UNIT-4

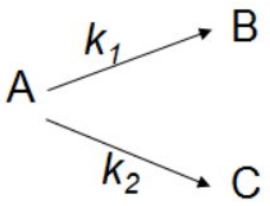
DESIGN OF SINGLE AND MULTIPLE REACTORS FOR MULTIPLE REACTIONS

More than one reaction occurs within a chemical reactor. Minimization of undesired side reactions that occur with the desired reaction contributes to the economic success of a chemical plant. The distinction between a single reaction and multiple reactions is that the single reaction requires only one rate expression to describe its kinetic behavior whereas multiple reactions require more than one rate expression. Multiple reactions are of two primary types: parallel reactions and series reactions.

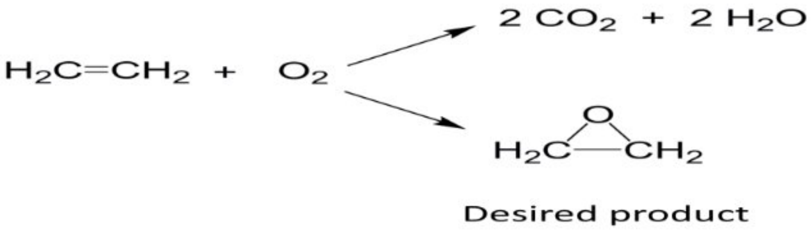
Multiple Reactions

1) Parallel or competing reactions

   When a reactant gives two product (desired, and undesired) simultaneously with different rate constant then this is called a parallel reaction.

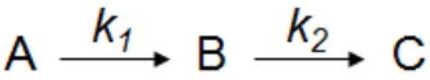


With an example

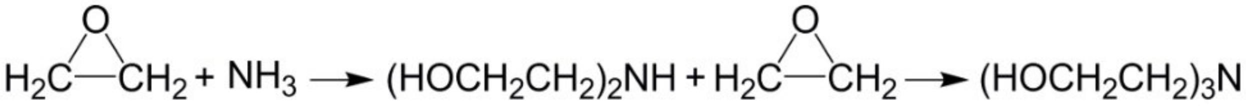


2) Series reactions

   When a reactant gives an intermediate (desired product) which decomposes to product



With an example



3) <u>Series-Parallel reactions</u>

Multiple reaction that consist of steps in series and steps in parallel reaction. In these reaction proper contacting pattern is very important.

The general representation of these reaction are

$$A + B \xrightarrow{k_1} R$$
$$R + B \xrightarrow{k_2} S$$
$$S + B \xrightarrow{k_3} T$$

Here the reaction is parallel with respect to reactant B and in series with A.

$$A \xrightarrow{+B,\, k_1} R \xrightarrow{+B,\, k_2} S \xrightarrow{+B,\, k_3} T$$

With an example

Halogenations of alkane is a example of this kind of reaction where reaction is parallel with respect to halogen

$$C_6H_6 \xrightarrow{+Cl_2} C_6H_5Cl \xrightarrow{+Cl_2} \cdots \xrightarrow{+Cl_2} C_6Cl_6$$
$$C_6H_6 \xrightarrow{+HNO_3} C_6H_5NO_2 \xrightarrow{+HNO_3} \cdots \xrightarrow{+HNO_3} C_6H_3(NO_2)_3$$
$$CH_4 \xrightarrow{+Cl_2} CH_3Cl \xrightarrow{+Cl_2} \cdots \xrightarrow{+Cl_2} CCl_4$$

PARALLEL REACTIONS

Qualitative Discussion About Product Distribution

Consider the decomposition of A by either one of two paths

$$A \xrightarrow{k1} D \quad \text{(Desired)} \quad r_D = k_1 C_A^{\alpha}$$

$$A \xrightarrow{k2} U \quad \text{(Undesired)} \quad r_U = k_2 C_A^{\beta}$$

The net rate of disappearance of A

$$r_A = r_D + r_U$$

$$S_{D/W} = \frac{r_D}{r_U} = \frac{k_1 C_A^{\alpha}}{k_2 C_A^{\beta}} = \frac{k_1}{k_2} C_A^{(\alpha-\beta)}$$

gives a measure of the relative rates of formation of D and U. This ratio is adjusted to be as large as possible

If $\alpha > \beta$ use high concentration of A. Use PFR.

If $\alpha < \beta$ use low concentration of A. Use CSTR

Now concentration is the only factor in this equation which we can adjust and control (k_1, k_2, $a_1(\alpha)$ and $a_2(\beta)$ are all constant for a specific system at a given temperature) and we can keep concentration, low throughout the reactor by any of the following means: by using a mixed flow reactor, maintaining high conversions, increasing inerts in the feed, or decreasing the pressure in gas-phase systems. On the other hand, we can keep CA high by using a batch or plug flow reactor, maintaining low conversions, removing inerts from the feed, or increasing the pressure in gas phase systems. For the reactions of whether the concentration of A should be kept high or low.

If $a_1 > a_2$ or the desired reaction is of higher order than the unwanted reaction, Equation shows that a high reactant concentration is desirable since it increases the R/S ratio. As a result, a batch or plug flow reactor would favor formation of product R and would require a minimum reactor size.

If $a_1 < a_2$ or the desired reaction is of lower order than the unwanted reaction, we need a low reactant concentration to favor formation of R. But this would also require large mixed flow reactor.

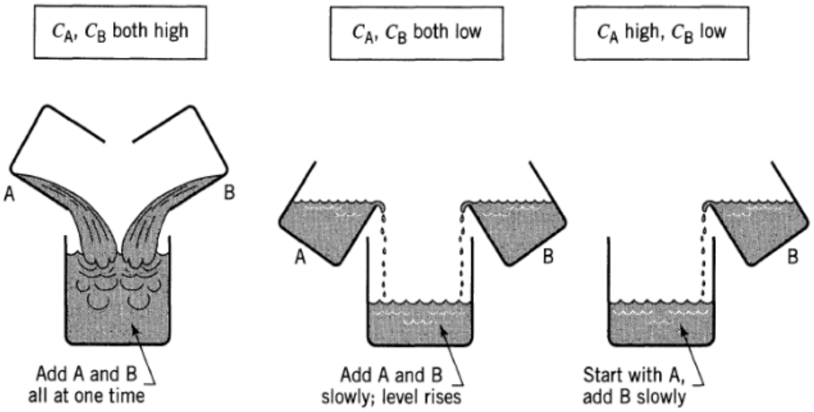
If $a_1 = a_2$ or the two reactions are of the same order, then only rate constant is the deciding authority

Hence, product distribution is fixed by k_2/k_1 alone and is unaffected by type of reactor used. We also may control product distribution by varying k_2/k_1. This can be done in two ways:

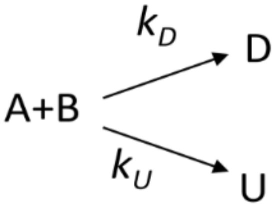
1. By changing the temperature level of operation. If the activation energies of the two reactions are different, k_2/k_1can be made to vary.

2. By using a catalyst. One of the most important features of a catalyst is its selectivity in depressing or accelerating specific reactions. This may be a much more effective way of controlling product distribution than any of the methods .

For reactions in parallel, the concentration level of reactants is the key to proper control of product distribution. A high reactant concentration favors the reaction of higher order, a low concentration favors the reaction of lower order, while the concentration level has no effect on the product distribution for reactions of the same order.



For example,another case in maximizing the desired product in parallel reactions



$$r_D \quad k_D C_A^{\alpha 1} C_B^{\beta 1}$$

$$\rightarrow r_D = A_D e^{\frac{-E_D}{RT}} C_A^{\alpha 1} C_B^{\beta 1}$$

$$r_U \quad k_U C_A^{\alpha 2} C_B^{\beta 2}$$

$$\rightarrow r_U = A_U e^{\frac{-E_U}{RT}} C_A^{\alpha 2} C_B^{\beta 2}$$

Rate of disappearance of A: $-r_A = r_D + r_U$

$$-r_A = A_D e^{\frac{-E_D}{RT}} C_A^{\alpha 1} C_B^{\beta 1} + A_U e^{\frac{-E_U}{RT}} C_A^{\alpha 2} C_B^{\beta 2}$$

Let α1 be the order of the desired reaction A + B → D and α2 be the order of the undesired reaction A + B → U. Let ED be the activation energy of the desired reaction and EU be the activation of the undesired reaction. We want to maximize selectivity. If α1 > α2: We want the concentration of the reactant to be as high as possible since C α1−α2 A has a positive exponent . If in the gas phase, the reaction should be run without inerts and at high pressure . If in the liquid phase, the reaction should be run without dilutents . A batch or PFR should be used since CA starts at a high value and drops over the course of the reaction whereas it is always at the lowest concentration in a CSTR (i.e. the outlet concentration) . If α2 > α1: We want the concentration of the reactant to be as low as possible since C α1−α2 .A has a negative exponent . If in the gas phase, the reaction should be run with inerts and at low pressure .If in the liquid phase, the reaction should be run without dilutents . A CSTR or recycle reactor should be used . If ED > EU : High temperature should .If EU > ED Low temperature should be used (but not so low that the desired reaction never proceeds) .For analyzing the effect of activatoin energies on selectivity, one can state the following if the reaction is A → D and A → U SD/U ∼ kD kU = AD AU e −[(ED−EU)/(RT)] . Let α1 and β1 be the order of the desired reaction A + B → D and α2 and β2 be the order of the desired reaction A + B → D if the reaction rates can be described by r = kCα AC β B. We want to maximize the selectivity of the desired product: If α1 > α2 and β1 > β2: Since C α1−α2 A and C β1−β2 B. Both have positive exponents, the concentration of both A and B should be maximized. Therefore, a tubular reactor or batch reactor should be used .High pressure for a gas phase reaction and a minimization of inerts should be considered .If $\alpha 1 > \alpha 2$ but $\beta 2 > \beta 1$: Since C $\alpha 1-\alpha 2$ .A has a positive exponent but C $\beta 1-\beta 2$ B has a negative exponent, the concentration of A should be maximized, but the concentration of B should be minimized.

There are two types of selectivity and yield: Instantaneous and Overall.

	Instantaneous	Overall
Selectivity	$S_{DU} = \frac{r_D}{r_U}$	$\tilde{S}_{DU} = \frac{F_D}{F_U}$
Yield	$Y_D = \frac{r_D}{-r_A}$	$\tilde{Y}_D = \frac{F_D}{F_{A0} - F_A}$
Example:	$A + B \xrightarrow{k_1} D$ desired product , $r_D = k_1 C_A^2 C_B$ $A + B \xrightarrow{k_2} U$ undesired product , $r_U = k_2 C_A C_B$ $S_{D/U} = \frac{r_D}{r_U} = \frac{k_1 C_A^2 C_B}{k_2 C_A C_B} = \frac{k_1}{k_2} C_A$ To maximize the selectivity of D with respect to U run at high concentration of A and use PFR	

Quantitative Treatment of Product Distribution and of Reactor Size.

If rate equations are known for the individual reactions, we can quantitatively determine product distribution and reactor-size requirements. For convenience in evaluating product distribution we introduce two terms, φ and **Φ.** First, consider the decomposition of reactant A, and let φ be the fraction of A disappearing at any instant which is transformed into desired product R. This is called as instantaneous fractional yield of R.

Thus at any *CA* .

φ = moles R formed/ moles *A* reacted

For any particular set of reactions and rate equations φ is a function of *CA,* and since *CA* in general varies through the reactor, φ will also change with position in the reactor. So let us define Φ as the fraction of all the reacted A that has been converted into R, and let us call this the overall fractional yield *of* R. The overall fractional yield is then the mean of the instantaneous fractional yields at all points within the reactor; thus we may write

φ = all R formed / all A reacted

It is the overall fractional yield that really concerns us for it represents the product distribution at the reactor outlet. Now the proper averaging for φ p depends on the type of flow within the reactor.

The Selectivity

The selectivity, is often used in place of fractional yield. It is usually defined as follows:

Selectivity = moles of desired product formed/moles of undesired material formed

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SERIES REACTIONS

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. In the first beaker, when the contents are being irradiated all at the same time, the first bit of light will attack A alone because only A is present at the start. The result is that R is formed. With the next bit of light both A and R will compete; however, A is in very large excess so it will preferentially absorb the radiant energy to decompose and form more R. Thus, the concentration of R will rise while the concentration of A will fall. This process will continue until R is present in high enough concentration so that it can compete favorably with A for the radiant energy. When this happens, a maximum R concentration is reached. After this the decomposition of R becomes more rapid than its rate of formation and its concentration drops. In the alternative way of treating A, a small fraction of the beaker's contents is continuously removed, irradiated, and returned to the beaker. Although the total absorption rate is the same in the two cases, the intensity of radiation received by the removed fluid is greater, and it could well be, 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. We note in the first method that the contents of the beaker remain homogeneous throughout, all changing slowly with time, whereas in the second a stream of highly reacted fluid is continually being mixed with fresh fluid. In other words, we are mixing two streams of different compositions. This discussion suggests the following rule governing product distribution for reactions in series.

For irreversible reactions in series the mixing of fluid of different composition is the key to the formation of intermediate. The maximum possible amount of any and all intermediates is obtained if fluids of different compositions and at different stages of conversion are not allowed to mix. As the intermediate is frequently the desired reaction product, this rule allows us to evaluate the effectiveness of various reactor systems. 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. 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.

Quantitative Treatment of Product Distribution and of Reactor Size.

A→ R→ S

The concentration- time curves for this reaction when it takes place in a mixed flow reactor. Again, 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

which for reactant A becomes

Noting that we obtain for A, on rearranging,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad \begin{aligned} -r_A &= k_1C_A \\ r_{B,net} &= k_1C_A - k_2C_B \end{aligned}$$

$$\frac{dF_A}{dV} = -k_1C_A \rightarrow \upsilon_0\frac{dC_A}{dV} = -k_1C_A \rightarrow C_A = C_{A0}e^{-k_1\tau}$$

$$\frac{dF_B}{dV} = k_1C_A - k_2C_B$$

$$\rightarrow \upsilon_0 \frac{dC_B}{dV} = k_1\left(C_{A0}e^{-k_1\tau}\right) - k_2C_B$$

$$\frac{V}{\upsilon_0} \quad \tau$$

Substitute

For component R the material balance, becomes and we obtain, on rearranging,

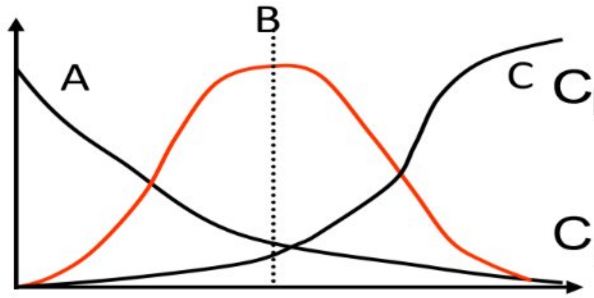
$$\rightarrow \frac{dC_B}{d\tau} = k_1\left(C_{A0}e^{-k_1\tau}\right) - k_2C_B$$

$$\rightarrow \frac{dC_B}{d\tau} + k_2C_B = k_1\left(C_{A0}e^{-k_1\tau}\right)$$

$$\rightarrow \frac{d\left(C_Be^{k_2\tau}\right)}{d\tau} = k_1C_{A0}e^{(k_2-k_1)\tau}$$

$$\rightarrow C_B = k_1C_{A0}\left(\frac{e^{-k_1\tau} - e^{-k_2\tau}}{k_2 - k_1}\right)$$

$$C_C = C_{A0} - C_A - C_B$$



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

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

$$C_C = C_{A0} - C_A - C_B$$

$$\tau_{opt} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$$

Example: Series Reaction in a batch reactor

$A \xrightarrow{k_1} B \xrightarrow{k_2} C$

This series reaction could also be written as

Reaction (1) $A \xrightarrow{k_1} B$: $-r_{1A} = k_1 C_A$

Reaction (2) $B \xrightarrow{k_2} C$: $-r_{2B} = k_2 C_B$

Mole Balance on every species

Species A:

Combined mole balance and rate law for a control volume batch reactor.

Batch Reactor $V = V_0$

$$\frac{1}{V_0} \frac{dN_A}{dt} = r_A$$

Net Rate of Reaction of A

$r_A = r_{1A} + 0$

Rate Law

$r_{1A} = -k_{1A} C_A$

Relative Rates

$r_{1B} = -r_{1A}$

$$\frac{dC_A}{dt} = -k_{1A} C_A$$

Integrating with $C_A = C_{A0}$ at t=0 and then rearranging $\boxed{C_A = C_{A0} \exp(-k_1 t)}$

Mole Balance

Species B: $\frac{dC_B}{dt} = r_B$

Net Rate of Reaction of B

$$r_B = r_{B\,NET} = r_{1B} + r_{2B}$$

Rate Law

$r_{2B} = -k_2 C_B$

Relative Rates

$$r_B = k_1 C_A - k_2 C_B$$

$$\frac{dC_B}{dt} = k_1 C_{A0} \exp(-k_1 t) - k_2 C_B$$

Combine

$$\frac{dC_B}{dt} + k_2 C_B = k_1 C_{A0} \exp(-k_1 t)$$

Using the integrating factor, i.f.:

$$\text{i.f.} = \exp\int k_2 dt = \exp(k_2 t)$$

Evaluate

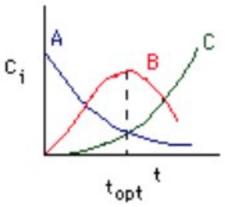
$$\frac{d[C_B \exp(k_2 t)]}{dt} = k_1 C_{A0} \exp(k_2 - k_1)t$$

at t = 0, $C_B = 0$

$$\boxed{C_B = \frac{k_1 C_{A0}}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)]}$$

Optimization of the Desired Product B

$$t = t_{opt} \text{ at } \frac{dC_B}{dt} = 0$$



Then $$t_{opt} = \left(\frac{1}{k_2 - k_1}\right) \ln \frac{k_2}{k_1}$$

Species C $C_C = C_{A0} - C_B - C_A$

And $$\boxed{C_C = \frac{C_{A0}}{k_2 - k_1}\left[k_2\left(1 - e^{-k_1 t}\right) - k_1\left(1 - e^{-k_2 t}\right)\right]}$$

The series reaction is when the reactant forms an intermediate product, which reacts further to form another product (e.g.. A → B → C) . The parallel reaction occurs when the reactant is consumed by two different reaction pathways to form different products (e.g. A breaks down to both B and C) .Complex reactions are multiple reactions that involve a combination of both series and parallel reactions . Independent reactions occur are reactions that occur at the same time but neither the products nor reactants react with themselves or one another (e.g. A → B + C and D → E + F) The selectivity is defined as S = rate of formation of desired product rate of formation of undesired product. The overall selectivity is defined as $\tilde{S}$ = exit molar flow rate of desired product exit molar flow rate of undesired product. For a CSTR, the overall selectivity and selectivity are identical . For a CSTR, the highest overall yield (i.e. most product formed)occurs when the rectangle under the rate vs. CA curve has the largest area .For a PFR, the highest overall yield (i.e. most product formed) occurs when the area under the (rate) vs, CA curve is maximized . If unreacted reagent can be separated from the exit stream and recycled, the highest overall yield (i.e. most product formed) is at the maximum of the (rate) vs. CA curve.

SERIES-PARALLEL REACTIONS

Multiple reactions that consist of steps in series and steps in parallel are called series-parallel reactions.

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

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

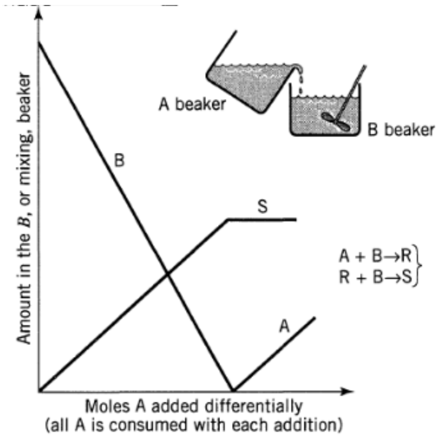
$d[A]/dt = -k_1[A][B]$

$d[B]/dt = -k_1[A][B]-k_2[R][B]$

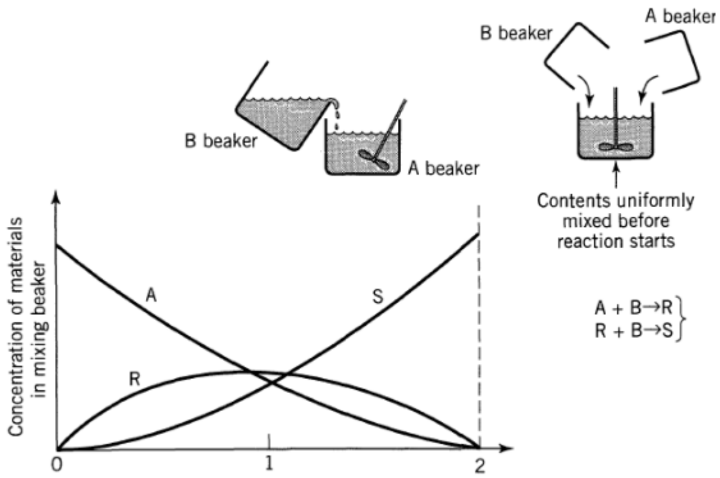
$d[R]/dt = k_1[A][B]-k_2[R][B]$

$d[S]/dt = k_2[R][B]$

Qualitative Discussion About Product Distribution.



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



There are two beakers, one containing A and the other containing B. 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.

(a) Add A ***Slowly to B.*** For the first alternative 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. 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, 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 build up 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 2 moles of B for each mole of A, we end up with a solution containing only S.

(c) Mix A and B Rapidly. Now consider the 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. 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 behavior of reactions in series. Thus, as far as A, R, and S are concerned, 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 it 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.

Quantitative Treatment, Plug Flow or Batch Reactor.

Quantitatively treat the reactions with the understanding that R, the intermediate, is the desired product, and that the reaction is slow enough so that we may ignore the problems of partial reaction during the mixing of reactants. In general, taking the ratio of two rate equations eliminates the time variable and gives information on the product distribution. We obtain the first-order linear differential equations . With no R present in the feed the limits of integration are CAO to *C*A for A and CRO = 0 for R, and the solution of this differential equation is given by mathematical calculation. This gives the relationship between CR and CA 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

CAO+CRO+CSO =CA+CR+CS

from which CS can be found as a function of CA and CR. Finally, a balance about B gives CB.

Quantitative Treatment, Mixed Flow.

Writing the design equation for mixed flow in terms of A and R gives rate equations. Rearranging, we obtain which the difference equation is corresponding to the differential equation. Writing CR in terms of CA then gives equations which can be solved mathematically. 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.