

# Catalytic Chemistry



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**Bruce C. Gates**  
University of Delaware



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# Preface

Most of the chemical reactions in industry and biology are catalytic, and many chemists and chemical engineers work to understand and apply catalysis. Catalysis is involved at some stage of the processing of a large fraction of the goods manufactured in the United States; the value of these products approaches a trillion dollars annually, more than the gross national products of all but a few countries in the world. Catalysis is the key to the efficiency of chemical conversions. In an age of increasingly limited energy and raw materials and concern for the environment, it is needed more and more. The technological needs are matched by the scientific opportunities: new techniques are bringing rapid progress in the understanding of molecular details of the workings of catalysts.

Notwithstanding these needs and opportunities, catalysis remains a neglected subject in chemical education. Students encounter it only as unconnected fragments in chemistry (organic, inorganic, and physical), biochemistry, and chemical engineering. The objective of this book is to integrate the fragments for students at the advanced undergraduate level.

Catalysis is a coherent subject, unified by concepts of chemical structure and reactivity, kinetics, and transport phenomena. It is developed in the following sequence:

**Chapter 1.** Introduction, with definitions and illustrations of catalysis and a brief review of kinetics.

**Chapter 2.** Catalysis in solutions, with emphasis on acid-base and organometallic catalysis. The ideas and mechanisms presented here are a foundation for the remainder of the book.

**Chapter 3.** Catalysis by enzymes. The amazing efficiency of each of nature's catalysts is related to the complementarity between its intricate structure and the structure of its particular reactant.

**Chapter 4.** Catalysis in and on synthetic polymers, ranging from swellable, solutionlike gels to rigid, porous solids with large internal sur-

faces. This chapter provides a transition from catalysis in solution to catalysis involving solids and surfaces.

**Chapter 5.** Catalysis within the molecular-scale cages of zeolites and other molecular sieves. The dramatic effects of shape selectivity at times allow a reversal of the reactivity patterns observed in solution catalysis.

**Chapter 6.** Catalysis on surfaces of inorganic solids, the most important industrial catalysts. This chapter is built on an introduction to the surface science of single crystals and extends to more complicated catalysts, including supported metal complexes, supported metals, metal oxides, and metal sulfides.

The principles are illustrated with catalytic cycles, reaction mechanisms, catalyst structures, and kinetics. The reader is led, with common threads of chemistry, from homogeneous solutions, to the confines of polymeric phases, enzyme pockets, cages, and surfaces. Catalysis is influenced by distributions of reactants and catalysts between phases and by geometric effects associated with groups bonded to catalyst molecules and surfaces. The complications and design possibilities of combinations of catalytic groups and the ideas of multifunctional catalysis are introduced from the beginning, paving the way to the enzymes and the complex surfaces of the solid catalysts used in industrial processes.

The central ideas are chemical, and the physical effects of diffusion, mass transfer, and heat transfer are integrated briefly within a context dictated by the chemistry. Industrial reactions and catalysts are emphasized to illustrate many of the principles, with tables and graphs of data included to provide concreteness and material for examples and problems. The selection of reactions and catalysts is intended to provide a sense of the great accomplishments represented by industrial catalytic processes, including alkylation, hydrogenation, hydroformylation, carbonylation, stereospecific polymerization, ammonia synthesis, ethylene oxidation, propylene ammoxidation, and cracking, reforming, and hydroprocessing of petroleum.

Students who have a foundation of undergraduate organic and physical chemistry and a beginner's familiarity with inorganic chemistry should be able to understand the book. Examples throughout the text and problems at the end of each chapter reinforce and test the student's grasp of the concepts.

This book was developed from notes used in one-semester courses at the University of Delaware (attended primarily by fourth-year students in chemical engineering) and the University of Munich (attended by students in physical chemistry). The Delaware catalysis course is paired with a course in kinetics and chemical reaction engineering, providing most chemical engineering students with their first integration of organic and inorganic chemistry into traditional chemical engineering. The course offers chemistry students an introduction to applied chemistry and some of the concepts of chemical engineering.

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Bruce C. Gates  
Newark, Delaware



## About the Author

**Bruce C. Gates** is the H. Rodney Sharp Professor of Chemical Engineering and Professor of Chemistry at the University of Delaware and has frequently been a visiting professor at the Institute of Physical Chemistry of the University of Munich. His research group is active in the investigation of catalytic hydroprocessing and catalysis by zeolites, superacids, and supported metals and organometallics. Professor Gates is a coauthor of *Chemistry of Catalytic Processes* (McGraw-Hill, 1979) and coeditor of *Metal Clusters in Catalysis* (Elsevier, 1986) and *Surface Organometallic Chemistry: Molecular Approaches to Surface Catalysis* (Kluwer, 1988).

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# Introduction

Nitrogen and hydrogen flow through a tube at high temperature and pressure, but they do not react to give ammonia, although the chemical equilibrium is favorable. When particles of iron are placed in the tube, however, the gases coming in contact with them are converted rapidly into ammonia. Millions of kilograms of this chemical are synthesized every year in such tubular reactors at a cost of a few cents per kilogram. Ammonia is a raw material for nitrate fertilizers needed to feed the world's population. Fertilizers are assimilated by the cells of plants in complex sequences of biological reactions. Further metabolic reactions take place as animals consume the plants, reconstructing their contents to provide energy and molecular building blocks for growth. All these biological reactions proceed under the direction of naturally occurring macromolecules called enzymes; without them, the processes of life could not take place.

What is an enzyme, and what does it have in common with the iron in the ammonia synthesis reactor? Each is a **catalyst**—a substance that accelerates a chemical reaction but is not consumed in the reaction and does not affect its equilibrium. Catalysts cause reactions to proceed faster than they would otherwise, and they can be used over and over again. Catalysts are the keys to the efficiency of almost all biochemical processes and most industrial chemical processes.

How do catalysts work? This book is an attempt to answer the question, but it is already evident from the book's length that there is no simple answer. Nonetheless, it is fitting to begin with an oversimplified answer and to improve upon it along the way: a catalyst provides a new and easier pathway for reactant molecules to be converted into product molecules. By analogy, consider instead of reactant molecules a group of climbers crossing a mountain range, breaking ground slowly over the steep crest. Alternatively, they might be guided rapidly along a less direct pathway, experiencing gentle ups and downs but circumventing the crest and crossing a low pass to reach the opposite valley in a short time. According to this rough analogy, the guidance along this new pathway—

more roundabout and complicated but faster—is provided by the catalyst. The catalyst participates in the reaction by somehow combining with the reactant molecules so that they rearrange into products (and regenerate the catalyst) more rapidly than they could if the catalyst were not present.

*A catalyst is by definition a substance that increases the rate of approach to equilibrium of a chemical reaction without being substantially consumed in the reaction.*<sup>1</sup> A catalyst usually works by forming chemical bonds to one or more reactants and thereby facilitating their conversion—it does not significantly affect the reaction equilibrium.

The definition of a catalyst rests on the idea of reaction rate, and therefore the subject of reaction kinetics is central, providing the quantitative framework. The qualitative chemical explanations of catalysis take the form of reaction mechanisms. These are models of reactions accounting for the overall stoichiometry, identifying the sequence of elementary reaction steps, and (insofar as possible) explaining, in terms of chemical bond strength and geometry, the interactions of the catalyst with reactants.

There are threads of continuity in the book that are provided by the families of catalytic reactions proceeding by similar mechanisms; the mechanisms commonly involve the transfer of ions (often hydrogen ions), electrons, and/or radicals. Catalytic reactions take place in various phases: in solutions, within the solutionlike confines of micelles and the molecular-scale pockets of large enzyme molecules, within polymer gels, within the molecular-scale cages of crystalline solids such as molecular-sieve zeolites, and on the surfaces of solids. This list of phases in which catalysis occurs forms a progression from the simplest toward the most difficult to characterize in terms of exact chemical structure. It also forms the outline of this book. A given catalytic reaction can take place in any of these phases, and the details of the mechanism will often be similar in all of them. Consequently, the next chapter (Chapter 2) concerns catalysis in homogeneous solutions because it is most thoroughly understood. The succeeding chapters build on this platform to explain catalysis in other phases.

A full account of how a catalyst works requires a description of how reactant molecules are transported to the catalyst and of how product molecules are transported away. Because the reactants and products are often concentrated in a phase separate from that holding the catalyst, it is necessary to consider transport between phases by diffusion and convection and to deter-

<sup>1</sup> This definition is close to that given by Wilhelm Ostwald in about 1895: A catalyst is a substance that changes the rate of a chemical reaction without itself appearing in the products. Ostwald's definition allows for negative catalysis, whereby the catalyst slows the reaction. It does not allow any conversion of the catalyst.

Sixty years earlier Jakob Berzelius had coined the term "catalysis" when he recognized that changes in compositions of numerous substances that came in contact with small amounts of various "ferments," liquids, or solids could be classified by a single concept. But his definition turned on undefined "forces" and did not stand the test of time. Many years earlier, alchemists had been aware of the actions of some of these "ferments" and other substances. Their awareness probably encouraged the futile search for a philosopher's stone and a way to turn base metals into gold.

mine how these transport processes affect the rates of catalytic reactions. For example, in the ammonia synthesis, the reactants  $H_2$  and  $N_2$  are concentrated in the gas phase flowing through the reactor, but the catalytic reaction occurs on the surface of the iron particles. Therefore, the rate of the reaction depends not only on what happens on the surface but also on how fast the  $H_2$  and  $N_2$  are transported to the surface and how fast the ammonia is transported away. The reaction occurs on the surface in the steady state at just the rate of transport of the reactants to the surface and the rate of transport of the products from the surface.

Some of the essential ideas defining catalysis can be learned from preliminary consideration of an example. The reaction of ethylene and butadiene in solution to give 1,4-hexadiene is of industrial importance in the manufacture of the polymer nylon. The reaction has been suggested to proceed via the cycle of elementary steps shown in Fig. 1-1. The species entering the cycle are  $H^+$ ,  $NiL_4$  (a complex of Ni with unspecified ligands L), ethylene (symbolized by the double bond,  $=$ ), and butadiene (symbolized by  $\diagup$ ). The species leaving the cycle are the hydrocarbon products, namely, three isomers of hexadiene. At this point it is not important what structures are formed from the reactants and the nickel complex. What is important is that the catalyst is formed from the reactants and the nickel complex and then converted cyclically through the various forms shown in the figure. The nickel is not consumed in the reaction once it has entered the cycle, but is repeatedly converted from one form to another in the cycle as the reactants are converted into products.

Catalysis always involves a cycle of reaction steps, and the catalyst is converted from one form to the next, ideally without being consumed in the overall process. The occurrence of a cyclic reaction sequence is a requirement for catalysis, and catalysis may even be defined as such an occurrence.

One might be tempted to designate  $NiL_4$ , the compound that enters the cycle, as the catalyst for the 1,4-hexadiene synthesis reaction. However, this choice would be arbitrary; any of the nickel compounds shown in the figure could with equal correctness be designated as the catalyst. The ambiguity in catalyst designation is typical, and the identification of one unique catalytic species is usually not possible. Reference to one species as the catalyst is imprecise but common because it is convenient.

Figure 1-1 shows that there is not just one cycle of reactions that converts reactants into products, but several parallel cycles. Many others, some involving nickel and some not, could also be imagined. They are not included because they are not kinetically significant; reaction via these imagined cycles is too slow to matter. A catalyst for a particular reaction always provides at least one pathway for conversion of reactants that is kinetically significant. The catalyst virtually always provides this pathway as a consequence of its becoming chemically bonded to reactants.

An inhibitor slows down a catalytic reaction; a competitive inhibitor slows down the reaction by competing with the reactants in bonding to the catalyst. A very strong inhibitor, one that bonds so strongly that it virtually excludes the reactants from bonding with the catalyst, is called a poison.

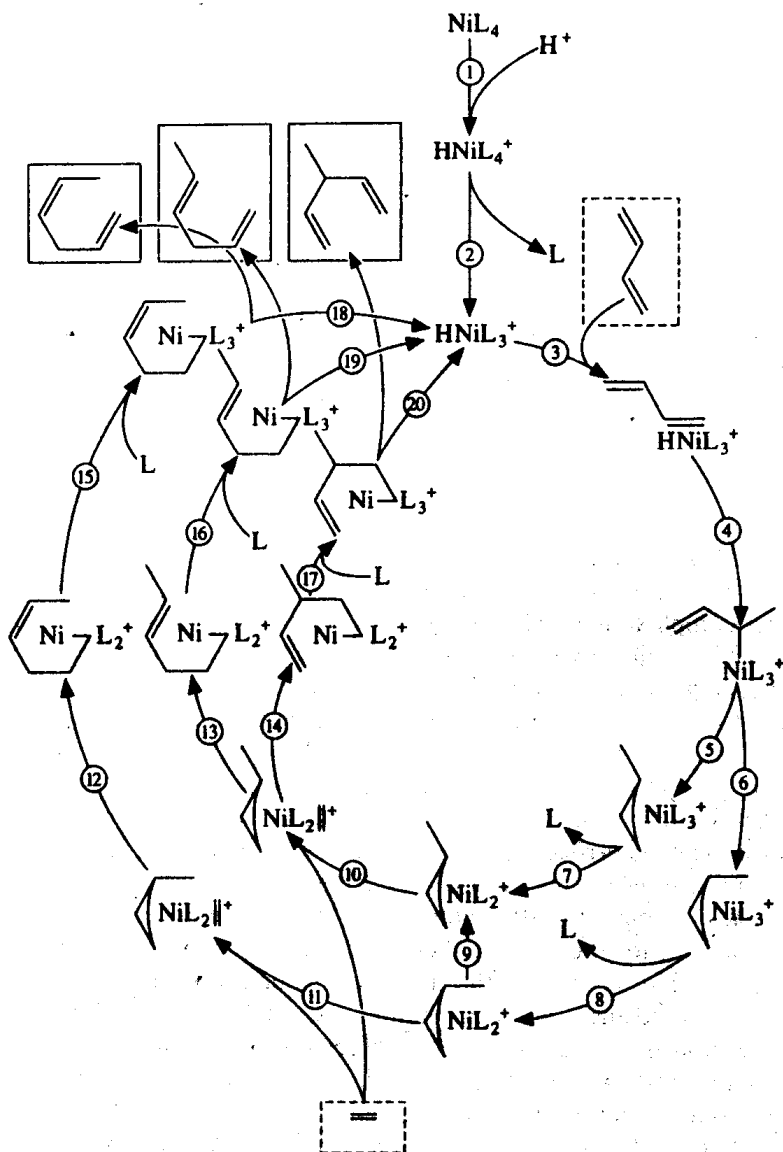


Figure 1-1

Catalytic cycles for the conversion of ethylene and butadiene into 1,4-hexadiene [1].

A quantitative measure of how fast a catalyst works is its **activity**, which is usually defined as the reaction rate (or a reaction rate constant) for conversion of reactants into products. Often products are formed in addition to those that are desired, and a catalyst has an **activity** for each particular reaction. A ratio of these catalytic activities is referred to as a **selectivity**, which is a measure of

the catalyst's ability to direct the conversion to the desired products. For a large-scale application, the selectivity of a catalyst may be even more important than its activity. In practice, catalysts are inevitably involved in side reactions that lead to their conversion into inactive forms (those not appearing in the catalytic cycle). Therefore, a catalyst is also chosen on the basis of its **stability**; the greater the stability, the lower the rate at which the catalyst loses its activity or selectivity or both. A deactivated catalyst may be treated to bring back its activity; its **regenerability** in such a treatment is a measure (often not precisely defined) of how well its activity can be brought back.

The definitions of activity, selectivity, and stability all rest on reaction kinetics, and it is important at the outset to be familiar with some elementary ideas of catalytic reaction kinetics. For illustration, consider the simple catalytic reaction of Fig. 1-2. The overall reaction is an isomerization,  $R \rightarrow P$ , where R and P respectively represent the hypothetical reactant and product, shown in the cycle as  $\boxed{R}$  and  $\boxed{P}$ .<sup>2</sup> The catalyst cycles between two forms: C and a complex incorporating the reactant, RC. (For simplicity, the form of catalyst initially entering the cycle is no longer shown.) Suppose that the following elementary reaction steps take place in the cycle:



This sequence of three steps indicates that the intermediate RC is formed from C and R and decomposes either to give back C and R, or to give C and the isomerized product P. Since each reaction is assumed to be an *elementary step* (or simply a step, i.e., a reaction taking place on the molecular level as written in the stoichiometric equation), the following rate expressions can be written directly from the stoichiometric equations:

$$r_1 = k_1 C_R C_C \quad (1-4)$$

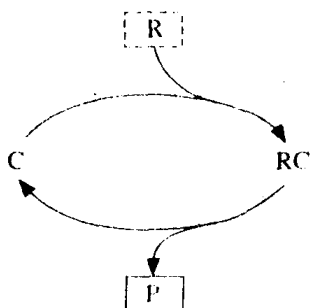
$$r_2 = k_2 C_{RC} \quad (1-5)$$

$$r_3 = k_3 C_{RC} \quad (1-6)$$

Here  $r$  is the rate,  $C$  is concentration, and the  $k$ s are exponentially dependent on absolute temperature according to the Arrhenius relation  $k = A e^{-E_{act}/RT}$ . If the reactions take place in an isothermal batch reactor with a negligible change in volume of reactants, then the reaction rates can be written as rates of change of concentration, for example,

<sup>2</sup> In most of the figures, reactants entering a cycle are indicated with a dashed rectangle,  $\boxed{\phantom{R}}$ , and products leaving the cycle are indicated with a closed rectangle,  $\boxed{\phantom{P}}$ .





**Figure 1-2**  
Hypothetical catalytic cycle for the isomerization  $R \rightarrow P$ .

$$r_1 = -\frac{dC_R}{dt} = k_1 C_R C_C \quad (1-7)$$

$$r_3 = \frac{dC_P}{dt} = k_3 C_{RC} \quad (1-8)$$

The analysis is carried further by application of one of the frequently used simplifying assumptions of chemical kinetics, called the steady-state approximation. Assume that the concentration of the intermediate RC, after a short induction period, achieves a nearly time-independent value, that is,  $dC_{RC}/dt \approx 0$ . This approximation is most nearly correct when the intermediate is highly reactive and short-lived, which implies that  $C_{RC}$  is small.

A mass balance on RC (i.e., a statement of the principle of conservation of mass) gives the following:

$$\frac{dC_{RC}}{dt} = k_1 C_R C_C - k_2 C_{RC} - k_3 C_{RC} \quad (1-9)$$

Invoking the steady-state approximation and rearranging the equation leads to

$$C_{RC} = \frac{k_1 C_R C_C}{k_2 + k_3} \quad (1-10)$$

and, from Eq. 1-8,

$$r_3 = \frac{k_1 k_3 C_R C_C}{k_2 + k_3} \equiv k' C_R C_C \quad (1-11)$$

This result shows that for the simple catalytic cycle of Fig. 1-2, the reaction is first order in the reactant concentration and first order in the catalyst concentration. These dependencies are especially simple and easy to remember. A convenient measure of the catalytic activity is the second-order rate constant  $k'$ , which is identified in Eq. 1-11 as a function of the rate constants of the three elementary steps. Alternatively, the catalytic activity could be