

Chapter 2

Kinetics and Chemical Equilibrium

The natural sciences are sometimes said to have no concern with values, nor to seek morality and goodness, and therefore belong to an inferior order of things. Counter-claims are made that they are the only living and dynamic studies. . . Both contentions are wrong. Language, Literature and Philosophy express, reflect and contemplate the world. But it is a world in which men will never be content to stay at rest, and so these disciplines cannot be cut off from the great searching into the nature of things without being deprived of life-blood. (Sir Cyril Norman Hinshelwood)

2.1 Affinity and Reactivity

The concept of the chemical bond, a concept which forms the basis of modern chemistry, had its roots in the idea of chemical affinity, inherited from the alchemist's vision of the interaction between objects as corresponding to the one between human beings. This idea occupied the minds of many leading chemists of the past in their attempts to rationalize the reactivity and behavior of chemical compounds, as well as their changes of physical state with temperature and pressure.

In particular Claude Louis Berthollet published, between 1800 and 1803, a new theory of affinity, forcing a re-evaluation of previous ideas on the subject and a basic revision of the nature of chemical reactions. He focused attention on the multiplicity of forces causing chemical reactions, in contrast to the specificity of the attractive forces between substances which represented the essence of the so-called elective affinity of the previous chemists and alchemists.

According to Berthollet, affinities were a manifestation of a universal attraction, all particles exerting an attraction towards all others, trying to bring them together in chemical combination. Hence, combinations between particles in variable proportions were likely to occur. This last assertion was inconsistent with Dalton's atomic theory and with Proust's principle of definite proportions and gave rise to a serious polemic that ended with the triumph of Proust's theory.

The concept of affinity survived for a good part of the nineteenth century and preserved his mysterious meaning, bound to an anthropomorphic vision of matter which associated bonds between atoms to attractions between human beings. Only through the development of classical physical theories such as thermodynamics and kinetics, associated with the study of thermal processes, were new horizons revealed in the understanding of the tendency of molecules to react.

Once the chemical community realized that statistical and thermodynamic factors govern the behaviour of chemical reactions, the idea started to develop that the same factors could also affect their reaction rates and that a measure of these rates could offer a direct evaluation of chemical affinity, as already suggested in 1777 by Karl Friedrich Wenzel (1740–1793). This idea then gave rise to one of the most important chapters in the newly emerging chemical physics, (Wenzel 1777) chemical kinetics, namely the study of the factors controlling reaction rates and responsible for the establishment of chemical equilibria in reversible reactions.

2.2 Chemical Equilibrium

The physico-chemical aspects of time evolution in chemical reactions were addressed for the first time in 1850 by Ludwig Ferdinand Wilhelmy (1812–1864) in the framework of a polarimetric investigation of the cane sugar inversion catalyzed by inorganic acids. Wilhelmy, who had a solid mathematical background, showed that the initial reaction rate was proportional to the sugar concentration and proposed (Wilhelmy 1850) a differential equation to describe its decrease in time. Wilhelmy's results remained practically ignored for a long time until they became known, thanks to Wilhelm Ostwald who was inspired by them to establish in 1884 an analytical method to measure the strength of acids from their ability to catalyze the sugar inversion. An important consequence of Wilhelmy's work was that the inversion rate is an exponential function of the inverse of the absolute temperature. Similar results were reached by the English chemist Augustus George Vernon Harcourt (1834–1919) in the study of the acid catalyzed clock reactions between iodide and hydrogen peroxide and between oxalic acid and potassium permanganate. The mathematician William Esson (1838–1916) interpreted then Harcourt's kinetics data in terms of differential equations not too different from those used today (Harcourt and Esson 1867).

Of great interest for the understanding of the kinetics of equilibrium reactions was a group of papers published by Marcellin Berthelot and Pean St. Gilles (Berthelot and St. Gilles 1862) relative to esterification reactions of the type $\text{RCOOH} + \text{R}'\text{OH} \rightleftharpoons \text{RCOOR}' + \text{H}_2\text{O}$. They studied the effects of temperature and of reactant's concentration on the direct reaction rate, concluding that it is proportional to the product of the concentration of the acid and of the alcohol.

A mechanistic attempt to explain the transformations occurring in a chemical reaction in equilibrium conditions was first made by the Austrian physicist Leopold

Pfaundler von Hadermur (1839–1920), professor at the University of Innsbruck, who treated the reactions in the framework of the kinetic theory of gases in terms of molecular collisions (Pfaundler von Hadermur 1867). Pfaundler assumed that at a given temperature the same number of molecules was formed and decomposed by collisions. This explanation implied that not all molecules had the same amount of translational and internal energy, since only a limited number of collisions was effective to give rise to the reaction, either by dissociating or by forming molecules. In Pfaundler's theory chemical affinity was thus defined in purely kinetic and statistical terms as involving all possible internal motions of the molecules. Later Berthelot took up, even if only qualitatively, in his *Essai de mécanique Chimique*, the ideas expressed by Pfaundler.

A more complete and general treatment of equilibrium displacements in chemical reactions was developed in the same period by two Norwegian scholars bound since their childhood by a fraternal friendship, Peter Waage (1833–1900) professor of chemistry at the University of Christiania and his brother in law Cato Maximilian Guldberg (1836–1902), a mathematician at the same university. Guldberg and Waage, whose collaboration started by studying Berthollet's affinity theory, realized that the concept of mass was not easily utilizable in a solution and that it was by far more convenient to use "active masses", i.e. concentrations. They started from the idea that for a generic equation $\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$, the direct reaction rate at equilibrium must be equal to that of the inverse reaction and that the two rates are proportional to the product of the concentrations of the reactants according to the reactions

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

where square parentheses indicate concentrations. By equalizing the two reaction rates, $v_{\text{dir}} = v_{\text{inv}}$, they obtained the equation known to all first year students of chemistry as the *mass action law*:

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

In 1862 Guldberg and Waage presented a short note to the Norwegian Academy of sciences with their first report on the problem. The note, entitled *Studier over Affiniteten*, was published in 1863 in Norwegian (Waage et al. 1864), a language unknown to European chemists, and remained therefore totally ignored. The same fate occurred to a second more detailed note, *Étude sur les affinités chimiques* (Guldberg et al. 1867), published this time in French in 1867. It was only in 1877 that Ostwald, once read this second paper confirmed its validity with a series of experiments. In 1877 van't Hoff, who also ignored Guldberg and Waage's paper, obtained the same law using the kinetic theory (van't Hoff 1877). At this point the two Norwegian friends decided to publish a new version of their work, this time in German (Guldberg et al. 1879), resuming in the discussion the ideas of Pfaundler. Eventually van't Hoff quoted their contribution, automatically acknowledging their priority.

In the late nineteenth century the chemist who best understood the importance of the new physical-chemical concepts in the study of chemical reactions was Jacobus van't Hoff (1852–1911) who had already achieved considerable fame in 1875 after the German translation of his 1874 paper that formulated the idea of the tetrahedral carbon atom, creating the basis of the new field of stereochemistry.

In 1870 van't Hoff, influenced by a paper of Wislicenus on the tri-dimensional representation of the isomers of lactic acid, developed the idea that the optical activity of organic compounds was due to the asymmetry of the carbon atom. Van't Hoff published a 13 pages essay with an unreadable Dutch title (van't Hoff 1874) in which he proposed to represent in three dimensions the structure of organic molecules, assuming that the four valences of the carbon atom were directed towards the vertices of a tetrahedron. A direct consequence of this idea was that when the carbon atom is asymmetric, i.e. when the four valences are saturated by four different atomic groups as in the case of lactic acid, two optically active isomers must exist, one being the mirror image of the other.

Almost at the same time The French Alsatian chemist Joseph Achille Le Bel (1847–1930) published an article (Le Bel 1874) based on Pasteur's hypothesis of the molecular asymmetry in which he reached the same conclusions of van't Hoff.

Van't Hoff's paper was translated in French and published in 1875 with the title *La chimie dans l'espace* (van't Hoff 1875) and after in German as *Die Lagerung der Atome im Raume* (van't Hoff 1877). An enlarged version of this paper, *Dix années dans l'histoire d'une théorie*, was later published at Rotterdam by van't Hoff in 1887 and at Paris in 1892 with the title *Stéréochimie*.

The German translation strongly contributed to the diffusion in Europe of van't Hoff's ideas and gave origin to a violent and ferocious polemics with Hermann Kolbe, the most important German chemist of the time, who attacked van't Hoff with a paper full of terrible insults published on the *Journal für Praktische Chemie* (Kolbe 1887). Van't Hoff theory was strongly appreciated by many important chemists such as Wislicenus and Wurtz, and gained his final consecration thank to the decisive support of Friedrich Wilhelm Ostwald, of Hans Heinrich Landolt, author of a fundamental book on the optical rotatory power of organic molecules (Landolt 1898), of Johann Friedrich Adolf Von Baeyer and of Emil Fischer. Finally in 1913 The two Braggs (see Chap. 4) determined experimentally the tetrahedral structure of the carbon in a diamond crystal.

Jacobus van't Hoff, after graduation at the polytechnic of Delft in 1871, decided to become a scientist, studying first mathematics at Delft for 1 year and then attending for about 6 months Kekulé's chemical laboratory in Bonn and for 1 year that of Wurtz at Paris. In 1874 he went back to the Netherlands where he obtained the Ph.D. at Utrecht with a thesis on the cyanoacetic and malonic acids entitled *Bijdrage tot de Kennis van Cyaanazijnzuren en Malonzuur*. In 1876 he was accepted as an assistant at the veterinary college of Utrecht and the year after moved to the same position of the University of Amsterdam. Only in 1878, when he was 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 accepted a move 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 his inaugural lecture *Verbeeldingskracht in de Wetenschap* (the power of imagination in science) that he held at the University of Amsterdam, he defended the role of imagination in scientific investigation (van't Hoff 1878), presenting a series of examples showing how several famous scientists had developed the ability to visualize the properties of imaginary objects without having seen them.

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. As he pointed out in his two-volume treatise, *Ansichten über die organische Chemie* (1878–1881), discoveries made in his studies of the spatial organization of the molecules persuaded him that the chemical properties of organic molecules depend essentially on their physical structure.

Van't Hoff entered by rights the chemical physics community with the book *Études de Dynamique chimique* (1884), in which he examined the problem of identifying the conditions that control the equilibrium of reversible reactions (van't Hoff 1884).

Reversible reactions had already studied by Berthollet in the framework of his research on affinity. In his books *Recherches sur les Lois de Affinité* (1801) and *Essai de statique chimique* (1803) he reached 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 (Berthollet 1801). Also, Williamson had studied reversible reactions during his research on ethers (Williamson 1850) concluding that in a reaction of the type $A + B \rightleftharpoons C + D$, the equilibrium is not static but dynamic. He concluded that the reactions takes place at the same rate in both directions, giving the impression of having stopped. The idea that equilibrium is reached when the rates of the two opposite reactions equalize, was also clearly stated almost at the same time by the Italian Faustino Malaguti (Malaguti 1853).

The principal interests of van't Hoff in the 1880s were concentrated on chemical reaction rates as a measure of chemical affinity. In 1884 he laid the mathematical basis of chemical kinetics, starting from the idea that each stoichiometric reaction is the sum of a series of elementary events in which the molecules enter in direct contact one with the other in order to react. The probability that the molecules react is therefore greater, the greater the concentration of the reacting species. In the simple case of a monomolecular reaction in which the reaction rate depends on the concentration c of a single chemical species, he formulated the differential equation

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

where k is a constant that he named *rate constant* since it represents the concentration decrease per unit time for an unitary concentration ($c = 1$). On the basis of the

number of molecules taking part in the elementary reaction event, van't Hoff classified the reactions in mono- and bi-molecular, showing that more complex reactions which apparently seem to involve the contemporary collision of several molecules, occur in reality through a succession of mono or bi-molecular processes.

As with all chemists of his time, van't Hoff was interested in measuring the affinity which, although considered responsible for chemical reactions, continued to be not easily quantifiable and translatable in measurable quantities. An attempt to find a numerical value for a quantity connected to the affinity had been made before, in 1844, by Eilhard Mitscherlich (1794–1863) who discovered isomorphism and who, working with Berzelius at the Karolinska Institutet in Stockholm, became interested in the affinity problem. Mitscherlich attempted to measure the attractive force of water of hydration in hydrate salts by controlling the decrease of the vapour tension in these crystals. By introducing crystals of the Glauber salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) in the empty space of a barometer, he observed that the mercury column would drop by 5.45 mm with respect to pure water that instead produced a decrease of 8.72 mm. From these data he deduced that the difference of 3.27 mm measured the affinity of sodium sulphate for hydration water, corresponding to a force of about 12 g/cm^2 (Mitscherlich 1844).

When van't Hoff read Mitscherlich's paper, he was surprised by the very low value of the hydration force, convinced that even the weakest chemical forces should have been much stronger. As he stated later, the botanist Hugo de Vries, whom he met in a street in Amsterdam, had told him that his colleague, the pharmacist and botanist Wilhelm Pfeffer (1845–1920), had observed a dependence of the osmotic pressure on the temperature, finding for each degree of temperature lowering a decrease of the osmotic pressure of about $1/270$.

The osmotic pressure is the hydrostatic pressure present in a solution in contact with the pure solvent through a semi-permeable membrane which allows only the solvent molecules to get across. The osmotic pressure, discovered in 1748 (Nollet 1748) by Jean Antoine Nollet (1700–1770), was at this time used essentially by botanists, being considered responsible of the motion of water in plants. Even if some chemists, like Thomas Graham and Justus von Liebig, had shown some interest in the problem essentially in relationship to their biological researches, osmotic pressure remained of limited interest for chemists. Van't Hoff instead immediately realized the importance of osmotic pressure measurements for the evaluation of chemical affinity and decided to use a cell of the type invented by Pfeffer to test his ideas.

Pfeffer (1887) had constructed a cell for osmotic pressure measurements in which a wall of porous ceramic holds a semi-permeable membrane of copper ferrocyanide separating the solution from the pure solvent. Using a diluted solution of cane sugar in water, van't Hoff was able to show that the attraction between water and sugar was about 100 times larger than that measured by Mitscherlich between the sulphate and the hydration water. From these measurements he further deduced a much more important and general result, i.e. that in diluted solutions the particles of the solute behave like the particles of an ideal gas and therefore that the osmotic pressure is proportional to the absolute temperature as the pressure in the gas phase.

In 1886 van't Hoff published a new text in French entitled *L'Équilibre chimique dans l'État dilué gazeux ou dissous* that presented his own ideas on the chemical physics of diluted solutions, establishing a perfect parallelism between ideal gases and diluted solutions in the form of the equation $\pi = \dot{i}cRT$ where π is the osmotic pressure, R the universal gas constant, T the absolute temperature, c the concentration and \dot{i} an empirical corrective coefficient. This equation, practically identical to the equation of state of the gases, $PV = nRT$, was found to be perfectly valid (van't Hoff 1887) for diluted solutions of organic compounds such as sugar with $\dot{i} = 1$. Van't Hoff, determined the numerical value of \dot{i} using different physical methods such as the increase of the boiling point or the decrease of the melting point. He realized that for solutions of inorganic acids, bases or salts \dot{i} assumed instead a value close to 2. Van't Hoff did not offer a valid explanation for the meaning of his empirical constant \dot{i} in these cases. Only in 1887 Arrhenius, informed by van't Hoff, suggested (Arrhenius 1887, p. 631) that a value of \dot{i} of the order of 2 was nothing else than a measure of the fact that the electrolytes were dissociated in solution and therefore that the number of particles of the solute was almost the double. Van't Hoff accepted without hesitation Arrhenius's explanation and re-interpreted his data in terms of ionic dissociation in a paper that he published the same year with the enthusiastic adhesion of Ostwald (van't Hoff 1887).

The analogy between diluted solutions and ideal gases was very useful in extending the second principle of thermodynamics to solutions (van't Hoff 1894). One of the important questions of chemical kinetics concerned in fact at that time the influence of temperature on reversible reactions. In 1884 van't Hoff developed the fundamental thermodynamic relationships controlling the displacement from equilibrium of a reaction with temperature (van't Hoff 1884). In his *Etudes de Dynamique Chimique* he explained the exponential dependence of the reaction rate from the inverse temperature assuming that the equilibrium constants obey the exponential relationship

$$k = Ae^{-\Delta G/RT}$$

where ΔG is the free energy variation (units of J/mole).

Although this equation was proposed by van't Hoff in 1884, it is universally known as the Arrhenius equation, since Svante Arrhenius was the first to offer in 1889 its physical interpretation (Arrhenius 1889). Van't Hoff actually had not made any hypothesis on the physical meaning of the pre-exponential factor A . Arrhenius instead suggested that, in order that a reaction could take place, the reacting molecules had to possess an energy greater than a limiting value that he called *activation energy* E_a . At the temperature T the fraction of molecules possessing a kinetic energy larger than E_a is given by the statistical distribution law of Boltzmann and is proportional to the factor $e^{-E_a/RT}$. 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 of E_a . Therefore the previous equation must be rewritten in the form

$$k = Ae^{-E_a/RT}$$

Van't Hoff used this equation to obtain a relationship that allowed the determination of the standard enthalpy variation ΔH° of a reactive process, avoiding the recourse to calorimetric measurements. From the Arrhenius equation, by calculation of the logarithm of the k constant one obtains,

$$\ln k = -\frac{\Delta G}{RT} = -\frac{\Delta H - T\Delta S}{RT}$$

and assuming that the temperature variation of the enthalpy ΔH ($\Delta H = \Delta H^0$) and of the entropy ΔS is negligible in a restricted temperature interval, one gets

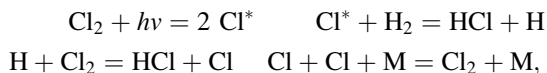
$$\left(\frac{\partial(\ln k)}{\partial T}\right)_p = \frac{\Delta H^0}{RT^2}$$

known as van't Hoff isochore since obtained the first time for a constant volume situation. Thus van't Hoff reached the conclusion that in a reversible reaction a shift of the equilibrium tends always to compensate the temperature variation. If the temperature is lowered the equilibrium shifts in the direction that produces heat, whereas a temperature increase gives rise to 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 Chatelier that states that *each system tends to counteract any change imposed from the exterior by minimizing his effect*. Henry Le Chatelier (1850–1936), son of a Parisian engineer who contributed to the creation of the French aluminum industry, was an applied chemist specializing in the production of cement who, after having formulated the principle that bears his name (Le Chatelier 1884), translated in 1899 the thermodynamic works of Gibbs in French to prove the validity of his principle.

2.3 The Quantum Mechanical Approach to Chemical Kinetics

The twentieth century witnessed an explosion of research into kinetics, due to its importance in the study of chemical reactivity. Central to the understanding of kinetic processes were the classical researches of Sir Cyril Hinshelwood (1897–1967) who studied in depth the effect of pressure on the kinetics of reaction in the gas phase (Stubbs et al. 1951). In particular he discussed the competition between effective collisions that supply the excess energy (activation processes) to trigger the reaction and inhibiting collisions in which an activated molecule loses his excess energy transferring it to another molecule or transforming it into kinetic energy. Sir Cyril Hinshelwood was awarded the 1956 chemistry Nobel Prize for his research into kinetics (Thompson et al. 1929) and for his fundamental contributions to the theory of chain reactions (Gibson and Hinshelwood 1928). The chain reaction's theory had been already started by Nernst who in 1918

conceived the mechanism of chain reactions to explain the high quantum yield of the photochemical reaction of chlorine with hydrogen (Nernst 1918a, b) according to the scheme



where M represents any object, for instance the walls of the reaction vessel, which eliminate the excess energy developed in the reaction. Nernst's theory was further developed by his successor at Berlin, Max Ernst August Bodenstein (1871–1942), who studied in detail gas phase reactions (Bodenstein 1913), in particular those of hydrogen with chlorine (Bodenstein and Dux 1913) and iodine and developed the quasi-stationary approximation which neglects the time variation of the concentration of intermediate species (Bodenstein 1922), assuming that the concentration variation of any highly reactive intermediate species is negligible in comparison to the speed of its formation and decay. The kinetic equation of the intermediate species is then substituted by an algebraic equation used to eliminate the corresponding concentration from the ensemble of the kinetic equations.

Hinshelwood studied several apparently simple elementary reactions as the one between molecules of hydrogen and oxygen to produce water, and showed their complexity. Hinshelwood was a key representative of the great scientific tradition of Oxford University. As a scientist with a strong classical and philosophical background and a passionate reader of Dante (he spoke perfectly Italian and) he created a style of humanistic-scientific writing of great elegance and courtliness through the refinement of his cultural formation. His books, *The Kinetics of Chemical Change* (1926), *The Structure of Physical Chemistry* (1951) and *The Chemical Kinetics of the Bacterial Cell*, continue to be famous and unsurpassed.

At the end of the 1930s Hinshelwood oriented his research to the study of bacterial growth, a complex problem that he faced using the same theoretical tools of his research in kinetics (Hinshelwood 1952). In this field he defined the total integration principle to characterize the ability of bacterial cells to adapt their enzymatic balance to the external environment (Hinshelwood 1953).

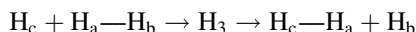
Fundamental for the understanding of chain reactions were also the contributions of the Russian Nikolay Semyonov (1896–1986), one of the greatest experts of combustion reactions and of explosive processes. Semyonov, who studied at St. Petersburg, was professor at the polytechnic institute from 1928 until 1931 when he went to direct the Chemical Physics Institute of the Russian Academy of Sciences. In the 1930s Semyonov founded the mathematical theory of auto-ignition reactions (Semyonov 1928) that allows the prediction of the auto-ignition temperature of mixtures from the knowledge of the rate and heat dissipation constants (Semyonov 1940). During the same period, he developed, with colleagues, the general theory of flame propagation processes in gases. These researches led to his interest in the chain reactions for which he developed, in parallel with Hinshelwood, a general theory of the reaction kinetics and of the branching processes and a detailed

analysis of the mechanisms of chain ignition (Semyonov 1929) as well as of those leading to the end termination of reactive chains. His treatise *Chain Reactions*, written in Russian in 1934 and translated into English the next year (Semyonov 1934), represented a milestone in the study of chain reactions. For his research activity he shared with Hinshelwood the chemistry Nobel Prize in 1956.

The link between classical kinetics, in particular the van't Hoff and Arrhenius theories, and the rising quantum mechanics was realized by Fritz London, Henry Eyring and Michael Polanyi soon after the publication of the seminal paper of Heitler and London on the calculation of the quantum energy of the hydrogen molecule (Heitler and London 1927).

Henry Eyring (1901–1981), was born and grew up in a Mormon community, and remained intimately bound to the religion all his life. He studied mining engineering, metallurgy and chemistry at the University of Arizona and obtained a Ph.D. degree in chemistry at Berkeley in 1927. After that he spent, thanks to a State fellowship, 1 year (1929–1930) at the Kaiser Wilhelm Institute of Berlin, where he met one of the most interesting personalities in Berlin society at the time, the Hungarian Michael Polanyi (1891–1976), chemist, philosopher and economist. Polanyi strongly influenced Eyring's scientific research showing him the road to the quantum mechanical treatment of kinetic processes. Michael Polanyi had started in 1919 to investigate gas phase reactions and had developed a theory which remained rather in the shadow (Polanyi 1932), of the works of Hinshelwood. When Eyring reached Berlin as a post-doctoral researcher with Polanyi, the idea that chemical reactions occurred through the displacement of the reactive system along a path on a multi-dimensional potential energy surface was already spreading. This idea was essentially based on a paper published in 1928 by Fritz London (London 1928a) in a collection of contributions of several authors to celebrate the 60 birthday of Sommerfeld (Sommerfeld Festschrift). In this paper, London, extending the theory developed with Heitler for the hydrogen molecule, discussed in detail in Chap. 4, presented an approximate calculation of the potential energy of a system made of one atom and one molecule of hydrogen (London 1928a, b, 1929), computed in terms of exchange and Coulomb energy between couples of atoms, leading to the formation of an unstable H_3 molecule.

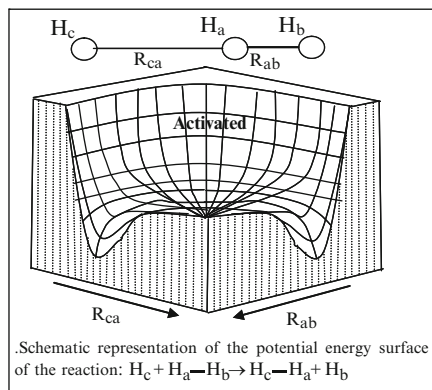
Starting from London's idea, Eyring and Polanyi developed in 1931 their transition state theory, and succeeded in performing the quantum mechanical calculation of the potential energy surface for the collinear reaction



between one hydrogen atom and one molecule of hydrogen (Eyring and Polanyi 1931), with formation of an unstable transition state, the H_3 ($H_c-H_a-H_b$) molecule (activated complex).

A three-dimensional potential energy surface of this reaction is schematically drawn in the figure below as a function of the relative position of all atoms involved and shows the energy path followed by the reagents in their evolution towards the final products. During the reaction they migrate from one to another

energy minimum, climbing a barrier h which shows the relative height of the intermediate stage to be crossed to reach the final products. The height and the position of the barrier h are completely defined by the level of accuracy of the quantum calculation.



The complete quantum mechanical calculation of the variation of the electronic energy in a chemical reaction was not feasible in the 1930s, since it requires to compute the energy for several tens of thousands of possible relative positions of the atoms as well as their representation with several variables functions, operations that require the use of powerful electronic computers available only at the end of the twentieth century. Nevertheless Eyring's approximate method of calculation, applied to the reaction of hydrogen with halogens, proved to be effective in predicting whether a reaction occurred through bimolecular collisions or through a mechanism at the atomic level. In 1955 the Japanese Shin Sato of the Technology Institute of Tokyo (Sato 1955) extended the calculations of potential energy surfaces to other reactions between an atom and a diatomic molecule.

At the end of 1930 Eyring went back to the United States where he continued to study the potential energy surfaces of elementary reactions (Eyring 1935). He developed the theory of the absolute reaction rates and of the activated complex and established an explicit expression for the pre-exponential Arrhenius factor in the form

$$k = \frac{k_B T}{h} e^{-\Delta G^*/RT}$$

where ΔG^* represents the activation energy, and where k_B and h are the Boltzmann and the Planck constants, respectively. Eyring became one of the fathers of the modern kinetic theory, author of several books and of more than 450 scientific papers.

The transition state theory was, however, not accepted with enthusiasm by the scientific community, since Eyring and Polanyi's papers were not easy to read and in addition introduced the concept of the activated complex, an object that for the

time being was purely hypothetical, did not possess a true physical reality and for many chemists did look as a kind of “Deus ex machina”. Several years had to pass before ultrafast laser technology could supply true spectroscopic evidence for the existence of short living molecules as intermediate stages of chemical reactions.

In 1933 Michael Polanyi moved from the Kaiser Wilhelm Institute for Physical Chemistry in Berlin to the University of Manchester, where he stayed until he became a Fellow at Merton College Oxford in 1959. At Manchester, after having developed independently from Eyring the theory of the absolute reaction rates in collaboration with Meredith Gwynne Evans (1904–1952) (Evans and Polanyi 1935), he continued for some years to work in kinetics until he abandoned definitively the field and devoted himself to problems of economics, politics and the philosophy of science. In 1928 Polanyi had actually joined a group including Leo Szilard and John von Neumann interested in understanding with Jacob Marschak, the Russian economic system. Polanyi visited Russia several times and in 1935, wrote a critical paper about the Soviet economy, published by the *Manchester School of Social and Economic Sciences*.

The research on reaction dynamics was, however, continued by his son John Polanyi, inventor of the infrared luminescence technique. John Polanyi was born in Germany but educated in England and emigrated in 1952 to Canada where he first worked at the National Council then moved in 1956 to the University of Toronto where he became professor in 1974. John Polanyi studied in depth the distribution of energy in the excited quantum levels of the reaction products, measuring their infrared emission in simple exothermic reactions (Cashion et al. 1958). Over the course of several years, he developed the technique of infrared emission for several reactive processes and succeeded in building a clear picture of the energy distribution in the vibro-rotational levels of the reaction products (Polanyi 1963, 1967). Of extreme interest was the experimental evidence of the existence of transition states that he collected by means of crossed molecular beams experiments (Polanyi et al. 1995). In 1986 John Polanyi obtained the Nobel Prize for chemistry together with Yuan Lee and Dudley Herschbach, authors of fundamental research in reactive systems by means of the molecular beams technique.

Dudley Robert Herschbach (1932–...), obtained a Ph.D. in chemical physics at Harvard in 1956 under the supervision of Bright Wilson Jr. with a thesis in microwave spectroscopy and in 1959 moved to the University of California at Berkeley, where he started a research project on reaction kinetics using molecular beam experiments, that made him known all over the world as a specialist in this new field (Herschbach et al. 1956). Returning to Harvard in 1963 as a professor, he started the study of a series of bimolecular reactions produced by the collision of alkali atoms with molecules (Herschbach 1966) and analyzed in detail the reactive collision as a function of several parameters (Miller et al. 1967) including incidence angles, particle speed, type of electronic state and so on. Amongst his most interesting experiments were those concerning the collisions between a deuterium atom and halogen molecules (McDonald et al. 1972), those relative to diffusion processes by reactive collisions (Herschbach 1973) as well as the multiple collision processes (King et al. 1973).

The study of reactive collisions in crossed molecular beams presents a large number of experimental difficulties that were resolved thanks to the cleverness and experimental ability of the Chinese Yuan Tseh Lee (1936–), born and educated in Taiwan, who in 1962 emigrated to Berkeley to obtain a Ph.D. in 1965. There he started the study of the reactions between ions and molecules by means of molecular beam experiments. In 1967 Lee moved to Herschbach laboratory at Harvard where he completed his scientific preparation (Lee et al. 1969) and started a brilliant career that brought him first to Chicago in 1968 and then again to Berkeley in 1974. Fundamental to the development of his research in reactive dynamics and for the identification of transition states was the technique of crossed beam experiments (Chen et al. 1973), that he developed to a high degree of sophistication (Zhang et al. 1997). In 1994, after having received the award of the Nobel Prize, he decided to go back to his native Taiwan where he dedicated himself to the social and scientific developments of the population, incurring, however, the hostility of students because of the excessive bureaucratization of his reforms and for the authoritarianism of his decisions.

The quantum theory of the dynamics of the reactive processes was extended in the period 1956–1965 by Rudolph Arthur Marcus (1923–) to oxidation-reduction reactions involving electron transfer processes from reactive centers of complex molecules in proteins, in semiconductors and in electrochemical aggregates in solution (Marcus 1956, 1965). Rudolph Arthur Marcus (1923–) born in Montreal in Quebec, Canada, was educated at McGill University where he graduated in 1956 in chemistry under the supervision of Carl A. Winkler, specialist in the study of the rates of chemical reactions who had been a student of Sir Cyril Hinshelwood at Oxford. As a young student at McGill he had the opportunity to attend the group of Edgar William Richard Steacie (1900–1962) an international figure in the study of free-radical reactions. In 1949 he moved to the United States where he worked first as post-doctoral student with Oscar K. Rice at the University of North Carolina at Chapel Hill, then at the Polytechnic Institute of Brooklyn, until in 1978 he accepted an offer from the California Institute of Technology to come there as Arthur Amos Noyes Professor of Chemistry.

At CalTech he started to work on the problem of reaction rates and, although still very young, was able to formulate a particular case of a theory of monomolecular gas phase reactions known as the Rice-Ramsperger-Kassel theory that he published in 1951 and in a more general formulation in 1952 (Marcus 1952).

Marcus and his group completed and extended the kinetic theory of monomolecular reactions and of intramolecular dynamics (Marcus 1952) started in 1921 by Frederick Alexander Lindemann (1886–1957), Viscount of Cherwell, who succeeded in explaining the first order kinetic of several monomolecular reactions, assuming that these were controlled by bimolecular collision processes followed by monomolecular dissociation events that define the determining stage of the reaction speed.

Lindemann's theory was developed by Sir Cyril Hinshelwood assimilating the molecular degrees of freedom to harmonic oscillators and using statistical methods to evaluate the collisional activation probability of the molecule (Levine and

Bernstein 1987). The theory was subsequently improved by Oskar Knefler Rice (1903–1978) and Herman Carl Ramsperger (1896–1932) (Rice and Ramsperger 1927, 1928). In the Rice-Ramsperger theory (RR theory) the dissociation rate of an excited molecule is treated as a function of its energetic content. In this theoretical approach the dissociation rate is assumed proportional to the number of internal degrees of freedom of the molecule and the dissociation is interpreted as due to the localization of a critical amount of energy in a given internal degree of freedom. The distribution of the excitation energy among the different molecular degrees of freedom had been independently discussed also by Louis S. Kassel (Kassel 1928) and by Marcus, so that the theory finally took the name of RRKM (Rice, Ramsperger, Kassel, Marcus) theory. In 1952 Rudolph Marcus (Marcus 1952) introduced in the framework of Eyring's transition state theory the idea that the molecular excitation energy could be separable into fixed and variable contributions and that only these latter, able to shift among the different degrees of freedom, were responsible for the reaction.

One of the most significant results of Marcus's electron transfer theory concerns the parabolic relationship between the driving force and the reaction rate. As the driving force increases, the reaction rate first increases, then reaches a maximum and finally decreases. The occurrence of an “inverted region” for the process was for some time seen with skepticism by the chemical community until it was experimentally documented (Miller et al. 1984; Deisenhofer et al. 1984).

2.4 Catalysis

Information concerning catalytic reactions was extremely limited before the beginning of the nineteenth century, when kinetic theory started to be an independent branch of chemistry, although humans had applied the principles for thousands of years in fermentation processes.

The first known catalytic processes involved reactions in solution catalyzed by the addition of small amounts of acid (homogeneous catalysis). This occurred in 1548 when the German physician and botanist Valerius Cordus (1515–1544) used oil of vitriol to transform ethyl alcohol in the corresponding ether, probably following an old recipe imported from Middle East by Portuguese explorers (Cordus 1548). At the end of the eighteenth century, acid catalysis started to play an important role in chemical kinetics, when several chemists, even without a rational explanation for it, realized that the addition of small amounts of an acid or of a basis, could modify and speed up reactions.

Antoine Augustin Parmentier realized for instance in 1781 that addition of acetic acid accelerated the transformation of potato flour into a sweet substance by means of cream of tartar and in 1811 the Russian Sigismund Konstantin Kirchhoff (1764–1833) found that the hydrolysis of starch in glucose was made faster by adding few drops of sulphuric acid (Kirchhoff 1811). Afterwards Ludwig Wilhelmy (1812–1864) found that the inversion process of cane sugar was made easier by

inorganic acids (Wilhelmy 1850) and Augustus George Vernon Harcourt (1834–1919) discovered the importance of acid catalysis in clock reactions (Shorter 1980).

At the beginning of the nineteenth century the interpretation of chemical processes was still dominated by the affinity concept, but slowly new results started to appear, suggesting that different mechanisms could contribute to orient the course of a reaction. 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, that they called *diastase*, and proved that at 100°C it loosed its activity (Payen and Persoz 1833). The starch fermentation was studied also by Johann Wolfgang Döbereiner who in 1822 found that starch transformed into alcohol only after having been converted in sugar (Döbereiner 1822). In 1877, the German physiologist Wilhelm Kühne (1837–1900), pupil of Claude Bernard and Virkow, isolated tripsine from gastric juice (Kühne 1877) and coined the word *ενζυμον*, enzyme, from the Greek, *εν* in and *ζυμον* ferment, to describe cellular fermentation:

Um Missverständnissen vorzubeugen und lästige Umschreibungen zu vermeiden schlägt Vortragender vor, die ungeformten oder nicht organisirten Fermente, deren Wirkung ohne Anwesenheit von Organismen und ausserhalb derselben erfolgen kann, als Enzyme zu bezeichnen.¹

Later the term *enzyme* was used only for non living systems and substituted by the word *ferment* for living organisms. Enzymes are essentially globular proteins and just from protein research derived the studies of enzymatic catalysis. At the beginning of the nineteenth century also metals were identified as reaction accelerators and in particular platinum gained a significant position in the catalysis world as a *prima donna* in heterogeneous catalysis.

In 1813 Louis Jacques Thenard (1777–1857) discovered that ammonia decomposed in nitrogen and hydrogen by flowing on red-hot metal. Subsequently, in collaboration with Pierre Dulong (Dulong and Thenard 1823a, b), later to be internationally known for the specific law of solids, Thenard showed that the ability to decompose ammonia decreased in the series copper, silver, gold and platinum. They proposed that this was due to electric charges on the metal. Furthermore, in 1817 Humphry Davy proved that platinum accelerated several organic reactions without being altered (Davy 1817) and in 1820 his cousin Edmund Davy (1785–1857) prepared a platinum sponge able to absorb large amounts of gas and realized that in the presence of finely divided platinum, alcohol vapors were transformed in acetic acid (Davy 1820). He showed also that boiling a mixture of platinum sulphate with ether and alcohol, one obtains a finely divided precipitate of platinum capable of absorbing

¹ In order to obviate misunderstandings and avoid cumbersome periphrases, the author, a lecturer, suggests to designate as “enzymes” the unformed or not organized ferments, whose action can occur without the presence of organisms and outside of the same.

hydrogen and possessing great catalytic properties, up to the point of becoming red-hot in the presence of a mixture of city gas and oxygen.

After some years Justus Liebig took up the idea and succeeded in preparing a platinum sponge able to absorb up to 250 times its volume of oxygen (Liebig 1829). In 1823 Johann Wolfgang Döbereiner discovered also the catalytic virtues of platinum, realizing that finely divided platinum in contact with hydrogen becomes red-hot while the hydrogen burns (Döbereiner 1823). In 1824 the Italian physicist and physician Ambrogio Fusinieri (1773–1853) from Vicenza re-interpreted Döbereiner's experiment, (Fusinieri 1824) putting forward the hypothesis that a solid layer of gas was adsorbed and continuously rebuilt on the platinum surface as the gas was consumed in the combustion reaction. The catalytic activity of platinum was studied also by William Henry, the author of the law bearing his name on the dissolution of gases in liquids, who discovered the inverse effect, namely that ethylene would stop the action of platinum on the mixture hydrogen–oxygen (Henry 1824). Soon after, Michael Faraday showed the ability of platinum to recombine hydrogen and oxygen obtained from the electrolysis of water (Faraday 1834).

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 1836), reviewed a large number of results on both homogeneous and heterogeneous catalytic reactions and proposed the existence of a “new catalytic force”, acting on the matter. He also coined the word catalysis, combining together 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 1839 Justus von Liebig, tied to the theory of organic radicals, postulated that the difference among the chemical properties of the elements forming a radical, could give rise to the break of their attraction, the breaking being favored by the temperature, by water, but also by a third body, the catalyst, which did not take part in the reaction (Liebig 1839).

A different interpretation of the catalytic mechanism was instead developed in 1845 by Julius Mayer who, in the frame of his thermodynamic researches, had devoted himself to the study of photosynthetic processes able to convert light into chemical energy. 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. In 1876, Mayer maintained that catalysis was a particular case of the more general concept of primer (Mayer 1876), a kind of chemical trigger able to start the reaction. The idea that the catalyst, without interacting with the reagents, could speed up the reaction producing intermediate products capable of opening new and faster paths to the reacting molecules, was developed by Christian Friedrich Schönbein (1799–1868), the discoverer of ozone and of gun cotton, who asserted that a reaction is not a single process, but occurs through a time ordered series of intermediate events (Schönbein 1848).

The possibility that a catalyst could release energy to facilitate the reaction, did show up again after some years in the catalysis theory proposed by the German Friedrich Stohmann (1832–1897) on the basis of his research into the combustion heat of foodstuffs. Stohmann thought that catalysis was a process in which the energy

released by the catalyst was transformed in motions of the atoms of the reacting molecules which reorganized themselves, giving rise to a more stable system by emission of energy (Stohmann 1894). Ostwald, however, did not agree with Stohmann and dedicated a large portion of a review of Stohmann's paper published on the *Zeitschrift für physikalische Chemie* (Ostwald 1894) to his own vision 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 several unstable systems exist such that their transformation into stable systems is so slow as to let them appear stable; the catalyst does nothing else than 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 metal catalytic effect was due to pure physical processes of adsorption in which the gases entered the cavities of the porous metals where their close contact, combined with local heating processes favored the reaction. In 1901 Ostwald synthetically formulated his own definition of catalysis (Ostwald 1902):

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

The theory of catalysis was the principal argument in favor of the award of the Nobel Prize to Ostwald in 1909 (Ostwald 1902) The Nobel lecture delivered by Ostwald at the Royal Academy of Sweden (Ostwald 1910) represented the definitive consecration of catalysis as one of the fundamental branches of chemical physics. In a short time it gained enormous influence on the development of the chemical industry.

Ostwald patented in 1902 the catalytic process for the production of nitric acid from ammonia. The procedure had been already developed and patented by *Charles Frédéric Kuhlmann* (1803–1881) more than 60 years before, but owing to the high price of ammonia was still considered as a pure academic exercise. 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 at that time the Fritz Haber ammonia synthesis (Haber and Le Rossignol 1910) was really effectual and the ammonia price became acceptable. Ammonia production in Germany was still controlled by BASF (*Badische Anilin und Soda Fabrik*) directed by Alwin Mittasch (1869–1953), pupil of Ostwald, who also maintained in 1930 that a catalysis was a particular case of chemical primer. The concept of primer was fashionable in the 1930s in Germany when the National Socialist regime encouraged the rhetoric of integration between nature and science for its autarkic programs. Several authors of the Nazi regime such as Walter Greiling (1900–1986), Karl Aloys Schenzinger (1886–1962) and Anton Zischka (1904–1997), used the concepts of primer and catalysis in books of Nazi propaganda.

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

Ostwald's process coupled to the Haber ammonia synthesis, led to large scale production of fertilizers and explosives, giving new breath to Germany during the first world war, when the guano import from Chile was blocked.

Support for Ostwald's theory of catalysis as a pure physical process came from the researches of the French chemist Jacques Duclaux (1877–1978), an expert of the chemistry of colloidal substances who, after the first world war, started a research project on the catalytic activity of colloids, based on the idea that catalysis was due to adsorption processes. Of the same idea was Henry Moissan, discoverer of fluorine who, studying in collaboration with Charles Moureu (1863–1929) the interaction of acetylene with finely divided metals, nickel, iron and cobalt (Moissan and Moureu 1896), was convinced that acetylene was adsorbed in the metal pores where by effect of heat a pyrolytic reaction took place, originating a mixture of carbon, benzene and hydrogen. Next year Paul Sabatier (1854–1941), professor at the University of Toulouse and his co-worker, the abbot Jean Baptiste Senderens (1856–1937), proved with a similar experiment on ethylene that Moissan's conclusions were wrong since ethylene in contact with the metal burns depositing carbon, but produces ethane and not hydrogen. From this they deduced that the action of nickel was to catalyze the attack to the ethylenic double bond, in other words to give origin to a true chemical reaction (Sabatier and Senderens 1897). On the basis of this result Sabatier and Senderens concluded that the 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 and confirmed a selective action of a pure chemical nature.

With this experiment and subsequent research (Sabatier 1897), Paul Sabatier made a fundamental contribution to heterogeneous catalysis, developing the catalytic hydrogenation technique by which ethylene was transformed in ethane using finely divided nickel as catalyst.

The catalytic hydrogenation method of Sabatier-Senderens initiated, in the period 1906–1919, a series of important papers in collaboration not only with Senderens but also with his students Alfonse Mailhe, Marcel Murat, Leo Espil and Georges Gaudion, published mostly in the *Comptes Rendus de l'Académie des Sciences* and in the *Bulletin de la Société Chimique de France*. In 1902 Sabatier and Senderens demonstrated also that by flowing a mixture of CO and H₂ in the ratio 1:3 in volumes on finely divided nickel at 250° one gets, with a 100% yield, methane and water



and that at higher temperature the same kind of reaction occurs also 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 1902a, b).

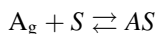
For his contributions to catalysis and in particular for the catalytic hydrogenation, illustrated in great detail in his famous 1913 treatise *La Catalyse en Chimie Organique*, Sabatier was awarded the Nobel Prize in 1912 together with Victor Grignard.

Sabatier was a very reserved man, very tied to Toulouse and indifferent to success to the point that he never agreed to move to Paris to the chair left vacant in 1907 by the death of Moissan. Nevertheless, when he became famous and particularly after the Nobel award, he incurred without understanding why, the resentment of Abbot Senderens, who felt denied official recognition for his contribution. As a consequence of their misunderstanding, their relationships which had lasted more than 30 years eventually deteriorated.

Later research on heterogeneous catalysis allowed several other elements to catalyze even very complex reactions, although elements belonging to group eight, in particular platinum, were the most prominent elements used for a good part of the century.

The understanding of the elementary mechanisms of heterogeneous catalysis took a great step forward in 1916 when Irvin Langmuir developed a theory of the chemisorptions of gases on metallic supports which rapidly became the starting point of the modern theories of heterogeneous catalysis (Langmuir 1916). According to Langmuir's model, a gas was adsorbed on a metallic surface thanks to residual valences, closely resembling those introduced by Thiele, Flürscheim and Lapworth in the discussion of molecules with conjugated bonds. In this way true compounds of variable composition were formed between the gas and the metal and these favored the reaction (Langmuir 1916, 1917, 1918).

Langmuir's theory offered a simple mechanism of attack of the gas molecules on the catalyst surface of the type



where A_g is a gas molecule and S an adsorption site. To simplify the mathematical treatment, Langmuir assumed that the metallic surface was uniform with adsorption sites S all equivalents, that there was a single adsorption mechanism, that the adsorbed molecules did not react together and that they formed at most a single monolayer.

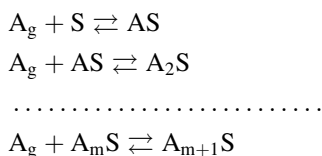
With these simplifications the theory allowed to connect at constant temperature the monolayer fraction θ of adsorbed gas molecules with the pressure P , according to the relationship

$$\theta = \frac{\alpha \cdot P}{1 + \alpha \cdot P}$$

where α was a constant characteristic of the bond energy between the gas and the substrate, representing the ratio between the equilibrium constants of the direct and inverse reactions. To a first approximation α was inversely proportional to temperature. The curves of θ as a function of P are known as Langmuir's adsorption isotherms.

In 1938, since the hypothesis of a single gas monolayer adsorbed on the metal surface was too limitative except at very low pressures, the Hungarian Stephen Brunauer (1903–1986) in collaboration with Paul Hugh Emmett (1900–1985) and with the future father of the atomic bomb Edward Teller (1908–2003) (Brunauer

et al. 1938) modified Langmuir's adsorption theory, developing a new one called BET from the initials of their names, taking into account the possibility of formation of multilayers of gaseous molecules A_g physisorbed at the sites S of the catalyst according to the reactions



In the analysis of the experimental data Langmuir's isotherms which predicts the occurrence of chemical bonds due to residual valences between the gas molecules and the atoms of the metallic surface, show in general a better agreement especially at low pressure and for chemisorptions processes, whereas the BET isotherms explain better the physisorption on non micro-porous materials in which the molecules are bound to the solid surface by weak van der Waals forces.

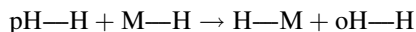
The first hypotheses on the mechanism involved in heterogeneous catalysis arose from the research of Adalbert and Ladislav Farkas, two Hungarian brothers who in 1927 went to the Fritz Haber Institute in Germany where both worked on molecular hydrogen and in particular on the ortho-para transformation catalyzed by tungsten. In 1933 the Farkas brothers were forced to flee Germany to escape Nazi persecution and being unable to go to the United States or England, emigrated to Israel. Later Adalbert went to the United States where he obtained academic positions, while Ladislav continued to work in the chemical industry.

After a seminal paper by Adalbert (Farkas 1931) and another by Ladislav in collaboration with Hans Sachsse (1906–1992) on the ortho-para transformation induced by the presence of paramagnetic (Farkas and Farkas 1934) and oxygen molecules, (Farkas and Sachsse 1933) the Farkas (Farkas and Farkas 1934) and in collaboration with Paul Karl Maria Harteck (1902–1985) (Farkas et al. 1934) proposed an interesting mechanism for the ortho-para transformation process following a previous treatment (Wigner 1933) by the famous physicist Eugene Paul Wigner (1902–1995), another high level Hungarian emigré. The theory assumed that changes from ortho- to para-hydrogen occur because the inhomogeneous magnetic field in the vicinity of a paramagnetic ion or molecule acts as a perturbation. In this way during a collision between a hydrogen molecule and the paramagnetic ion on the metal surface, the otherwise forbidden ortho-para transition can occur.

The reaction mechanism proposed by the Farkas brothers for the ortho-para transformation process opened the road to intense research activity on the elementary mechanisms of the catalytic processes. After a few years the transformation was also studied by one of the best English experts of catalysis, the chemist Eric Rideal starting from the idea, borrowed from the BET isotherms theory that on the solid surface multilayer's of adsorbed molecules could be deposited.

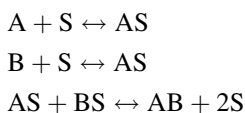
Eric Keightley Rideal (1890–1974) after a period of postdoctoral training in Germany from 1910 to 1913, first at Aachen and then at Bonn, acquired

considerable experience in heterogeneous catalysis working with Hugh S. Taylor (1890–1974) at the Haber-Bosch process for the ammonia synthesis from hydrogen and nitrogen. In 1930 he became professor at Cambridge where he founded a world-renowned known laboratory of colloid chemistry. For the conversion reaction of para to ortho molecular hydrogen Rideal proposed the mechanism bearing his name that assumes that a para H_2 molecule, weakly physisorbed in the second layer on the solid surface (M), reacts with an hydrogen atom strongly chemisorbed in the underlying layer (Rideal 1939) exchanging an H atom according to the scheme



The same type of mechanism known as the Eley-Rideal, was proposed successively by Daniel Douglas Eley and by Rideal himself for reactions between two molecules, one adsorbed on the catalyst and the other coming from the gas phase (Eley and Rideal 1940, 1941). Eley who had started his research activity with Michael Polanyi (Eley and Polanyi 1935) entered later Rideal's research group and eventually became editor of the famous series *Advances in Catalysis* (Academic Press, New York).

A more efficient mechanism, based on Langmuir's adsorption theory and known as the Langmuir-Hinshelwood mechanism, was developed by Sir Cyril Norman Hinshelwood (Hinshelwood 1940) starting from the idea that two molecules A and B, both adsorbed on the catalyst surface could give rise to a bimolecular reaction according to the scheme (Gadsby et al. 1946)



In the first half of the twenty-first century the industrial applications of catalysis had a substantial boost from the work of the Muscovite Vladimir Nikolaevich Ipatieff (1867–1952) who as a young man took up a military career studying at the famous Russian military academy *Mikhailovskaia artilleriiskaia akademiia*. After his graduation in chemistry at the University of St. Petersburg in 1907 he reached the highest grades in the Czar's Nicholas II army up to the position of general. After the October revolution Ipatieff remained in the Soviet Union where in 1927 he founded the high pressure institute and where he was even awarded the prestigious Lenin prize.

In 1931 to escape Stalin's purges he took advantage of a trip abroad to escape to the United States where he became research director at the Universal Oil Products at Des Plaines as well as professor of chemistry at the Northwestern University. In the same year a young Polish chemist, Herman Pines (1902–1996), joined his group and became his closest coworker up to his death. Ipatieff and Pines set right in the 1930s the catalytic technique of addition of a paraffin molecule to the double bond of an olefin in the presence of a strong acid, operation considered impossible until

then since paraffins were considered chemically inert molecules as stated by their Latin name *parum affinis*. In 1932 they proved that isobutane reacts at -35°C with olefins and this alkylation reaction opened the road to the synthesis of gasoline with high octane number. The synthesis of iso-octane from butene and isobutane that they patented in 1938 allowed to produce high quality fuel that played a decisive role for the Royal Air Force victory during the Aerial Battle of Britain in 1941.

In 1928 Johannes Nicolaus Brønsted (Brønsted 1928) reconsidered the problem of homogeneous acid and basic catalysis, correlating the free energy variation to the activation energy and showing that strongly exothermic reactions possess a low activation energy. A mathematical form of this concept was produced in 1936 by Brønsted's pupil Ronald Percy Bell (1907–1996) (Bell 1935, 1936) and after him by Meredith G. Evans and Michael Polanyi, when this latter joined the University of Manchester. These authors tackled the problem in terms of the potential energy surface (Evans and Polanyi 1937) and in order to simplify the numerical calculations approximated the form of the potential energy curve with pieces of linear segments, producing a linear relationship between the activation energy ε_a and the free energy ΔG in the form $\varepsilon_a = k_1 + k_2\Delta G$ (Evans and Polanyi 1938) where the constants k_1 and $k_2 > 0$ depend on the inclination of the segments of curve. The linear relation between the free energy ΔG and the activation energy is known as the *Bell-Evans-Polanyi principle*. A more accurate representation, due to Rudolph Arthur Marcus (Marcus 1968), approximated the potential energy curve with two parabolas centered at the two energy minima and added a quadratic term to the previous equation.

In the period 1930–1960, research was mostly oriented to individuate the role played by the electronic structure of metals and semiconductors in catalytic processes. In this way the electronic theory of catalysis developed as a valid combination of solid state physics and adsorption theories. The electronic theory of catalysis was essentially a phenomenological one and had a considerable development in Russia after the pioneering research of the Ukrainian Lev Vladimirovich Piszrzhnevsky (1871–1938), the first who correlated in 1916 the catalytic activity of solids with their electronic structure (Piszrzhnevsky 1955). The contribution of the Russian school to heterogeneous catalysis is well documented in the book of Georgii K. Borekov, “Heterogeneous Catalysis” (Borekov 2003) and reached its heights with the institution in 1958 of the Soviet Institute of catalysis dedicated today to its founder and first director Borekov, a great supporter of the importance of the chemical nature of heterogeneous catalysis. In 1953 he formulated the rule of the approximate perseverance of the catalytic capacity of substance with the same chemical composition. Even if unable to explain the intimate mechanisms of catalysis, the electronic theory opened the road to the applications of the concepts of transition state and of collective surface effects later incorporated in the quantum theory of catalysis.

The concept of surface collective phenomena was introduced in the catalysis theory by Dennis Albert Dowden (1950) and after by Karl Hauße (1950) and Fyodor F. Vol'kenshtein (Vol'kenshtein 1960), who contributed a large amount

of experimental research to correlate catalytic activity to the chemical structure of semiconductors and alloys used in heterogeneous catalysis.

With the coming of quantum mechanics and of the physics of surfaces it became clear that on the metallic surfaces were present sites particularly active in catalysis. A fundamental contribution to this problem was given by the Berliner Georg-Maria Schwab (1899–1984) who started his interest in catalysis working at the catalytic decomposition of methane and ammonia (Schwab and Pietsch 1926) in collaboration with Erich Pietsch (1902–1979) who later would become one of the principal figures of scientific divulgation in Germany as editor of the *Gmelin Handbuch der anorganischen Chemie*. In 1929 they developed together the “adlineation” theory describing the reaction along the line between two surface phases, that assigns particular catalytic efficiency to structures with high density of adsorption (Schwab and Pietsch 1929). Schwab discussed in detail the catalytic activity of lattice defects and dislocations at the surface of solid catalysts that expose to adsorption different crystal faces giving rise to an increase of the density of adsorbed gas molecules on particularly active sites. In 1929 in collaboration with Erika Cremer (1900–1996) a German pioneer in gas-chromatography, he introduced in his kinetic approach to catalysis the concept of compensation effect that he named the “theta rule”, referring to the thermal preparation used to fix the thermodynamic distribution of catalytic centers (Cremer 1929). In 1930 Schwab and Hermann Schultes discussed also the importance of finely divided metal catalysts dispersed on a support of metal oxides, argument that Schwab reconsidered in 1950 (Schwab 1950). He wrote in 1931 his comprehensive treatise *Katalyse vom Standpunkt der Kemischen Kinetik* (Verlag J. Springer, Berlin 1931) translated in English in 1937 as *Catalysis from the Standpoint of Chemical Kinetics*, (D Van Nostrand Co 1937) and acted as editor of the *Handbuch der Katalyse* (Springer Verlag, Wien) from 1940 to 1957. In 1939 he emigrated to Greece as director of the chemical physics department of the Nikolaos Kanellopoulos Institute in the Piraeus, until in 1950 he went back to Germany as director of the Institute of Chemical Physics of the University of Munich where he directed a broad research project on catalysis.

With the development of new experimental techniques such as LEED (*Low Energy Electron Diffraction*), UPS (*Ultraviolet photoelectron Spectroscopy*) and STM (*Scanning tunneling Microscope*) which revolutionized the study of surfaces in the second half of the twentieth century, the understanding of the elementary mechanisms of catalysis made a significant quality jump.

The LEED technique is a sophisticated application of the discovery of electron diffraction made in 1927 by Clinton Joseph Davisson (1881–1958) and his assistant Lester Halbert Germer (1896–1971) (Davisson and Germer 1927) following the hypothesis postulated in 1924 by Louis de Broglie. One month after George Paget Thomson, son of J.J. Thomson with his coworker Alexander Reid, published their electron diffraction obtained with electron kinetic energy thousand times higher than that used by Davisson and Germer (Thomson and Reid 1927). These two experiments opened a new era for the application of electron diffraction to the study of matter.

Electron diffraction did not, however, become a popular tool for the study of surfaces until the early 1960s, owing to the difficulty of correctly monitoring the

directions and intensities of the diffracted beams with the available vacuum techniques and detection methods. In the early 1960s ultra high vacuum became widely available and better detection methods were devised and thus the LEED technique experienced an intensive diffusion in catalytic laboratories, thanks also to the realization of new techniques for the reconstruction of clean metal surfaces. Its operability as a true research instrument in chemical physics for the determination of bond angles and bond lengths of metal surfaces and of molecular systems adsorbed on them, became a true reality only when a new dynamical electron diffraction theory which took into account the possibility of multiple scattering was realized.

Another important physical technique for the study of catalytic surfaces is the Scanning tunneling Microscopy developed in 1981 by the German Gerd Binnig (1947–) and the Swiss Heinrich Rohrer (1933–) at the IBM research laboratories in Zurich (Binnig et al. 1986). The tunnelling microscope technique is based on the tunnel effect realized by letting a small conducting tip to approach very closely a surface so that electrons can tunnel through the vacuum when a voltage difference is applied among them. With this kind of microscope a resolution of Ångströms can be easily obtained, well suited to image individual atoms and to explore the presence of impurities attached to a surface. An important advantage of this technique with respect to LEED is that it can be applied not only in ultra high vacuum but also in air, or in a liquid and even at high temperatures.

The intelligent application of these techniques characterized the research of the German Gerhard Ertl and of the Hungarian Gabor Somorjai, the two figures who have contributed most to the development of modern catalysis theories.

Gerhard Ertl (1936–) was born in Stuttgart where he graduated in 1961 after a post doctoral period in Paris first and then at the München Technische Universität where he completed his Ph.D. thesis in 1965. In his research he faced the study of the surface structure of metallic catalysts and semiconductors and developed avant-garde techniques allowing observation of atoms or molecules absorbed on very clean surfaces, with active sites completely free from adsorbed atmospheric oxygen or nitrogen molecules.

In 1974, by coupling LEED measurements of electron diffraction to desorption techniques and to theoretical models, he succeeded in explaining how hydrogen is tight to palladium (Conrad, Ertl, Latta 1974) and nickel (Christmann et al. 1974) metallic surfaces. In 1977 he worked out a theory of the molecular mechanisms in the famous Haber Bosch ammonia synthesis, concentrating his attention on the process that he considered the determining step for the reaction rate constants, namely the dissociation of the N_2 molecules into single atoms of nitrogen. Ertl first showed that nitrogen atoms derived from the breaking of the $N \equiv N$ triple bond are present on the iron catalyst surface (Bozso et al. 1977) and proposed a model of the iron-nitrogen bond. He proved also that the activation energy is different for different crystallographic planes of the iron, pointing out the greater efficiency of the (111), (110) e (100) planes and clarified the details of the reaction mechanism (Ertl and Huber 1980).

Later Ertl studied the non linear mechanisms involved in the classical oxidation reaction of carbon monoxide CO on platinum and palladium catalysts (Skottke et al.

1987). He identified at the microscopic level the causes of the non linear behaviour of the reaction and the conditions that give rise to oscillating reactions (Cox et al. 1985) and contributed to the theory underlying the production of catalytic exhaust pipes for cars and of combustion cells. He investigated also the formation of molecular aggregates on the surface of tiny crystallites of ice in the stratosphere, responsible for reactions that damage the ozone layer protecting the Earth from solar radiation. For his researches Gerhard Ertl received in 2007 the Nobel Prize for chemistry.

Of equal importance is the research and under many aspects equivalent are the researches of the Hungarian Gabor Arpad Somorjai (1935–), who as a child escaped the holocaust thanks to the help of the Swedish diplomat Raoul Wallenberg who in 1944 procured for him and his mother false Swedish passports. Somorjai studied chemical engineering at Budapest but in 1956, having taken part in the Hungarian revolution, escaped to the United States where he obtained the Ph.D. in 1960 (Somorjai 1960) at the University of California, Berkeley, where he still works as a teacher and a researcher since 1964, after a period at the IBM research laboratories at Yorktown Heights, New York. At Berkeley Somorjai discovered that inhomogeneous catalytic reactions occur where there are defects on the catalyst surface: when these defects break down, new bonds are formed between the atoms, with creation of new organic compounds.

Since 1965 Somorjai has directed a research project concerning the study of the molecular bases of heterogeneous catalysis by characterizing the structure of the crystal surfaces and determining the nature of the bonds with adsorbed molecules.

In these researches Somorjai utilized single crystals of transition metals in a large number of catalytic reactions both in high pressure cells and under high vacuum, applying advanced techniques to control *in situ* the catalyst surface during the reactions. Since 1994 he has been interested in nanostructures (Somorjai and Park 2008) produced either by lithography through bombardment with electrons, or by epitaxial growth (Habas et al. 2007), as well as in photo lithography and in colloidal science, studying among others the hardness and the resistance to friction of the catalysts using either atomic force microscopy (AFM or SFM) or generation of overtones by non linear optics.

In the 1990s Somorjai started an important collaboration with his colleague at Berkeley Yuen-Ron Shen (1935–), one of the greatest experts of non-linear optics. Together they developed the technique of overtone generation by frequency sum or difference (Cremer et al. 1996) which Somorjai applied to the study of catalytic reactions on surfaces (Somorjai and McCrea 2000).

Somorjai, from his interest in the Haber-Bosch process, reached different conclusions from those of Ertl as far as the slow stage of the reaction is concerned. According to Somorjai the slow stage is the one in which the ammonia molecules are detached from the catalyst. Somorjai derived this idea from the knowledge of the fact that in the industrial synthetic process several molecules of NH_3 are produced at the same time and these partially fill the catalyst surface preventing the adsorption of new nitrogen molecules (Spencer et al. 1982).

The tradition of heterogeneous catalysis studies, established at Cambridge by Rideal and Eley, was successfully continued by the Welshman John Meurig Thomas who complemented his efforts in the elucidation of catalysis with an equally powerful interest in general culture and in the popularization of science. His balance of interests was shown through his position as director of the Royal Institution, a role that identified him as the natural heir of his scientific hero, Michael Faraday. He celebrated this in 1991 in a beautiful book entitled *Michael Faraday and the Royal Institution: The Genius of Man and Place*, (Taylor and Francis 1991)

Born in the small mining town of Llanelli in South Wales, he graduated in 1958 from the University of Wales, Swansea under the supervision of Keble Sykes, completing his Ph.D. work through a collaboration with the Queen Mary College, University of London. After a year he joined the Department of Chemistry at the University of Wales, Bangor, where he started his academic career until in 1969 he became professor of chemistry at the University College of Wales, Aberystwyth. In 1978, he was appointed Head of the Department of Physical Chemistry at the University of Cambridge and in 1986 succeeded George Porter as Director of the Royal Institution of Great Britain. In his research, Thomas has used different chemical-physical techniques in particular synchrotron radiation, high-resolution X ray diffraction and spectroscopy to investigate the nature and the location of active sites of solid catalysts under operating conditions (Wright et al. 1986) and to devise new mesoporous (Raja et al. 2003), micro-porous, and molecular sieve catalysts. He has also contributed to the development of industrial applications of heterogeneous catalysis, inventing the solvent-free (Thomas et al. 2001) catalytic synthesis of ethyl acetate, which has reached today a production of 200,000 t/year in the UK (Ballantine et al. 1984). He has also devised a single-step, solvent-free process for the production of caprolactam, the raw material for nylon-6 (Thomas et al. 2005).

References

- Arrhenius S (1887) Über die Dissociation der im Wasser gelösten Stoffe. Z Phys Chem 1:631
Arrhenius S (1889) Über die Reaktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Säuren. Z Phys Chem 4:226–248
Ballantine JA, Purnell JH, Thomas JM (1984) Sheet silicates: broad spectrum catalysts for organic synthesis. J Mol Catal 27:157–167
Bell RP (1935) The theory of reactions involving proton transfers. Trans Faraday Soc 31:875
Bell RP (1936) The theory of reactions involving proton transfers. Proc R Soc Lond 154A:414
Berthelot M, St. Gilles P (1862) De la formation et de la décomposition des éthers. Ann Phys Chim 65:385
Berthollet CL (1801) Recherches sur les lois de l'affinité. Baudouin, an IX, Paris
Berzelius JJ (1836) Quelques Idées sur une nouvelle Force agissant dans les Corps Organiques. Ann Chim Phys 61:146
Binnig G, Rohrer H (1986) Scanning tunneling microscopy. IBM J Res Dev 30:4

- Bodenstein M (1913) Eine theorie der photochemischen reaktionsgeschwindigkeiten. *Z Phys Chem* 85:329–397
- Bodenstein M (1922) Chemische Kinetik. *Erg Exakt Naturwiss* 1:197–209
- Bodenstein M, Dux W (1913) Photochemische Kinetik des Chlor-knallgases. *Z Phys Chem* 85:297
- Boreskov GK (2003) Heterogeneous catalysis. traduzione inglese di K.I. Zamaraev e A. V. Kzasin, Nova Science Publisher, Hauppauge
- Bozso F, Ertl G, Grunze M, Weiss M (1977) Interaction of nitrogen with iron surfaces. 1. Fe(100) and Fe(111). *J Catal* 49:18–41
- Brønsted JN (1928) Acid and basic catalysis. *Chem Rev* 5:231–338
- Brunauer S, Emmett PH, Teller E (1938) Adsorption of gases in multi molecular layers. *J Am Chem Soc* 60:309
- Cashion K, Polanyi JC (1958) Infrared chemiluminescence from the gaseous reaction atomic H plus Cl₂. *J Chem Phys* 29:455
- Chen CH, Siska PE, Lee YT (1973) Intermolecular potentials from crossed beam differential elastic scattering measurements, VIII. *J Chem Phys* 59:601–610
- Christmann K, Schöber O, Ertl G, Neumann M (1974) Adsorption of hydrogen on nickel single crystal surfaces. *J Chem Phys* 60:4528
- Conrad H, Ertl G, Latta EE (1974) Adsorption of hydrogen on palladium single-crystal surfaces. *Surf Sci* 41:435–446
- Cordus V (1548) *Pharmacorum Conficiendorum Ratio*. Jacobus Gazellus, Paris
- Cox MP, Ertl G, Imbihl R (1985) Spatial self-organization of surface-structure during an oscillating catalytic reaction. *Phys Rev Lett* 54:1725
- Cremer E, Schwab GM (1929) Zusammenhang zwischen Aktivierungswärme und Aktivität. *Z Physikal Chem* 144:243
- Cremer PS, Su XC, Shen YR, Somorjai GA, (1996) *Ethylene hydrogenation on Pt(111) monitored in situ at high pressures using sum frequency generation*. *J. Am. Chem. Soc.*, 118, 2942–2949
- Davison C, Germer LH (1927) Reflection of electrons by a crystal of nickel. *Nature* 119:558–560
- Davy H (1817) Some new experiments and observations on the combustion of gaseous mixtures, with an account of a method of preserving a continued light in mixtures of inflammable gases and air without flame. *Philos Trans* 107:77–85
- Davy E (1820) On some combinations of platinum. *Philos Trans* 110:108–125
- Deisenhofer J, Epp O, Miki K, Huber R, Michel H (1984) X-ray structure analysis of a membrane protein complex. Electron density map at 3 Å resolution and a model of the chromophores of the photosynthetic reaction center from *Rhodospseudomonas viridis*. *J Mol Biol* 180:385
- Döbereiner JW (1822) Zur Gährungs-Chemie und Anleitung zur Darstellung verschiedener Arten künstlicher Weine, Biere u.s.w. Aug. Schmid, Jena
- Döbereiner JW (1823) Propriétés nouvelles et remarquables reconnues au sus-oxide de platine, au sulphure oxidé et à la poussiere du même métal. *Ann Chim Phys* 24:91
- Down DA (1950) Heterogeneous catalysis. Part I. Theoretical basis. *J Chem Soc* 242–265
- Dulong PL, Thenard L (1823a) Note sur la Propriété que Possèdent Quelques Métaux de Faciliter la Combinaison des Fluides Élastiques. *Ann Chim* 23:440–444
- Dulong PL, Thenard L (1823b) Nouvelles Observations Sur la Propriété Dont Jouissent Certains Corps de Favoriser la Combinaison des Fluides Élastiques. *Ann Chim* 24:380–387
- Eley DD, Polanyi M (1935) Catalytic interchange of hydrogen with water and alcohol. *Trans Faraday Soc* 32:1388–1397
- Eley DD, Rideal EK (1940) Parahydrogen conversion on tungsten. *Nature* 146:40
- Eley DD, Rideal EK (1941) The catalysis of parahydrogen conversion by tungsten. *Proc R Soc Lond A* 178:429–451
- Ertl G, Huber M (1980) Mechanism and kinetics of ammonia decomposition on iron. *J Catal* 61:537–539
- Evans MG, Polanyi M (1935) Some applications of the transition state method to the calculation of reaction velocities, especially in solution. *Trans Faraday Soc* 31:875
- Evans MG, Polanyi M (1937) On the introduction of thermodynamic variables into reaction kinetics. *Trans Faraday Soc* 33:448

- Evans MG, Polanyi M (1938) Inertia and driving force of chemical reactions. *Trans Faraday Soc* 34:11–28
- Eyring H (1935) The activated complex in chemical reactions. *J Chem Phys* 3:107
- Eyring H, Polanyi M (1931) Über einfache Gasreaktionen. *Z Phys Chem Abt B* 12:279–311
- Faraday M (1834) Experimental researches in electricity. VI. *Philos Trans R Soc* 124:55
- Farkas A (1931) Aktivierungsenergie der p-H₂-Umwandlung an Nickel. *Z Phys Chem B* 14:371
- Farkas A, Farkas L (1934) Experiments on heavy hydrogen. Part I. *Proc R Soc Lond A* 144:467–480
- Farkas L, Sachsse H (1933) Über die homogene Katalyse der Para-Orthowasserstoff umwandlung. *Z Phys Chem B*, 23, 1, 19
- Farkas A, Farkas L, Harteck P (1934) Experiments on heavy hydrogen. II. The ortho-para conversion. *Proc R Soc Lond A* 144:481–493
- Fusineri A (1824) Sulla Causa delle Combustione di Sostanze Gaseose per Mezzo delle Superficie di Alcuni Metalli. *Giorn Fis* 7:371–376, 443–449
- Gadsby J, Hinshelwood CN, Sykes KW (1946) The kinetics of the reactions of the steam-carbon system. *Proc R Soc Lond A* 187:151–187
- Gibson CH, Hinshelwood CN (1928) The influence of nitrogen peroxide on the union of hydrogen and oxygen. A problem of trace catalysis. *Trans Faraday Soc* 24:559
- Guldberg CM, Waage P (1867) *Études sur les Affinités Chimiques*. Christiania University Press, Oslo
- Guldberg CM, Waage P (1879) Concerning chemical affinity. *Erdmann's Journal für Praktische Chemie* 19: 69–114. Translated in German by Abegg in *Ostwald's Klassiker der Exacten Wissenschaften*, vol 104. Wilhelm Engleman, Leipzig, pp 126–171, 1899
- Habas SE, Lee H, Radmilovic V, Somorjai GA, Yang P (2007) Shaping metal nanocrystals through epitaxial seeded growth. *Nat Mater* 6:692–697
- Haber F, Le Rossignol R (1910) Über die Darstellung des Ammoniaks aus Stickstoff und Wasserstoff. *Z Elektrochem* 16:244
- Harcourt AV, Esson W (1867) On the laws of connexion between the conditions of a chemical change and its amount. *Philos Trans* 157:117
- Hauffe K (1950) *Reaktionen in und an festen Stoffen B*, vol Band 2. Springer, Berlin, p 696
- Heitler W, London F (1927) Wechselwirkung neutraler Atome und homöpolare Bindung nach der Quantenmechanik. *Z Phys* 44:455–472
- Henry W (1824) On the action of finely divided platinum on gaseous mixtures and its application to their analysis. *Philos Trans* 114:266–289
- Herschbach DR (1966) Reactive scattering in molecular beams. *Adv Chem Phys* 10:319–393
- Herschbach DR (1973) Reactive scattering. *Faraday Discuss Chem Soc* 55:233–251
- Herschbach DR, Johnston HS, Pitzer KS, Powell RE (1956) Theoretical pre-exponential factors for twelve bimolecular reactions. *J Chem Phys* 25:736–741
- Hinshelwood CN (1940) *The kinetics of chemical change*. Clarendon, Oxford
- Hinshelwood CJ (1952) Reaction patterns in bacterial metabolism. *Bull World Health Organ* 6:3–17.
- Hinshelwood CJ (1953) *Chem. Soc, Autotynthesis*, 1947–1956
- Kassel LS (1928) Studies in homogeneous gas reactions. II. Introduction of quantum theory. *J Phys Chem* 32:1065–1079
- Kilkenny B. C. and Hinshelwood C. (1952) An Investigation of some Adaptive Changes in Yeast Cells, *Proc. R. Soc. Lond. B* vol. 139, 575–583
- King DL, Herschbach DR (1973) Facile four centre exchange reactions. *Faraday Discuss Chem Soc* 55:331–343
- Kirchhoff SK (1811) Die Entdeckung der leichten Umwandlung der Stärke in Zucker. *Bull Neusten Wiss Naturwiss* 10:88–92
- Kolbe H. (1887) Zeichen der Zeit, *Journal für Praktische Chemie* 15, 473
- Kühne W (1877) Über das Trypsin (Enzym des Pankreas). In: *Verhandlungen des naturhistorisch-medizinischen Vereins zu Heidelberg*, vol 1. Neue Folge, Heidelberg, pp 194–198
- Landolt H. (1902), *The optical rotating power of organic substances and its practical applications*: Easton, Pa., Chemical Pub. Co.

- Langmuir I (1916) The constitution and fundamental properties of solids and liquids. I. Solids. *J Am Chem Soc* 38:2221
- Langmuir I (1917) The constitution and fundamental properties of solids and liquids. II. Liquids. *J Am Chem Soc* 39:1848
- Langmuir I (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. *J Am Chem Soc* 40:1361–1402
- Le Bel J. A. (1874) Sur les relations qui existent entre les formules atomiques des corps organiques et le pouvoir rotatoire de leurs dissolution, *Bulletin de la Société Chimique de Paris* 22, 337
- Le Chatelier HL (1884) Sur un énoncé général des lois des équilibres chimiques. *Comptes Rendus* 99:786
- Lee YT, McDonald JD, LeBreton PR, Herschbach DR (1969) Molecular beam reactive scattering apparatus with electron bombardment detector. *Rev Sci Instrum* 40:1402
- Levine RD, Bernstein RB (1987) *Molecular reaction dynamics and chemical reactivity*. Oxford University Press, New York
- Liebig J (1829) Über Edmund Davy's schwarzen Platinniederschlag und über die Eigenschaft des Platinschwamms, das Wasserstoffgas zu entzünden. *Ann Phys* 93:101–114
- Liebig J (1839) Über die Erscheinungen der Gährung, Fäulniss und Verwesung, und ihre Ursachen. *Ann Pharm* 30:250–287
- London F (1928a) *Probleme der moderne Physik (Sommerfeld Festschrift)*, vol 104. Hirzel, Leipzig
- London F (1928b) Zur Quantenmechanik der homöopolaren Valenzchemie. *Z Phys* 46:455
- London F (1929) Quantenmechanische Deutung der Vorgänge der Aktivierung. *Z Elektrochem* 35:552–555
- Malaguti F (1853) Exposition de Quelques Faits relatifs a l'action réciproque, des sels solubles. *Ann Chim* 37:198–206
- Marcus RA (1952) Unimolecular dissociations and free radical recombination reactions. *J Chem Phys* 20:359
- Marcus RA (1956) On the theory of oxidation-reduction reactions involving electron transfer. I. *J Chem Phys* 24:966
- Marcus RA (1965) On the theory of electron-transfer reactions. VI. Unified treatment of homogeneous and electrode reactions. *J Chem Phys* 43:679
- Marcus RA (1968) Theoretical relations among rate constants, barriers, and Bronsted slopes of chemical reactions. *J Phys Chem* 72:891
- Mayer JR (1876) *Die Torricellische Leere und über Auslösung*. Verlag der J. G. Cotta'schen Buchhandlung, Stuttgart
- McDonald JD, LeBreton PR, Lee YT, Herschbach DR (1972) Molecular beam kinetics: reactions of deuterium atoms with halogen molecules. *J Chem Phys* 56:769–788
- Miller WB, Safron SA, Herschbach DR (1967) Exchange reactions of alkali atoms with alkali halides: a collision complex mechanism. *Discuss Faraday Soc* 44:108–122
- Miller JR, Calcatera LT, Gloss GL (1984) Intramolecular long-distance electron transfer in radical anions. The effects of free energy and solvent on the reaction rates. *J Am Chem Soc* 106:3047
- Mitscherlich E (1844) *Lehrbuch der Chemie*, 4th edn. Mittler, Berlin, p 617
- Moissan H, Moureu Ch (1896) Action de l'acétylène sur le fer, le nickel et le cobalt réduits par l'hydrogène. *Comptes Rendus* 122:1241
- Nernst W (1918a) Zur Anwendung des Einsteinschen photochemischen Äquivalentgesetzes. I. *Z Elektrochem* 24:335–336
- Nernst W (1918b) *Des neuen Wärmesatzes*. Verlag von Wilhelm Knapp, Halle
- Nollet L'Abbé (1748) *Recherches sur les Causes du Bouillonnement des Liquides*. Mem Acad R Sci Paris
- Ostwald W (1894) Definition der Katalyse. *Z Phys Chem* 15:705–706
- Ostwald W (1902) Über Katalyse. *Nature* 65:522 (Summary of a lecture hold by Ostwald at Amburg in 1901 at the Deutsche Naturforscher Versammlung)
- Ostwald W (1910) Über Katalyse. *Ann Naturphilos* 9:1–25
- Payen A, Persoz J-F (1833) Mémoire sur la diastase, les principaux produits de ses réactions et leurs applications aux arts industriels. *Ann Chim Phys* 53:73–92

- Pfaundler von Hadernur L (1867) Beiträge zur chemischen Statik. Pogg Ann, 131
- Pfeffer WFP (1887) Osmotische Untersuchungen. W. Engelmann, Leipzig
- Pisarzhevsky LV (1955) Selected works on catalysis. Izd Acad Nauk USSR Kiev, in Russian
- Polanyi M (1932) Developments of the theory of chemical reactions. *Naturwissenschaften* 20:289–296
- Polanyi JC (1963) Infrared chemiluminescence. *J Quant Spect Rad Trans* 3:471
- Polanyi JC (1967) Dynamics of chemical reactions. *Discuss Faraday Soc* 44:293
- Polanyi JC, Zewail AH (1995) Direct observation of the transition state. *Accounts Chem Res* (Holy Grail Issue) 28:119
- Raja R, Thomas JM, Jones MD, Johnson BFG, Vaughan DEW (2003) A constraining asymmetric organometallic catalysts within mesoporous supports boosts their enantioselectivity. *J Am Chem Soc* 125:14982–14983
- Rice OK, Ramsperger HC (1927) Theories of unimolecular gas reactions at low pressures. *J Am Chem Soc* 49:1617–1629
- Rice OK, Ramsperger HC (1928) Theories of unimolecular gas reactions at low pressures. *J Am Chem Soc* 50:617–620
- Rideal EK (1939) Parahydrogen conversion on tungsten. *Proc Camb Philos Soc* 35:130
- Sabatier P (1897) Action du Nickel sur l'Éthylène. *Compt Rend* 124:616–618
- Sabatier P, Senderens J-B (1897) Action du nickel sur l'éthylène. Synthèse de l'éthane. *CR Acad Sci Paris* 124:1358–1360
- Sabatier P, Senderens JB (1902a) New synthesis of methane. *Compt Rend* 134:514–516
- Sabatier P, Senderens JB (1902b) New synthesis of methane. *J Chem Soc* 82:333
- Sato S (1955) Potential energy surface of the system of three atoms. *Chem Phys* 23:592, 2465
- Schönbein CF (1848) On some chemical effects produced by platinum. *Mem Proc Chem Soc* 3:17
- Schwab GM (1950) On compact-dispersed silver. *J Phys Chem* 54:576–580
- Schwab GM, Pietsch E (1926) Thermische Spaltung von Methan am Glühdraht. *Z Elektrochem* 32:430–434
- Schwab GM, Pietsch E (1929) Zur Topoehemie der Kontakt-Katalyse. II. Über einen experimentellen Fall der Adlineation. *Z Phys Chem B* 2:262–264
- Semyonov NN (1928) Zur Theorie des Verbrennungsprozesses. *Z Phys* 48:571
- Semyonov NN (1929) Kinetics of chain reactions. *Chem Rev* 6:347–379
- Semyonov NN (1934) Chain reactions (in Russian). Goskhimizdat, Leningrad. English edition: Semyonov NN (1935) Chain reactions. Oxford Press
- Semyonov NN (1940) Study of properties of solutions of kinetic equations. *Usp Fiz Nauk* 23:251
- Shorter J (1980) A. G. Vernon Harcourt. *J Chem Educ* 57:411–416
- Skottke M, Behm RJ, Ertl G, Penka V, Moritz W (1987) LEED structure analysis of the clean and (2×1)H covered Pd(110) surface. *J Chem Phys* 87:6191
- Somorjai G (1960) A small angle x-ray study of metallized catalysts. Ph.D. thesis, University of California, Berkeley
- Somorjai GA, McCrea KR (2000) Sum frequency generation: surface vibrational spectroscopy studies of catalytic reactions on metal single-crystal surfaces. *Adv Catal* 45:385–438
- Somorjai GA, Park JY (2008) Evolution of the surface science of catalysis from single crystals to metal nanoparticles under pressure. *J Chem Phys* 128:182504
- Spencer ND, Schoonmaker RC, Somorjai GA (1982) Iron single crystals as ammonia synthesis catalysts: effect of surface structure on catalyst activity. *J Catal* 74:129–135
- Stohmann F (1894) Über dem Wärmewerth der Bestandtheile der Nahrungsmittel. *Z Biol* 31:364–391
- Stubbs FJ, Hinshelwood CN (1951) The thermal decomposition of hydrocarbons. *Discuss Faraday Soc* 10:129
- Thomas JM, Raja R (2005) Design of a “green” one-step catalytic production of ϵ -caprolactam (precursor of nylon-6). *Proc Natl Acad Sci* 102:13732–13736
- Thomas JM, Raja R, Sankar G, Johnson BFG, Lewis DW (2001) Solvent-free routes to clean technology. *Chem-Eur J* 7:2972–2978
- Thompson HW, Hinshelwood CN (1929) The mechanism of the homogeneous combination of hydrogen and oxygen. *Proc R Soc Lond A* 122:170

- Thomson GP, Reid AA (1927) Diffraction of cathode rays by a thin film. *Nature* 119:890
- Van't Hoff (1874), Voorstel tot Uitbreiding der Tegenwoordige in de Scheikunde gebruikte Structuurformules in de Ruimte: benevensen daarmee samenhangende Opmerking omtrent het Verband tusschen Optisch Actief Vermogen en chemische Constitutie van Organische Verbindingen, *Archives neerlandaises des sciences exactes et naturelles*, 9, 445–454, Greven, Utrecht, 1874
- van't Hoff JH (1877) Die Grenzebene ein Beitrag zur Kenntniss Esterbildung. *Chem Ber* 10:669
- van't Hoff JH (1878) De verbeeldingskracht in de wetenschap. P.M. Bazenijk, Rotterdam
- van't Hoff JH (1884) *Etudes de Dynamique Chimique*. Frederik Muller, Amsterdam, pp 114–118
- van't Hoff JH (1887) Die Rolle des osmotischen Druckes in der Analogie zwischen Lösungen und gases. *Z Phys Chem* 1:481–508
- van't Hoff JH (1894) Wie die Theorie der Lösungen entstand. *Ber Deut Chem Ges* 27:6–19
- van't Hoff JH (1898) Vorlesungen über Theoretische und Physikalische Chemie. Friedrich Viewig und Sohn, Braunschweig
- Vol'kenshtein FF (1960) *Elektronnaya teoriya kataliza na poluprovodnikakh*. English edition: Fizmatgiz M (1963) *The electronic theory of catalysis on semiconductors* (trans: Anderson NG). Pergamon Press, Oxford
- Waage P, Guldberg CM (1864) *Forhandlinger: Videnskabs-Selskabet i Christiana* 35
- Wenzel KF (1777) *Lehr von der Verwandtschaft der Körper*. (V. D. H. Gründel) Dresden
- Wigner EP (1933) Über die paramagnetische Umwandlung von Para-Orthowasserstoff. *Z Phys Chem B* 23:28
- Wilhelmy L (1850) Über das Gesetz, nach welchem die Einwirkung der Säuren auf den Rohrzucker stattfindet. *Ann Phys* 81:413–428, 499–526
- Williamson AW (1850) Theory of aetherification. *Philos Mag* 37:350–356
- Wright PA, Thomas JM, Cheetham AK, Nowak AK (1986) Localizing active sites in zeolitic catalysts: neutron-powder-profile analysis and computer simulation of deuterio-pyridine bound to gallozeolite-L. *Nature* 318:611–614
- Zhang J, Lee YT (1997) Crossed molecular beam study of the reaction $\text{Cl} + \text{O}_3$. *J Phys Chem A* 101:6485–6495

<http://www.springer.com/978-3-642-28179-2>

Pathways to Modern Chemical Physics

Califano, S.

2012, XII, 288 p., Hardcover

ISBN: 978-3-642-28179-2