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From the Onset to the First Large-Scale Industrial Processes

1.1 Origin of the Catalytic Era

Chemists have always known, even before becoming scientists in the modern term (i.e., during the long alchemist era), how to increase reaction rates by raising the temperature. Only much later on, they realized that the addition to the reaction of a third chemical substance, the catalyst, could give rise to the same effect.

Formerly the word "affinity" was used in chemical language to indicate the driving force for a reaction, but this concept had no direct connection with the understanding of reaction rates at a molecular level.

The first known processes involving reactions in solution accelerated by the addition of small amounts of acids are normally defined today as homogeneous catalysis. Experimental evidence for such processes dates back to the sixteenth century, when the German physician and botanist Valerius Cordus published posthumously in 1549 his lecture notes with the title *Annotations on Dioscorides*.

Valerius Cordus (1515–1544), born in Erfurt, Germany, organized the first official pharmacopoeia (*φαρμακοποιΐα*) in Germany. He wrote a booklet that described names and properties of medicaments, completing and improving the famous pharmacopoeia written by the Roman natural philosopher Pliny the Elder and listing all known drugs and medicaments. In 1527, he enrolled at the University of Leipzig where he obtained his bachelor's degree in 1531. During these years, he was strongly influenced by his father Euricius, author in 1534 of a systematic treatise on botany (*Botanologicon*). Valerius Cordus, after completing his training in the pharmacy of his uncle at Leipzig, moved in 1539 to Wittenberg University. As a young man, he also made several trips to Europe, the last one to Italy where he visited several Italian towns, including Venice, Padua, Bologna, and Rome. There he died in 1544 at the age of only 29 and was buried in the church of Santa Maria dell'Anima.

His role in pharmacy was based on the *Dispensatorium*, a text he prepared in 1546 that, using a limited selection of prescriptions, tried to create order in

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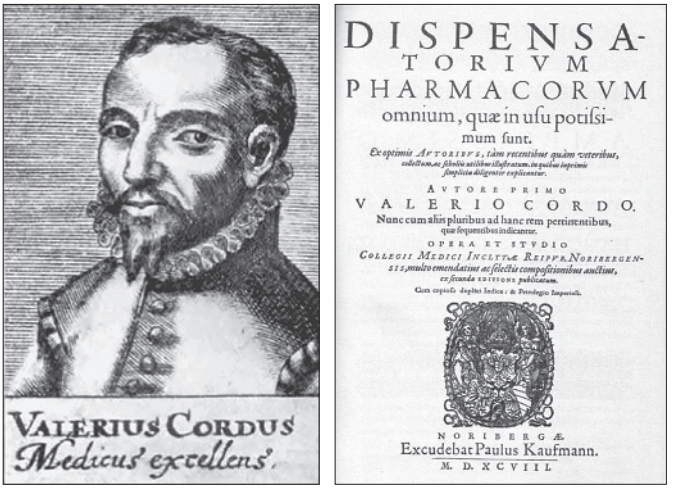


(a) (b)

Figure 1.1 (a) Valerius Cordus, discoverer of ethyl ether formation from ethyl alcohol in the presence of an acid (oil of vitriol). (b) Cover page of *Dispensatorium Pharmacorum*. Images in the public domain.

the unsystematic corpus of medicaments existing at that time. Soon his dispensatory became obligatory for the complete German territory. In 1540 Cordus discovered ether and described the first method of preparing this special solvent in the *De artificiosis extractionibus liber*. Following a recipe imported to Europe from the Middle East by Portuguese travelers, he discovered how to synthesize ethyl ether by reacting oil of vitriol, "*oleum dulci vitrioli*" (sweet oil of vitriol), with ethyl alcohol (Califano, 2012, Chapter 2, p. 40). The synthesis was published in 1548 (Cordus, 1548) after his death and again later in the *De artificiosis extractionibus liber* (Cordus, 1561) (Figure 1.1).

He, of course, did not grasp the fact that the presence of an acid in the solution had a catalytic effect on the reaction. Only at the end of the eighteenth century did chemists realize that a few drops of acid or even of a base added to a solution could speed up reactions in solutions, giving rise to the era of homogeneous catalysis.

The chemical importance of these processes became evident only several years later, when the French agronomist and nutritionist Antoine-Augustin Parmentier (1737–1813) realized in 1781 that the addition of acetic acid accelerated the transformation of potato flour into a sweet substance. Parmentier was known for his campaign in which he promoted potatoes as an important source of food for humans not only in France but also throughout Europe (Block, 2008) (Figure 1.2).

(a) (b)

Figure 1.2 (a) Augustin Parmentier (1737–1813) and (b) Anselme Payen (1795–1871) (images in the public domain). Parmentier discovered the accelerating action of acetic acid in the transformation of potato flour into a sweet substance. Payen attributed the starch transformation induced by few drops of sulfuric acid previously discovered by Constantin Kirchhoff to the concomitant action of a particular biological substance named *diastase*. Thus, we can consider him a true precursor of the modern *enzyme* science (vide infra: Chapter 8).

During the Seven Years' War, while performing an inspection at the first front lines, Parmentier, captured by a Prussian patrol, was sent on probation to the shop of a German pharmacist Johann Meyer, a person who became his friend and had a great influence on his scientific formation. After his return to Paris in the year 1763, he pursued his research in nutrition chemistry. His prison experience came back to his mind in 1772 when he proposed, in a contest sponsored by the Academy of Besançon, to use the potato as a convenient food for dysenteric patients, a suggestion that he soon extended to the whole French population. This suggestion, complemented in 1794 by the book *La Cuisinière Républicaine* written by Madame Mérigot, definitely promoted the use of potatoes as food for the common people first in France and subsequently over the entire continent. In 1772, he won a prize from the Academy of Besançon with memoirs in which he further emphasized the praise of the potato as a source of nutrients (Parmentier, 1773, 1774).

An additional early example of catalytic processes was found by the Russian chemist Gottlieb Sigismund Constantin Kirchhoff (1764–1833) born in Teterow in the district of Rostock, in Mecklenburg-Western Pomerania (Germany), who was working in St. Petersburg as an assistant in a chemist's

shop. In 1811, he became the first person who succeeded in converting starch into sugar (corn syrup), discovering that the hydrolysis of starch in glucose was made faster by heating a solution to which he had added only a few drops of sulfuric acid (Kirchhoff, 1811a, b). This gluey juice was a kind of sugar, eventually named glucose. Kirchhoff showed at a meeting of the Imperial Academy of Sciences in St. Petersburg three versions of his experiments. He apparently discussed the problem with Berzelius who then told the Royal Institute in London about Kirchhoff's experiments, remarking upon the treatment with sulfuric acid.

At the suggestion of Sir Humphry Davy, members of the Royal Institution in London repeated his experiment and produced similar results. It was, however, only in 1814 that the Swiss chemist Nicolas-Théodore de Saussure showed that the syrup contained dextrose.

1.2 Berzelius and the Affinity Theory of Catalysis

The first who coined the name *catalysis* was Berzelius, one of the founders of modern chemistry, in 1836. Born in 1779 at Väversunda in Östergötland, Sweden, although in continual financial difficulties and suffering many privations, he was able to study at the Linköping secondary school and then enroll at Uppsala University to study medicine during the period between 1796 and 1801, thanks to the moral support of Jacob Lindblom, Bishop of Linköping. At Uppsala, he studied medicine and chemistry under the supervision of Anders Gustaf Ekeberg, the discoverer of tantalum and supporter of the interest in the chemical nomenclature of Lavoisier.

He worked then, as a medical doctor near Stockholm, until Wilhelm Hisinger, proprietor of a foundry, discovered his analytical abilities and decided to provide him with a laboratory where he could work on his research on looking for new elements.

In 1807, the Karolinska Institute appointed Berzelius as professor in chemistry and pharmacy. In 1808, he was elected as a member of the Royal Swedish Academy of Sciences and, in 1818, became secretary of the Academy, a position that he held until 1848. During his tenure, he revitalized the Academy, bringing it into a significant golden era (Figure 1.3).

In 1822, the American Academy of Arts and Sciences nominated him as Foreign Honorary Member, and in 1837, he became a member of the Swedish Academy. Between 1808 and 1836, Berzelius worked with Anna Sundström, who acted as his assistant (Leicester, 1970–1980).

Berzelius developed a modern system of chemical formula notation in which the Latin name of an element was abbreviated to one or two letters and superscripts (in place of the subscripts currently used today) to designate the number of atoms of each element present in the atom or molecule.

Figure 1.3 Jöns Jacob Berzelius (1779–1848) (image in the public domain), one of the founders of modern chemistry. He coined the word *catalysis*.

Berzelius discovered several new elements, including cerium and thorium. He developed isomerism and catalysis that owe their names to him. He concluded that a new force operates in chemical reactions, the *catalytic force* (Califano, 2012, Chapter 2, p. 42).

A first attempt to interpret the mechanism of catalysis was made by Berzelius who, in a report to the Swedish Academy of Sciences of 1835 published in 1836 (Berzelius, 1836a), had collected a large number of results on both homogeneous and heterogeneous catalytic reactions that he reviewed, proposing the existence of a "new catalytic force," acting on the matter. In 1836, he wrote in the *Edinburgh New Philosophical Journal* (Berzelius, 1836a):

> *The substances that cause the decomposition of H_2O_2 do not achieve this goal by being incorporated into the new compounds (H_2O and O_2); in each case they remain unchanged and hence act by means of an inherent force whose nature is still unknown… So long as the nature of the new force remains hidden, it will help our researches and discussions about it if we have a special name for it. I hence will name it the catalytic force of the substances, and I will name decomposition by this force catalysis. The catalytic force is reflected in the capacity that some substances have, by their mere presence and not by their own reactivity, to awaken activities that are slumbering in molecules at a given temperature.*
>
> *Berzelius J. J. Quoted by Arno Behr and Peter Neuber, Applied Homogeneous Catalysis, Wiley-VCH Verlag GMbH and &Co KGaA, 2012*

He coined also the word catalysis, combining the Greek words κατά (down) and λύσις (solution, loosening). According to Berzelius a catalyst was a

substance able to start a reaction without taking part in it and thus without being consumed. In his famous paper of 1836 (Berzelius, 1836b), he wrote:

> *the catalytic power seems actually to consist in the fact that substances are able to awake affinities, which are asleep at a particular temperature, by their mere presence and not by their own affinity*.
> Berzelius J. J., the *Edinburgh New Philosophical Journal* XXI, 223, 1836c

In 1839, Justus von Liebig, one of the most important organic chemists of his time, tried an interpretation of catalysis based on the concept that a third body, the catalyst, added to the reactants, although not taking part in the reaction, was able to speed up the process (Liebig, 1839). After a few years, the German physicist and physician Julius Robert von Mayer, in the framework of his studies of photosynthetic processes, developed in 1845 a different interpretation of the catalytic mechanism. Mayer put forward the idea that the catalyst was able to release large amounts of *sleeping energy* that could allow the reaction to break out. Christian Friedrich Schönbein (1799–1868), discoverer of ozone, further developed the idea that the catalyst, without interacting with the reagents, could speed up the reaction producing intermediate products able to open new and faster paths to the reacting molecules. He asserted that a reaction is not a single process but occurs as the consequence of a time-ordered series of intermediate events (Schönbein, 1848). After some years, the German Friedrich Karl Adolf Stohmann (1832–1897) proposed the possibility that a catalyst could release energy to facilitate the reaction. He pointed out that catalysis is a process in which the energy released by the catalyst transforms into the motions of the atoms of the reacting molecules. These in turn reorganize themselves, giving rise to a more stable system by emission of energy (Stohmann, 1894).

The research of Ludwig Wilhelmy (1812–1864) complemented Berzelius's idea of the existence of substances activating the ability of chemical compounds to react. He found that the addition of inorganic acids made the inversion process of cane sugar easier. Augustus George Vernon Harcourt, who discovered the importance of acid catalysis in clock reactions (Shorter, 1980), reached the same conclusion (1834–1919). In 1896, the Scottish mathematician William Esson (1838–1916) interpreted Harcourt's data in terms of a differential equation.

1.3 Discovery of the Occurrence of Catalytic Processes in Living Systems in the Nineteenth Century

In the same period, it became evident that catalytic effects also occur in living systems. Actually, the fact that living organisms contain substances able to facilitate or even trigger chemical reactions was known for a long time, but was never considered the consequence of catalytic processes occurring in the

body. As documented in the chapter 8 devoted to enzymes, the use of yeasts for the production of wine was, for instance, a very old technique, already known to the Bronze Age Minoan and Mycenaean civilizations. The ability of the acid juice contained in the stomach of animals to digest meat and even bones was demonstrated by the French scientist René Antoine Ferchault de Réaumur (1683–1757), and later by the Italian biologist Lazzaro Spallanzani (1729–1799) and by the Scottish physician Edward Stevens (1755–1834).

The occurrence of different mechanisms involving living substances and contributing to orient the course of a reaction was proved by a series of fundamental research at the beginning of the nineteenth century. In 1833, Anselme Payen (1795–1871) and Jean-François Persoz (1805–1868) attributed the starch transformation, discovered by Kirchhoff, to the action of a particular biological substance. They called it *diastase* and further proved that at 100°C it loosed its catalytic activity (Payen and Persoz, 1833).

Anselme Payen studied chemistry at the École Polytechnique under the supervision of the chemists Louis Nicolas Vauquelin and Michel Eugène Chevreul. Besides the discovery in 1833 of the first enzyme (diastase), the synthesis of borax from soda and boric acid and a process for refining sugar can be attributed to him. He also isolated and named the carbohydrate cellulose (Payen, 1838). In 1835 Payen became a professor at the École Centrale and later at the Conservatoire National des Arts et Métiers in Paris. His friend Jean-François Persoz was *préparateur* of Louis Thénard at the Collège de France, before becoming professor of chemistry at the University of Strasbourg. In 1830 he had become director of the École de Farmacie and in 1850 succeeded Jean-Baptiste Dumas at the Sorbonne. Persoz studied the solubility of chemical compounds and their molecular volumes. His collaboration with Payen led to the discovery of diastase and of its presence in human saliva.

In 1835, in collaboration with Jean-Baptiste Biot, he showed how to follow experimentally the inversion of cane sugar, simply observing with a polarimeter the variation of its rotatory power after acidification.

The German Johann Wolfgang Döbereiner (1780–1849), who became famous for his discovery of similar triads of elements that paved the route to Mendeleev's organization of the elements in the famous periodic table, also investigated starch fermentation. In 1822, he was one of the first to observe the fermentative conversion of starch paste into sugar and gave a correct explanation of alcoholic fermentation, finding that starch transforms into alcohol, only after conversion to sugar (Döbereiner, 1822). Döbereiner, son of a coachman, had in his youth a poor education. Despite very poor schooling, he succeeded in attending the University of Jena where he eventually reached the position of professor.

In the field of catalysis, he worked on the use of platinum as catalyst. For his discovery of the action of solid catalysts, he is considered as one of the initiators of heterogeneous catalysis.

In 1877 the German physiologist Wilhelm Kühne (1837–1900), a pupil of several outstanding chemists and physiologists of the time, including Claude Bernard in Paris, isolated trypsin from gastric juice (Kühne, 1877) and coined the word *ἐνζυμων* (enzumon), enzyme, from the Greek, *ἐν* in and *ζυμων* ferment, to describe cellular fermentation.

1.4 Kinetic Interpretation of Catalytic Processes in Solutions: The Birth of Homogeneous Catalysis

The first interpretation of catalytic events at the beginning of the nineteenth century dealt mainly with reactions occurring in solution. At that time the affinity concept dominated the interpretation of chemical processes. This idea, inherited from the alchemist's vision of the interaction between chemical elements or compounds, formally corresponded to the attraction between human beings. This metaphoric explanation of catalysis, however, did not satisfy the members of the new branch of chemical physics, educated by their training in mechanics and thermodynamics to a mechanistic approach toward the interpretation of chemical reactions. The route to this new comprehension of chemical reaction was paved by the pioneering work of Ludwig Ferdinand Wilhelmy (1812–1864), usually credited for publishing the first quantitative study of chemical kinetics.

Wilhelmy, born in 1812 at Stargard in Pomerania, studied pharmacy in Berlin. After a period spent in an apothecary shop, he studied chemistry and physics at Berlin, Giessen, and Heidelberg, where he obtained his PhD in 1846.

In his life Wilhelmy was always an amateur, not bound to the university system. He conducted the largest part of his research in his private house, a villa that he reorganized as his private laboratory. Nevertheless, he was highly respected in the German physical society that he had founded with Heinrich Gustav Magnus (1802–1870). Together with Paul du Bois-Reymond, Rudolf Clausius, Hermann von Helmholtz, and Carl Wilhelm Siemens, he was considered by all his friends as a leader of the young European chemical physics. After traveling chiefly in Italy and Paris, he returned to Heidelberg and became a *Privatdozent* in 1849. He remained at the university for only five years.

In 1850 Wilhelmy, in the framework of a series of polarimetric research, studied the inversion of cane sugar catalyzed by inorganic acids and proved experimentally that this reaction leads to the conversion of a sucrose solution into a 1:1 mixture of fructose and glucose (Figure 1.5). Under the assumption that the initial velocity of the reaction is proportional to the concentration of both

the cane sugar and the acid and counting the time from the moment in which the sugar solution is brought in contact with the acid, Wilhelmy succeeded in describing the time evolution of the process in terms of the differential equation

$$dZ/dt = MZS$$

where Z and S are the amount (concentration) of sugar and acid at time t, respectively, whereas M is a "velocity coefficient," which is constant over a large time interval (Califano, 2012, Chapter 2).

Wilhelmy wrote in his paper that the

> *process is certainly only one member of a greater series of phenomena which all follow general laws of nature*

and that these laws can be expressed mathematically. The time, however, was not yet mature to appreciate the importance of his work, and it remained practically ignored for a long time, until Wilhelm Ostwald, the true father of modern chemical physics, realized its importance and even developed a quantitative analytical method to measure the strength of the acids from their ability to catalyze the sugar inversion.

The English chemist George Vernon Harcourt (1834–1919) complemented Wilhelmy's research (Figure 1.5). In the early 1860s Harcourt embarked on a research project on the rates of chemical reactions. He settled on two reactions for which, during definite time intervals, the amount of chemical change could be accurately measured. In close partnership with William Esson, mathematical fellow and tutor of Merton College, he studied the acid-catalyzed clock reaction of iodide and hydrogen peroxide (Harcourt and Esson, 1866a) as well as the oxidation of oxalic acid with potassium permanganate (Harcourt and Esson, 1866b), showing that the reaction rate was proportional to the concentration of reactants present. Their work for the first time gave detailed treatments of the kinetics of different types of reactions, anticipating several later formulations of equilibrium reactions. In 1912, when they both were well in their seventies, they again collaborated on the effect of temperature on the rates of chemical reactions (Harcourt and Esson, 1913). An interesting outcome of this work is that they predicted a "kinetic absolute zero" at which all reaction ceases; their value of −272.6°C is in remarkable agreement with the modern value of −273.15°C.

The results obtained by Wilhelmy and Harcourt were later formalized by the chemist Peter Waage and his brother-in-law Cato Maximilian Guldberg as the law of mass action (Figure 1.4).

The Norwegian mathematician and chemist Cato Maximilian Guldberg (1838–1902) entered the University of Christiania in 1854. He worked

Figure 1.4 From left to right: Cato Maximilian Guldberg (1838–1902) and Peter Waage (1833–1900) (image in the public domain). They jointly formulated the famous law of mass action concerning the variation of equilibrium in chemical reactions that is the milestone of chemical kinetics.

independently on advanced mathematical problems, and his first published scientific article won the Crown Prince's Gold Medal in 1859. In 1862, he became professor of applied mechanics and professor at the Royal Military College the following year. In 1869, he developed the concept of "corresponding temperatures" and derived an equation of state valid for all liquids of certain types.

His friend Peter Waage (1833–1900) was also born in Norway. He attended the University of Christiania and passed his matriculation examination in 1854, the same year as Guldberg. After graduation in 1859, in 1861 the University of Christiania appointed him as lecturer in chemistry and promoted him professor in 1866. He became Guldberg's brother-in-law, marrying in 1870 one of Guldberg's sisters.

Cato Guldberg and Peter Waage's names normally occur together, not because of their family relations but for their joint discovery in 1864 of the famous law of mass action, concerning the variation of equilibrium in chemical reactions that is the milestone of chemical kinetics.

For a generic reaction

$$\alpha A + \beta B \rightleftarrows \gamma C + \delta D \tag{1.1}$$

the velocity of the direct reaction is equal to that of the inverse reaction, and both are proportional to the concentrations of the reagents, according to the equations

$$v_{dir} = k_{dir}[A]^{\alpha}[B]^{\beta} \text{ and } v_{inv} = k_{inv}[C]^{\gamma}[D]^{\delta} \tag{1.2}$$

where square brackets indicate concentrations. By equalizing the two velocities $v_{dir} = v_{inv}$, they obtained the relationship

$$\frac{[A^{\alpha}][B^{\beta}]}{[C^{\gamma}][D^{\delta}]} = K \tag{1.3}$$

well known to all first-year chemistry students (Guldberg and Waage, 1864).

An important step toward the understanding of the external factors influencing the reaction rates was realized by the publication of papers by Marcellin Berthelot and his student Léon Armand Pean Saint-Gilles (Berthelot and Saint-Gilles, 1862) concerning the kinetics of the esterification reactions of the type

$$RCOOH + R'OH \rightleftarrows RCOOR'$$

for which they demonstrated that the direct reaction rate is proportional to the product of the concentration of the two reactants (Califano, 2012, Chapter 2).

The Parisian chemist, science historian, and politician Pierre Eugène Marcellin Berthelot (1827–1907), author in 1854 of a PhD thesis *Sur les combinaisons de la glycérine avec les acides*, in 1859 became professor of organic chemistry at the École Supérieure de Pharmacie and in 1865 at the Collège de France (Figure 1.5). He was also involved in social and political activities: he was general inspector of higher education in 1876, life senator in 1881, minister of public instruction in 1886, and minister of foreign affairs in 1895–1896.

Berthelot was an adversary of the *vis vitalis* theory supported by Berzelius, the most important chemist of the time, who maintained that the formation of organic substances was controlled by interactions different from those occurring in the inorganic world (Berthelot, 1860). Berthelot proved instead with the synthesis of several hydrocarbons, natural fats, and sugars that organic compounds obey the same laws that control the formation of the inorganic compounds. His opposition to the vitalistic approach and his belief that the organic world was controlled by the same mechanical laws that operate in the universe gave rise to his interests in thermochemistry and calorimetry, producing an enormous number of experiments and two books on these arguments, *Essai de mécanique chimique fondée sur la thermochimie* (Berthelot, 1879) and *Thermochimie* (Berthelot, 1897).

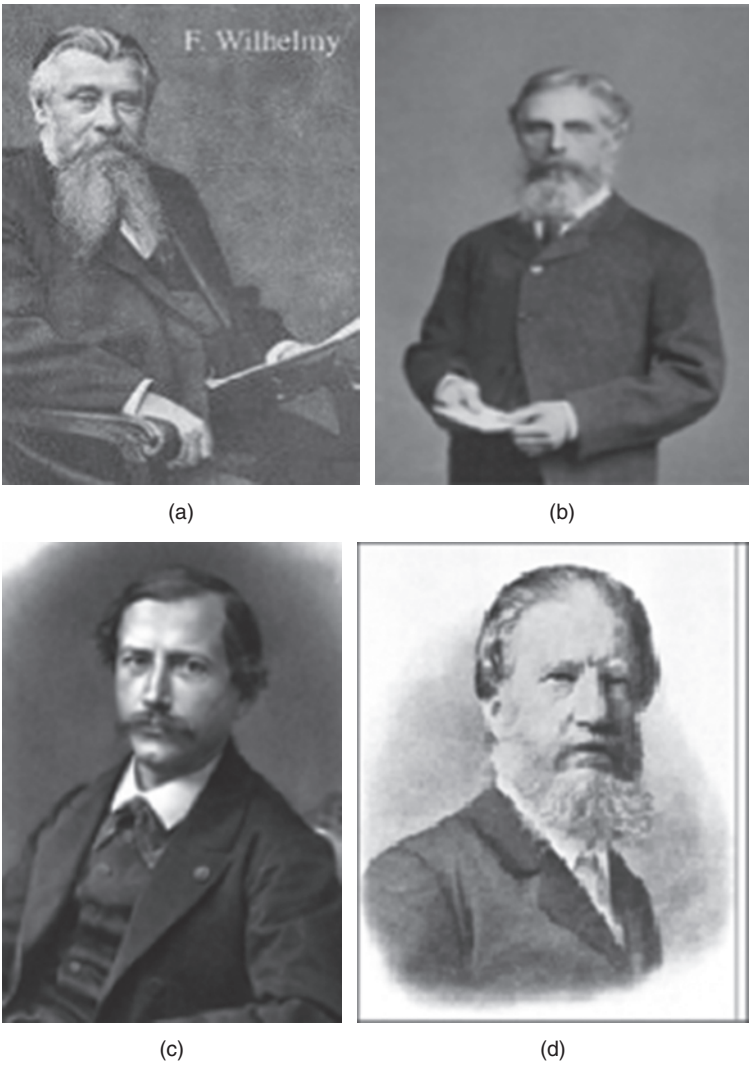


Figure 1.5 (a) Ludwig F. Wilhelmy (1812–1864), (b) George Vernon Harcourt (1834–1919), (c) Marcellin P. Berthelot (1827–1907), and (d) Leopold Pfaundler von Hadermur (1839–1920). They are the main protagonists of the onset of chemical kinetics. *Source*: (a) The Wilhelmy image reuse is free because it is of uncertain source and can be considered as an orphan work. (b) The Harcourt image is in the public domain. (c) Author of Berthelot image (public domain): Magnus Manske. (d) Hardemur image is by courtesy of Oesper Collections in the History of Chemistry, University of Cincinnati.

Berthelot was also convinced that reactions producing heat (exothermic reactions) are spontaneous, whereas those absorbing heat (endothermic) are not. Berthelot's idea, even if plausible, was not correct, since there are spontaneous reactions that are not exothermic as well as reactions proceeding spontaneously and absorbing heat from the external world.

His research on the heat of reaction led him to study the theory of explosives (Berthelot, 1872). In the important book *La chimie au moyen âge* (1893), he wrote the following general reflection about chemistry:

> *La chimie est née d'hier: il y a cent ans à peine qu'elle a pris la forme d'une science moderne. Cependant les progrès rapides qu'elle a faits depuis ont concouru, plus peut-être que ceux d'aucune autre science, à transformer l'industrie et la civilisation matérielle, et à donner à la race humaine sa puissance chaque jour croissante sur la nature. C'est assez dire quel intérêt présente l'histoire des commencements de la chimie. Or ceux-ci ont un caractère tout spécial: la chimie n'est pas une science primitive, comme la géométrie ou l'astronomie; elle s'est constituée sur les débris d'une formation scientifique antérieure; formation demi-chimérique et demi-positive, fondée elle-même sur le trésor lentement amassé des découvertes pratiques de la métallurgie, de la médecine, de l'industrie et de l'économie domestique.*

In a period in which the legacy of the mechanistic philosophers was overwhelming all other theoretical approaches, it was natural to describe kinetic processes in terms of collisions between particles. Already in 1620, at the beginning of the seventeenth century, Bacon (1620; Rossi, 1978) had used the concept of intestine motion to explain chemical processes.

Similarly Franciscus de la Boë, better known as Franciscus Sylvius (1614–1672), professor of medicine in Leyden in 1658, had also suggested to his friend René Descartes that heat might correspond to some kind of "intestine" motion of either the molecules or the underlying ether, a view later supported in 1798 by Count Rumford and in 1799 by Humphry Davy. The discussion of Bacon's vitalistic idea of the "intestine motion" played an important role in the chemistry of that time up to the beginning of the twentieth century.

The association of heat with the translational motions of molecules was, however, due essentially to the development of the kinetic theory of gases (Herzfeld, 1925).

The true origin of the kinetic theory dates back to the eighteenth century to the *Hydrodynamica* published by Daniel Bernoulli in 1738 (Bernoulli, 1738) in which he maintained that gases consist of great numbers of molecules moving in all directions and that their impact on a surface causes the gas pressure.

Despite the attempts made by both John Herapath (1821–1847) (Herapath, 1821) and John Waterston in 1846 (Waterston, 1893), this theory did not attract general agreement until the 1850s. In the second part of the century, it was revived by Krönig (1856) and Clausius (1857) in Germany as well as by Joule (1851) and Maxwell (1860) in England.

A reaction mechanism based on molecular collisions was actually proposed in 1867 by a young Austrian physicist, Leopold Pfaundler von Hadermur (1839–1920), professor at the University of Innsbruck from 1867 to 1881 and then at Graz, where he succeeded Boltzmann (Califano, 2012, Chapter 2, p. 29) (Figure 1.5). He applied Boltzmann's kinetic theory of gases to equilibrium reactions, assuming that the rate of the direct and of the inverse process was the same (Pfaundler, 1867).

At the age of 28, he published his seminal paper on the application of the kinetic theory of matter and heat to chemical reactions. In 1887, he became a full member of the Vienna Academy of Sciences.

Pfaundler was the first to rationalize the law of mass action in terms of the number and frequency of molecular collisions and anticipated significant aspects of both the collision and the transition-state theories of chemical kinetics via his concepts of critical threshold energies and collision complexes. According to him, not all molecules had the same amount of internal and translational energy. Therefore only a limited number of molecular collisions were effective in determining the reaction, either by forming or by dissociating molecules.

Pfaundler was also the first to interpret chemical affinity in pure mechanistic terms, relying primarily on the work of the French chemist Henri Sainte-Claire Deville and his coworkers on the experimental behavior of equilibrium systems of the type

$$\text{Heat} + \text{CaCO}_3(\text{s}) \rightleftarrows \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$$

involving either solid or gaseous dissociation and concerning the general phenomenon of reversible reactions (Sainte-Claire Deville, 1856, 1865, 1869). On the basis of the analogy of the behavior of equilibrium resulting from the thermal dissociation of solids or from the evaporation of pure liquids, he concluded that, just as with vapor pressure, the dissociation increased with increasing temperature and decreased with decreasing temperature (Sainte-Claire Deville, 1866, 1867).

Pfaundler's work remained practically unknown, until it aroused the attention of the German thermochemist Alexander Nicolaus Franz Naumann, professor at the University of Giessen, who extensively quoted it in a review on dissociation phenomena (Naumann, 1867). In 1868 August Horstmann (1842–1929) attempted to quantify Pfaundler's qualitative arguments by using a probability distribution to calculate the change in the degree of dissociation of various vapors as a function of temperature (Horstmann, 1868) and tried to

develop a quantitative theory of dissociation using the kinetic theory of gases (Horstmann, 1873).

Pfaundler's views consequently were criticized after 1870 by several scientists including Horstmann, Pattison Muir (1848–1931) (Pattison Muir, 1885), Bancroft (1861–1953) (Bancroft, 1897), and Pierre Duhem in 1898 (Duhem, 1898), all upholders of a purely thermodynamic approach based on either the maximization of the entropy function or on minimization of the Gibbs free energy. Pfaundler published a rejoinder to Horstmann's critics (Pfaundler, 1876), not fully convincing for the scientific community, including the same Naumann in 1882 who, after a first enthusiastic agreement to Pfaundler's ideas, became disillusioned by 1873 with the kinetic approach, in large part because he felt that it failed to explain why pure solids did not exert a mass action effect.

Finally, the Dutch chemist Jacobus Henricus van't Hoff (1852–1911) mentioned Pfaundler's name in the introduction to the first edition of his *Études de dynamique chimique* of 1884.

The most important representative of the history of science among the critics of Pfaundler was undoubtedly the French philosopher and physicist Pierre Maurice Marie Duhem (1861–1916), an important member of the French cultural milieu of the end of the nineteenth century. In his youth, Duhem was profoundly influenced by his teacher Jules Moutier, an ingenious theorist who had published a number of texts, including *La thermodynamique et ses principales applications*.

In 1882 Duhem enrolled at the École Normale Supérieure where he received a *license* in mathematics and another in physics at the end of the academic year 1883–1884. During the academic year 1884–1885, Duhem presented a doctoral thesis in physics entitled *Le potentiel thermodynamique et ses applications à la mécanique chimique et à l'étude des phénomènes électriques*, which was rejected by the doctoral committee, probably a political decision. The prestigious French scientific publisher, Hermann, published, however, a version of the thesis the following year. At a time when French scientists were predominantly liberal and anticlerical, Duhem was instead openly conservative and deeply religious.

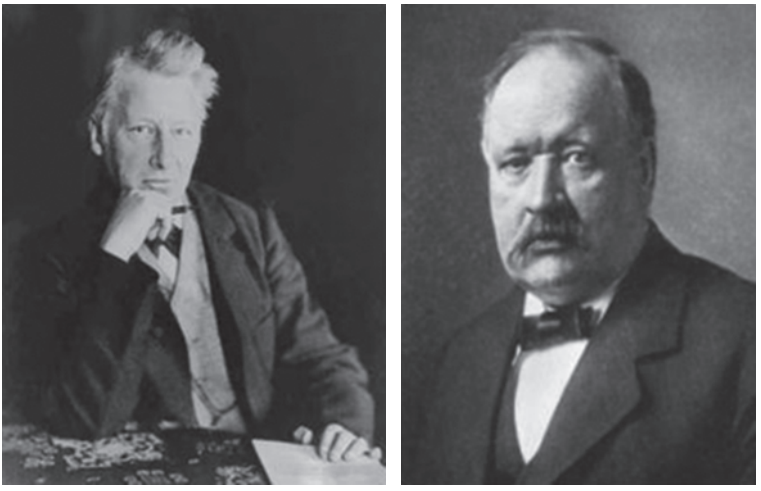
Duhem was one of the first to appreciate the work of Josiah Willard Gibbs, writing the earliest critical examination of Gibbs's *On the Equilibrium of Heterogeneous Substances* in 1887. In the mid-1890s, Duhem published his first essays on the history of science that led him in 1904 to a new understanding of the history of science, considered as a continuity between medieval and early modern science. This path culminated in important historical works such as the *Études sur Léonard de Vinci* and the *Le système du monde*.

The true father of the theoretical approach to catalysis in terms of the kinetic theory developed by Maxwell and Celsius was, however, Jacobus van't Hoff, the first chemist able to assign to chemical physics the structure of the theoretical core of modern chemistry.

Jacobus van't Hoff (1852–1911), after graduation at the Polytechnic of Delft in 1871, studied mathematics at Delft and then attended the laboratory of Kekulé at Bonn and that of Wurtz in Paris. In 1874, he obtained a PhD at Utrecht. In 1876, he was an assistant at the Veterinary College of Utrecht and the following year at the University of Amsterdam. Only in 1878, when already known all over Europe for his theory of the stereochemistry of the carbon atom, he was promoted to the position of professor of chemistry, mineralogy, and geology, a position that he maintained for 18 years until he moved to Berlin as honorary professor and member of the Real Academy of Prussia. A romantic dreamer, lover of music and poetry, van't Hoff was a convinced supporter of the importance of fantasy in scientific research. In the inaugural lecture *Verbeeldingskracht in de Wetenschap* (the power of imagination in science) that he gave at the University of Amsterdam, he defended the role of imagination in scientific investigation.

Trained as an organic chemist, he was one of the first to become interested in chemical physics, thanks to his excellent preparation in mathematics and physics.

Van't Hoff deservedly joined the chemical physics community with the book *Études de dynamique chimique* (1884), in which he faced the problem of identifying the conditions that control the equilibrium of reversible reactions (van't Hoff, 1884a, b) (Figure 1.6).



(a) (b)

Figure 1.6 (a) Jacobus H. van't Hoff (1852–1911), awarded the 1901 Nobel Prize in Chemistry (image in the public domain: author Nicola Persheid), and (b) Svante Arrhenius (1859–1927), awarded the 1903 Nobel Prize in Chemistry (image in the public domain). They formulated the fundamental laws of chemical kinetics.

In 1886 van't Hoff published a new text in French entitled *L'équilibre chimique dans l'etat dilué gazeux ou dissous* (van't Hoff, 1886) that presented his own ideas on the chemical physics of diluted solutions (van't Hoff, 1887).

The equation

$$k = Ae^{-E_a/RT} \tag{1.4}$$

proposed by van't Hoff in 1884 (Califano, 2012, Chapter 2, p. 33) is universally known as the Arrhenius equation, since Svante Arrhenius was the first to offer in 1889 its physical interpretation (Arrhenius, 1889) (Figure 1.6).

Arrhenius suggested that, in order for a reaction to take place, the reacting molecules have to possess energy greater than a limiting value, what he called *activation energy* E_a. At the temperature T, the fraction of molecules possessing a kinetic energy larger than E_a is defined by the statistical distribution law of Boltzmann and is proportional to the factor $e^{-Ea/RT}$. In the Arrhenius equation, the fraction of free energy available to give rise to the reaction is thus only the one superior to the value E_a.

Arrhenius also supplied a convenient graphical method to evaluate k_a. This procedure is normally used to evaluate the activation energy in homogeneous and heterogeneous processes.

Van't Hoff also studied the effect of temperature on the equilibrium constant of reversible reactions and formulated the famous van't Hoff isochore. From this equation, the conclusion can be derived that in a reversible reaction a shift of the equilibrium tends always to compensate the temperature variation. At lower temperature, the equilibrium shifts in the direction that produces heat, whereas a temperature increase produces the opposite effect (van't Hoff, 1898). This conclusion is in reality a particular case of the more general principle formulated in 1885 by the French chemist Le Châtelier (1850–1936) that states that *each system tends to counteract any change imposed from the exterior by minimizing its effect* (Le Châtelier, 1884).

In 1884, van't Hoff laid down the mathematical basis of chemical kinetics, starting from the idea that each reaction is the sum of a series of elementary events in which the molecules collide and give rise to a reaction (van't Hoff, 1884a, b). The probability that the collision gives origin to a reaction is greater than the concentration of the reacting species. In the case of a monomolecular reaction in which the reaction rate depends on the concentration c of a single species, he formulated the differential equation

$$v = -\frac{dc}{dt} = kc \tag{1.5}$$

where k is a constant that he named *rate constant* because it represents the concentration decrease per unit time for a unitary concentration. The analogy between diluted solutions (van't Hoff, 1894) and ideal gases allowed him to extend the second principle of thermodynamics to solutions and to develop

the fundamental relationships controlling the displacement from equilibrium of a reaction with temperature in the form

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \tag{1.6}$$

Integration of this equation allowed van't Hoff to obtain the exponential dependence of the reaction rate constant k (Arrhenius equation) from the inverse temperature.

The dependence of the rate constant on temperature had actually been described even before van't Hoff and Arrhenius by John J. Hood on the basis of his experiments on the oxidation of ferrous sulfate by potassium dichromate (Hood, 1878), but he gave no valid explanation of this effect. As van't Hoff said in the 1884 paper (van't Hoff, 1884a, b),

> *the equilibrium is to be regarded as a result of two changes taking place with the same velocity in opposite directions.*

In 1850 the English chemist Alexander William Williamson (1824–1904) advanced a similar idea, when commenting on the formation of ethers by the reaction of sulfuric acid and alcohols (Williamson, 1850).

Reversible reactions had already been studied by Berthollet in the framework of his research on affinity, reaching the conclusion that chemical reactions do not always proceed up to the end but often reach an equilibrium situation that depends on the amount of reactants involved. Almost at the same time, the Italian chemist Faustino Malaguti (1802–1878) (Malaguti, 1853) also stated that equilibrium is reached when the rates of the two opposite reactions equalize. Malaguti, born near Bologna, joined the University of Bologna where he graduated in pharmacy. Banished for political reasons from Italy, he immigrated to Paris where he became an assistant at the Gay-Lussac laboratory of the École Polytechnique. Malaguti is better known for his research in chemical physics, concerning affinity and chemical equilibria. With this research he anticipated the law of mass action of Guldberg and Waage, who enthusiastically quoted his work.

1.5 Onset of Heterogeneous Catalysis

If van't Hoff played a fundamental role in the development of the theory of reaction rates in solution, no less important was the research of the second man of genius of nineteenth-century chemistry, Wilhelm Ostwald (1853–1932). Ostwald was the leading figure in the study of chemical affinity, who faced the central theoretical question in the chemistry of his time, establishing the theoretical basis of heterogeneous catalysis and even encouraging its industrial applications. Ostwald received the Nobel Prize award in 1909.

At the beginning of the nineteenth century, enough experimental evidence had been already accumulated on the fact that some solid compounds, in particular platinum, could affect the reaction rate without being consumed, that is, they could be true heterogeneous catalysts able to facilitate or even trigger chemical reactions.

Earlier, in 1815, Humphry Davy, during his research that led to the miners' safety lamp, discovered that a combustible gas could be oxidized by atmospheric oxygen on the surface of a platinum wire without the production of a flame and yet with the emission of enough heat to keep the platinum incandescent (Figure 1.7). In 1817, he prepared a platinum sponge able to absorb large quantities of gas and realized that, in the presence of finely divided platinum, alcohol vapors transformed in acetic acid (Davy, 1820). In 1818, the French chemist Louis Jacques Thénard discovered that finely divided Pt favors the decomposition of H_2O_2 into water and oxygen (Thénard, 1818) (Figure 1.7). Furthermore, in 1823, Johann Wolfgang Döbereiner, the German chemist later famous for the theory of triads that gave origin to the periodic system of the elements, noticed that mere contact with Pt powder causes the formation of water from hydrogen and oxygen already at room temperature without alteration of the metal (Figure 1.7).

Döbereiner's experiment (Döbereiner, 1823) attracted the attention of the Italian physicist Ambrogio Fusinieri (1775–1853) who, in the period from 1823 to 1826, researched into the catalytic activity of platinum and suggested that a solid layer of gas adsorbed on the platinum surface was continuously rebuilt as the gas was consumed in the combustion (Fusinieri, 1824). According to him, the platinum catalyst acted like a candlewick with the laminae burning like candle wax. As an explanation of the burning of the concrete laminae, he proposed the concept of "native caloric" (Robertson, 1975). Even Michael Faraday was involved in the study of the catalytic activity of platinum, showing its ability to recombine hydrogen and oxygen obtained from the electrolysis of water (Faraday, 1834). In his monumental paper of 1834, he proposed the idea (increasingly supported since the research of Langmuir) of simultaneous adsorption of both reactants on a platinum surface.

In 1834, he proposed that the reactants have to adsorb simultaneously at the surface but did not offer a reasonable explanation for the process. Later Ostwald gave a more reasonable explanation, suggesting that a catalyst does not influence the thermodynamic equilibrium of reactants and products but only affects the rate of the chemical reactions.

Platinum in the form of wires in sponges became in a few years the most important solid catalyst of the time. In 1824, William Henry, author of the law describing the dissolution of gas in liquids, discovered the inverse process, the one in which ethylene would stop the catalytic action of platinum on the hydrogen–oxygen mixture (Henry, 1824). In 1831, Peregrine Phillips, a vinegar manufacturer in Bristol, England, patented a new process (British

Figure 1.7 (a) Humphry Davy (1778–1829) (image in the public domain), (b) Louis Jacques Thénard (1777–1857) (image in public domain), and (c) Johann Wolfgang Döbereiner (1780–1927) (image in the public domain: authors Carl A. Schwerdgeburth, engraver, and Fritz Ries, painter). Together with Peregrine Phillips, this group of contemporary scientists discovered in the period 1818–1831 the catalytic properties of platinum in gas oxidation (Davy), hydrogen peroxide decomposition (Thénard), hydrogen–oxygen reaction (Döbereiner), and SO_2 to SO_3 oxidation reaction (Phillips).

Patent No. 6096), concerning the instantaneous union of sulfur dioxide with atmospheric oxygen when passing the mixture over platinum heated to a strong yellow heat. Sulfur trioxide formed rapidly when in contact with water to produce concentrated sulfuric acid. In 1838, the French chemist Charles Frédéric Kuhlmann (1803–1881), professor at the University of Lille and owner since 1829 of a chemical company, later merged into the Pechiney–Ugine–Kuhlmann group, producing sulfuric acid, succeeded in transforming nitric oxide into ammonia by using a Pt sponge in the presence of hydrogen. Kuhlmann (1803–1881), born in Colmar, started his scientific career at the University of Strasbourg. Upon arriving in Lille, he gave lectures on chemistry and soon founded a society for the production of sulfuric acid. In a little time, he also started on the production of hydrochloric acid, sodium sulfate, nitric acid, and chlorine in new plants.

In 1863, Henry Debus showed likewise that methylamine is produced when a mixture of hydrogen and hydrocyanic acid is passed over platinum black heated to 110°C (Debus, 1863). A similar reaction, involving the synthesis of benzyl amine, was later suggested by Mendius (1862), normally referred to as the Mendius reaction. Only few years later, in 1874, Prosper De Wilde (1835–1916), professor of chemistry at the University of Brussels, discovered that acetylene could be hydrogenated to ethylene and then to ethane over a platinum catalyst (De Wilde, 1874).

Significant support to the theory of catalysis based on the idea that the catalytic process was due to an adsorption mechanism came from the research of the French chemist Jacques Duclaux (1877–1978). The same idea was held by the French chemist Henri Moissan, who won the 1906 Nobel Prize in Chemistry for his discovery of fluorine, studying in collaboration with Charles Moureu (1863–1929) the interaction of acetylene with finely divided nickel, iron, and cobalt metals (Moissan and Moureu, 1896). He was convinced that acetylene was adsorbed in the metal pores where, by the effect of heat, a pyrolytic reaction took place, creating a mixture of carbon, benzene, and hydrogen.

The following year the French chemist Paul Sabatier (1854–1941), professor at the University of Toulouse, in collaboration with the abbot Jean Baptiste Senderens (1856–1937) proved that Moissan's conclusions were wrong (Califano, 2012, Chapter 2, p. 44), since ethylene in contact with the metal produces ethane and not hydrogen. From this result they deduced that the action of nickel was to catalyze the breaking of the ethylene double bond, in other words to give origin to a true chemical reaction (Sabatier and Senderens, 1897). This result drove Sabatier and Senderens to reach the conclusion that catalysis was not, as maintained by Ostwald, a purely physical process but that finely divided metals were able to absorb large amounts of gas and that this property was very specific, confirming a selective action of a pure chemical nature (Figure 1.8).

Figure 1.8 (a) Jean Baptiste Senderens (1856–1937), (b) Paul Sabatier (1854–1941), and (c) Wilhelm Ostwald (1853–1932) (images in the public domain). They are considered as the originators of catalysis science. Paul Sabatier obtained the 1909 Nobel Prize *for his method of hydrogenating organic compounds in the presence of finely disintegrated metals.* Wilhelm Ostwald received the 1912 Nobel Prize *in recognition of his work on catalysis and on the fundamental principles governing chemical equilibria and rates of reactions*.

Paul Sabatier (1854–1941), born at Carcassonne, entered in 1874 the École Normale Supérieure where he graduated three years later. He then moved to the Collège de France in 1878 as assistant to Berthelot and received the degree of doctor of science in 1880.

He became professor of chemistry in 1884 at the University of Toulouse, a post that he retained until his retirement in 1930. He was ever faithful to Toulouse and turned down many offers of attractive positions elsewhere, notably the succession to Moissan at the Sorbonne in 1908.

Sabatier's earliest research concerned the thermochemistry of sulfur and metallic sulfates, the subject for his thesis leading to his doctorate, and in Toulouse, he extended his physicochemical investigations to sulfides, chlorides, chromates, and copper compounds. He also studied the oxides of nitrogen and nitrosodisulfonic acid and its salts and carried out fundamental research on partition coefficients and absorption spectra.

In 1834, Michael Faraday had proposed the idea that catalytic processes occur on a platinum surface thanks to the simultaneous adsorption process of the reactants (Faraday, 1834). As soon as Sabatier started his investigations into the phenomenon of catalysis, he pointed out anomalies in Faraday's physical theory of catalysis and formulated his alternative chemical theory, postulating the formation of unstable intermediaries.

His subsequent accurate research concerning the use of metal catalysts under very finely divided forms gave rise to modern oil hydrogenation and synthetic methanol industries. He also proved the selectivity of catalytic processes and the sensitivity of catalysts to poisons, introducing the use of supports to enhance the catalytic activity.

Sabatier's work is accurately recorded in the publications of several learned societies. His most important book, *La catalyse en chimie organique* (catalysis in organic chemistry), was first published in 1913, with a second edition in 1920, of which an English translation was published in 1923.

For his method of hydrogenating organic compounds in the presence of finely divided metals, Sabatier was awarded the Nobel Prize in Chemistry for 1912, sharing the prize with Victor Grignard, who received it on account of his discovery of the so-called Grignard reagent. In an interesting paper devoted to the biography of Sabatier and his scientific contributions, Michel Che asked why the Nobel committee did not use the word catalysis in the nomination concerning the Sabatier Nobel Prize in 1912 (Che, 2013).

Paul Sabatier gave with this experiment and with following research (Sabatier and Senderens, 1897) a fundamental contribution to heterogeneous catalysis developing the catalytic hydrogenation technique by which ethylene was transformed in ethane using finely divided nickel as catalyst. Undoubtedly, Sabatier was one of the basic founders of heterogeneous catalysis.

In 1902, Sabatier and Senderens, intrigued by the discovery in 1890 of the reaction between nickel and carbon monoxide made by the German Jewish

chemist Ludwig Mond (1839–1909), also demonstrated that by flowing a mixture of CO and H_2 in the ratio 1:3 in volumes on finely divided nickel at 250°C, there is a 100% yield of methane and water. At higher temperatures, the same kind of reaction occurs with a mixture of carbonic anhydride and hydrogen in the ratio 1:4. This type of reaction became known as the "Sabatier process" (Sabatier and Senderens, 1902):

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O \quad CO_2 + 4H_2 \rightleftarrows CH_4 + 2\,H_2O$$

By 1911 Sabatier reported at length on many hydrogenation and dehydrogenation reactions that could be carried out in the laboratory, and became the leading authority on catalysis. The catalytic hydrogenation method of Sabatier–Senderens gave rise in the period 1906–1919 (Sabatier and Mailhe, 1904; Sabatier and Murat, 1912) to a series of important papers, which were published mostly in the *Comptes Rendus de l'Académie des Sciences* and in the *Bulletin de la Société Chimique de France* (Califano, 2012, Chapter 2, p. 44).

Subsequent research on heterogeneous catalysis extended to the ability of several other elements to catalyze even very complex reactions.

The metals classified by Sabatier as active in hydrogenation (or hydrogen activation) catalysis included not only Pt (the ubiquitous catalyst) but also other finely divided transition metals like Pd, Ni, Fe, and Co (Sabatier, 1913). This observation led to the discovery of the Haber–Bosch and Fischer–Tropsch (FT) processes where activation of hydrogen on Fe and Co catalysts plays a central role. Since Sabatier's time, hydrogenation catalysts with industrial applications (heterogeneous and homogeneous) have been based on these metals, particularly Pt, Pd, and Ni. The official award statement the Nobel Prize, where it mentions that the hydrogenation reactions are carried out on *finely disintegrated metals*, is interesting because the role of surface phenomena in determining the catalytic events is implicit in this expression.

In the book *La catalyse en chimie organique*, Sabatier enounced his famous principle stating that the interactions between the catalyst and the substrate should be neither too strong nor too weak but *just right*. On the one hand, if the interaction is too weak, the substrate will fail to bind to the catalyst and no reaction will take place. On the other hand, if the interaction is too strong, the catalyst is blocked by the substrate or by products that fail to dissociate. This intuition was fully confirmed by the subsequent observations in the twentieth century about the catalytic activity of the metallic elements of the periodic table. In fact, when the bond between the surface atoms and hydrogen is sufficiently weak (as it occurs, for instance, in Pt, Pd, and Ni), hydrogenation of adsorbed olefins occurs at room temperature. By contrast, when the bond between the surface metal atoms and H is too strong, as happens with W, Mo, Cr, Ti, and so on (which form stable hydrides), the catalytic activity is weakened or even absent.

Sabatier was a very reserved man, tied to Toulouse, and indifferent to success to the point that he never accepted a move to Paris to the chair left

vacant in 1907 by the death of Moissan. Nevertheless, when Sabatier became famous after the Nobel award, he attracted, without even understanding why, the displeasure of the abbey Senderens, who believed himself to have been driven out from the official Nobel recognition. In consequence of their misunderstanding, their relationship, which had lasted for more than thirty years, eventually deteriorated.

To end the list of results on the catalytic properties of metals, it is appropriate to recall that in 1884 William Ramsay tried, without success, to react directly hydrogen and nitrogen, using Pt as catalyst. Only 30 years later did Fritz Haber successfully perform this reaction.

The contribution to catalytic science of Wilhelm Ostwald (1853–1932), by far the most important representative of the modern chemical physics, is outstanding and comparable to that of Sabatier (Figure 1.8). Ostwald, born in Riga, graduated from the University of Tartu, Estonia, in 1875, where he received his PhD in 1878 under the guidance of Carl Schmidt. He taught at the Riga Polytechnicum from 1881 to 1887. In 1887, he moved to Leipzig as professor of physical chemistry where he worked for the rest of his academic life with only a short interruption for one term, as exchange professor at Harvard University in 1904–1905.

He started his contribution to catalysis by criticizing severely the Stohmann's ideas on the mechanism of catalysis. He dedicated a large portion of a review of Stohmann's paper published in the *Zeitschrift für physikalische Chemie* (Ostwald, 1894) to his own view of the problem, asserting that the catalyst did not alter the reaction mechanism but simply accelerated its kinetics, lowering the energy barrier necessary to prime the reaction. He maintained that a catalyst does nothing but speed up the reaction, which in any case would have occurred without its presence, although at a much slower rate.

In particular, for gas-phase reactions, Ostwald suggested that the catalytic effect of a metal was due to pure physical processes of adsorption in which the gases entered the cavities of the porous metal where their close contact, combined with local heating processes, favored the reaction. This suggestion does not introduce a clear concept of chemical interaction between the catalyst surface and the substrate. Accordingly, Sabatier and Senderens later developed the fundamental concept of the interaction between the substrate and the catalyst surface.

In 1894, Ostwald synthetically formulated his own definition of catalysis as (Califano, 2012, Chapter 2, p. 43):

> *jeder Stoff, der den Vorgang nicht erst hervorruft, sondern nur einen vorhandenen Vorgang beschleunig*[1]

1 Any substance that does not originate from the process but is only accelerating a previous process.

and in 1901 gave a more precise definition (Ostwald, 1902):

> *Ein Katalysator ist jeder Stoff, der, ohne im Endprodukt einer chemischen Reaktion zu erscheinen, ihre Geschwindigkeit verändert.*[2]

This definition is still valid today. In a short time it gained an enormous influence on the development of the chemical industry. The theory of catalysis was the principal reason for of the Nobel award to Ostwald in 1909 (Califano, 2012, p. 43). The Nobel lecture, delivered by Ostwald at the Royal Academy of Sweden (Ostwald, 1910), effectively confirmed catalysis as one of the fundamental branches of chemical physics. In the Ostwald lecture presentation, Hans Hildebrand, president of the Royal Academy of Sciences, summarized the Ostwald catalysis concept in the following way:

> *catalytic action consists in the modification, by the acting substance, the catalyst, of the rate at which a chemical reaction occurs, without that substance itself being part of the end-products formed*.

In connection with Ostwald's statement, a definition of heterogeneous reaction was emerging referring to the situation where gaseous or liquid reactants passed over the surface of a solid acting as catalysts. As a solid contains an infinite number of atoms, this differentiated the heterogeneous catalysts from the homogeneous parents, where only a discrete number of atoms are usually involved in the catalyst center. This difference cannot be taken too rigidly, since the borderline between the particles of finely dispersed solids and some homogeneous catalysts based on metal clusters is often elusive.

1.6 First Large-Scale Industrial Processes Based on Heterogeneous Catalysts

1.6.1 Sulfuric Acid Synthesis

In term of tonnage, sulfuric acid production, whose importance grew strongly when the production of explosives increased during the First World War, is the first true industrial process. Even today, sulfuric acid is a very important chemical commodity, and indeed, a nation's sulfuric acid production is a good indicator of its industrial strength.

In the nineteenth century, sulfuric acid was produced using lead condensing chambers, invented in 1746 by the English inventor John Roebuck. Together

2 A catalyst is a substance that alters a chemical reaction rate without being part of the final product.

with the Birmingham merchant Samuel Garbett, Roebuck built in 1749 a factory in Scotland, which for several years had the absolute monopoly of the production of this essential component of the industrial revolution in England.

The leaden condensing chambers were then gradually adopted worldwide and became the dominant method for the production of sulfuric acid.

The Anglo-German chemist Rudolph Messel (1848–1920), born at Darmstadt and educated at the universities of Zurich, Heidelberg, and Tubingen, later collaborator of J. C. Calvert and of Sir Henry Roscoe at Manchester, devised, in 1870, a contact process for producing concentrated fuming sulfuric acid (oleum) by passing the vapor of ordinary sulfuric acid over finely divided platinum at red heat (Figure 1.9). A patent was filled by Messel's partner Squire (1875), and the process was made operative, an account being given to the Chemical Society (Messel and Squire, 1876). In 1878, Messel became the managing director of the company known as *Squire, Chapman & Messel Ltd*, holding the position until his retirement in 1915. At that time, some thousands of tons a week were already being produced worldwide by the process he had developed. Messel's multistep process was very complicated because it involved heating sulfuric acid (from the chamber method) in a platinum vessel to decompose it into water, sulfur dioxide, and oxygen, followed by a water-condensing

(a) (b)

Figure 1.9 (a) Rudolph Messel (1848–1920) (image by courtesy of the Society of Chemical Industry) and (b) Clemens Winkler (1838–1904) (image in the public domain). They greatly contributed to the catalytic synthesis of sulfuric acid. Messel developed the contact process for producing concentrated sulfuric acid (oleum) with finely divided platinum. Winkler, discoverer of germanium, proposed the use of platinized asbestos in the production process. *Source*: (a) Reproduced with permission of Anne Pinheiro.

step and a third step where the mixed gases were passed over finely divided platinum to form sulfur trioxide. The final step was the dissolution of sulfur trioxide in sulfuric acid to give oleum.

An innovation came in 1886 when Clemens Alexander Winkler (1838–1904), professor of chemistry and director of the Freiberg School of Mines, proposed using platinized asbestos in a production process (Winkler, 1875) (Figure 1.9). Winkler was a German chemist who discovered the element germanium in 1886, solidifying Dmitri Mendeleev's theory of periodicity.

Winkler, born in Freiberg, entered Freiberg University of Mining and Technology in 1857. Sixteen years later, Winkler was appointed professor of chemical technology and analytical chemistry at the same university.

In 1886 Winkler obtained a new mineral from the Himmelsfürst mine, near Freiberg. The mineral *argyrodite* that was Winkler's start toward finding germanium is now known to be a double sulfide with formula $GeS_2 \cdot 4Ag_2S$.

Mendeleev, in order to insert germanium into the periodic table, suggested that it might be the element *ekacadmium*, the existence of which he had predicted earlier. In contrast, Lothar Meyer favored the identification of germanium with *ekasilicon*, a different predicted element.

Winkler's production process was similar to that previously proposed by Peregrine (1832) employing sulfur dioxide and oxygen in stoichiometric proportions (Cook, 1926). This process represented a significant advance on the ones previously used, since until then experts had attempted to use finely divided metals without the asbestos support. Before 1920 the industrial catalyst for concentrated sulfuric acid production was Pt supported on kieselgur or silica. The important step of the Pt-based contact process is the oxidation of sulfur dioxide to sulfur trioxide following the scheme

$$2SO_2(g) + O_2(g) \rightleftarrows 2SO_3(g)$$

catalyzed by finely divided platinum, here acting as in the Ostwald process of ammonia oxidation as an oxidation catalyst. In other words, Pt is able to activate not only hydrogen (as largely investigated by Sabatier) but also oxygen. The state of oxygen on the Pt surface has since been debated. With the advent, after 1970, of the modern physical and computational methods, the state of oxygen (molecular or atomic) on the surface of platinum or other noble metal surfaces has been clarified. The coexistence of molecular (Gustafsson and Anderson, 2004) and dissociated species on the surface of platinum has been only recently demonstrated (Bocquet, Cerda, and Sautet, 1999). A detailed discussion concerning the experimental and theoretical results can be found in the recent W. F. Schneider and coworkers contribution (McEwen *et al*., 2012).

Only after 1920 the expensive Pt catalyst was substituted by vanadium pentoxide (Thomas, 1970; Farrauto and Bartholomew, 1997; Lloyd, 2011), whose catalytic properties had been discovered several years before (1899) by Charles

R. Meyers. An effective vanadium catalyst for the contact process was developed in 1921 and employed in Germany by the Badische Company (Slama and Wolf, 1921). Today the catalyst consists of vanadium pentoxide supported on a SiO_2-based substrate containing promoters. The surface chemistry of vanadium pentoxide has been the subject of many studies in the twentieth century, and only with the advent of surface science methods was his composition and structure correctly understood.

We will return to the surface structure of active sites in a later chapter, when partial oxidation reactions will be discussed (Weckhuysen and Keller, 2003). This final formulation is the result of continuous trial-and-error investigations and accumulated experience based on the studies of a great number of researchers working in industrial laboratories. The contact process (still relying on supported vanadium pentoxide catalyst) was significantly improved only in 1963 when the Bayer AC announced the first double contact adsorption process that reduced the unreacted SO_2 emissions in the atmosphere.

1.6.2 Ammonia Problem

At the beginning of the twentieth century, sodium nitrate extracted by English companies from existing sediments of Chilean guano was practically the only chemical fertilizer utilized in agriculture. The realization that guano could be exhausted in a few years, coupled with the need for European countries to obtain other sources of nitrogen rich material, had, for some time, prompted applied research groups to produce synthetic ammonia. Ammonia, whose name derived from the ancient Egyptian deity Amun, known to the Greeks as Ammon, is the basic compound for the synthesis of nitric acid and of nitrates of enormous importance not only in agriculture but also in the production of explosives. In the latter years of the nineteenth century, the scientific community was strongly involved in the discussion on what later became known as "the nitrogen problem," earnestly addressed by Sir William Crookes in his speech at the meeting of the British Association for the Advancement of Science in Bristol in September 1898 (Crookes, 1898; Topham, 1955):

> *… all civilized nations stand in deadly peril of not having enough to eat. … the fixation of atmospheric nitrogen is one of the great discoveries awaiting the ingenuity of chemists.*

Crookes was very concerned to show that, owing to the fast rate of increase of the population, the world's supplies of wheat would soon prove insufficient and the land would not continue to produce the same yield year after year, unless adequate quantities of nitrogenous manure were used to fertilize the soil. In a number of European countries, afraid that in the event of war, the Chile nitrates

might well prove to be inaccessible, the need to obtain chemical compounds such as ammonia in large amounts was complemented with a similar demand for supplies of nitric acid in the manufacture of explosives.

The problem of succeeding in the fixation of atmospheric nitrogen became a central one in Europe. Nitrogen fixation is a general term to describe the conversion of atmospheric nitrogen N_2 into a form used by plants. One method to fix nitrogen mimicked the natural fixation of nitrogen by lightning. The process involved subjecting air to a high-voltage electric arc to produce nitric oxide:

$$N_2 + O_2 \rightarrow 2NO(g)$$

The nitric oxide was then converted into nitric acid and combined with limestone to produce calcium nitrate. The problem with this process was that the procedure required large amounts of energy and was economically feasible only when there was a cheap supply of electricity.

In 1828 Michel Desfossés, apothecary at Besançon, conceived the possibility of fixing atmospheric nitrogen through chemical reactions. He observed that mixtures of alkali metal oxides and carbon react at high temperatures with nitrogen. With the use of barium carbonate as starting material, the first commercially used process, developed by Louis Joseph Frederic Margueritte and Alfred Lalouel Sourdeval, became available in the 1860s. The resulting barium cyanide could be reacted with steam-yielding ammonia. In 1898 Adolph Frank and Nikodem Caro decoupled the process producing calcium carbide and then reacted it with nitrogen to obtain calcium cyanamide. They founded the Cyanid-Gesellschaft mbH, which would later become the Bayerischen StickstoffWerke AG (BStW) in Trostberg in southeast Bavaria, where today is located in the Trostberg Chemical Park, home for the three major companies AlzChem, Badische Anilin und Soda Fabrik (BASF), and Evonik–Degussa. The Frank–Caro process dominated the industrial fixation of nitrogen until the discovery of the Haber process in 1909.

Another way to fix nitrogen is the synthesis of ammonia. The conversion of hydrogen and nitrogen into ammonia had been studied since the mid-1800s, but serious work on the subject did not occur until the turn of the century.

In 1901 Henry Le Châtelier made the first attempt to produce ammonia by subjecting a mixture of hydrogen and nitrogen to a pressure of 200 atmospheres and a temperature of 600°C in a heavy steel bomb (Le Châtelier, 1936) (Figure 1.10). Contamination with oxygen led to a violent explosion, and Le Châtelier abandoned his attempts to synthesize ammonia. Toward the end of his life, Le Châtelier said (van Klooster, 1938):

> *I let the discovery of the ammonia synthesis slip through my hands. It was the greatest blunter of my scientific career*.

At the beginning of the twentieth century, the fear of shortage of Chile's guano convinced many European scientists to help in finding solutions for

Figure 1.10 (a) Henry Le Châtelier (1850–1936), (b) Fritz Haber (1868–1934), (c) Carl Bosch (1874–1940), and (d) Paul Alwin Mittasch (1869–1953) (images in the public domain). They are the protagonists of the ammonia synthesis under high pressure. The first attempt to perform the synthesis under high pressure is attributed to Le Châtelier. Haber (1918 Nobel Prize) was the first to succeed in performing the reaction. Bosch (1931 Nobel Prize) and Mittasch developed the catalysts of the industrial Haber–Bosch process.

their countries' long-term needs. One such man was botanist Wilhelm Pfeffer (1845–1920), professor at the University of Bonn who in 1901 expressed his concern about the need for supplies of fixed nitrogen (Pfeffer, 1887) to his friend Ostwald who at this time was investigating the effects of catalysts on chemical reactions. Ostwald's response was immediate; it was obviously his duty as a chemist to play his part in making his country independent of Chile saltpeter and in obtaining nitric acid from other sources.

1.6.3 Ammonia Oxidation Process

Ostwald, in the initial years of the twentieth century, decided to give his attention to the oxidation of ammonia to nitric acid since he was aware of the fact that Charles Frédéric Kuhlmann had already discovered such a process by passing a mixture of ammonia and air over platinum sponge heated to about 300°C in a glass tube. In 1838 Kuhlmann had also filled a patent application for this invention. In the course of a paper presented to the Société des Sciences of Lille in the same year, Kuhlmann made these prophetic remarks:

> *If in fact the transformation of ammonia to nitric acid in the presence of platinum and air is not economical, the time may come when this process will constitute a profitable industry and it may be said with assurance that the facts presented here should serve to allay completely any fears felt by the government on the difficulty of obtaining saltpetre in sufficient quantities in the event of war.*

It was, however, clear to Ostwald that the theoretical basis of the ammonia oxidation reaction had to be well clarified before its industrial organization could be planned on a large scale. He thus decided to convince his private assistant and later his son-in-law, Eberhard Brauer, to work on this problem. In the first experiments, ammonia and air were passed over the catalyst (platinized asbestos) in known quantities and with known velocities, and it was at once clear that the conversion to nitric acid was practicable. A new apparatus and systematic variations of reaction conditions (gas velocities, ammonia–air ratio, and catalyst temperature) finally gave a conversion of 85%. Thanks to this systematic investigation, the foundations of the technical process for producing nitric acid from ammonia were laid on a solid basis in 1902, since then known as the Ostwald–Brauer process. The translation from idea to practice presented many problems before the project became economically convenient. The main problem of the original Ostwald–Brauer process was the large amount of platinum necessary to carry out the reaction. Very soon, however, Karl Kaiser at the Technische Hochschule in Charlottenburg patented the utilization of platinum gauzes that gave much better yields. Furthermore addition of small quantities of rhodium to platinum improved the catalyst activity. A small factory was

available to Ostwald and Brauer, and here a pilot chemical plant became operative. Ostwald filed patents for his procedure in 1902, although his German patent was disallowed because of Kuhlmann's earlier disclosures of more than 60 years before (Califano, 2012, Chapter 2, p. 43).

The later date of 1908 is often reported for Ostwald's patent starting time, probably because of the unavoidable bureaucratic delays to make it operative or perhaps because only by then was the Fritz Haber ammonia synthesis (Haber and Le Rossignol, 1910) really effectual and the ammonia price became acceptable.

1.6.4 Ammonia Synthesis

The problem of ammonia synthesis from atmospheric nitrogen found a practical solution in 1908 when the German chemist Fritz Haber, professor at the University of Karlsruhe, discovered the catalytic procedure for the synthesis of ammonia from hydrogen and atmospheric nitrogen (Figure 1.10).

Before describing the ammonia synthesis from H_2 and N_2 discovered by Haber following the reaction

$$N_2 + 3H_2 \rightarrow 2NH_3$$

it is appropriate to summarize the state of the knowledge concerning the industrial production of H_2 whose purity is essential for the ammonia synthesis process. In the first years of the twentieth century, hydrogen was obtainable from the coal gasification when steam is put in contact with incandescent coke (at about 1000°C) following the reaction

$$C + H_2O \rightarrow CO + H_2$$

As CO is a poison for the catalysts used in the ammonia synthesis, liquefaction or copper liquor scrubbing was used to remove it from the ($CO + H_2$) gas mixture. Both methods are, however, not applicable to large-scale production. A catalytic process was consequently needed to remove the CO from the mixtures. In 1914 Bosch and Wild (Bosch and Wild, 1914) discovered that oxides of iron and chromium could convert a mixture of steam with CO into CO_2 at 400–500°C, according to the reaction in the gas phase (water gas shift reaction)

$$CO + H_2O \rightarrow CO_2 + H_2$$

a process generating additional hydrogen for the Haber process. The water gas produced from the carbonaceous source by steam reforming was passed over the iron–chromium catalyst to convert the CO to CO_2 by the water gas shift reaction. Iron-based catalysts are still used today industrially to transform CO to CO_2 by the water gas shift reaction even if other catalytic systems are also employed.

In modern times the H_2 production is based nearly exclusively on methane, following the Ni-catalyzed process

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

Fritz Haber (1868–1934), born in one of the oldest Jewish families of Breslau, studied chemistry in the period 1886–1891 first at the University of Heidelberg in Bunsen's laboratory, then at the University of Berlin under A. W. Hoffmann, and finally at the Königlichen Technischen Hochschule in Berlin, Charlottenburg (today the technical University of Berlin) under Carl Liebermann. There he obtained his PhD (Haber, 1891). After completing his PhD thesis, he decided to start a university career in chemistry under the supervision of Ludwig Knorr at Jena. In 1894, he obtained a position as an assistant professor of Hans Bunte at the Technische Hochschule of Karlsruhe. In 1898, he published his treatise on electrochemistry *Grundriss der technischen Elektrochemie auf theoretischer Grundlage* and started the study of reduction processes at the cathode.

At the beginning of the twentieth century, Haber was already well known for his papers on the combustion of hydrocarbons (Haber and van Oordt, 1904) and for his research in electrochemistry and thermodynamics. For these he obtained in 1906 the position of professor of chemical physics and electrochemistry at the University of Karlsruhe. In 1911, he succeeded as director of the Institute for Physical and Electrochemistry at Berlin-Dahlem, where he remained until 1933.

The biography of Haber is significant owing to its connection with the tragic German history between the two world wars. Haber was of Jewish origin and a patriotic German proud to serve the German homeland during the World War I. As a chemist, he was assigned to the section for the preparation of poisonous gases where he became leader of the teams developing chlorine gas and other deadly gases, despite the proscription by the Hague Convention of 1907, to which Germany was a signatory. In particular, he was indirectly involved in the creation of Zyklon (a compound used in Auschwitz–Birkenau and Majdanek extermination camps during the Nazi regime). He also participated in the production of the grünkreuz gas, a variation of "mustard gas," invented in France in 1854 by the pharmacist Alfred Riche (1829–1908) and better developed by another Nobel Prize winner, the French chemist Victor Grignard of the University of Nancy. Due to the involvement of Haber in the warfare program and in the development of poisonous gases, it is thought that his wife, Clara Immerwahr, a brilliant chemist and the first woman to receive a doctorate from Breslau University, was so deeply hurt that she committed suicide in May 1915. On the same day the German patriot Fritz Haber, although seriously heartbroken by his wife's tragedy, traveled to the Eastern Front. In the new Germany of the Weimar Republic, Haber continued to strive patriotically, but he was forced to witness the growth of vicious anti-Semitism, spreading around

him and, by the early 1930s, realized that his patriotism had no more place in Germany. In 1933, the Nazi race laws compelled nearly all his staff to resign.

Rather than agreeing to this, Haber himself resigned. Sir William Pope then invited him to go to Cambridge, England, and there he remained for a while. He suffered, however, for some time from heart disease and, fearing the English winter, moved to Switzerland, where he died on January 29, 1934, at Basel. The personal history of Haber is relatively common among scientists. In fact, in the period between the two world wars and even beyond, many scientists (chemists and physicists) faced the contradiction between patriotic and humanitarian behavior.

In 1908, he discovered the direct synthesis from N_2 and H_2, a chemical process that has virtually changed the economy of the world, making it possible for the production of millions of tons of fertilizers. Haber succeeded in reacting hydrogen with nitrogen, one of the less reactive existing gases, using a catalyst based on finely dispersed osmium and uranium at a temperature of about 500°C and a pressure of about 150–200 atmospheres. The collaboration of Haber with the British chemist Robert Le Rossignol (1884–1976) from University College London was essential for the realization of the ammonia synthesis. Le Rossignol worked in Germany in the period 1908–1909 with Haber and was instrumental in the development of the high-pressure devices used in the Haber process, eventually producing a tabletop apparatus that worked at 200 atmospheres pressure (Haber and Le Rossignol 1907, 1908a, b). Le Rossignol was interned in Germany in 1914 at the outbreak of the World War I, but was released to work for the industrial firm Auergesellschaft during the war. Le Rossignol returned to the United Kingdom after the war.

Haber was awarded the 1918 Nobel Prize in Chemistry (awarded in 1919) for his discovery that virtually "made bread from the air" and recognized the assistance received from Le Rossignol, whose name appears on Haber's patents for the process.

In 1910, BASF purchased the Haber initial process and charged one of his best chemists, Carl Bosch and his assistant Paul Alwin Mittasch (1869–1953), to transform it into a large-scale industrial process (Figure 1.10). Haber's catalysts were, however, too expensive and not sufficiently stable to be utilized at an industrial level. Bosch and Mittasch therefore conducted a systematic research of possible catalysts at BASF, covering practically the full periodic system and in two years reached the conclusion that finely dispersed iron with the addition of few percent of alumina and small quantities of potassium and calcium supplied an excellent catalyst, well reproducible, and with a long-lasting lifetime (Haber, 1922). The BASF chemists also solved the problem of a reactor able to work without risks at high temperature and pressure and developed the necessary methods of purification of hydrogen and nitrogen. The intensive collaboration between Haber and Bosch made possible the large-scale commercial

production of ammonia. As the war between Germany and the other big world powers began, several European countries were excluded from the possibility of importing guano from South America, since England had complete control of the oceanic routes as well as of the Chilean and Peruvian sediments. The Haber process became therefore of fundamental importance, and Germany would not have been able to afford to continue the war without the massive production of ammonium nitrate that was realized thanks to the BASF plants built with the advice of Fritz Haber and the direction of Carl Bosch.

The first "Stickstoffwerke" became operative at Oppau, in Germany in 1913, with a production of 30 tons of ammonia per day, and a larger plant at Leuna, in Saxony, East Germany, soon followed. Leuna is today the center of the great German synthetic chemical industry. Bosch became managing director of BASF in 1919 and in 1925 was nominated director of the IG Farbenindustrie Aktiengesellschaft and in 1935 general director of the IG Farbenindustrie.

Another German industrial chemist who played a basic role in the development of high-pressure devices for the ammonia synthesis was Friedrich Bergius (1884–1949). He studied first at the University of Breslau in 1903 and then at the University of Leipzig where he received a PhD in chemistry in 1907, under the supervision of Arthur Rudolf Hantzsch. In 1909, Bergius worked with Fritz Haber and Carl Bosch at the University of Karlsruhe in the development of the Haber–Bosch process. The collaboration with Haber and Bosch was of extreme importance for his development as a real expert of high-pressure catalytic processes, to the point that by 1913 he succeeded in developing a new and original method of production of liquid hydrocarbons for use as synthetic fuel by hydrogenation of high-volatile bituminous coal lignite at high temperature and pressure. Lignite has a high content of volatile matter, which makes it easy to convert into gas and liquid petroleum products. Together with Carl Bosch, he won the Nobel Prize in Chemistry in 1931 in recognition of their contributions to the invention and development of chemical high-pressure methods.

Both Bosch and Mittasch continued their research of catalytic synthesis at the industrial level. Strangely enough the Nobel committee ignored Paul Mittasch, who had given fundamental contributions to the high-pressure catalytic synthesis. Carl Bosch was critical about Nazi policies and for this reason was gradually relieved from his high position, falling into despair and alcoholism. He died in Heidelberg.

Beside the Haber–Bosch process, other processes based on the same catalysts were developed in Italy and France in the period 1920–1930 (Ammonia Casale, Fauser–Montecatini, and Claude processes).

Luigi Casale (1882–1927), an Italian chemist and industrialist, who developed a new process for the synthesis of ammonia, founded the Ammonia Casale Company.

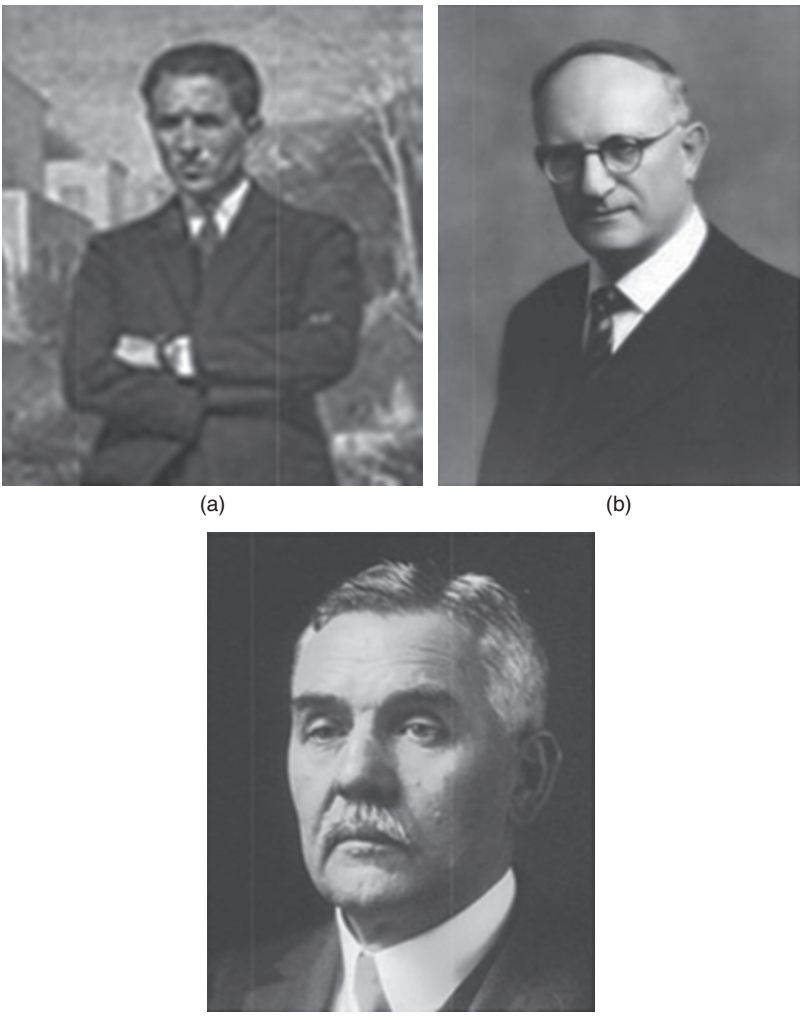
Casale graduated at the University of Turin where he spent the initial years of his career as assistant professor in the Institute of Chemistry. Then he visited

for a year the laboratory directed by Nernst at the University of Berlin, where he studied the engineering aspects of the ammonia synthesis. Back in Italy in 1919, he constructed the first plant for the synthesis of ammonia based on an innovative design. This plant, located at Rumianca site in Domodossola, operating at pressure different with respect to that of BASF, produced 200 kg/day of NH_3. In 1921 he founded the Società Ammonia Casale, the founding company of the Casale Group, which is one of the oldest companies active in the field of synthetic ammonia production, established in Lugano (Switzerland). The Casale process was in direct competition with the Haber–Bosch process, developed at BASF. Contrary to the BASF process, Casale's was the only one offered on the market, and this secured a substantial success at the time, which continues to this day.

In the same period the Fauser–Montecatini company developed another process, carrying the name of Giacomo Fauser (1892–1971) (Figure 1.11). This industrial researcher of Swiss origin, after graduation at the Politecnico of Milano, had the chance to visit the BASF plant in 1919. When he returned to Italy, he proposed a new process characterized by lower operation pressures and temperatures with respect to the Haber–Bosch one. He constructed a pilot plant in Novara producing 90 kg/day NH_3. This achievement attracted the attention of Guido Donegani, president of the Società Generale Montecatini, who promoted the construction of a new larger plant. For this reason the process was patented as Fauser–Montecatini. Both the Casale and Fauser–Montecatini processes are now adopted in numerous plants, worldwide.

For his contribution to ammonia synthesis, Guglielmo Marconi made Giacomo Fauser in 1935 a member of the Italian *Consiglio Nazionale delle Ricerche*. In 1957 he became also a member of the *Accademia Nazionale dei Lincei*.

In France, Georges Claude (1870–1960) started working on an ammonia process in 1917 (Figure 1.11). Besides ammonia synthesis, Georges Claude is known for his early work on the industrial liquefaction of air in the invention and commercialization of neon lighting. Following Linde, Claude had been expert in separating air from its components by cooling to low temperatures (liquefaction of air) since 1896. Claude established Air Liquide in 1902 and built a number of oxygen plants in France and other countries in the following years. In 1919 he constructed the first ammonia plant. Air Liquide and Saint-Gobain established the Société de la Grande Paroisse Azote et Produits Chimiques for the development and exploitation of the Claude ammonia process. Considered by some to be the *Edison of France*, he was an active collaborator of the German occupiers of France during World War II: for this reason he was imprisoned in 1945 and stripped of his honors. To end the chapter devoted to ammonia synthesis, it can be added that after the war, the original patents from BASF, Casale, Fauser–Montecatini, and Claude expired,



(a) (b)

(c)

Figure 1.11 (a) Luigi Casale (1882–1927), (b) Giacomo Fauser (1892–1971), and (c) Georges Claude (1870–1960) (images in the public domain). They developed the first commercialized ammonia synthesis processes other than the Haber–Bosch process. *Source*: (a) Courtesy of Casale SA.

and new competitors came on the market. However, the catalyst formulation did not change substantially.

The problems of the ammonia synthesis mechanism and of the atomic or molecular structure of adsorbed nitrogen have been at the origin of stimulating scientific debate for several decades. The debate has seen the confrontation of two hypotheses. The first hypothesis on the mechanism of the ammonia synthesis requires as a starting point the dissociation of the N_2 molecules into adsorbed N atoms that can be successively hydrogenated into the final products. The rate of the N_2 dissociation is determined by the height of the potential barrier. In addition the interaction of the N atoms on the catalyst surface should be sufficiently weak (following the Sabatier intuition) to allow the creation of new empty sites on the surface where fresh N_2 molecules can dissociate. Hydrogen also needs to dissociate, but this reaction is fast and hydrogen binds more weakly to the surface than nitrogen.

An alternative mechanism was based on the hypothesis that N_2 is adsorbed in molecular form and is progressively hydrogenated with the formation of hydrazine-type intermediates followed only at the end by the formation of ammonia. The hypothesis of a role of a molecular form received a substantiated credit by the isolation in the second half of the twentieth century of molecular complexes where N_2 is end bonded or bridged to metal centers (Allen and Senoff, 1965; Fryzuk and Johnson, 2000).

Due to this controversy, the challenging problem of the state of N_2 on the catalyst did not escape the attention of the surface scientists and theoretical chemists operating in the last quarter of the twentieth century when new physical and computational methods became available. While the contribution of classical surface science methods will be thoroughly described when the G. Ertl (2007 Nobel Prize) results are illustrated, we anticipate that the computer modeling results, in particular those from Christensen and Nørskov (2008), have confirmed Ertl's model.

As for the catalyst is concerned, it can be underlined that only about 80 years later the industrial production of ammonia partially switched to the utilization of ruthenium instead of iron-based catalysts (the Kellogg Advanced Ammonia Process (KAAP)) because ruthenium is a more active catalyst and allows milder operating pressures.

The mechanism of the synthesis on Ru surfaces has also been studied with computational methods (Christensen and Nørskov, 2008). It has been confirmed that N_2 dissociates on the surface and that the most active sites are those where the two N atoms originated from the dissociation of a N_2 molecule are stabilized by bonding to five atoms on the surface. One N atom is bound to three Ru atoms, whereas the other N atom is bound to two. None of the Ru atoms within the active site are bound to more than one N atom at a

time. This gives stronger Ru–N bonds, resulting in a more stabilized transition state. Successive molecular beam experiments on the dissociation probability of N_2 on Ru surface confirmed these conclusions (Murphy *et al*., 1999). Bjørk Hammer, professor of physics and astronomy at the Aarhus University in Denmark, and his group predicted this mechanism by density functional theoretical calculations (Mortensen *et al*., 1997) in the framework of a research project on the factors determining the reactivity of simple molecules adsorbed on metallic catalysts (Kratzer, Hammer, and Nørskov, 1996a, b; Kinnersley *et al*., 1996).

The rate of ammonia synthesis over a nanoparticle of ruthenium catalyst was computed recently by a quantum chemical treatment using the density functional theory theoretical approach (Honkala *et al*., 2005).

Ammonium nitrate, the fertilizer generated from ammonia produced by the Haber process, is estimated to be responsible for sustaining one-third of the Earth's population. Ammonium nitrate is, however, a very dangerous material that requires careful handling and can explode via auto-combustion or in mechanical accidents. For this reason, his large-scale production has caused several serious disasters. Among them we recall the September 1921 explosion in the BASF plant at Oppau with 561 casualties, the April 1942 explosion in the town of Tessenderlo in Belgium with 189 casualties, and the explosion on April 1947 of a French cargo in the harbor of Texas City with 570 casualties. In addition the nearby Monsanto chemical storage facility exploded, killing 234 workers. More recently, on September 2001, an explosion of ammonium nitrate occurred in Toulouse, France, with 31 deaths and 2442 injured. The danger connected to the handling of ammonium nitrate has therefore prompted all governments to establish severe controls and to impose particularly restrictive conditions on its storage and utilization in agriculture in the hope of eliminating for the future the causes, not always purely accidental, of its explosions.

1.7 Fischer–Tropsch Catalytic Process

Another important catalytic process, which was found during the first quarter of the twentieth century, is the FT process discovered by Franz Fischer (1877–1947) and Hans Tropsch (1889–1935) at the Kaiser Wilhelm Institute for Coal Research in the Ruhr (Fischer and Tropsch, 1926a, b) (Figure 1.12). To illustrate the continuity of the German school of catalysis, it is interesting to recall that before becoming director of the Kaiser Wilhelm Institute in 1913, Franz Fischer worked with Wilhelm Ostwald and Emil Fischer. From 1920 to 1928, he collaborated with Hans Tropsch, a Bohemian industrial chemist, who graduated at Prague, where he received his PhD under the supervision of Hans Meyer. In 1928, Hans Tropsch became professor at the new Institute for Coal Research in Prague. He later accepted a position in the United States

(a) (b)

Figure 1.12 (a) Franz Fischer (1877–1947) and (b) Hans Tropsch (1879–1935). *Source*: Courtesy of Max Planck Institut für Kohlenforschung. They discovered the process for converting carbon monoxide and hydrogen into liquid hydrocarbons.

at the laboratories of Universal Oil Products and at the Armour Institute of Technology in Chicago in 1931. Hans Tropsch returned to Germany in 1935, where he died shortly after arrival.

The FT process converts a mixture of carbon monoxide and hydrogen to liquid hydrocarbons using finely dispersed iron as catalyst according to the scheme

$$n\mathrm{CO} + (2n + 1)\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{H_2O}$$

As already mentioned, the mixture of CO and H_2 gas (syngas) was obtained from coal, via the reaction $C + H_2O \rightarrow H_2 + CO$ (coal gasification).

As H_2O can further react with CO following the scheme $CO + H_2O \rightarrow CO_2 + H_2$(water gas shift reaction), a small amount of CO_2 is always present in the mixture.

Depending on the catalysts and on the operative conditions, the Fischer–Tropsch synthesis (FTS) made feasible not only the production of practically contaminant-free transportation fuels (e.g., diesel) but also the synthesis of other valuable chemicals (e.g., short-chain alkenes) from coal and other feedstock alternatives to oil (for instance, natural gas and, later, biomass). Furthermore, alcohols are also formed on iron-based catalysts.

Iron-based catalyst precursors consist of nanometer-sized iron oxide crystallites often added with promoters to improve the catalyst performance. A typical catalyst contains promoters like copper (to improve reducibility) and potassium

(to improve CO dissociation), along with some silica or zinc oxide to improve the catalyst dispersion. A complex catalytic system indeed!

The catalyst precursor is treated in H_2, CO, or syngas to convert it to its active form, a complex mixture of metallic iron, carbidic iron, and iron oxides.

The iron-based FT catalyst system is one of the oldest and perhaps most studied system known in the field of heterogeneous catalysis. However, even after more than 80 years of research, many important questions remain unanswered. In particular, the exact structural composition of the active site in these catalysts is still not unambiguously identified. Also the reaction mechanism for the formation of hydrocarbons and alcohols is still debated (Schulz, 1999; de Smit and Weckhuysen, 2008). Cobalt- and ruthenium-based catalysts (with appropriate promoters) are also good for FTS, ruthenium being the best for the production of long-chain hydrocarbons (waxes).

Franz Fischer and Hans Tropsch, being aware of the carbon- and carbide-forming tendency of iron catalysts, proposed CO dissociation as the primary step and, respectively, iron carbides as intermediates. Prior to dissociation, carbon monoxide was thought to be adsorbed through the carbon end on one or more metal atoms to form linear and bridged carbonyls. The existence of these precursor species was confirmed about fifty years later by spectroscopic and theoretical methods. The carbidic carbon was thought to be hydrogenated to CH_2 species, and these were thought to polymerize. This "carbide theory" was, however, discarded when no carbide phases were discovered using cobalt and ruthenium as the catalysts (Pichler, 1952). The exact mechanism for the production of hydrocarbons over iron carbide phases is largely unknown. In fact, even though it is observed that carburized iron is an active catalyst, it is still disputed in the literature whether bulk carbide phases themselves play an active role in the synthesis (Niemantsverdriet and van der Kraan, 1981). The problem of which metals are active in FTS has been discussed in a recent paper of a group of researchers at the Van't Hoff Institute of Molecular Sciences, University of Amsterdam. They established a clear correlation between the experimental and calculated heats of adsorption of CO and H_2 on several transition metals with expected FT activity, as can also be inferred from recent DFT calculations (Toulhoat and Raybaud, 2013; Bligaard *et al*., 2004).

A qualitative explanation of the better performance of Ru in catalyzing the formation of long-chain hydrocarbons is related to the small decrease of the metal–carbon (Me—C) bond strength on passing from Fe to Ru, a fact that favors the formation of C—C bonds and hence the polymerization of adsorbed (CH_2) groups to form hydrocarbon chains. In relation to this point, it must be mentioned that the FTS has also been attempted, without substantial success, by means of homogeneous complexes of Co, Fe, and Ru (Badhuri and Mukesh, 2000).

The presence of oxygen-containing organic compounds in the product ion of FTS on Fe inspired Henry Herman Storch, Norma Golumbic, and Robert B. Anderson in their famous volume (Storch, Golumbic, and Anderson, 1951) to postulate a mechanism where the atomic hydrogen is first added to the adsorbed CO to form an oxymethylene species. This idea received much attention and was a common belief for many years. Famous authors like Emmett (Kummer and Emmett, 1953) tried to substantiate this hypothesis.

One of the problems of the FT reaction is the production of water, which can keep the metal in a partially oxidized form. This implies that a mixture of phases is always present under reaction condition***s*** and that the fraction of oxidized metal decreases on passing from Fe, Co to Ru. This fact suggested that hydrocarbon chains are formed on the bare metal surfaces, while the formation of oxygenated products (like alcohols) requires the presence of an oxide phase (for instance, Fe_2O_3).

The simultaneous presence of multiple phases is the reason why the identification of a fully accepted mechanism remained controversial for several years. For this reason the surface chemistry of all potential catalytically active phases Fe, Fe_2O_3, Co, Ru, and the reactivity toward CO, H_2, and H_2O has been the object of numerous surface science studies. The novel surface science techniques, which became available in the 1970s and 1980s boosted research efforts for identifying the surface structures and the adsorbed species (in particular, CH_3, CH_2, CH, and carbidic groups) with the aim of correlating them to the catalytic performance of the materials (Barteau *et al*., 1985). Bent (1996) made an extensive review of the numerous investigations concerning the properties of CH_3, CH_2, CH, and carbidic species present on the surface of many metals. With the advent of modern computing facilities at the end of twentieth century and the initial years of the twenty-first century, theoretical methods were extensively applied. The completely new and innovative consequence of this development is that experimental synthesis, characterization, and testing were rapidly becoming interwoven with theoretical calculations (Dellamorte, Barteau, and Lauterbac, 2009; Nørskov and Bligaard, 2012).

Since the FT process opened the possibility to obtain gasoline from coal, several political reasons influenced the application of this process. Historically the interest in this alternative production route of hydrocarbons has paralleled the crises in the oil feedstock supply chain. A clear-cut example is the production of transportation fuels from coal in Germany during the Second World War, which was cut off from oil supplies by allied forces. A few decades later, South Africa invested significant research in the FT process during its 1970s–1980s oil sanctions. During that same decade, the 1973 and 1979 energy crises initiated new worldwide initiatives for transportation fuels and chemicals from alternative feedstock, including FT.

Today the Fe-based catalysts, being especially suited for the production of liquid hydrocarbon products from biomass, are attracting new attention.

1.8 Methanol Synthesis

An important process, strictly connected with the FT process, is methanol synthesis. In fact the industrial synthesis of methanol is obtained from synthesis gas ($CO/H_2/CO_2$ mixture) or methane using an appropriate catalyst (Oliveira, Grande, and Rodrigues, 2010).

The use of methanol in making other chemicals (for instance, formaldehyde, an important intermediate for plastics, paint, etc.) has stimulated the studies of the synthesis of methanol starting from the second decade of the twentieth century. More recently further incentive is derived by the use of methanol as an important liquid fuel that can be supplied to modified internal combustion engines or fuel cells and by the conversion of methanol to hydrocarbons such as paraffins or olefins. The methanol to olefin process will be illustrated in the chapter devoted to zeolitic and microporous materials. The first industrial catalyst was a mixed ZnO/Cr_2O_3 oxide consisting of about 70% ZnO and 30% Cr_2O_3 (high-temperature, high-pressure methanol synthesis catalysts). The discovery, in 1923, was made by the German chemist Matthias Pier (1882–1965) (Pier, 1923). Pier, working for BASF, developed a means to convert synthesis gas (a mixture of CO and H_2 derived from coke and used as a source of hydrogen in synthetic ammonia production) into methanol. The process used a zinc chromate catalyst and required extremely vigorous conditions, that is, pressures ranging from 30–100 MPa (300–1000 atm) and temperatures of about 400°C.

The biography of this important industrial researcher is relevant for the discovery of this process because it shows the importance of the German chemical school in catalysis in the first part of the twentieth century. In fact, after graduation in Heidelberg he moved to Berlin where, from 1906–1910, he served as assistant to Emil Fischer and Walther Nernst. After this period he became chemist at BASF (Leuna site) where he successfully synthesized methanol. The zinc chromate catalyst has high activity and selectivity and is resistant to sulfur poisoning, fundamental properties when syngas produced from coal gasification is used (as was the case in Germany). An even earlier discovery of methanol and aldehydes synthesis process (which, however, never went into production) is ascribed to the French chemist Georges Patart, inspector of the Bureau of the Explosives, who took out a patent in 1921 describing the preparation of methanol by hydrogenation under pressure of CO in the presence of a catalyst (Patart, 1921).

Indeed the problem of the discovery has been debated, and evidence of this debate can be found in the *Industrial and Engineering Chemistry Journal* (Patart, 1925) where the BASF statement on one side and the Georges Patart

reply (where he admits that BASF was the first to market synthetic methanol) on the other side are reported. As a matter of fact during the war, and in the years immediately following, BASF was exploring the possibility of obtaining methyl alcohol from carbon monoxide and hydrogen, under pressure. In 1923, the technical production of synthetic methanol had reached 10 tons per day, and the output was rapidly increasing. Up to 1925, large-scale production of this compound by this method was in the hands of the Badische Company alone. In 1930, Giulio Natta and M. Strada also discussed the synthesis of higher alcohols from CO and hydrogen (Natta and Strada, 1930).

However, as early as 1935, it was recognized that copper-based catalysts provided considerable advantages for methanol synthesis, allowing considerably lower pressures and, above all, lower temperatures. These catalysts proved to be extremely sensitive to sulfur components. Consequently only after the development of suitable syngas purification systems, mainly to remove sulfur, was the first low-pressure methanol process brought onto the market by the Imperial Chemical Industries Ltd, Great Britain, in 1966, based on a catalyst, which is a mixture of copper oxide, zinc oxide, and alumina. At that time Lurgi Gesellschaft für Wärme und Chemoteknik from Germany also developed a similar low-pressure methanol process.

Most of the methanol plants built in the last twenty years of the twentieth century operate according to the ICI or Lurgi processes, while numerous high-pressure units were converted to the low-pressure system in the second half of the nineteenth century.

The most active catalysts have high Cu content (optimum of about 60% Cu), the maximum quantity being limited by the need for sufficient refractory oxide to prevent Cu sintering. While it is accepted that Al_2O_3 prevents sintering, the role of ZnO in the catalyst has been debated, because pure ZnO is able to catalyze the synthesis of methanol (Strunk *et al*., 2009a). It must be underlined that ZnO interacts with Al_2O_3 to form a spinel that provides a robust catalyst support. It is generally assumed that the coordination, chemisorption, and activation of carbon monoxide take place on Cu^0 or Cu^+ and that the splitting of hydrogen is heterolytic and takes place on ZnO. However, different points of view on the location and coordination state of Cu^+ sites still exist.

The catalytic mechanism has been at the center of several discussions and reviews, which animated the last quarter of the twentieth century (Behrens *et al*., 2012).

A further impulse on methanol synthesis studies is the hydrogenation of carbon dioxide. This topic has attracted worldwide research interest in the past fifteen years because the use of CO_2, the most important greenhouse gas, as an alternative feedstock replacing CO in the methanol production can potentially afford an effective way of CO_2 utilization. A recent study shows that a mixture of a proper proportion of CO_2 and CO can increase the yield of methanol (Liu *et al*., 2003).

As happened for other industrial processes, the methanol synthesis process has stimulated the application of advanced surface science methods to the study of the surface properties of pure Cr_2O_3, ZnO (Zecchina *et al*., 1996), and nanosized Cu particles (Armelao *et al*., 2006).

Supported gold nanoparticles are also utilized in methanol synthesis. However, their extensive industrial application is still not adopted (Haruta, 1997; Bond, 2002; Strunk *et al*., 2009b). The catalytic activity of finely divided gold particles was initially considered in contrast with accepted opinion on the inactive character of gold. This is early evidence of the "quantum size effect," which states that the physical properties of nanosized particles are different from those of the bulk solid.

1.9 Acetylene Production and Utilization

Acetylene C_2H_2 was discovered in 1836 by Edmund Davy, who identified it as a "new carbure of hydrogen". The French chemist Marcellin Berthelot rediscovered it in 1860 and coined the name acetylene. From 1900 to 1950 it was prepared by the hydrolysis of calcium carbide, a reaction discovered in 1862 by Friedrich Wöhler (1800–1882), pupil of Gmelin and for a while collaborator of Berzelius, who is better known for the synthesis of urea. The well-known reaction is

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

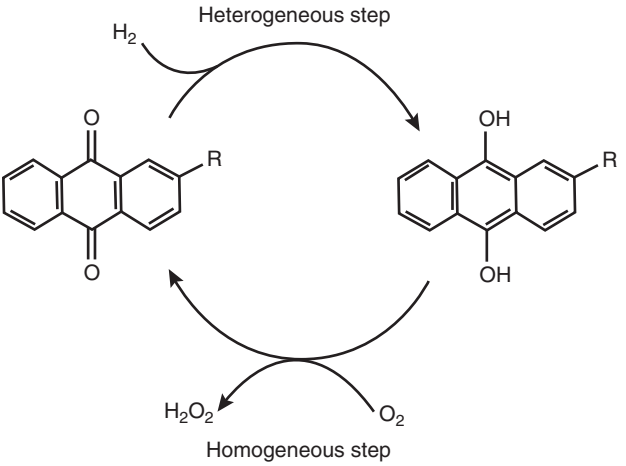
Calcium carbide production requires extremely high temperatures from coke and lime, necessitating the use of an electric arc oven, following a method discovered in 1982 by Henri Moissan (1906 Nobel Prize in Chemistry). Today acetylene is mainly produced by the partial combustion of methane or appears as a side product in the ethylene stream from the cracking of hydrocarbons. Approximately 400,000 tonne are produced this way, annually.

Acetylene can react with many molecules to give a wide range of industrially significant chemicals, via several reactions, often collected under the name of "Reppe chemistry" from the name of their discoverer, the German chemist Walter Reppe (1892–1969). The chemistry of acetylene was an extremely important chapter of German chemical industry in the period between the World Wars I and II. The discovery and application of homogeneous Reppe catalysts in the first quarter of the twentieth century gave us the opportunity to underline that, when considered from an historical point of view, homogeneous and heterogeneous catalysis developed in a parallel way. We will return to discuss the catalysts involved in the Reppe chemistry in the chapter devoted to homogeneous catalysis.

1.10 Anthraquinone Process for Hydrogen Peroxide Production

Another extremely important process today is the catalytic hydrogenation of anthraquinone, which is one of the two-step reactions for the industrial production of hydrogen peroxide. Anthraquinone is obtained industrially in several ways, including extraction from tar by the Friedel–Crafts reaction of benzene and phthalic anhydride in presence of $AlCl_3$ and by acid-catalyzed dimerization of styrene to give a 1,3-diphenylbutene, which then can be transformed to the anthraquinone.

The whole process of H_2O_2 synthesis is illustrated in the following scheme:



This reaction is playing a fundamental role for the synthesis of the green oxidant H_2O_2, whose current production is increasing at a steady space of 4% and today is estimated to be about 2.2 million ton.

As shown in the scheme reported earlier, the whole process consists of two separate steps, one heterogeneous (hydrogenation) and the other homogeneous (oxidation of reduced molecule to give back anthraquinone). The industrial process was developed in the period 1935–1936 by two researchers of BASF Hans-Joachim Riedl and George Pfleiderer (Riedl and Pfleiderer, 1936). The first commercial production was operated by IG Farbenindustrie in Germany during the World War II. Even today the production of bulk H_2O_2 is based on this process. To illustrate the history of the very innovative ideas that are at the basis of the whole process, in particular, the generation of hydrogen peroxide by reaction of oxygen with hydroquinones under homogeneous

Figure 1.13 Wilhelm Manchot. His fundamental contribution on autoxidation reactions was the basis for the anthraquinone process developed by Hans-Joachim Riedl and George Pfleiderer at BASF in 1936. Source: Photo by Eduard Manchot.

conditions, it is necessary to go back to the early observations in 1901 of the German chemist Wilhelm Manchot (1869–1945) (Manchot, 1901), a scientist of Hungarian origin who in 1895 obtained his PhD at the Technical University of Munich under the supervision of Friedrich Karl Johannes Thiele (Figure 1.13). In 1903 he was nominated professor of inorganic and analytical chemistry at the University of Würzburg where he started to work on problems of autoxidation and activation of catalysts (Manchot and Herzog, 1900, 1901). The fundamental works on autoxidation form the basis of the homogeneous part of the process of H_2O_2 synthesis. The fact that autoxidation could be catalyzed by the presence of certain metallic ions, for instance, copper, iron, manganese, cobalt, and nickel, was studied in detail by James H. Walton and George W. Filson in 1932 (Walton and Filson, 1932). More information can be found in the paper of Goor (1992). As for the heterogeneous step, it is also worthy to underline that the selective reduction of anthraquinone (where only the C=O groups should be attacked by hydrogen leaving the rings unaltered) is not trivial and that the choice of the best hydrogenation (heterogeneous) catalyst has been the subject of many research efforts even in the 1950–2000 period (Campos-Martin, Blanco-Brieva, and Fierro, 2006). Raney nickel catalyst was used initially. However, this catalyst had two serious drawbacks: excessive hydrogenation and rapid deactivation. The second generation of catalysts, based on palladium, was more selective, but due to the excessive activity, hydrogenation of the aromatic rings could not be completely avoided. Thus the need for a highly selective catalyst hydrogenating only the carbonyl group and leaving the aromatic ring intact stimulated the creation (~2000) of a new generation of catalysts based on Ni/B and Ni/Cr/B alloys.

In principle, the obvious alternative to the AO process could be the direct synthesis of H_2O_2 from H_2 and O_2. The first patent on the direct H_2O_2 synthesis

using a Pd catalyst was awarded in 1914 to Hugo Henkel and Walther Weber researchers of the Henkel & Cie, in Düsseldorf (Henkel and Weber, 1914). However, little progress was made in the following fifty years because of safety issues (H_2–O_2 mixtures are flammable). Due to the increasing demand for H_2O_2, the direct process attracted renewed interest after 1960, and several industrial and academic laboratories became involved after 1970. Unfortunately, no industrial application has been accomplished to date for the production of bulk H_2O_2, although some successful attempts were realized at DuPont. It is evident that the successful development of a commercialized process would be a major breakthrough in the oxidation process technology. The catalysts used were invariably based on Pd and Pd–Au alloys supported on various oxides, on zeolitic materials, and on resins (Chanchal, 2008). The major problem is the selectivity because the catalysts favoring the synthesis are also very active in the decomposition. For the future of the direct synthesis of hydrogen peroxide, photocatalysis on TiO_2-based catalysts seems to be a good candidate.

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