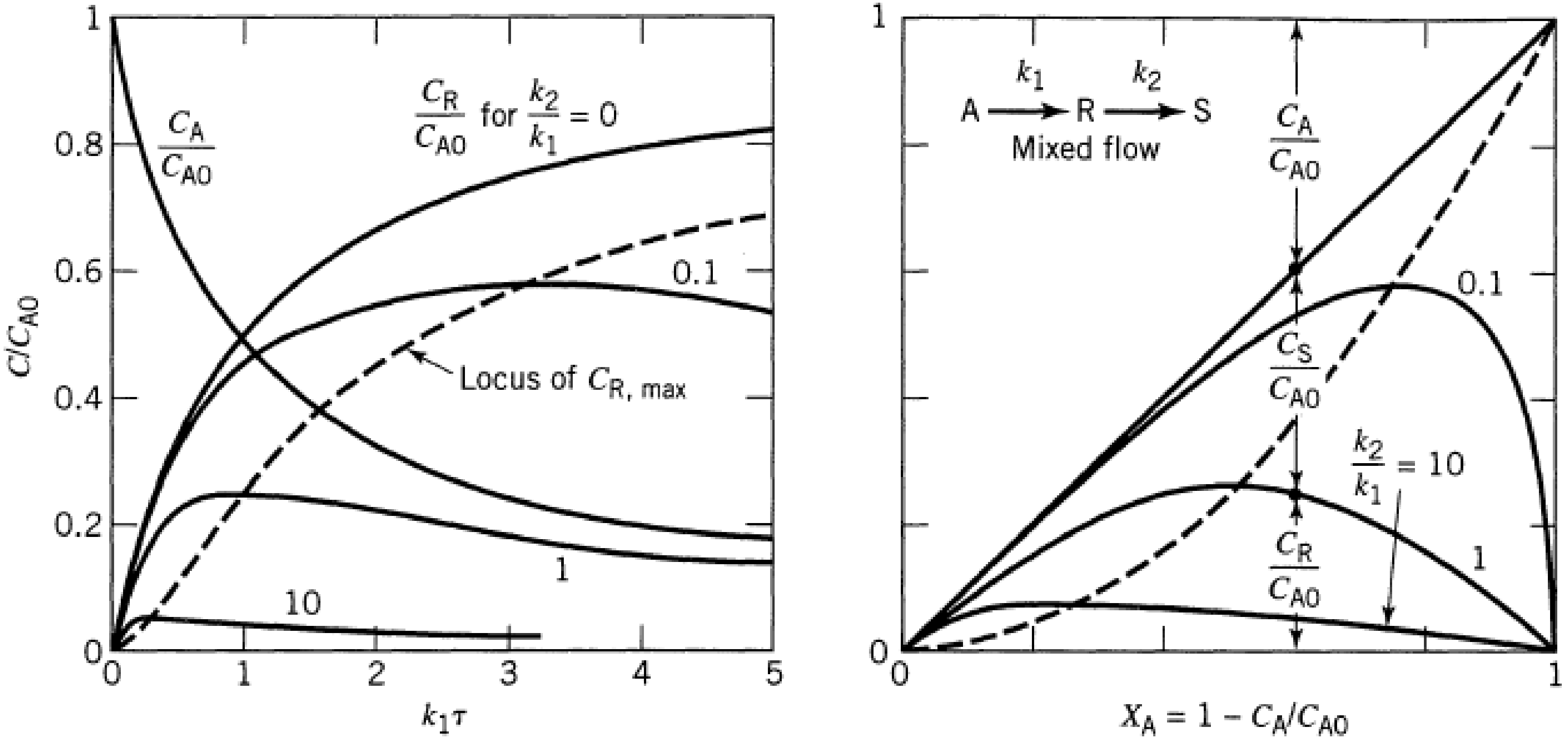
- The location and maximum concentration of R are found by determining $dC_R/d\tau_m$, = 0. Thus

$$\frac{dC_{\mathrm{R}}}{d\tau_m} = 0 = \frac{C_{\mathrm{A0}}k_1(1+k_1\tau_m)(1+k_2\tau_m) - C_{\mathrm{A0}}k_1\tau_m[k_1(1+k_2\tau_m)+(1+k_1\tau_m)k_2]}{(1+k_1\tau_m)^2(1+k_2\tau_m)^2}$$

$$\tau_{m,\mathrm{opt}} = \frac{1}{\sqrt{k_1k_2}}$$

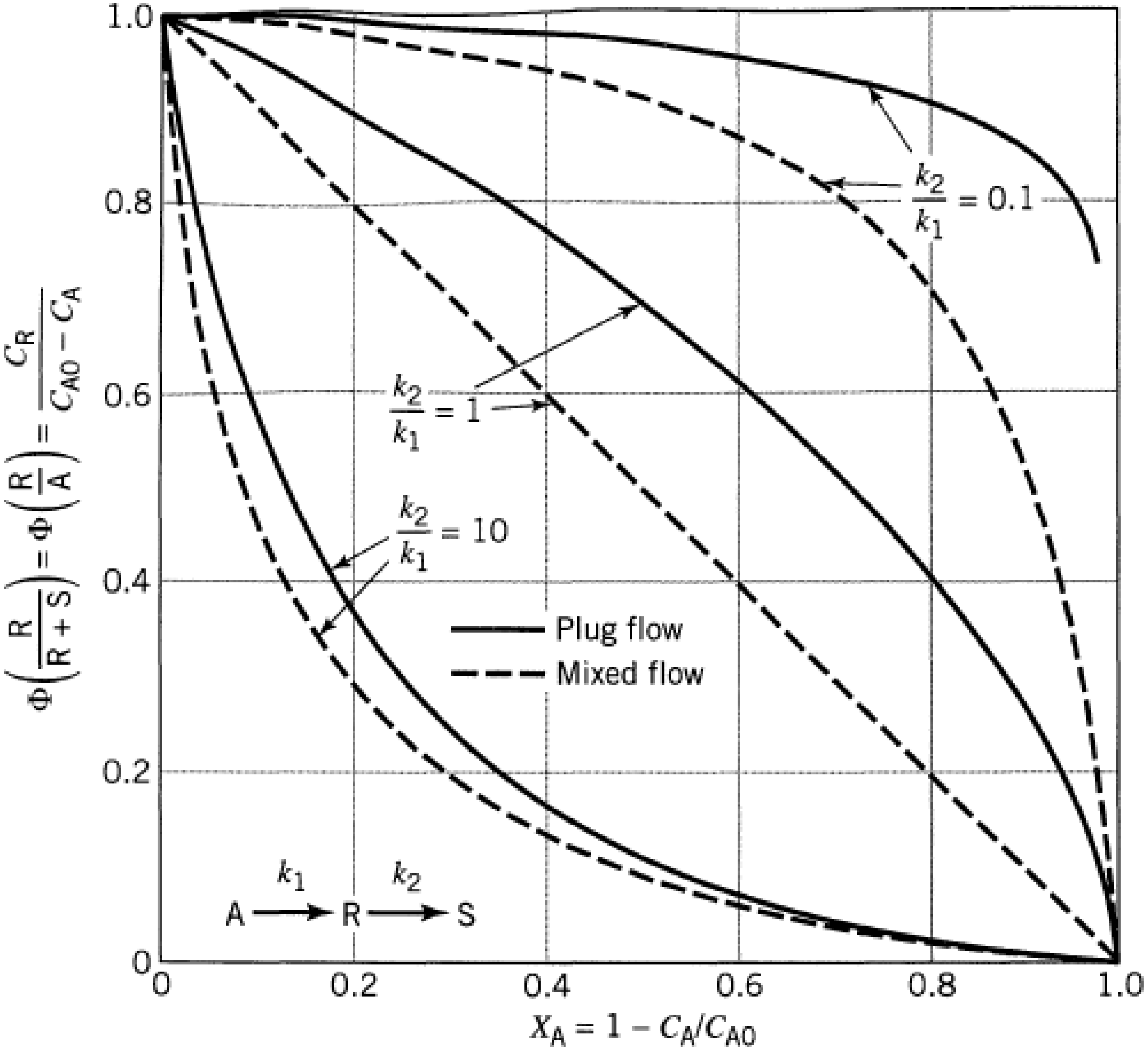
$$\frac{C_{\mathrm{R,max}}}{C_{\mathrm{A0}}} = \frac{1}{[(k_2/k_1)^{1/2}+1]^2}$$

Typical concentration-time curves for various ***k_2/k_1*** values are shown. A time-independent plot, relates the concentrations of reactant and products.



Comparison of these figures shows that except when ***k*$_1$ = *k*$_2$** the plug flow reactor always requires a smaller time than does the mixed reactor to achieve the maximum concentration of R.

- time-independent plots, show the distribution of materials during reaction.
- Such plots find most use in kinetic studies because they allow the determination of k_2/k_1 by matching the experimental points with one of the family of curves on the appropriate graph.
- Though not shown in the figures, Cs can be found by difference between C_{A0}, and $C_A + C_R$.



Graph presents the fractional yield curves for intermediate R as a function of the conversion level and the rate constant ratio.

- These curves clearly show that the fractional yield of R is always higher for plug flow than for mixed flow for any conversion level.
- A second important observation in this figure concerns the extent of conversion of A we should plan for If for the reaction considered ***k_2/k_1*** is much smaller than unity, we should design for a high conversion of A and probably dispense with recycle of unused reactant.
- However, if ***k_2/k_1*** is greater than unity, the fractional yield drops very sharply even at low conversion.
- Hence, to avoid obtaining unwanted S instead of R we must design for a very small conversion of A per pass, separation of R, and recycle of unused reactant.
- In such a case large quantities of material will have to be treated in the A-R separator and recycled, and this part of the process will figure prominently in cost considerations.

FIRST-ORDER FOLLOWED BY ZERO-ORDER REACTION

$$\mathrm{A} \xrightarrow[n_1=1]{k_1} \mathrm{R} \xrightarrow[n_2=0]{k_2} \mathrm{S} \qquad \left.\begin{aligned} -r_\mathrm{A} &= k_1 C_\mathrm{A} \\ r_\mathrm{R} &= k_1 C_\mathrm{A} - k_2 \end{aligned}\right\} \quad \text{where } K = \frac{k_2/C_{\mathrm{A}0}}{k_1}$$

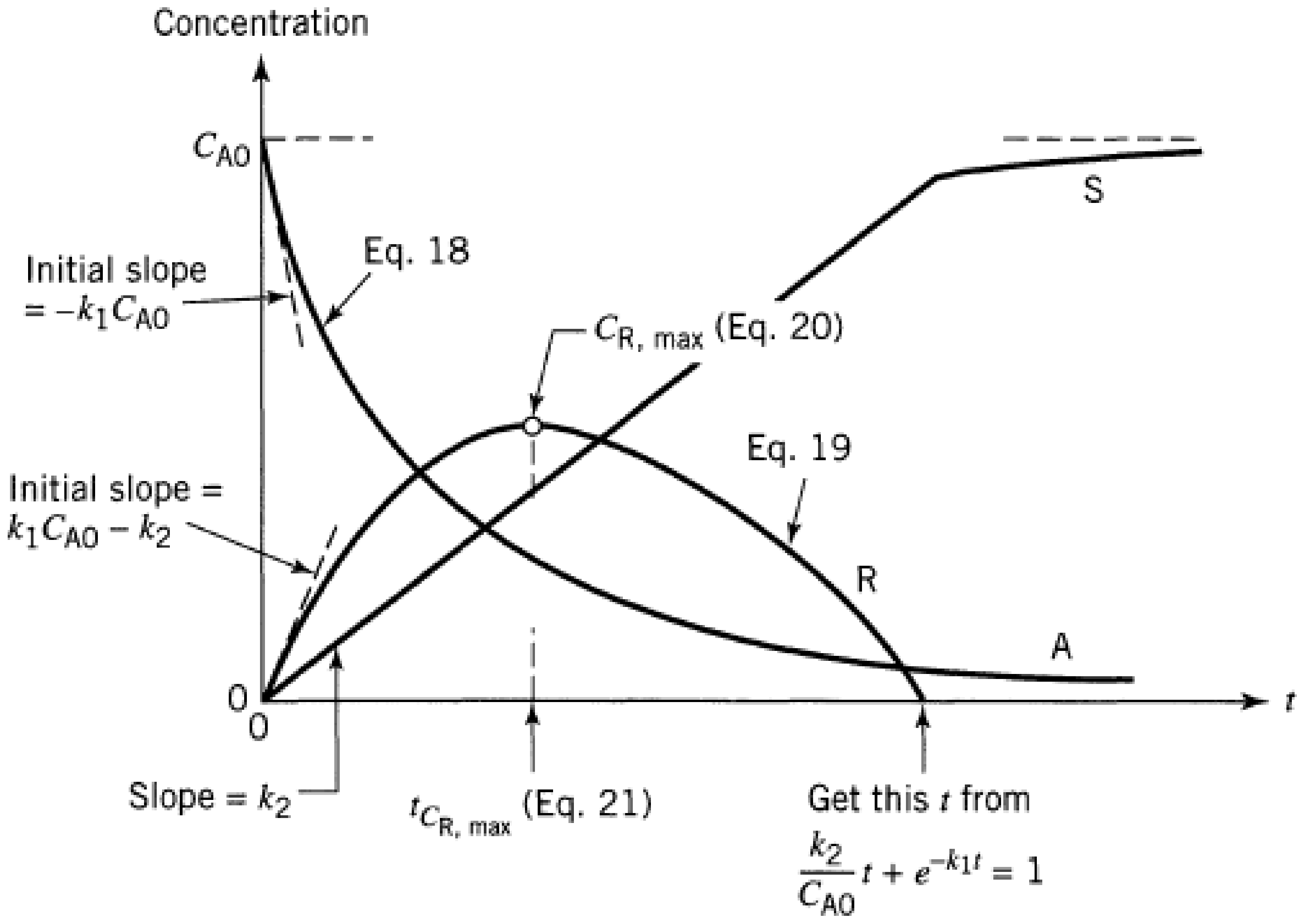
For *batch or plug flow* with $C_{\mathrm{R}0} = C_{\mathrm{S}0} = 0$ integration gives

$$\frac{C_\mathrm{A}}{C_{\mathrm{A}0}} = e^{-k_1 t}$$

$$\frac{C_\mathrm{R}}{C_{\mathrm{A}0}} = 1 - e^{-k_1 t} - \frac{k_2}{C_{\mathrm{A}0}} t \qquad \frac{C_{\mathrm{R,max}}}{C_{\mathrm{A}0}} = 1 - K(1 - \ln K)$$

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

Product distribution for the reactions $A \xrightarrow{n=1} R \xrightarrow{n=0} S$



ZERO-ORDER FOLLOWED BY FIRST-ORDER REACTION

$$A \xrightarrow[n_1=0]{k_1} R \xrightarrow[n_2=1]{k_2} S \qquad \left.\begin{array}{l} -r_A = k_1 \\ r_R \begin{cases} = k_1 - k_2 C_R & \text{A present} \\ = -k_2 C_R & \text{A absent} \end{cases} \end{array}\right\} \quad K = \frac{k_2}{k_1/C_{A0}}$$

for *batch or plug flow with* $C_{R0} = C_{S0} = 0$ integration gives

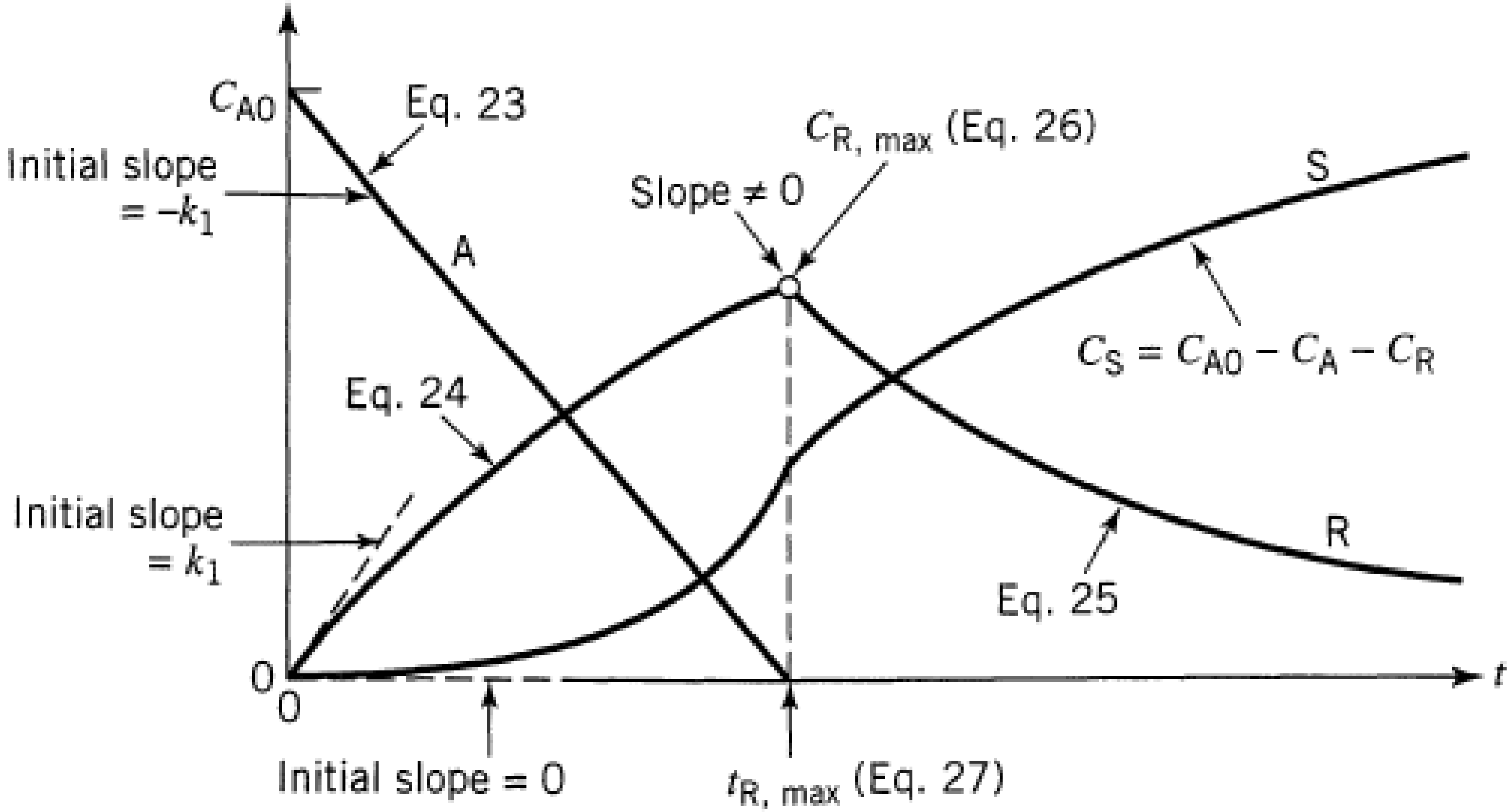
$$\frac{C_A}{C_{A0}} = 1 - \frac{k_1 t}{C_{A0}}$$

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

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

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

Product distribution for the reactions $A \xrightarrow{n=0} R \xrightarrow{n=1} S$



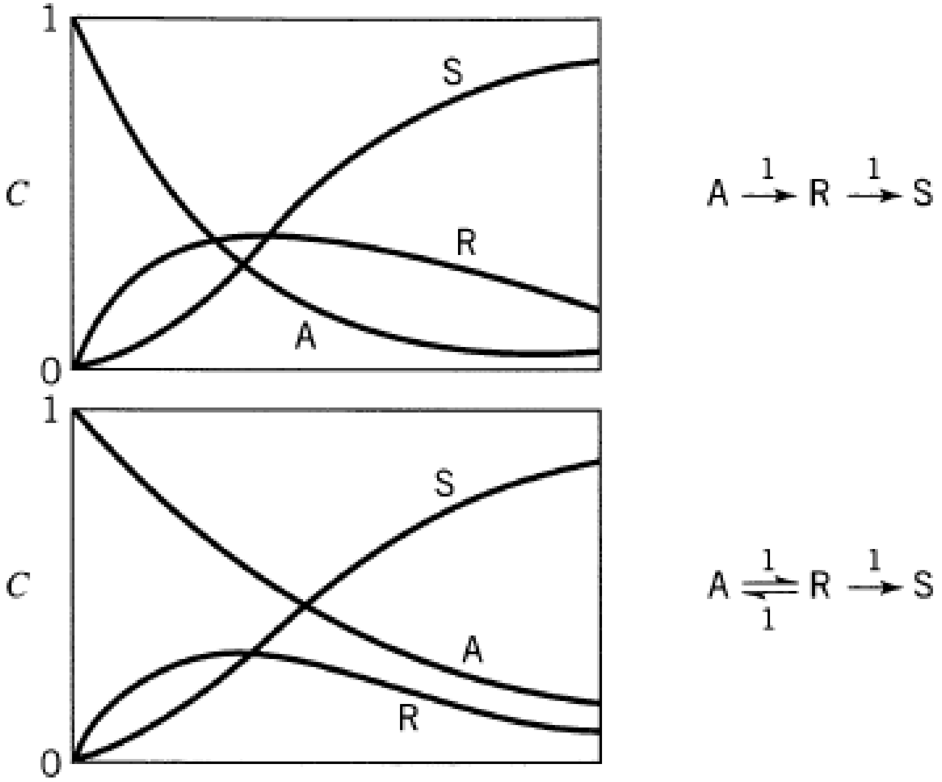
SUCCESSIVE IRREVERSIBLE REACTIONS OF DIFFERENT ORDERS

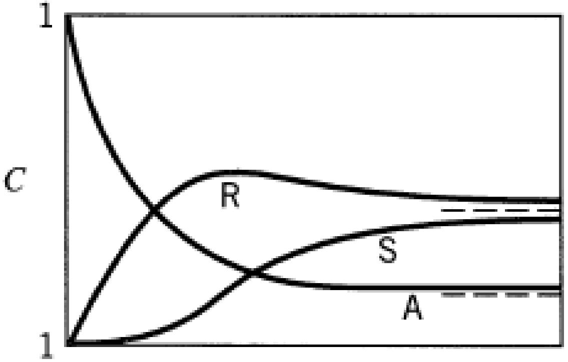
- In principle, concentration-time curves can be constructed for successive reactions of different orders.
- For the plug flow or batch reactor and for the mixed reactor explicit solutions are difficult to obtain.
- Thus, numerical methods provide the best tool for treating such reactions.
- Concentration-time curves are of little generality for they are dependent on the concentration of reactant in the feed.
- As with reactions in parallel, a rise in reactant concentration favors the higher-order reaction.
- A lower concentration favors the lower-order reaction.
- This causes a shift in C_{Rmax} and this property can be used to improve the product distribution.

REVERSIBLE SERIES REACTIONS

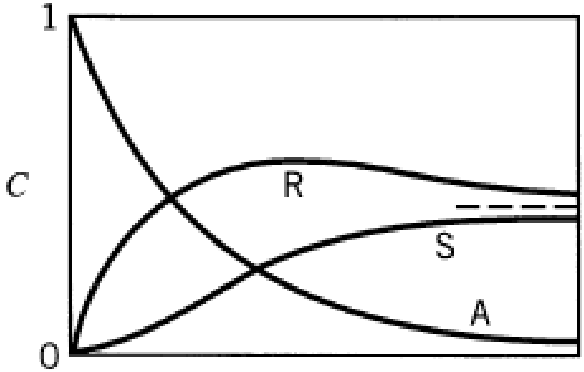
- Solution of the equations for successive reversible reactions is quite formidable even for the first-order case
- Concentration of intermediate in reversible series reactions need not pass through a maximum
- Concentration-time curves for the elementary reversible reactions shown

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R \underset{k_4}{\overset{k_3}{\rightleftharpoons}} S$$

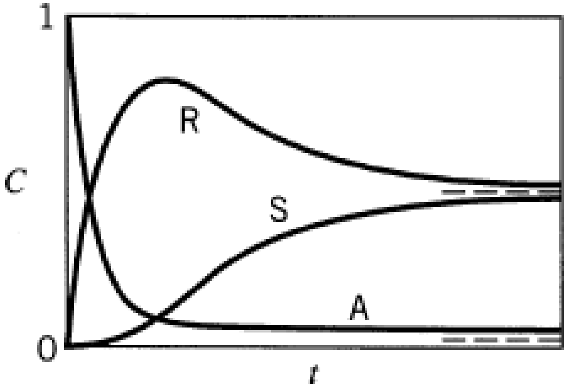




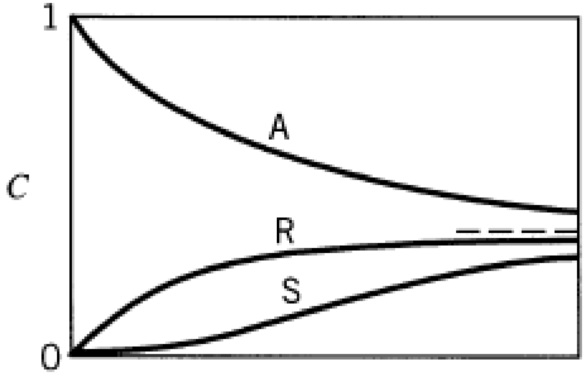
$$A \underset{1}{\overset{3}{\rightleftarrows}} R \underset{1}{\overset{1}{\rightleftarrows}} S$$



$$A \xrightarrow{1} R \underset{1}{\overset{1}{\rightleftarrows}} S$$



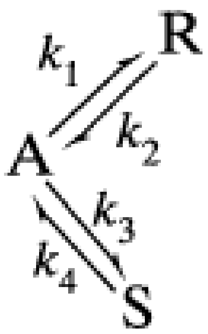
$$A \underset{1}{\overset{10}{\rightleftarrows}} R \underset{1}{\overset{1}{\rightleftarrows}} S$$

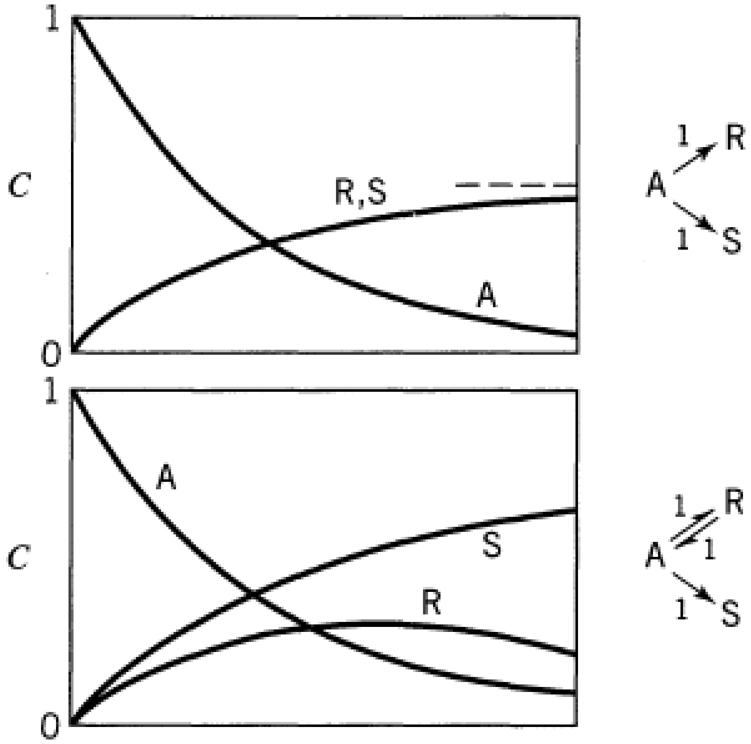


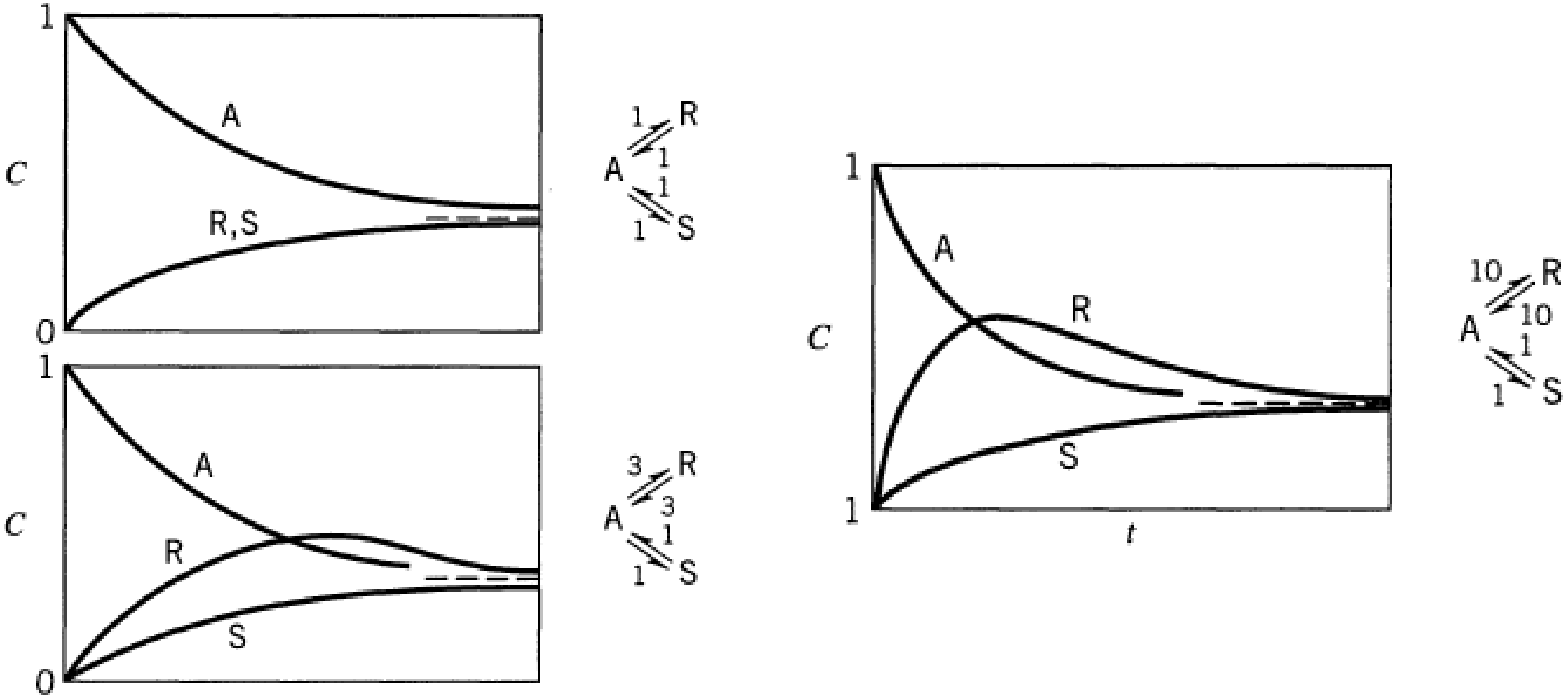
$$A \underset{1}{\overset{1}{\rightleftarrows}} R \underset{1}{\overset{1}{\rightleftarrows}} S$$

Reversible parallel reactions

- Shows that a product may pass through a maximum concentration typical of an intermediate in the irreversible series reaction; however, the reactions may be of a different kind.
- Concentration-time curves for the elementary reversible parallel reactions shown







A comparison of these figures shows that many of the curves are similar in shape, making it difficult to select a mechanism of reaction by experiment, especially if the kinetic data are somewhat scattered.

- Probably the best clue to distinguishing between parallel and series reactions is to examine initial rate data.
- Data obtained for very small conversion of reactant.
- For series reactions the time-concentration curve for S has a zero initial slope, whereas for parallel reactions this is not so.

IRREVERSIBLE SERIES-PARALLEL REACTIONS

- Multiple reactions that consist of steps in series and steps in parallel are called series-parallel reactions.
- From the point of view of proper contacting, these reactions are more interesting than the simpler types already considered.

IRREVERSIBLE SERIES-PARALLEL REACTIONS

- A larger choice of contacting is usually possible, leading to much wider differences in product distribution.
- Let us develop our ideas with a reaction type that represents a broad class of industrially important reactions.
- We will then generalize our findings to other series-parallel reactions.
- The general representation of these reactions is

$$\left.\begin{aligned} A + B &\xrightarrow{k_1} R \\ R + B &\xrightarrow{k_2} S \\ S + B &\xrightarrow{k_3} T \end{aligned}\right\} \qquad A \xrightarrow{+B,\, k_1} R \xrightarrow{+B,\, k_2} S \xrightarrow{+B,\, k_3} T$$

Two-Step Irreversible Series-Parallel Reactions

- Examples of such reactions may be found in the successive substitutive halogenation (or nitration) of hydrocarbons.
- Another important example is the addition of alkene oxides, say ethylene oxide, to compounds of the proton donor class such as amines, alcohols, water, and hydrazine.

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

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

$$r_B = \frac{dC_B}{dt} = -k_1 C_A C_B - k_2 C_R C_B$$

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

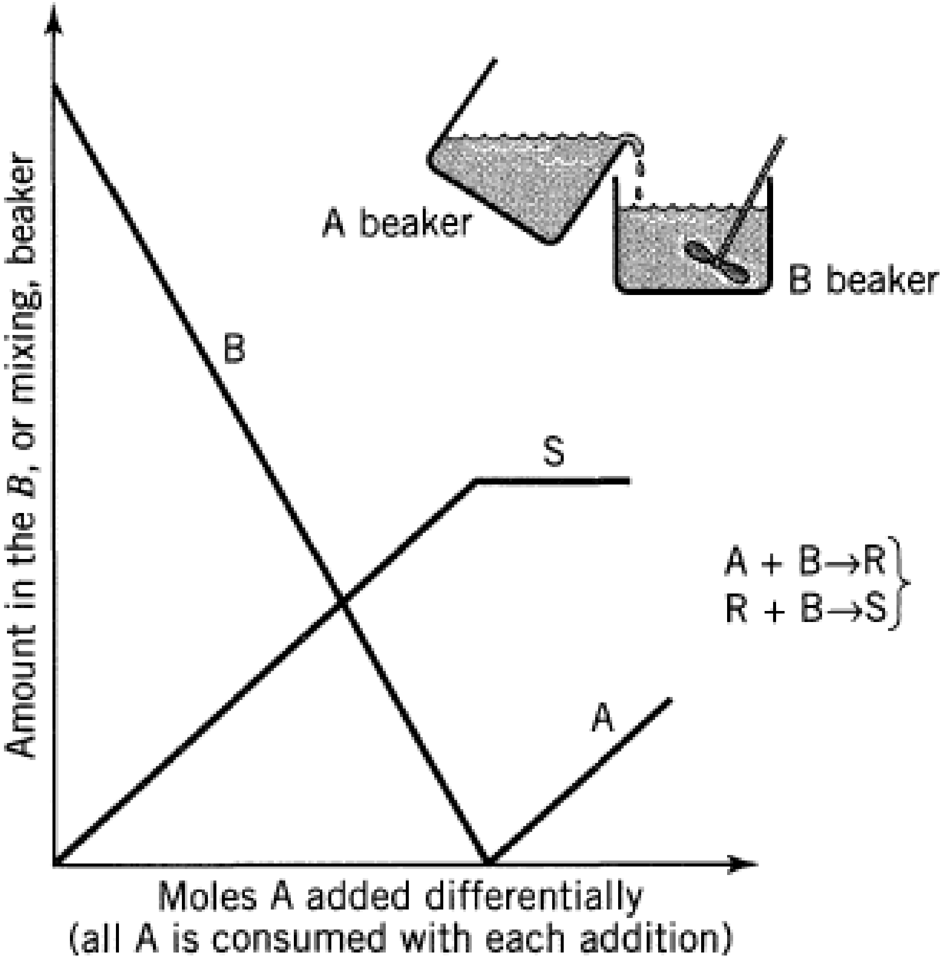
$$r_S = \frac{dC_S}{dt} = k_2 C_R C_B$$

Qualitative Discussion About Product Distribution.

- To get the "feel" for what takes place when A and B react according to Eq.
- Imagine that we have two beakers, one containing A and the other containing B.
- Should it make any difference in the product distribution how we mix A and B?
- To find out, consider the following ways of mixing the reactants:
  - (a) add A slowly to B,
  - (b) add B slowly to A, and finally
  - (c) mix A and B together rapidly.

Distribution of materials in the B beaker for the method of mixing shown

Add A Slowly to B



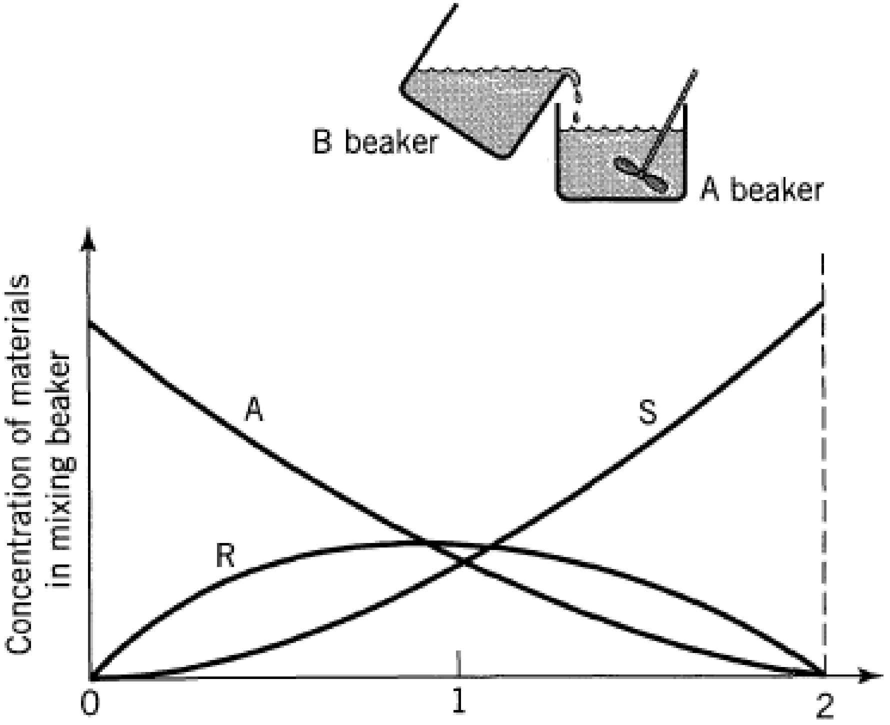
Pour A a little at a time into the beaker containing B, stirring thoroughly and making sure that all the A is used up.

(a) Add A Slowly to B

- Reaction stops before the next bit is added.
- With each addition 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.

(b) Add B Slowly to A

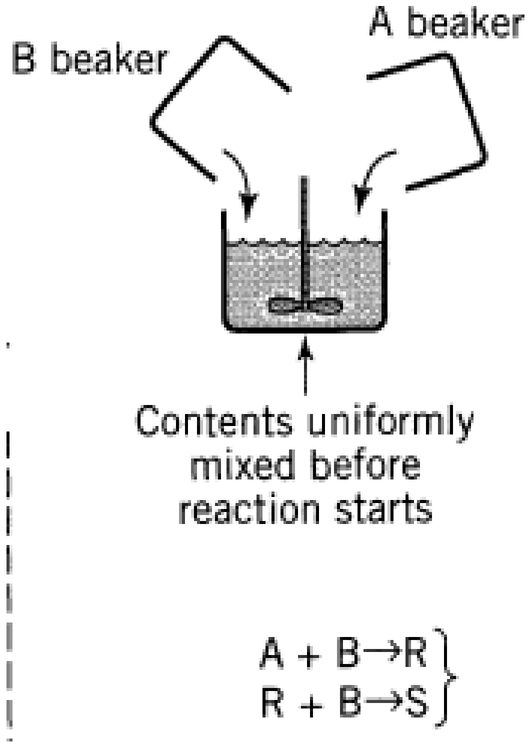
- Now pour B a little at a time into the beaker containing A, again stirring thoroughly.



- 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.
- Since A is in very large excess it will react with most of the B, producing even more R.

R is high enough, it can compete favorably with A for the B added. The concentration of R reaches a maximum, then decreases. Finally, after addition of 2 moles of B for each mole of A, we end up with a solution containing only S.

(c) Mix A and B Rapidly.



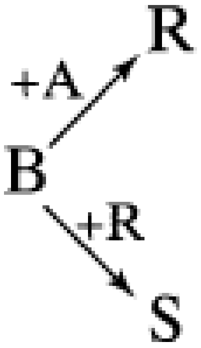
- The two beakers are rapidly mixed together,
- The reaction being slow enough so that it does not proceed to any appreciable extent before the mixture becomes uniform.
- During the first few reaction increments R finds itself competing with a large excess of A for B and hence it is at a disadvantage.
- Carrying through this line of reasoning, we find the same type of distribution curve as for the mixture in which B is added slowly to A.

  (Similar to previous graph)

- The product distribution are completely different.
- Thus, when A is kept uniform in composition as it reacts, then R is formed.
- However, when fresh A is mixed with partly reacted mixture, then no intermediate R forms.
- But this is precisely the behaviour of reactions in series.
- Thus, as far as A, R, and S are concerned, we may view the reactions as

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

- A second observation is that the concentration level of B, whether high or low, has no effect on the path of the reaction and on the distribution of products.
- But this is precisely the behavior of parallel reactions of the same order. So with respect to B can be looked at as



Irreversible series-parallel reactions can be analyzed in terms of their constituent series reactions and parallel reactions in that optimum contacting for favorable product distribution is the same as for the constituent reactions.

For the above reactions where R is desired this rule shows:

- That the best way of contacting A and B is to react A uniformly, while adding B in any convenient way.
- This is a powerful generalization which, without needing specific values for the rate constants, can already show in many cases which are the favorable contacting patterns.
- It is essential, however, to have the proper representation of the stoichiometry and form of rate equation.

Quantitative Treatment, Plug Flow or Batch Reactor.

$$\left.\begin{array}{l} A + B \xrightarrow{k_1} R \\ R + B \xrightarrow{k_2} S \end{array}\right\} \Rightarrow \left.\begin{array}{l} r_R = \dfrac{dC_R}{dt} = k_1 C_A C_B - k_2 C_R C_B \\ r_A = \dfrac{dC_A}{dt} = -k_1 C_A C_B \end{array}\right\} \longrightarrow \frac{r_R}{r_A} = \frac{dC_R}{dC_A} = -1 + \frac{k_2 C_R}{k_1 C_A}$$

With no R present in the feed the limits of integration are C_{AO} to C_A for A and $C_{RO} = 0$ for R, and the solution of this differential equation is

$$\frac{C_R}{C_{A0}} = \frac{1}{1 - k_2/k_1}\left[\left(\frac{C_A}{C_{A0}}\right)^{k_2/k_1} - \frac{C_A}{C_{A0}}\right], \qquad \frac{k_2}{k_1} \neq 1$$

$$\frac{C_R}{C_{A0}} = \frac{C_A}{C_{A0}} \ln \frac{C_{A0}}{C_A}, \qquad \frac{k_2}{k_1} = 1$$

With maximum C_R at

$$\frac{C_{R,max}}{C_{A0}} = \left(\frac{k_1}{k_2}\right)^{k_2/(k_2-k_1)}, \qquad \frac{k_2}{k_1} \neq 1$$

$$\frac{C_{R,max}}{C_{A0}} = \frac{1}{e} = 0.368 \qquad \frac{k_2}{k_1} = 1$$

This gives the relationship between C_R and C_A in a batch or in a plug flow reactor.

To find the concentrations of the other components, simply make a material balance. An A balance gives

$$C_{A0} + C_{R0} + C_{S0} = C_A + C_R + C_S$$

$$\Delta C_A + \Delta C_R + \Delta C_S = 0$$

from which C_S can be found as a function of C_A and C_R.

Finally, a balance about B gives

$$\Delta C_B + \Delta C_R + 2\Delta C_S = 0$$

from which C_B can be found.

Quantitative Treatment, Mixed Flow.

- Design equation for mixed flow in terms of A and R gives

$$\tau_m = \frac{C_{A0} - C_A}{-r_A} = \frac{-C_R}{-r_R}$$

$$\tau_m = \frac{C_{A0} - C_A}{k_1 C_A C_B} = \frac{-C_R}{k_2 C_R C_B - k_1 C_A C_B} \quad \Longrightarrow \quad \frac{-C_R}{C_{A0} - C_A} = -1 + \frac{k_2 C_R}{k_1 C_A}$$

Writing C_R in terms of C_A then gives

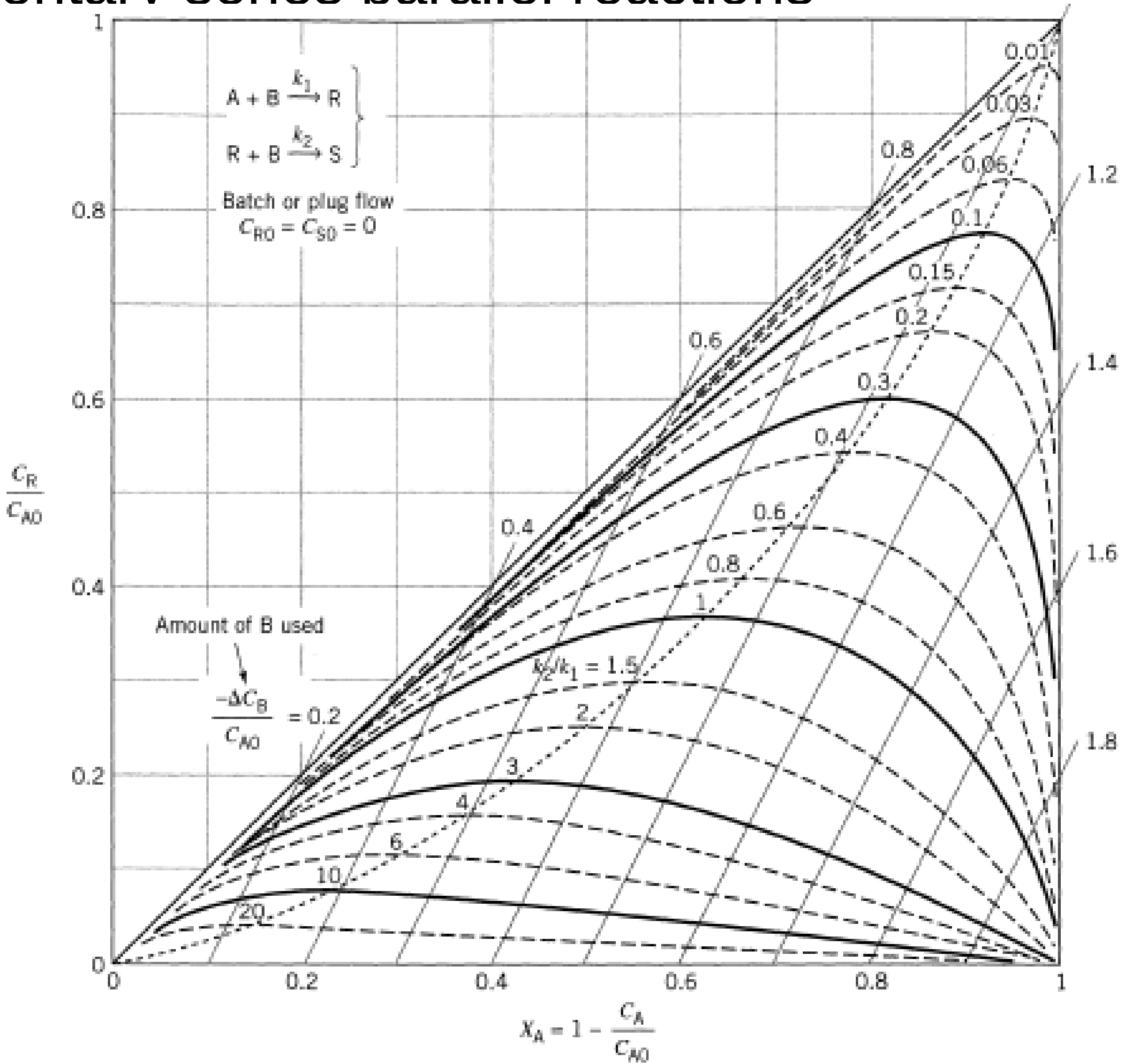
$$C_R = \frac{C_A (C_{A0} - C_A)}{C_A + (k_2/k_1)(C_{A0} - C_A)}$$

$$\frac{C_{R,\max}}{C_{A0}} = \frac{1}{[1 + (k_2/k_1)^{1/2}]^2}$$

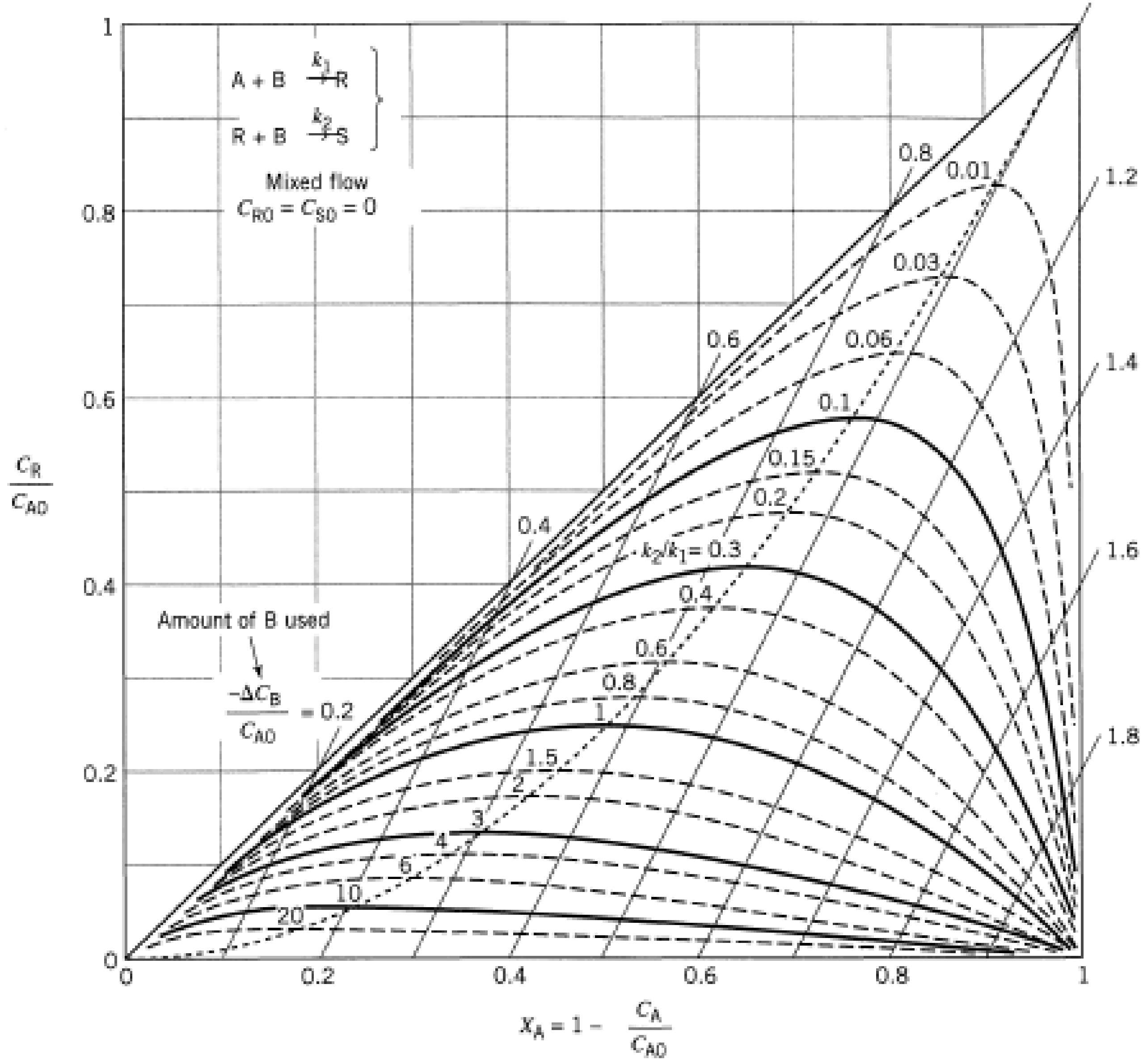
Material balances about A and B in plug flow, hold equally well for mixed flow and serve to complete the set of equations giving complete product distribution in this reactor.

Graphical Representation

Distribution of materials in a batch or plug flow reactor for the elementary series parallel reactions



Distribution of materials in a mixed flow reactor for the elementary series-parallel reaction



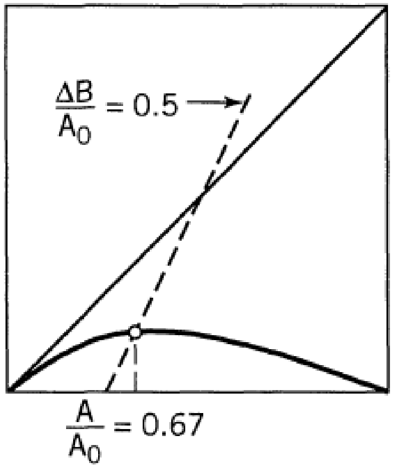
KINETICS OF SERIES-PARALLEL REACTION

- From each of the following experiments (mixed flow reactor), what can we say about the rate constants of the multiple reactions

$$A + B \xrightarrow{k_1} R$$

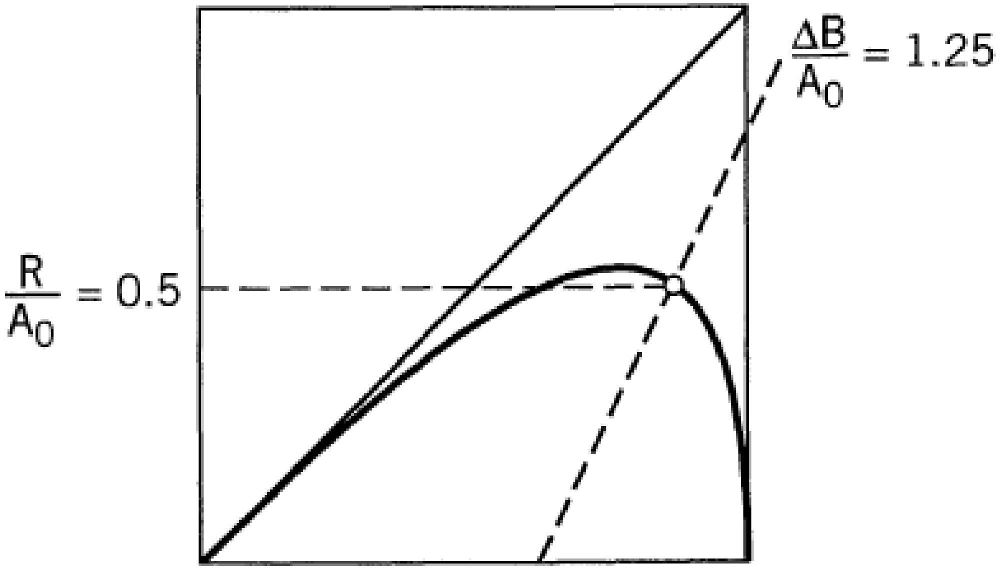
$$R + B \xrightarrow{k_2} S$$

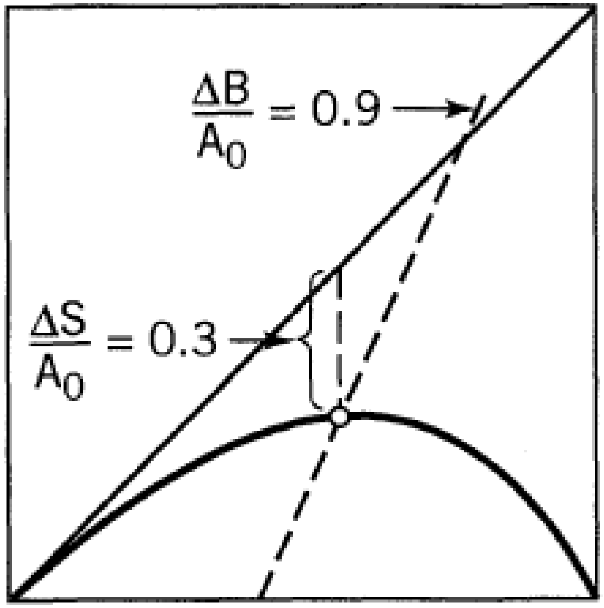
(a) Half a mole of B is poured bit by bit, with stirring, into a flask containing a mole of A. The reaction proceeds slowly, and when B is entirely consumed 0.67 mole of A remains unreacted.



(a) $k_2/k_1 = 4$,

(b) One mole of A and 1.25 moles of B are rapidly mixed, and the reaction is slow enough so that it does not proceed to any appreciable extent before homogeneity in composition is achieved. On completion of the reaction, 0.5 mole of R is found to be present in the mixture.





(c) One mole of A and 1.25 moles of B are rapidly brought together. The reaction is slow enough so that it does not proceed to any appreciable extent before homogeneity in A and B is achieved. At the time when 0.9 mole of B is consumed, 0.3 mole of S is present in the mixture

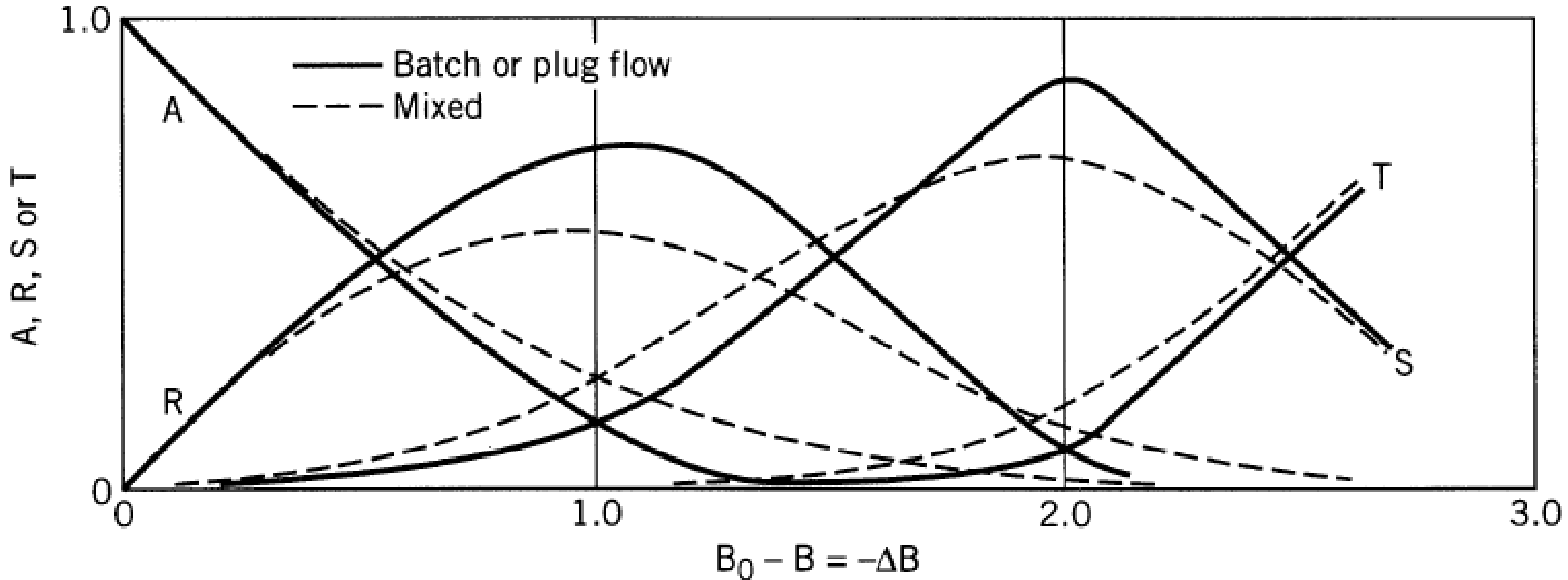
Extensions and Applications

Three or More Reactions

Analysis of three or more reactions can be made by procedures analogous to those presented.

Again, as with the two-reaction set, we find that a plug flow reactor yields a higher maximum concentration of any intermediate than does a mixed flow reactor.

$$\begin{array}{lcl} A + B \xrightarrow{k_1} R + U & & C_6H_6 + Cl_2 \xrightarrow{k_1} C_6H_5Cl + HCl \\ R + B \xrightarrow{k_2} S + U & \text{or} & C_6H_5Cl + Cl_2 \xrightarrow{k_2} C_6H_4Cl_2 + HCl \\ S + B \xrightarrow{k_3} T + U & & C_6H_4Cl_2 \xrightarrow{k_3} C_6H_3Cl_3 + HCl \end{array}$$

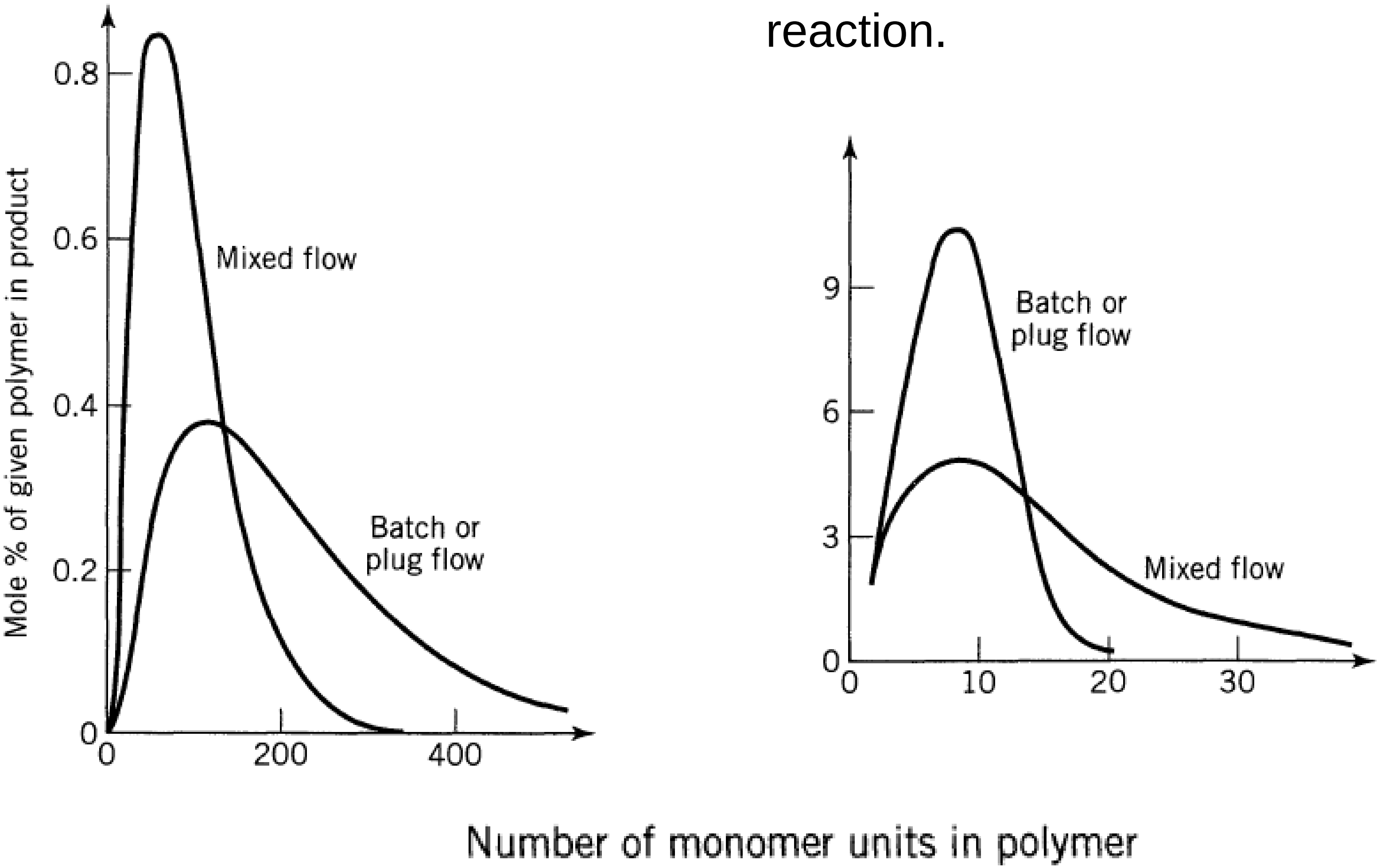


Polymerization

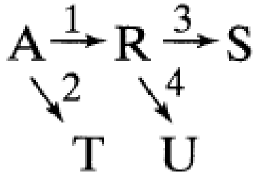
- The field of polymerization affords an opportunity for a fruitful application of these ideas.
- Often hundreds or even thousands of reactions in series occur in the formation of polymers,
- Since the mode of mixing of monomers with their catalysts profoundly affects product distribution, great importance must be paid to this factor if the product is to have the desired physical and chemical properties.

(a) Duration of polymerization reaction (life of active polymer) is short compared to the reactor holding time;

(b) duration of polymerization reaction is long compared to the reactor holding time, or where polymerization has no termination reaction.



THE DENBIGH REACTIONS AND THEIR SPECIAL CASES



$$\left.\begin{aligned} -r_A &= k_{12}C_A \\ r_R &= k_1C_A - k_{34}C_R \\ r_S &= k_3C_R \\ r_T &= k_2C_A \\ r_U &= k_4C_R \end{aligned}\right\} \begin{aligned} k_{12} &= k_1 + k_2 \\ k_{34} &= k_3 + k_4 \end{aligned}$$

$$C_{A0} + C_{R0} + C_{S0} + C_{T0} + C_{U0} = C_A + C_R + C_S + C_T + C_U$$