# CHEMICAL REACTION ENGINEERING

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## Contents

## Summary

Chemical reactors are key parts of any chemical plant. The design and operation of chemical reactors are the subjects, of part of chemical engineering, called "Chemical Reactor (or Reaction) Engineering".

The chapter describes main principles of chemical reaction engineering: fundamentals of reactor modeling, reaction equilibrium and kinetics, flow models and mixing in

chemical reactors, and different kinds of reactors (catalytic reactors, polymerization reactors, bioreactors, electrochemical reactors, photoreactors, multifunctional reactors, and microreactors).

## 1. Introduction

A chemical reactor is a vessel, in which a chemical change is taking place. In the case of biochemical changes, the vessel is called a bioreactor.

The part of chemical engineering, dealing with chemical reactors, is called chemical reaction (or reactor) engineering (CRE).

A chemical reactor is the heart of every industrial process in chemical and related industries.



Figure 1. A reactor for steam cracking (breaking the molecules of heavier hydrocarbons into smaller ones) occupies central part of a plant in BASF, Ludwigshafen, Germany (copyright BASF).

In many cases, the performance of the chemical reactor can be the key to the success or failure of the whole industrial process. For example, if the reactor produces the desirable product together with large amount of an undesirable byproduct (low selectivity), the subsequent separation and purification procedure may be so complicated as to make the whole process economically unattractive. It also means less effective use of the raw materials, which, in view of the shortness of available resources, is detrimental for sustainable economy. Similarly, if the degree of conversion of substrates to products is low (low yield), then large amount of material leaving the reactor must be recycled, causing additional cost and again influencing the economy of the process.

The performance of a reactor depends on its design, the way it is operated, and a number of chemical and physical phenomena occurring in it. These phenomena include fluid flow, influencing mixing of substrates, mass transfer, influencing the concentration distribution of the reagents, heat transfer, influencing the temperature distribution, and, above all, the chemical reaction equilibrium and kinetics.

The design of a chemical reactor may be very different from the simplest mixing tanks or empty pipes (so called tubular reactors) to complicated structures, containing heat exchangers, membranes, catalyst layers and so on.

They may also be operated in different ways. In batch (periodical) reactors the reactants are just filled into the reactor and left there until the reaction is completed, and then the products are discharged. In continuous reactors the reacting mixture flows continuously through the reactor, entering it at one point (the inlet), and leaving at another one (the outlet). In the semi-batch (or semi-continuous) reactors some substrates are filled into the reactor at the beginning of the process, while others are gradually added during the course of reaction. There may be also situation in which products are continuously withdrawn from the reactor during the reaction course.

The complexity of the physical and chemical phenomena occurring in the reactor and influencing its performance is the reason why the course of a chemical process may be (and usually is) different in reactors of different size (different scale). For example, the amount of heat released in the course of an exothermic reaction depends on the reactor volume (proportional to the cube of its linear dimension), whereas the rate of heat exchanged with the environment depends on the reactor outer surface (proportional to the square of linear dimension). The rate of the temperature rise would therefore be much higher in a reactor of greater size than in that of smaller size. These (and similar) facts are the reason why generally the chemical process proceeds differently in reactors of different size, e.g. laboratory glass vessel and large industrial reactor.

The problem of scaling-up a reactor (i.e. to predict its behavior in a bigger scale on the basis of its behavior in a smaller scale) has been a challenge for chemical engineers for a long time.

For many years chemical reactors were designed and constructed on an empirical basis, by successively constructing bigger and bigger vessels, thus gradually passing from laboratory scale to full industrial scale. The early theoretical approach was based on the theory of similarity, using non-dimensional expressions, called similarity criteria. Equal values of these criteria for two reactors of two different scales should ensure similar behavior of these reactors. Four such criteria were proposed by G. Damköhler (1937). However, usually it is impossible to maintain equality of all the similarity criteria describing the behavior of the reactor, which renders this approach impracticable.

The fully rational approach, based on mathematical modeling, has only been possible relatively recently, with the development of sufficiently powerful computers and sufficiently detailed mathematical models.

## 2. Fundamentals of Reactor Modeling

Formulation of a proper mathematical model of a computer is difficult because of the complexity of phenomena occurring in a process taking place in a reactor.

As mentioned earlier, the performance of a reactor may depend on the fluid flow characteristics, the mass transfer rates, the heat transfer rates, as well as the reaction equilibrium and kinetics.

A set of equations, describing the above factors, includes:
- balance equations (overall mass balance and mass – or mole – balance of each component energy balance, in some cases also population balances (of crystals, bubbles, drops, cells, etc.);
- equations describing mass transfer rates (for each component);
- equations describing heat transfer rate;
- equilibrium equations (for each reaction, and, in the case of polyphasic systems, phase equilibria for each component);
- reaction rate equations (for each reaction taking place in the reactor).

## 3. Balances

The balance equations are based on the obvious principle:

$$Input = Output + Accumulation - Generation \tag{1}$$

where by input is understood the quantity of an extensive property inflowing into the system, output the quantity flowing out of the system, accumulation is the quantity amassed in the system, and generation – the quantity produced (or, if negative, used) in the system.

By an extensive property is understood a property whose amount in a system is proportional to the size of the system. It may be mass, energy, momentum, number of elements, etc. In contrast, an intensive property is a property independent of the size of a system, such as density, viscosity, conductivity, etc.

Balance equation can be written for a macroscopic system (so called shell balance), or a differential element of the system volume. In the first case a general form of the balance equation is an integral equation, in the second case – a partial differential equation. Needless to say, an important task of an engineer is to simplify such equations to bring them to a solvable form.

A solution of the macroscopic (integral) balance equation supplies information about the whole system, while a solution of the differential balance equation supplies information about the distribution of the property in question over the system volume, often expressed in terms of an intensive property (e.g. density in the case of mass balance, or temperature in the case of energy balance). This somewhat abstract introduction shall become clearer when applied to concrete properties.

In the case of the macroscopic mass balance written for a vessel with one inlet and one outlet, the balance equation is:

$$\frac{dm}{dt} = Q_{in}\rho_{in} - Q_{out}\rho_{out} \tag{2}$$

where: $m$ – total mass of the system; $t$ – time; $Q_{in}$ and $Q_{out}$ – inlet and outlet volumetric flow rate, respectively; $\rho_{in}$ and $\rho_{out}$ - inlet and outlet stream density, respectively.

The left hand side of the equation is the rate of accumulation of mass in the system, the first term on the right hand side is mass inflow, the second – mass outflow. As, according to the mass conservation principle, in chemical processes mass in neither generated nor destroyed, the generation term is equal to zero.

Similarly, macroscopic energy balance written for the same system would read:

$$\frac{d(em)}{dt} = Q_{in}\rho_{in}h_{in} - Q_{out}\rho_{out}h_{out} + q - w \tag{3}$$

where: $e$ is energy per unit mass; $h$ – enthalpy per unit mass; $q$ – rate of heat exchange with the system surroundings; $w$ – work done by the system.

In an analogous way one can write balance equations for momentum, or a population of separate elements such as crystals, bubbles, drops, living cells, etc.

A mass balance equation can also be written for a chemical reaction. In this case it relates the amount of reacted substrates (expressed in moles), with the amount of products (also expressed in moles). Such equation, called stoichiometric equation, takes a general form

$$\sum_i \upsilon_i A_i = 0 \tag{4}$$

where $\upsilon_i$ is the stoichiometric coefficient of the reactant $A_i$ (positive for products, negative for substrates).

For example, if one mole of reactant A reacts with two moles of reactant B to give one mole of product, the above equation, after rearrangement, takes the form

$$A + 2B = C \tag{5}$$

An energy balance for a reaction carried out at standard conditions (i.e. at 25° and 1 bar) reads

$$\Delta H_{\mathrm{rs}} = \sum_i \upsilon_i H_i^{\mathrm{o}} \tag{6}$$

where $\Delta H_{\mathrm{rs}}$ is the heat (enthalpy) of the reaction, and $H_i^{\mathrm{o}}$ denotes so called standard heat of formation of the reactant $A_i$. For other temperatures the heat of reaction may be calculated as

$$\Delta H_{\mathrm{r}} = \Delta H_{\mathrm{rs}} + \int_{T_{\mathrm{S}}}^{T} \Delta C_{\mathrm{p}} dT \tag{7}$$

where $T_{\mathrm{s}}$ – standard temperature (25°C); $T$ – temperature at which the reaction is carried out, and

$$\Delta C_{\mathrm{p}} = \sum_i \upsilon_i C_{\mathrm{p}i} \tag{8}$$

where $C_{\mathrm{p}i}$ – molar specific heat of the reactant $A_i$.

The heat of reaction is necessary for determination of the generation term in the energy balance equation for a reacting system.

As mentioned before, differential balances are necessary to determine distributions of such intensive properties like density, temperature, etc.

Two other kinds of such balances are very important in modeling of chemical reactors: the momentum balance and balances of reactants.

The differential momentum balance, after suitable transformations, gives so called equation of motion, known also as the Navier-Stokes equation. The solution of this differential equation gives the velocity distribution in the system, which in turn helps to determine the mixing conditions in the reacting mixture.

Extremely important for reactor modeling are the mass (or mole) balances of reactants. Such balance equations may be written for every reactant in the system. In the macroscopic form they supply information about the degree of conversion of any reactant, provided the stoichiometric equation, the reaction equilibrium and the reaction kinetics are known. The reaction kinetics depends in turn on the concentrations of the reactants in a given space element within the reactor volume, i.e., the concentration distribution, which is determined on the basis of the differential balances of the reactants. In both cases these equations follow the general principle expressed by Eq. (1), which gives for the macroscopic balance

$$\frac{dm_i}{dt} = Q_{\mathrm{in}} c_{i,\mathrm{in}} - Q_{\mathrm{out}} c_{i,\mathrm{out}} + M_i R_i V \tag{9}$$

where $m_i$ – mass of reactant $A_i$ in the system, $c_{i,\text{in}}$, $c_{i,\text{out}}$ – concentration of this reactant in the inflowing and outflowing streams, respectively; $M_i$ – molar mass of the reactant; $R_i$ – molar rate of production of this reactant in the chemical reaction carried out in the reactor (per unit time and unit reactor volume); $V$ – reactor volume.

For the differential element of reactor volume the mass balance of a reactant $A_i$ reads

$$\frac{\partial c_i}{\partial t} + \nabla \cdot N_i = R_i \tag{10}$$

where $c_i$ – local concentration of this reactant; $N_i$ – molar flux of the reactant; $R_i$ – molar rate of production of the reactant in the chemical reaction. For more detailed information on the balances see "Principles of momentum, mass and energy balances" and "Generalized mass balances".

## 4. Equilibrium Equations

Any isolated system left alone for sufficiently long time reaches the state of equilibrium. The distance from equilibrium, measured by a suitable intensive property, such as temperature or concentration, influences the rate at which the system approaches equilibrium (for example heat or mass transfer rate) and is called driving force.

The state of equilibrium can be determined from the thermodynamic principles. For a chemical reaction the equilibrium is described by the equilibrium constant, defined as:

$$K = \prod_i a_i^{\upsilon_i} \tag{11}$$

where $a_i$ is the so called activity of a reactant in the reacting mixture.

For example, for the reaction involving substances A, B, P and R

$$\upsilon_A A + \upsilon_B B \rightarrow \upsilon_P P + \upsilon_R R \tag{12}$$

the equilibrium constant takes the form

$$K = \frac{a_P^{\upsilon_P} a_R^{\upsilon_R}}{a_A^{\upsilon_A} a_B^{\upsilon_B}} \tag{13}$$

The value of $K$ can be determined from the relation

$$K = \exp\left(\frac{-\Delta G^o}{RT}\right) \tag{14}$$

where $\Delta G^o$ is the standard Gibbs free energy of the reaction, which can be determined in different ways from the thermodynamic principles; $R$ is the gas constant, and $T$ is absolute temperature.

In practice, it is easier to use the equilibrium constant expressed in concentrations rather than activities, namely:

$$K_C = \prod_i c_i^{v_i} \tag{15}$$

Knowing the relation between $a_i$ and $c_i$, one can transform $K$ into $K_C$.

If the reacting system is composed of more than one phase (polyphasic or multiphasic system), then the knowledge of the phase equilibria is needed.

Generally speaking, a phase equilibrium equation is the equation relating concentration (or activity) of a reactant in one phase to the concentration (or activity) of this reactant in another phase, in the state of equilibrium. Again, thermodynamics supplies the necessary tools to determine these relationships. For more information see "Thermodynamics" and "Thermodynamics of chemical processes".

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**Biography Sketch**

**Professor Ryszard Pohorecki** studied chemistry at Warsaw University of Technology (WUT), where he received MSc in 1959 and PhD in 1964. In the years 1965/66 he was visiting scholar at the University of Cambridge, UK, which he also visited in 1986 and 2000. In 1970 he received DSc ("habilitation") at WUT. In 1988/89 he was teaching and doing research in France (Toulouse and Nancy). For most of his scientific career he was employed at WUT, where he was head of the Chemical Reactor and Bioprocess Engineering Division, and director of the Centre of Biotechnology. Now he is Emeritus Full Professor of Chemical Engineering at WUT. For several years he served as Vice President for Science, European Federation of Chemical Engineering, and Vice President for Europe, Alliance of Universities for Democracy. He is member of the Polish Academy of Sciences, honorary member of the Czech Society of Chemical Engineering, holder of the Purkyne Medal, Czech Academy of Sciences, and Villermaux Medal, European Federation of Chemical Engineering. He is author or co-author of 6 books, and over 250 research papers. His main scientific interests include chemical reaction engineering and bioprocess engineering.