

1

Introduction

1.1 The Beginnings of Catalytic Research

In the second half of the eighteenth century, as scientists were developing an art of chemical experimentation that besides qualitative aspects, also considered quantitative issues and made use of exact measurements and mass balances for chemical reactions, an increasing number of reactions were described that marked the beginnings of catalytic research in chemistry. Table 1.1 provides an overview. At the same time, the first steps toward research into catalysis in biology and physiology were taken. From the beginning of this period, it was already clear that the phenomenon of catalysis encompassed synthesis as well as decomposition reactions, as exemplified by the catalytic formation of water from its elements (oxyhydrogen gas reaction) and the catalytic decomposition of hydrogen peroxide. The establishment of stoichiometry (J. B. Richter, 1792–1793) and the formulation of the law of constant (J. L. Proust, 1799) and multiple proportions (J. Dalton, 1803) were important foundations for recognizing two essential aspects of catalysis, namely that trace quantities of a substance (“substoichiometric quantities”) can induce chemical reactions and that this substance is not consumed by the reaction.

1.1.1 Homogeneously Catalyzed Reactions

Understanding was achieved gradually. Thus, for example, it took 30 years from the observation that boiling potato starch with tartaric and acetic acids formed sugar (1781) before it was understood that the acids were not consumed. In 1801, it was discovered that other acids could also decompose starches. Experiments on the effect of the concentration of the acid led to the finding that ultimately it was water that split the starch and that “. . . ‘boiling for a sufficient length of time’ with water alone must be able to achieve the same goal!” (Döbereiner, 1808). In 1811–1812, it was finally recognized by Kirchhoff and Vogel that the sulfuric acid used in these experiments

Table 1.1 Beginnings of catalysis research in chemistry (adapted from Mittasch [1]).

Year	Author	Discovery
1781	A. A. Parmentier	Saccharification of starches by boiling in acid
1782	C. W. Scheele	Esterification of acids (acetic acid, benzoic acid, . . .) with alcohol in the presence of a mineral acid; saponification
1783	J. Priestley	Conversion of alcohol into ethene and water on heated clay (catalytic dehydration of alcohol)
1796	M. van Marum	Conversion of alcohol into aldehyde on glowing metals (catalytic dehydrogenation of alcohol)
1806	C. B. Desormes, N. Clément	Investigation of the lead chamber process; nitrogen oxides as oxygen carriers for sulfurous acid
1811	G. S. C. Kirchoff	Extensive investigation of starch saccharification by acids and recognition that the acids are not consumed
1812	H. Davy	Recognition that lead chamber crystals (nitrosylsulfuric acid) are of substantial significance in the lead chamber process
1813	L. J. Thénard	Decomposition of ammonia on heated metals, especially iron
1815	J. L. Gay-Lussac	Cleavage of hydrogen cyanide on iron
1816	A. M. Ampère	Hypothesis of alternating formation and cleavage of metal nitrides during ammonia decomposition on metals
1817	H. Davy	Combustion of methane and alcohol on glowing platinum wire
1818	L. J. Thénard	Decomposition of hydrogen peroxide on metals, oxides, and organic substances
1821	J. W. Döbereiner	Oxidation of alcohol into acetic acid on platina mohr (platinum black) at ordinary temperature
1823	J. W. Döbereiner	Inflammation of hydrogen in the presence of platinum sponge at ordinary temperature
1824	J. S. C. Schweigger	Active sites on metal surfaces in processes defined above
1831	P. Phillips	Generation of sulfuric acid through oxidation in air of SO ₂ , yielding SO ₃ , on heated platinum
1833	E. Mitscherlich	“Contact reactions”: Decomposition of H ₂ O ₂ on Pt, Au, . . . and of ClO ₃ ⁻ on MnO ₂ ; formation of ether from alcohol in the presence of acid
1835	J. J. Berzelius	Catalysis: Name assignment and definition

remained unchanged and the significance of the acid concentration for the reaction rate was emphasized, as Döbereiner had previously done (summarized and cited from [2], p. 6).

The production of sulfuric acid by burning sulfur with saltpeter, first in glass vessels and then in lead chambers, had already long been familiar. The lead chamber process was first performed in 1746 without admitting air (Roebuck) and from 1793 onwards with an air supply (Desormes and Clément). In 1806, the latter two then also described the effect of nitrous gases in the lead chamber process as an oscillating transition between two known reactions, namely the oxidation of SO₂ by NO₂ and the reoxidation of NO by O₂. In 1812, Davy described the lead chamber crystals

[(NO)HSO₄] as an intermediate stage. With these two findings, obtained about 200 years ago, it was first recognized that in the course of a homogeneously catalyzed reaction, the catalyst is directly involved in the reaction and opens a reaction pathway that cannot be achieved without it.

Around 1800, it was found that when diethyl ether was produced by distillation of alcohol with sulfuric acid, the acid could be used repeatedly and no component of the sulfuric acid would be contained in the diethyl ether. The opinion prevalent at the time was that sulfuric acid formed ether through its dehydrating action. The formation of ethyl sulfate, which was also observed, was ascribed to a side reaction. In 1828, Hennell characterized it as an intermediate in the formation of ether such that the alternating formation and decomposition of ethyl sulfate gave rise to the continuous formation of ether. Finally, in 1833–1834, Mitscherlich demonstrated experimentally that the dehydrating effect of sulfuric acid is not critical for formation of ether. Mitscherlich concluded that the sulfuric acid “. . . [derives] no ‘advantage’ from the result, so it behaves as an eager, selfless mediator, hence acting purely ‘by contact’;” he generalized that instances of “. . . decomposition and combination that are produced in this way occur very frequently; we will call them *decomposition and combination by contact*” (quoted from [2], p. 30).

1.1.2

Heterogeneously Catalyzed Reactions

In heterogeneous reactions, the special characteristics of catalytic reactions are more apparent. In 1783, Priestley was the first to describe the catalytic dehydration of alcohol, in a process in which alcohol vapor was directed through a heated tobacco pipe. In 1795, Deimann took this as the starting point for systematically studying the influence of the tobacco pipe – which is now known to be the catalyst – on the course of the reaction. He stated that a glass pipe by itself will not induce the reaction, but a glass pipe filled with clay fragments will. The individual components of the clay and other substances were also studied for their ability to dehydrate alcohol.

H. Davy studied the effect of platinum on combustion processes and discovered in 1816 that heated platinum wire, even below the annealing temperature, caused the (flameless!) combustion of methane (and other substances such as hydrogen, ether, alcohol) in air, and the resulting heat caused the wire to glow.¹⁾ In 1818, Erman proved that the oxyhydrogen gas reaction only required the platinum wire to be heated to 50 °C. In 1823, Döbereiner showed that platinum sponge causes a flameless reaction of oxyhydrogen gas at ordinary temperatures, and only a few days later he reported that almost instantaneous inflammation occurs when the hydrogen

1) Davy also invented (in 1815) the safety lamp for coal mines that now bears his name, in which the flame of an oil lamp is separated from the outside air by a narrow-mesh wire cylinder. Later, he incorporated a platinum spiral in his mining lamp. If the lamp was extinguished due to excessive methane content in the air, the spiral began to glow and thus allowed the miners to orient themselves in the dark.

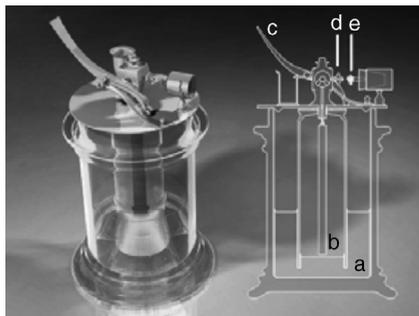


Figure 1.1 Döbereiner's lamp. It corresponds in principle to a Kipp generator filled with sulfuric acid (a), which comes into contact with the zinc rod (b) when the faucet (c) is opened. This produces hydrogen, which is released from the nozzle (d) and ignites on the platinum sponge (e).

is directed onto platinum sponge produced by thermal decomposition of “platinum salmiac” (ammonium chloroplatinate, $[\text{NH}_4]_2[\text{PtCl}_6]$) so that the hydrogen can mix with air beforehand. He stated that “... the spongy powder behaves somewhat like electrical sparks with respect to oxyhydrogen gas” (quoted from [3], p. 20). This is the basis of Döbereiner's lamp (Figure 1.1), which spread rapidly (with almost 20 000 in use by 1828). Döbereiner did not profit financially from the invention.²⁾

In 1813, Thénard extensively studied the decomposition of ammonia on heated metals and found that the most pronounced effect occurred with iron, which in the process changed its appearance, becoming brittle and loose. The cause was later assumed to be the formation of a nitride as an intermediate, which was proven experimentally in 1829. Thénard obtained hydrogen peroxide by treatment of barium peroxide with hydrochloric acid/sulfuric acid in 1818. He then studied the decomposition of H_2O_2 on numerous metals and metal oxides. Ag and Ag_2O (which is reduced to silver) proved the most effective. Even organic materials such as fibrin and various kinds of tissues caused H_2O_2 to decompose. In summary, he expressed that these substances can exert their effects without themselves undergoing a change, and that behind this action is one and the same “force” for all substances, including animal and plant materials.

²⁾ Döbereiner was a professor at the University of Jena, in the Duchy of Saxe-Weimar-Eisenach, from 1810 onwards. He kept the responsible minister of state, J. W. von Goethe (author of *Faust* and other influential works, both literary and scientific), informed of his research, and served him in many ways as an advisor on chemical issues. He also presented him with one of his lighters, and Goethe wrote to Döbereiner “[I] always remember you with gratitude, since every day I have at hand the lighter you so cleverly invented.” (cited from [3], p. 29).

1.2

The Catalysis Definitions of Berzelius and Ostwald

1.2.1

Berzelius' Catalysis Concept

From 1821 to 1847, Jöns Jakob Berzelius (1779–1848) compiled the new results from the physical sciences (physics, chemistry, mineralogy, geology) into annual reports. The reports were presented to the Swedish Academy of Sciences and also translated into German.³⁾ In the chapter on plant chemistry in his 1835 report, covering the year of 1834 (German translation dated 1836), Berzelius points to several of the phenomena mentioned previously and sums them up as follows:

“Thus, it has been demonstrated that many bodies, simple or compound, in solid or dissolved form, possess the property of exerting an influence on compound bodies quite different from conventional chemical affinity, whereby they cause in the body a conversion of the components, without themselves taking part with their components, although this can sometimes be the case.

This is a new force in both inorganic and organic nature of causing chemical activity, that may well be more widespread than previously thought, and whose nature is still hidden to us. If I call it a new force, it is in no way my belief that it should be declared a capability independent of the electrochemical relations of matter; on the contrary, I can only assume that it is a special kind of manifestation of these. As long as their interrelation may remain hidden, however, it will facilitate our research to regard it provisionally as a force of its own, and it will likewise facilitate our proceedings for us to give it a name of its own. Therefore, in order to make use of a derivation well known in chemistry, I will call it the *catalytic force* of the bodies, and will call their decomposition *catalysis*, just as we use the word analysis to indicate the separation of the components of the bodies by virtue of conventional chemical affinity. The catalytic force seems essentially to consist of the property that bodies, by their mere presence, and not by their affinity, are able to awaken affinities that are dormant at this temperature, so that . . .”

In keeping with the conception of the time, a reaction between two “bodies” (modern term: “substances”) presupposed their “chemical affinity.” *Catalysts* were now seen as “bodies,” which thanks to their *catalytic force* triggered reactions (“awaken dormant affinities”), without themselves having “affinities” to the reacting “bodies.” Berzelius referred thereby not only to homogeneously *and* heterogeneously catalyzed reactions, but also included (to use the current term) enzymatically catalyzed reactions.

3) J. Berzelius, *Jahres-Bericht über die Fortschritte der physischen Wissenschaften*, Tübingen (*Jber. Berz.*). From Vol. 21 (1842) *Jahres-Bericht über die Fortschritte der Chemie und Mineralogie*.

Berzelius contrasted the new term “catalysis” (Greek: *κατάλυσις* = dissolution) with “analysis.” In this context, “analysis” meant a reaction induced by “conventional chemical affinity,” while catalysts triggered a reaction by their mere presence.

Berzelius used the concept of catalysis to bring together a group of phenomena that could not be explained within the doctrine of reactions being caused by chemical affinity. Thus, the term was originally purely descriptive, and Berzelius intentionally refrained from attempting to explain the nature of catalysis. Berzelius did call the “catalytic force” a new force, but emphasized that he expected to be able to explain its operation within the framework of his electrochemical theory. Liebig attacked Berzelius several times for his definition of catalysis, with his criticism focusing on the “creation of a new force through a new word that does not explain the phenomenon.”

1.2.2

Ostwald's Definition of Catalysis

In 1850, the physicist Ludwig Wilhelmy (1812–1864) studied the acid-catalyzed inversion of cane sugar and formulated the “law by which the action of acids on cane sugar occurs.” It explicitly defines, for the first time, the chemical rate (reaction rate), which is the foundation of chemical kinetics. An exact definition of the rate of a chemical reaction is a precondition for recognizing the acceleration of a reaction by a catalyst, which is the focus of the “kinetic definition of catalysis” by Wilhelm Ostwald (1853–1932). In recognition of his work on catalysis and for his investigations into the fundamental principles governing chemical equilibria and reaction rates, he was granted the Nobel Prize in Chemistry in 1909.

With the goal of measuring the strength of acids, in the course of his experiments on the influence of acids on the hydrolysis of esters (1883), Ostwald discovered the close relationship between the strength of acids and their catalytic effect. In his experiments on the acid-catalyzed oxidation of hydrogen iodide by bromic acid (1887), he studied for the first time a system in which the reaction ran at a measurable rate even without a catalyst, so “the nature of catalysis is to be sought not in the *inducement* of a reaction, but in its *acceleration*.” In the “*Zeitschrift für physikalische Chemie*” (1894, 15, 705), in a short review of a work by F. Strohmann, Ostwald gave the definition of catalysis that has prevailed ever since:

“... If the referee were confronted with the problem of characterizing the phenomenon of catalysis in general, he would consider something like the following expression as most suitable: **Catalysis is the acceleration of a slow-running chemical reaction via the presence of a foreign substance.**

... It is thus misleading to regard the catalytic action as a force that brings about something that would not occur without the substance that acts catalytically; still less can it be assumed that the latter performs work. It will perhaps contribute to an understanding of the problem if I especially point out that time is not involved in the concept of chemical energy; thus, if the chemical energy relations are given such that

a particular process must occur, then they determine only the initial and final states and the whole series of intermediate states which must be passed through, but in no way the time during which the reaction must occur. **This time depends on conditions that lie outside the two main laws of energetics. . . .**

Ostwald thoroughly summarized the state of knowledge about catalysis in a lecture in 1901. Referring to a homogeneous system that can be transformed into products with lower free energy, he states:

“. . . However, the most secure foundation for general conclusions that we know, the laws of energetics, require that the transformation actually occur. They dictate no numeric figure for the rate that must be adhered to; they only require that this rate not be strictly zero, but rather have a finite value.

In this way, we obtain at once a definition for a catalyst for this case as well.

A catalyst is any substance that, without appearing in the final product of a chemical reaction, changes its rate. . . .

Already in this lecture (1901), and later in his Nobel lecture (1909), Ostwald also pointed out, regarding the theory of catalysis, that:

“. . . none . . . has prospered better than Clement and Désormes' theory of *intermediate reactions*. This is based precisely on the participation of the catalyst in the reactions actually occurring, in the sum of which, however, the catalyst is not directly involved, although the partial reactions contain the catalyst as a major chemical component of the process. . . .”

Such a reaction course was initially only considered for homogeneously catalyzed reactions. At the beginning of the 1920s, Irving Langmuir (1881–1957; Nobel Prize in Chemistry, 1932) showed in his work on chemisorption that intermediate reactions are also of fundamental importance in heterogeneously catalyzed reactions.

At the end of his Nobel lecture Ostwald asserted that “. . . until a way has been found whereby a rate of chemical reaction can generally be calculated in advance . . ., the catalysis problem cannot satisfactorily be answered.” It was not until after Ostwald's death that Henry Eyring (1901–1981) provided an important theoretical foundation for an answer with transition state theory (1935).

Ostwald's insight into the nature of catalysis, which he himself designated his “most independent and successful chemical achievement,” enabled targeted research into the area of catalysis and its deliberate technical application. Ostwald studied the iron-catalyzed synthesis of ammonia starting from the known fact (see Table 1.1) that ammonia passed over weakly glowing iron decomposes into its elements almost completely, and from his recognition that a catalyst only hastens the achievement of equilibrium, and thus accelerates both the forward and reverse reaction in equal measure. In his memoirs, Ostwald wrote that his patent application, submitted in 1900, contained all the basic ideas of the Haber-Bosch process implemented in 1913. However, the lack of reproducibility of the results led Ostwald

to allow his application to lapse. In 1901, a familiar demonstration experiment, in which a glowing spiral of platinum wire continues to glow in a mixture of NH_3 and air with the formation of nitrogen dioxide, served him as the starting point for the “Ostwald process” for synthesis of nitric acid [4], which now meets practically the entire demand for HNO_3 .

Wilhelm Ostwald had established catalysis as the fundamental principle for overcoming kinetic inhibition of chemical reactions, and thus created the preconditions for scientifically-based catalysis research and targeted catalyst development.