

Introduction to Ideal Reactors

Basic Description and Design

1 Basic Purposes of Reactors

- Mixing of substrates, contacting catalyst
- Mass transfer (G/L, L/L, G/S, L/S)
- Heat transfer
- Control of environment
- Containment (protection from/of environment)

2 Basic Reactor Concepts

2.1 Batch Operation

Batch operation has the following characteristics

- 1) Time variant conditions
- 2) Discontinuous production
- 3) Downtime for cleaning and filling
- 4) Flexibility

Many reactors particularly in the fine chemical industry are operated in a pure batch manner as shown below. During the reaction period there is a change in substrate and product concentration with time; the other periods, e.g. emptying, cleaning, filling, are time lost.

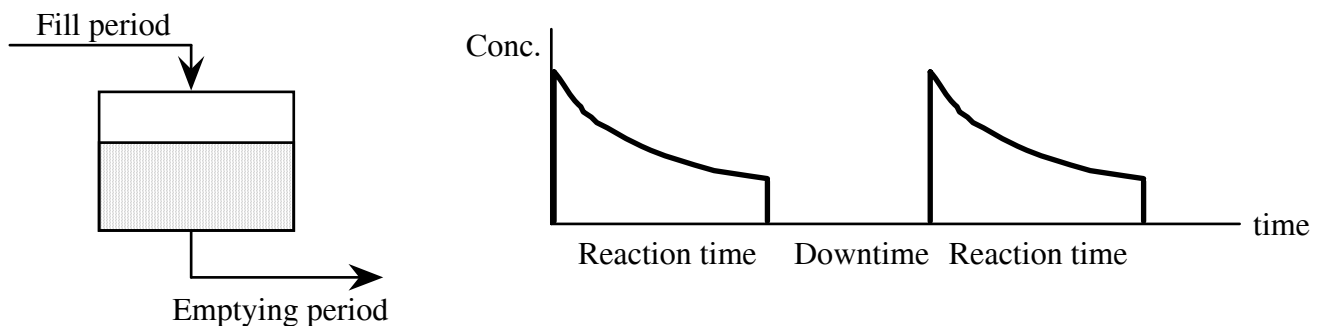


Figure 1. Batch operation

1. Batch operation is most flexible. Reactors can be used for multiple purposes. This is particularly important for the fine chemical industry where multiple products are produced in one plant.

2.2 *Continuous Operation*

has the following characteristics:

1. Continuous production
2. Steady state after start-up period (usually)
3. No variation of concentrations with time
4. Constant reaction rate
5. Ease of balancing to determine kinetics
6. No down-time for cleaning, filling, etc.

The steady state will develop only after a start up period usually 4 times the residence time ($t = V/F$). Continuous reactors are mainly used for large-scale production. Frequent use is made of continuous reactors in the laboratory for studying kinetics.

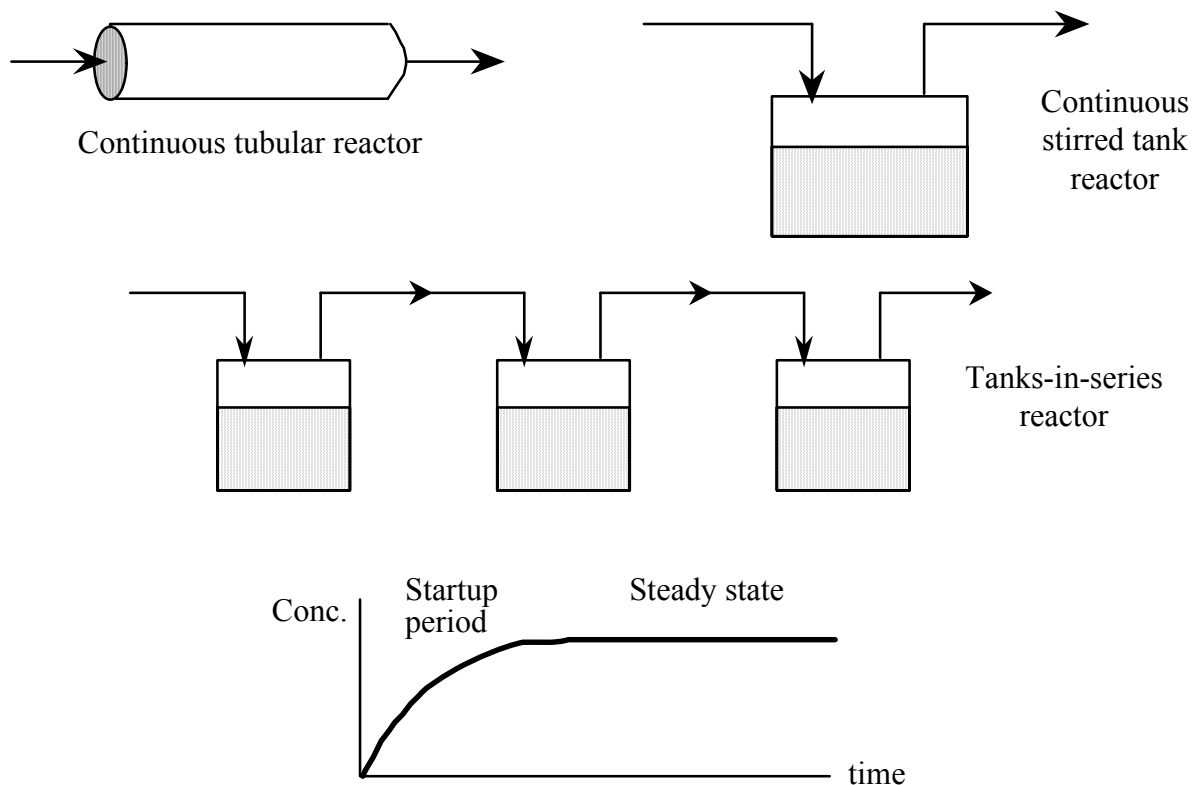


Figure 2. Continuous operation

In the tanks-in-series reactor configuration the effluent of one reactor is entering a second one and so on. In this way a plug flow reactor behavior can be approached by increasing the number of tanks. Advantages compared to the PFR are the improved controllability and mixing. It is much easier to adjust e.g., an optimal temperature or concentration profile in such a multistage CSTR than in a PFR. The reactor analysis for each reactor is identical to a single CSTR.

2.3 *Batch versus Continuous Operation*

Table 1. Comparison of batch and continuous operation (A- advantage; D- disadvantage)

Batch operation	Continuous operation
Usually better for small-volume production (A).	Better for indefinitely long production runs of one product or set of products (A).
More flexible for multi-product (multipurpose) operation (A)	Flexibility usually low (D)
Capital cost usually relatively low (A)	Capital cost usually relatively high (D)
Easy to shut down and clean for fouling service (A)	Shut down for cleaning very demanding and costly (D)
Inherent down-time between batches (D)	No down-time except for scheduled and emergency maintenance (A); but loss of production in lengthy stoppages can be costly (D)
Unsteady-state operation means process control and obtaining uniformity of product is more difficult (D)	Operating cost relatively low (A)
Process control and obtaining uniform product quality more difficult because of unsteady-state operation (D)	Process control and obtaining uniformity of product easier because of steady-state operation (A)
Coupling with continuous down-stream processing requires buffering tanks (D)	Steady-state operation allows easy coupling with continuous down-stream operation (A)

2.4 *Semi-batch and Semi-continuous Operation*

Semi-continuous operation is very common in the fine chemical industry and in biotechnological processes. One type of operation is fed-batch, which is often applied in biochemical processes. Here a substrate feed stream is being slowly added to the reactor. This type of operation is also often used to increase selectivity or to improve safety. In some cases products are removed, e.g. water in esterification reactions. In other situations gas (e.g. oxygen or chlorine) is supplied continuously to a batch reactor. Semi-continuous operation is typical in heterogeneous catalysis

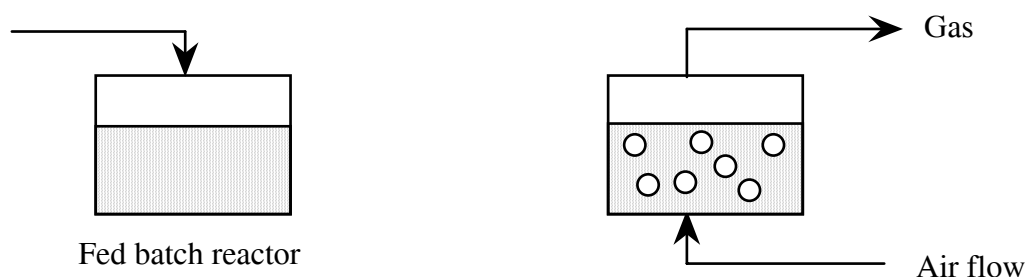


Figure 3. Semi-batch and semi-continuous operation of reactors

Various feeding policies for reactor control would be possible:

1. Slow constant feeding which results in constant reaction rate and low accumulation.
2. Exponential feeding to maintain S constant and give exponential growth in fermentation.
3. Feeding with feedback control based on measurements such as temperature or concentration.
4. Removal of reactant in equilibrium reactions, e.g. water in esterification.

Characteristics of semi-continuous operation are:

1. Good for small-scale production (A).
2. Capital cost usually between batch and continuous operation (A,D)
3. Easy adjustment for increased reaction selectivity (A)
4. Better than batch operation for many runaway –type reactions (A)
5. Operating cost may be relatively high compared to batch operation (D)
6. Inherent down time (D)
7. Unsteady-operation requires optimal feed or often complex control strategy (D)
8. Design of reactor may be more complicated (D). Dynamic modeling improves situation.

2.5 Preliminary Comparison of Reactor Operation Modes

A comparison of batch, continuous and semi-continuous reactor characteristics is given in Table 2.

Table 2. Summary of Reactor Modes

Mode of Operation	Advantages	Disadvantages
Batch	Equipment simple; suitable for small production because of multi-product flexibility	Downtime for loading and cleaning; reaction conditions change with time
Continuous	Provides high production; better product quality due to constant conditions; good for kinetic studies	Requires flow control, longevity of catalyst necessary, stability of organisms required
Semi-batch Semi-continuous	Control of environmental conditions e.g. substrate concentration (inhibition), induction of product formation; most flexible for selecting optimal conditions; most frequently used in biotechnological processes and in fine chemical industry	Requires feeding strategy e.g. to keep constant temperature or substrate concentration.

3 Quantitative Description of Ideal Reactors

There are numerous criteria to select the optimal reactor. In typical fine chemical and fermentation plants, reactors are already installed and process conditions have to be adjusted to fit into the available equipment. In this case mainly feeding strategies can be optimized as far as the reactor is concerned. On the other hand, dedicated continuous processes are installed for large-scale production. Reactor choice is mainly possible when building a new plant or in certain cases of retrofitting an existing one.

To improve understanding it is useful to study ideal reactors first. These reactors are the batch reactor (BR), the plug flow reactor (PFR) and the continuous stirred tank reactor (CSTR).

3.1 The Ideal Batch Reactor (BR)

The material balance for component A for a ideal batch reactor

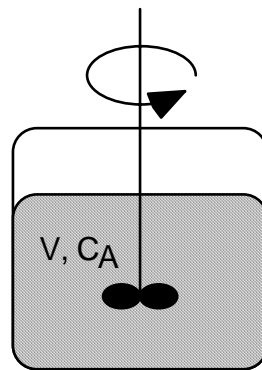


Figure 4. The batch reactor and its variables.

with a simple reaction $A \rightarrow \text{products}$ is

$$\frac{d(C_A V)}{dt} = r_A V$$

rearrangement and integration gives

$$\int_{C_{A0}}^{C_A} \frac{d(C_A V)}{r_A V} = t$$

For a constant density (volume) system we get

$$\int_{C_{A0}}^{C_A} \frac{dC_A}{r_A} = t$$

t is the time required to reach concentration C_A starting from C_{A0} . Graphically this can be presented by plotting $-1/r_A$ versus concentration as depicted in Fig.5. The left hand side of the figure shows a typical decay reaction. The right part shows an auto-catalytic type of process, e.g. biomass (X) growth. The required residence time to reach a desired conversion is then given by the area.

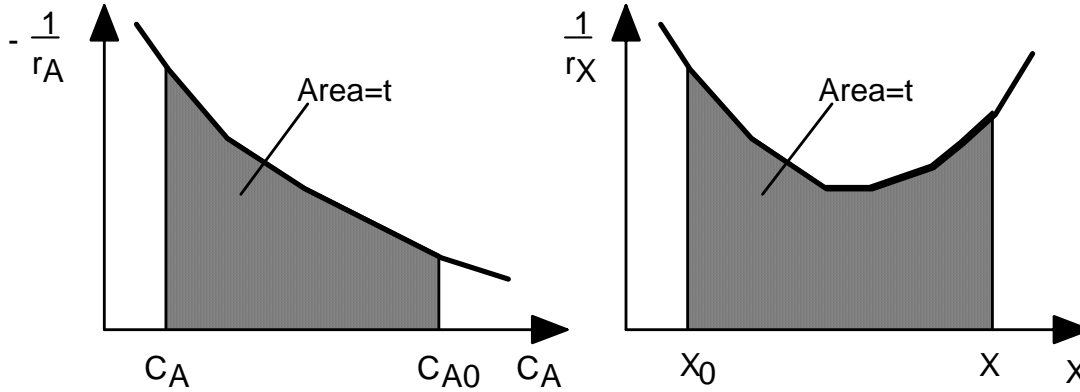


Figure 5 Estimation of batch reactor residence time in a decay reaction (left side) and an autocatalytic reaction, biomass growth (right side)

3.2 Continuous Stirred Tank Reactor (CSTR)

In the CSTR substrate is continuously fed to a reactor and immediately mixed with the entire reactor content. There are no gradients of concentration with respect to location. Therefore, the effluent concentration is equal to the reactor concentration.

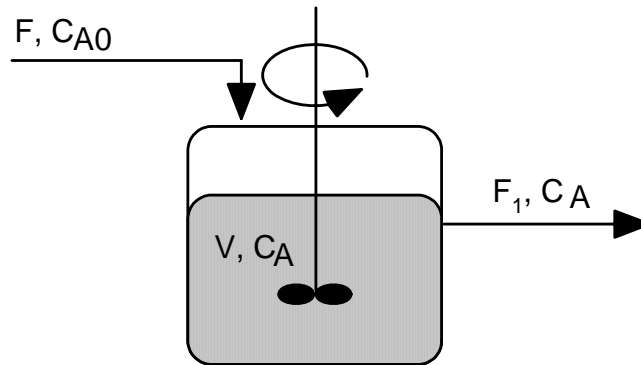


Figure 6. The CSTR and its variables.

The component material balance for a component A in a steady-state ($dc_i/dt=0$) continuous reactor is

$$0 = FC_{A0} - F_1C_A + Vr_A$$

and further for constant volume, where $F=F_1$

$$\tau = \frac{V}{F} = -\frac{C_{A0} - C_A}{r_A}$$

The graphical presentation of this equation is given in Figure 7. The CSTR operates at the reactor outlet condition which is at low substrate concentration and therefore low reaction rate. Such low concentrations can, however, be beneficial for the improvement of reaction selectivity, for autocatalytic type reactions and for the reduction of chemical hazard.

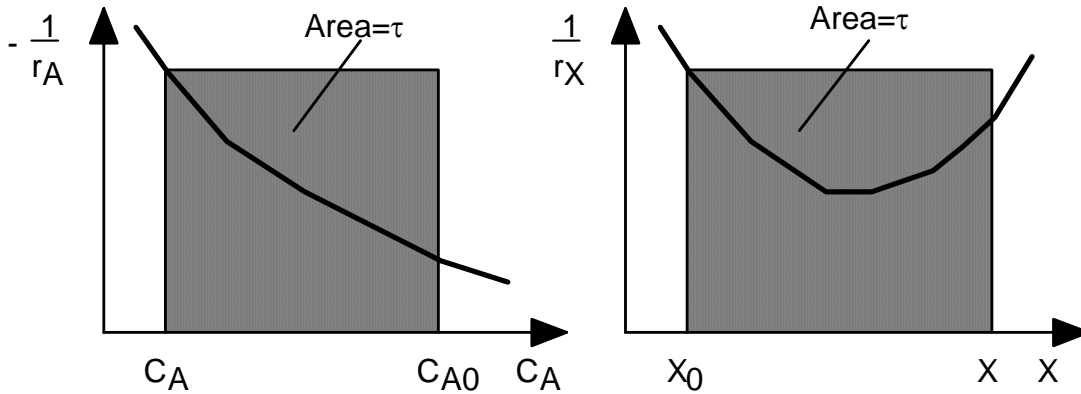


Figure 7. Estimation of steady-state mixed flow reactor residence time in a decay reaction (left side) and an autocatalytic reaction, here biomass growth (right side).

3.3 Steady-State Plug Flow Reactor (PFR)

The material balance for a component A in a steady-state ($dC_i/dt=0$) plug flow reactor element of volume dV as depicted in Figure 8 is

$$0 = F(C_A - (C_A + dC_A)) + r_A dV$$

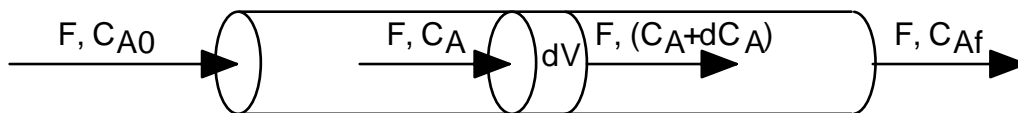


Figure 8 Plug flow reactor

At constant density (constant volumetric flow rate F) over the whole reactor, rearrangement of the above equation and integration over the whole reactor volume yields

$$\tau = \frac{V}{F} = \int_{C_{A0}}^{C_A} \frac{dC_A}{r_A}$$

This equation is identical with the batch reactor. Correspondingly Figure 5 is also valid for the steady-state plug flow reactor.

3.4 Comparison of the Performance of the Basic Reactor Types

For simple decay reactions, the BR and the PFR are always superior to the CSTR. In such reactions the inverse rate curve is always increasing from feed to exit concentrations.

In Table 2 and in Figure 10, reactors are compared for a second order reaction ($n=2$) with constant volume.

Table 3: Reactor comparison for given reaction Damköhler Number ($k \tau C_{A0}$).

Given Damköhler Number $k \tau C_{A0}$	6	11	20
Conversion in BR and PFR (%)	86	92	95
Conversion in CSTR (%)	67	74	80

The reason for the differences in conversion in the different reactor types can be shown by the differences in concentration profiles (Figure 9).

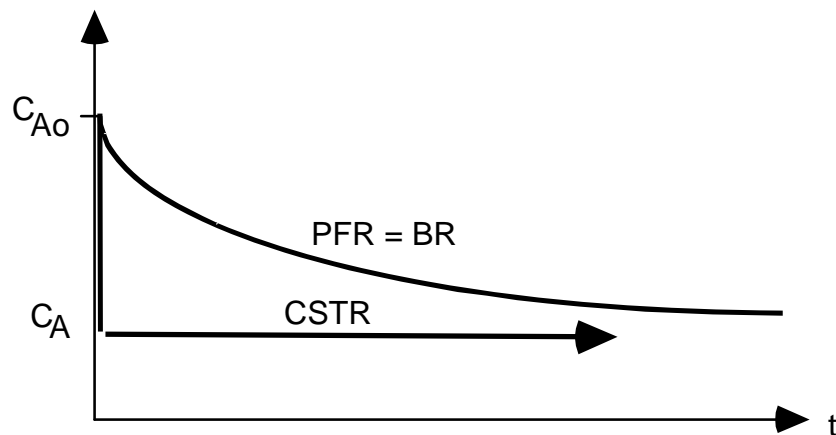


Figure 9. Concentration profiles in a plug-flow reactor (PFR), a stirred batch reactor (BR) and a continuous stirred-tank reactor (CSTR).

After entry into the CSTR the substrates are immediately diluted from feed concentration C_{A0} to effluent concentration C_A . Therefore, $-r_A$ is always on its lowest possible value. In the BR and in the PFR the concentration is decreasing during reaction and the rates are always higher compared to the CSTR.

The CSTR is, however, better for an auto-catalytic reaction, e.g. growth of microorganisms, as shown in the right part of Figures 5 and 7, if the final concentration is close to the minimum of the curve.

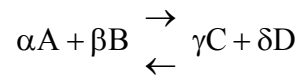
In more complex cases and particularly in the case of the semi-batch reactor, which is most frequently used in fermentation and fine chemical industry, a detailed comparison of reactor performance is most easily done using simulation. This method of analysis is useful for complex kinetics, for more complex reactor configurations, e.g. with recycle, or for any type of semi-batch reactor.

4 Nonisothermal Reactors

The basic design equations, rate laws, thermodynamic and stoichiometric relationships derived also still valid for the design of nonisothermal reactors. The major difference lies in the method of evaluating the design equation when temperature varies along the length of a PFR or when heat is removed from a CSTR. In this chapter we first introduce the importance of equilibrium as function of temperature. Then we derive design equations for batch reactor (BR), for the ideally mixed continuous stirred tank reactor (CSTR) and for the plug flow reactor (PFR). Finally we present methods for solving the equations including a complex example.

4.1 Equilibrium Constant

For a general reaction



the equilibrium constant K_a is defined as

$$K_a = \frac{a_C^\gamma a_D^\delta}{a_A^\alpha a_B^\beta}$$

where a are the activities and $\alpha, \beta, \gamma, \delta$ are the stoichiometric coefficients. In most cases we can assume ideal behavior and can set $a=C$, where C is concentration. Then

$$K_C = \frac{C_C^\gamma C_D^\delta}{C_A^\alpha C_B^\beta}$$

We define a pressure equilibrium constant K_P

$$K_P = \frac{P_C^\gamma P_D^\delta}{P_A^\alpha P_B^\beta}$$

Using the ideal gas equation $pV=nRT$ we get

$$K_P = K_C (RT)^\varepsilon$$

with

$$\varepsilon = \gamma + \delta - \alpha - \beta$$

The relationship between the change in Gibbs free energy, G, enthalpy, H, and entropy, S, is

$$\Delta G = \Delta H - T\Delta S$$

The equilibrium constant at temperature T can be calculated from the change in the Gibbs free energy using

$$\Delta G = -RT \ln(K)$$

The dependency of the equilibrium constant on temperature is given by the van't Hoff relationship

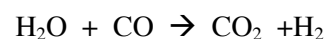
$$\frac{d(\ln K)}{dT} = \frac{\Delta H}{RT^2}$$

For constant ΔH integration gives

$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

From this relationship we can see that K is decreasing with increasing temperature in an exothermic reaction, whereas in an endothermic reaction K is increasing with increasing temperature.

Example: Equilibrium of water-shift reaction to produce hydrogen



At 1000 K and 10 atm the Gibbs free energies of formation are: $G_{\text{CO}} = -47860 \text{ cal mol}^{-1}$; $G_{\text{CO}_2} = -94630 \text{ cal mol}^{-1}$; $G_{\text{H}_2\text{O}} = -460400 \text{ cal mol}^{-1}$; $G_{\text{H}_2} = 0 \text{ cal mol}^{-1}$.

$$\Delta G = G_{\text{H}_2\text{O}} + G_{\text{H}_2} - G_{\text{CO}} - G_{\text{CO}_2}$$

$$\Delta G = -46040 + 0 - (-47860) - (-94630)$$

$$\Delta G = -730 \text{ cal mol}^{-1}$$

and

$$\ln(K) = \frac{-(-730 \text{ cal mol}^{-1})}{(1.987 \text{ cal (mol K)}^{-1})(1000 \text{ K})}$$

$$K = 1.44$$

assuming activity coefficients to be 1, and using the ideal gas law we get

$$K = \frac{C_{\text{CO}_2} C_{\text{H}_2}}{C_{\text{CO}} C_{\text{H}_2\text{O}}} = \frac{P_{\text{CO}_2} P_{\text{H}_2}}{P_{\text{CO}} P_{\text{H}_2\text{O}}}$$

At constant volume conversion is defined as

$$X_A = \frac{C_{A0} - C_A}{C_{A0}}$$

With equimolar feed, $C_{A0} = C_{B0}$, we obtain

$$K = \frac{C_{\text{CO}_2,0} X_e C_{\text{CO}_2,0} X_e}{C_{\text{CO}_2,0} (1 - X_e) C_{\text{CO}_2,0} (1 - X_e)} = \frac{X_e^2}{(1 - X_e)^2}$$

$$K = 1.44$$

solving for X_e , the equilibrium conversion gives $X_e = 0.55$

4.2 Equilibrium Conversion and Temperature

Using the equation of van't Hoff one can calculate equilibrium conversion as function of temperature. For exothermic reactions with $\Delta H < 0$, X_e , the equilibrium conversions decreases with temperature. The reaction rate is depending on concentration, temperature and for an equilibrium reaction also from the backward reaction. For exothermic reactions lines of equal reaction rate reach a maximum at a certain temperature. Higher temperature will favor the backward reaction. In the case of an endothermic reaction rates are always higher when increasing temperature.

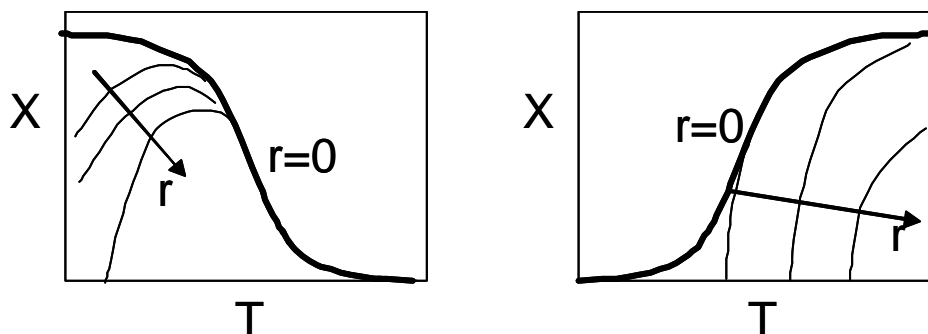
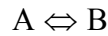


Figure 10. Equilibrium conversion for exothermic and endothermic reactions as function of temperature.

Example: Equilibrium conversion

Determine the equilibrium conversion between 0 und 100° C for a liquid phase reaction.



With $\Delta G_{298} = -7290$ cal/mol and $\Delta H_{298} = -75240$ cal/mol

$$K = K_{298} e^{-\left(\frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{298}\right)\right)}$$

and

$$X_e = \frac{K}{1 + K}$$

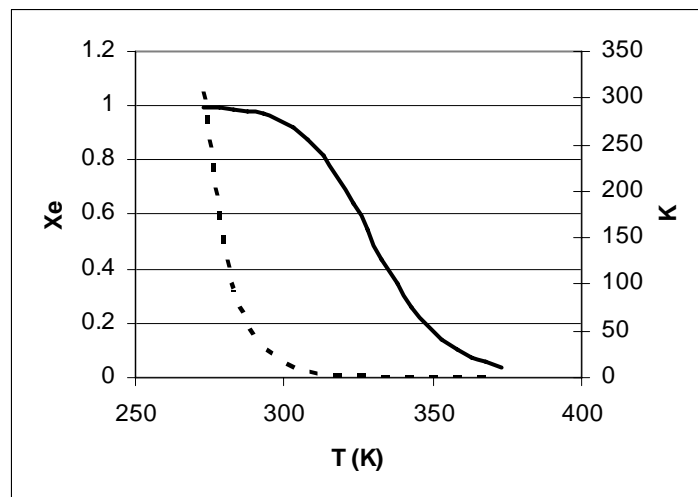


Figure 11. Equilibrium constant, K - dashed line, and equilibrium conversion, X_e - full line, of an exothermic reaction.

A few important remarks concerning thermodynamics:

- The equilibrium constant, K , is independent on pressure, on the presence of inert materials and on kinetics, i.e., on the presence of a catalyst.
- K is essentially a function of temperature.
- Since K is independent on pressure and inert materials, the equilibrium conversion depends on these variables.
- $K \gg 1$ irreversible reaction
- $K \ll 1$ no reaction
- Endothermic reaction (e.g. dehydrogenation): equilibrium conversion increases with increasing temperature

Exothermal reaction (e.g. hydrogenation): equilibrium conversion decreases with increasing temperature.

- Gas reactions: conversion increases with pressure, if number of moles decreases during reaction and it decreases with pressure, if number of moles increases during reaction.
- Increasing inert material content is equivalent to decreasing pressure.

4.3 *The Energy Balance*

For the quantitative description of non-isothermal reactor performance material and energy balances are needed. In the chapter **Basic Concepts** the energy balance was derived in the most simplified form

$$V\rho c_p \frac{dT_1}{dt} = F_0\rho c_p(T_0 - T_1) + r_Q V + UA(T_a - T_1)$$

In this form the dependency of ΔH and c_p on temperature are assumed to be negligible. In cases of multiple reactions the heat production rate is

$$r_Q V = V \sum_{j=1}^R \frac{r_{ij}}{\nu_{ij}} (-\Delta H_j)$$

4.4 *Batch Reactor (BR)*

In a batch reactor all flow terms are 0. The material balance for a component i is therefore

$$\frac{d(VC_i)}{dt} = r_i V$$

$$V\rho c_p \frac{dT_1}{dt} = r_Q V + UA(T_a - T_1)$$

or

$$\frac{dT_1}{dt} = \frac{r_Q}{\rho c_p} + \frac{UA(T_a - T_1)}{V\rho c_p}$$

Isothermal operation

Isothermal operation means $dT_1/dt=0$ and therefore

$$0 = \frac{r_Q}{\rho c_p} + \frac{UA(T_a - T_1)}{V\rho c_p}$$

and therefore

$$0 = \frac{r_Q}{\rho c_p} + \frac{UA(T_a - T_1)}{V\rho c_p}$$

and

$$-r_Q V = UA(T_a - T_1)$$

which means that at any instant of time the heat production has to be compensated by corresponding heat removal.

Adiabatic Operation

For a single reaction $A \rightarrow B$ with reaction enthalpy ΔH and constant volume and substituting $C_A = C_{A0}(1-X)$ we obtain

$$-C_{A0} \frac{dX}{dt} = r_A$$

and since

$$r_Q = r_A \Delta H$$

$$\frac{dT}{dt} = \frac{r_A \Delta H}{\rho c_p} + \frac{UA(T_a - T)}{V\rho c_p}$$

Combining with the component mass balance

$$dT = \frac{-C_{A0} \Delta H}{\rho c_p} dX$$

Integration with $X_0=0$ gives

$$T = T_0 + \frac{C_{A0}(-\Delta H)}{\rho c_p} X$$

This equation corresponds to a straight line in the following figure

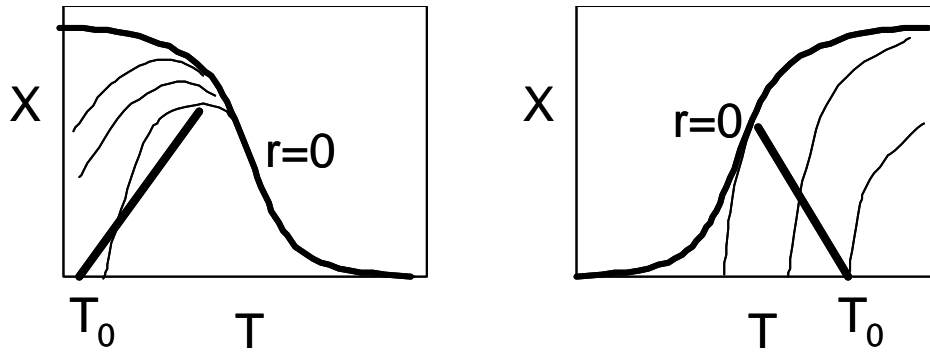


Figure 12. Equilibrium conversion for exothermic and endothermic reactions and adiabatic temperature changes.

Non-isothermal batch reactor design

The general design equation is still valid and may also be expressed in terms of fractional conversion, X.

$$t = \int_{C_{A0}}^{C_A} \frac{dC_A}{r_A} = C_{A0} \int_0^X \frac{dX}{(-r_A)}$$

4.5 Continuous Stirred Tank Reactor (CSTR)

In a CSTR all accumulation terms are 0. The material balance for a component A is therefore

$$0 = F(C_{A0} - C_A) + Vr_A$$

$$0 = F\rho c_p(T_0 - T_1) + r_Q V + UA(T_a - T_1)$$

and since

$$r_Q = r_A \Delta H(T)$$

and

$$C_A = C_{A0}(1 - X)$$

we get an expression to calculate the fractional conversion

$$X = \frac{F\rho c_p(T_0 - T) + UA(T_a - T)}{F C_{A0} \Delta H(T)}$$

Aidabatic Operation

For adiabatic operation U=0 and we obtain

$$X = \frac{\rho c_p (T_0 - T)}{C_{A0} \Delta H(T)}$$

or identical to the BR and PFR

$$T = T_0 + \frac{C_{A0} (-\Delta H(T))}{\rho c_p} X$$

This equation corresponds to a straight line in the following Figure 13, which compares BR, CSTR and PFR for exothermic and endothermic reactions.

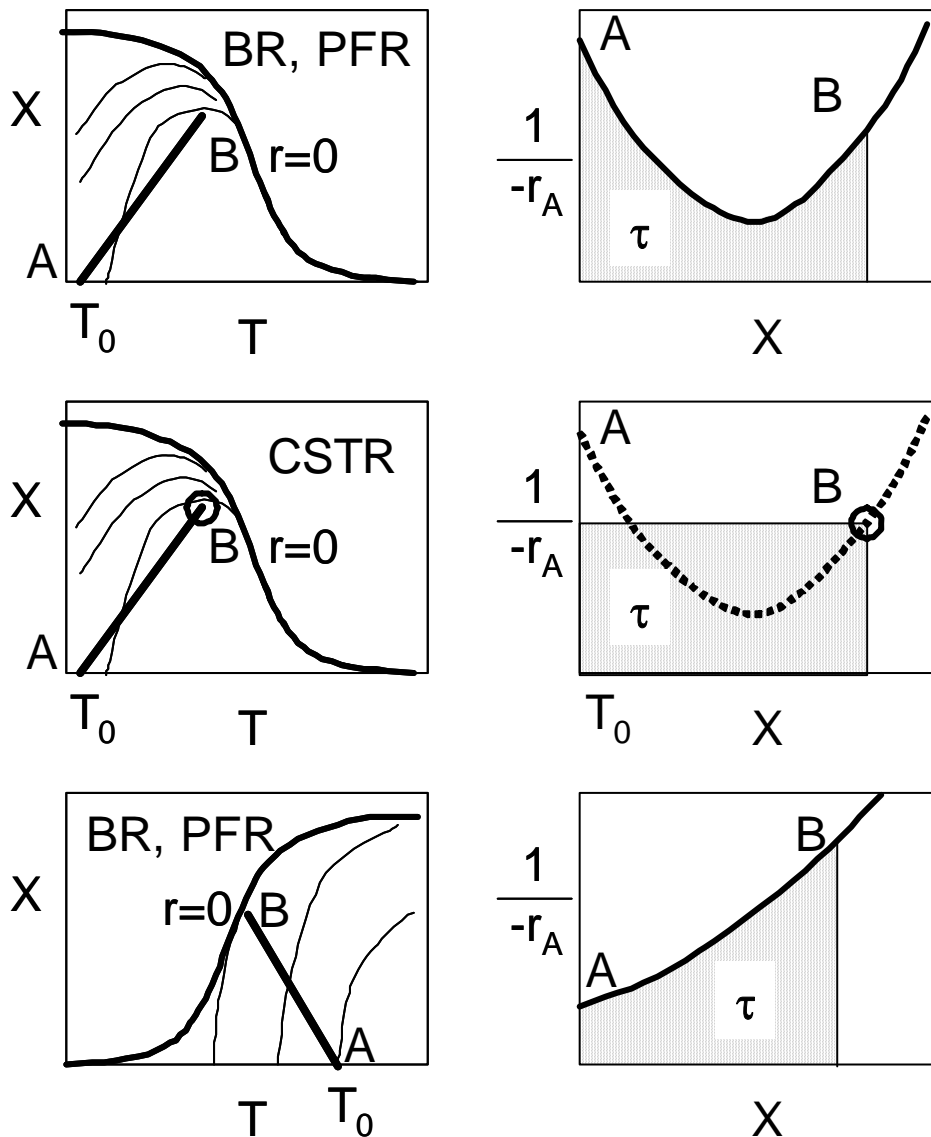


Figure 13. Equilibrium conversion for exothermic and endothermic reactions and adiabatic temperature changes.

The design of non-isothermal reactors is most easily done by simulation (See example REVREACT of exercise).

5 General Concepts of Reactor Design

Reactor design may follow three basic types of approaches:

Empirical Approach: Measure productivity for all combinations of reactor operating conditions, and make correlations.

- Advantage: Little thinking necessary
- Disadvantage: Many experiments required.

Regime Analysis Approach: Compares characteristic variables (e.g. time constants, characteristic lengths) to determine the rate limiting step.

- Advantage: Relatively simple, rather fast.
- Disadvantage: Good solution only if rate limiting step clearly identified. Results difficult to interpret if several steps have similar influence.

Modeling Approach: Establish a model and determine the important variables from the model. Compare the model behavior with the experimental measurements

- Advantages: Fewer experiments and greater understanding. In most cases simplified material and energy balances are sufficient.
- Disadvantages: Effort for model setting up, complete material, energy and momentum balancing not feasible today.

In the modeling approach it is necessary to combine physical and chemical quantitative knowledge to a reactor model which can then be used for reactor design and optimization as depicted schematically in Fig. 14.

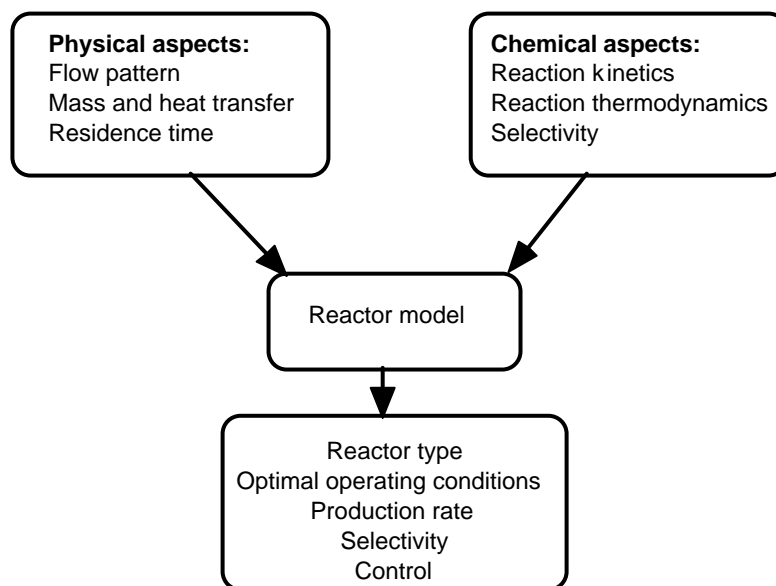


Figure 14 Information needed for reactor design using the modeling approach