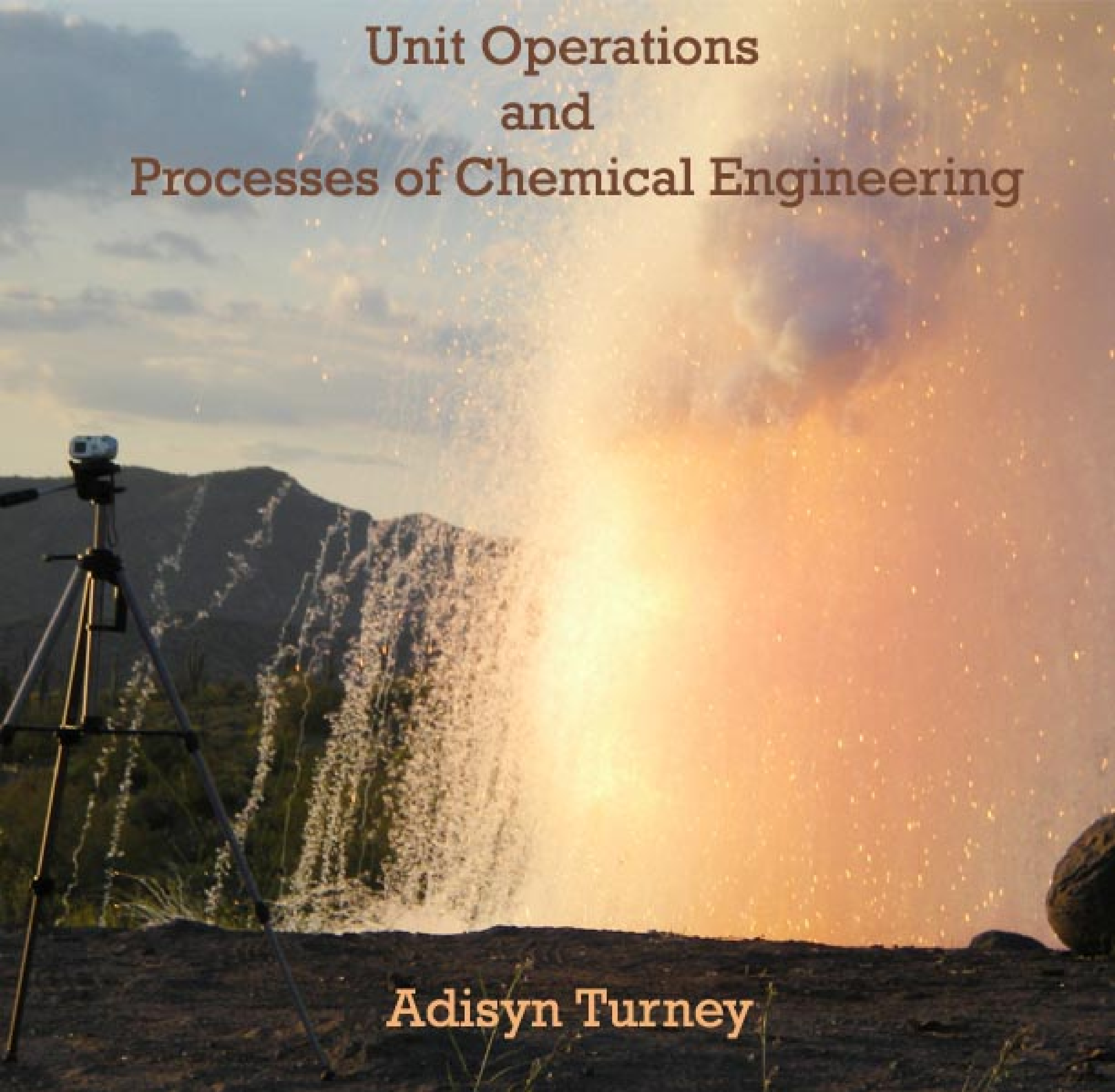
Unit Operations
and
Processes of Chemical Engineering



Adisyn Turney

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Chemical Reaction Engineering and Chemical Synthesis

Chemical Reaction Engineering

Chemical reaction engineering (reaction engineering or reactor engineering) is a specialty in chemical engineering or industrial chemistry dealing with chemical reactors. Frequently the term relates specifically to catalytic reaction systems where either a homogeneous or heterogeneous catalyst is present in the reactor. Sometimes a reactor *per se* is not present by itself, but rather is integrated into a process, for example in reactive separations vessels, retorts, certain fuel cells, and photocatalytic surfaces.

Origin of Chemical Reaction Engineering

Chemical reaction engineering as a discipline started in the early 1950s under the impulse of researchers at the Shell Amsterdam research center and the university of Delft. The term chemical reaction engineering was apparently coined by J.C. Vlugter while preparing the 1st European Symposium on Chemical Reaction Engineering which was held in Amsterdam in 1957.

Discipline

Chemical reaction engineering aims at studying and optimizing chemical reactions in order to define the most optimal reactor design. Hence, the interactions of flow phenomena, mass transfer, heat transfer, and reaction kinetics are of prime importance in order to relate reactor performance to feed composition and operating conditions. Although originally applied to the petroleum and petrochemical industries, its general methodology combining reaction chemistry and chemical engineering concepts allows to optimize a variety of systems where modeling or engineering of reactions is needed. Chemical reaction engineering approaches are indeed tailored for the development of new processes and the improvement of existing technologies.

A few Chemical Reaction Engineering books

- Chemical Reaction Engineering (3rd Edition), Octave Levenspiel, 1999, John Wiley & Sons
- Elements of Chemical Reaction Engineering (4th Edition), H. Scott Fogler, 2005, Prentice Hall
- Chemical Reactor Analysis and Design (2nd Edition), Gilbert F. Froment and Kenneth B. Bischoff, 1990, John Wiley & Sons
- Fundamentals of Chemical Reaction Engineering (1st Edition), Mark E. Davis and Robert J. Davis, 2003, The McGraw-Hili Companies, Inc.

Chemical Reaction Engineering symposia

The most important series of symposia are the International Symposia on Chemical Reaction Engineering or ISCRE conferences. These three-day conferences are held every two years, rotating among sites in North America, Europe, and the Asia-Pacific region, on a six-year cycle.

Chemical synthesis

In chemistry, **chemical synthesis** is purposeful execution of chemical reactions to get a product, or several products. This happens by physical and chemical manipulations usually involving one or more reactions. In modern laboratory usage, this tends to imply that the process is reproducible, reliable, and established to work in multiple laboratories.

A chemical synthesis begins by selection of compounds that are known as reagents or reactants. Various reaction types can be applied to these to synthesize the product, or an intermediate product. This requires mixing the compounds in a reaction vessel such as a chemical reactor or a simple round-bottom flask. Many reactions require some form of work-up procedure before the final product is isolated . The amount of product in a chemical synthesis is the reaction yield. Typically, chemical yields are expressed as a weight in grams or as a percentage of the total theoretical quantity of product that could be produced. A **side reaction** is an unwanted chemical reaction taking place that diminishes the yield of the desired product.

The word *synthesis* in the present day meaning was first used by the chemist Adolph Wilhelm Hermann Kolbe.

Strategies

Many strategies exist in chemical synthesis that go beyond converting reactant A to reaction product B. In cascade reactions multiple chemical transformations take place within a single reactant, in multi-component reactions up to 11 different reactants form a single reaction product and in a telescopic synthesis one reactant goes through multiple transformations without isolation of intermediates.

Organic synthesis

Organic synthesis is a special branch of chemical synthesis dealing with the synthesis of organic compounds. In the total synthesis of a complex product it may take multiple steps to synthesize the product of interest, and inordinate amounts of time. Skill in organic synthesis is prized among chemists and the synthesis of exceptionally valuable or difficult compounds has won chemists such as Robert Burns Woodward the Nobel Prize for Chemistry. If a chemical synthesis starts from basic laboratory compounds and yields something new, it is a purely synthetic process. If it starts from a product isolated from plants or animals and then proceeds to a new compounds, the synthesis is described as a semisynthetic process.

Other meanings

The other meaning of **chemical synthesis** is narrow and restricted to a specific kind of chemical reaction, a *direct combination reaction*, in which two or more reactants combine to form a single product. The general form of a direct combination reaction is:

$$A + B \rightarrow AB$$

where A and B are elements or compounds, and AB is a compound consisting of A and B. Examples of combination reactions include:

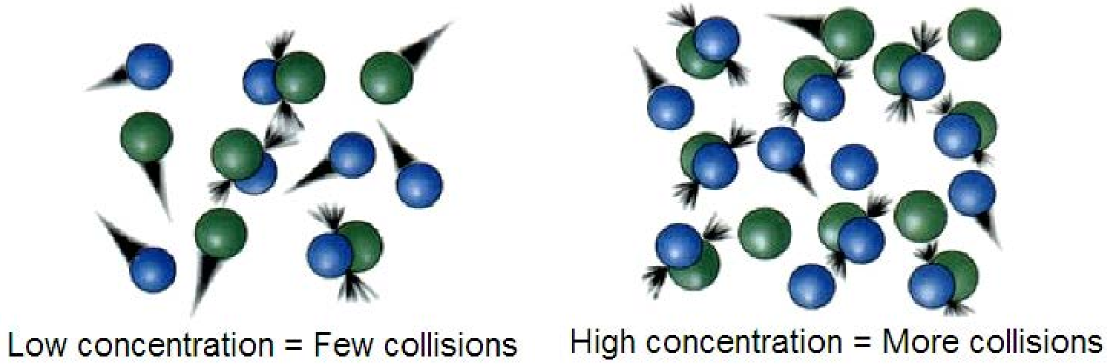
$2Na + Cl_2 \rightarrow 2\,NaCl$ (formation of table salt)
$S + O_2 \rightarrow SO_2$ (formation of sulfur dioxide)
$4\,Fe + 3\,O_2 \rightarrow 2\,Fe_2O_3$ (iron rusting)
$CO_2 + H_2O \rightarrow H_2CO_3$ (carbon dioxide dissolving and reacting with water to form carbonic acid)

4 special synthesis rules:

metal-oxide + $H_2O \rightarrow$ metal(OH)
non-metal-oxide + $H_2O \rightarrow$ oxi-acid
metal-chloride + $O_2 \rightarrow$ metal-chlorate
metal-oxide + $CO_2 \rightarrow$ metal(CO_3)

Chapter 2

Chemical Kinetics



Low concentration = Few collisions High concentration = More collisions

Reaction rate tends to increase with concentration - a phenomenon explained by collision theory.

Chemical kinetics, also known as **reaction kinetics**, is the study of rates of chemical processes. Chemical kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction. In 1864, Peter Waage and Cato Guldberg pioneered the development of chemical kinetics by formulating the law of mass action, which states that the speed of a chemical reaction is proportional to the quantity of the reacting substances.

Chemical kinetics deals with the experimental determination of reaction rates from which rate laws and rate constants are derived. Relatively simple rate laws exist for zero-order reactions (for which reaction rates are independent of concentration), first-order reactions, and second-order reactions, and can be derived for others. In consecutive reactions the rate-determining step often determines the kinetics. In consecutive first-order reactions, a steady state approximation can simplify the rate law. The activation energy for a reaction is experimentally determined through the Arrhenius equation and the Eyring equation. The main factors that influence the reaction rate include: the physical state of the reactants, the concentrations of the reactants, the temperature at which the reaction occurs, and whether or not any catalysts are present in the reaction.

Factors affecting reaction rate

Nature of the reactants

Depending upon what substances are reacting, the reaction rate varies. Acid/base reactions, the formation of salts, and ion exchange are fast reactions. When covalent bond formation takes place between the molecules and when large molecules are formed, the reactions tend to be very slow. Nature and strength of bonds in reactant molecules greatly influences the rate of its transformation into products. The reactions which involve lesser bond rearrangement proceed faster than the reactions which involve larger bond rearrangement.

Physical state

The physical state (solid, liquid, or gas) of a reactant is also an important factor of the rate of change. When reactants are in the same phase, as in aqueous solution, thermal motion brings them into contact. However, when they are in different phases, the reaction is limited to the interface between the reactants. Reaction can only occur at their area of contact, in the case of a liquid and a gas, at the surface of the liquid. Vigorous shaking and stirring may be needed to bring the reaction to completion. This means that the more finely divided a solid or liquid reactant, the greater its surface area per unit volume, and the more contact it makes with the other reactant, thus the faster the reaction. To make an analogy, for example, when one starts a fire, one uses wood chips and small branches—one doesn't start with large logs right away. In organic chemistry, On water reactions are the exception to the rule that homogeneous reactions take place faster than heterogeneous reactions.

Concentration

Concentration plays a very important role in reactions, because according to the collision theory of chemical reactions, molecules must collide in order to react together. As the concentration of the reactants increases, the frequency of the molecules colliding increases, striking each other more frequently by being in closer contact at any given point in time. Think of two reactants being in a closed container. All the molecules contained within are colliding constantly. By increasing the amount of one or more of the reactants it causes these collisions to happen more often, increasing the reaction rate.

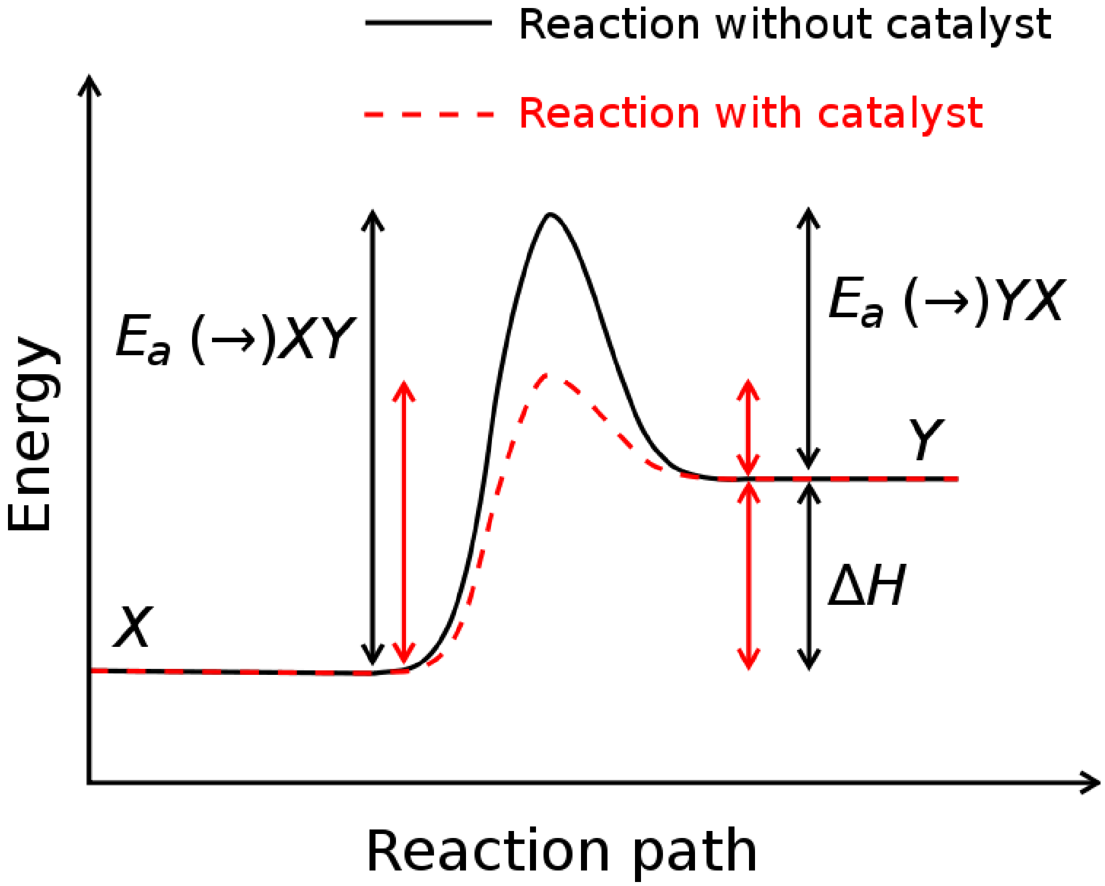
Temperature

Temperature usually has a major effect on the rate of a chemical reaction. Molecules at a higher temperature have more thermal energy. Although collision frequency is greater at higher temperatures, this alone contributes only a very small proportion to the increase in rate of reaction. Much more important is the fact that the proportion of reactant molecules with sufficient energy to react (energy greater than activation energy: $E > E_a$) is significantly higher and is explained in detail by the Maxwell–Boltzmann distribution of molecular energies.

The 'rule of thumb' that the rate of chemical reactions doubles for every 10 °C temperature rise is a common misconception. This may have been generalized from the special case of biological systems, where the Q_{10} (temperature coefficient) is often between 1.5 and 2.5.

A reaction's kinetics can also be studied with a temperature jump approach. This involves using a sharp rise in temperature and observing the relaxation rate of an equilibrium process.

Catalysts



Generic potential energy diagram showing the effect of a catalyst in an hypothetical endothermic chemical reaction. The presence of the catalyst opens a different reaction pathway (shown in red) with a lower activation energy. The final result and the overall thermodynamics are the same.

A catalyst is a substance that accelerates the rate of a chemical reaction but remains chemically unchanged afterwards. The catalyst increases rate reaction by providing a different reaction mechanism to occur with a lower activation energy. In autocatalysis a reaction product is itself a catalyst for that reaction leading to positive feedback. Proteins that act as catalysts in biochemical reactions are called enzymes. Michaelis-Menten kinetics describe the rate of enzyme mediated reactions. A catalyst does not affect the position of the equilibria, as the catalyst speeds up the backward and forward reactions equally.

In certain organic molecules, specific substituents can have an influence on reaction rate in neighbouring group participation.

Agitating or mixing a solution will also accelerate the rate of a chemical reaction, as this gives the particles greater kinetic energy, increasing the number of collisions between reactants and therefore the possibility of successful collisions.

Pressure

Increasing the pressure in a gaseous reaction will increase the number of collisions between reactants, increasing the rate of reaction. This is because the activity of a gas is directly proportional to the partial pressure of the gas. This is similar to the effect of increasing the concentration of a solution.

Equilibrium

While chemical kinetics is concerned with the rate of a chemical reaction, thermodynamics determines the extent to which reactions occur. In a reversible reaction, chemical equilibrium is reached when the rates of the forward and reverse reactions are equal and the concentrations of the reactants and products no longer change. This is demonstrated by, for example, the Haber–Bosch process for combining nitrogen and hydrogen to produce ammonia. Chemical clock reactions such as the Belousov–Zhabotinsky reaction demonstrate that component concentrations can oscillate for a long time before finally attaining the equilibrium.

Free energy

In general terms, the free energy change (ΔG) of a reaction determines whether a chemical change will take place, but kinetics describes how fast the reaction is. A reaction can be very exothermic and have a very positive entropy change but will not happen in practice if the reaction is too slow. If a reactant can produce two different products, the thermodynamically most stable one will generally form except in special circumstances when the reaction is said to be under kinetic reaction control. The Curtin–Hammett principle applies when determining the product ratio for two reactants interconverting rapidly, each going to a different product. It is possible to make predictions about reaction rate constants for a reaction from free-energy relationships.

The kinetic isotope effect is the difference in the rate of a chemical reaction when an atom in one of the reactants is replaced by one of its isotopes.

Chemical kinetics provides information on residence time and heat transfer in a chemical reactor in chemical engineering and the molar mass distribution in polymer chemistry.

Applications

The mathematical models that describe chemical reaction kinetics provide chemists and chemical engineers with tools to better understand and describe chemical processes such as food decomposition, microorganism growth, stratospheric ozone decomposition, and the complex chemistry of biological systems. These models can also be used in the design or modification of chemical reactors to optimize product yield, more efficiently separate products, and eliminate environmentally harmful by-products. When performing catalytic cracking of heavy hydrocarbons into gasoline and light gas, for example, kinetic models can be used to find the temperature and pressure at which the highest yield of heavy hydrocarbons into gasoline will occur.