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Volume 19

RAYNAL TO SARRAUT



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"LET KNOWLEDGE GROW FROM MORE TO MORE  
AND THUS BE HUMAN LIFE ENRICHED."



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## Volume 19

### RAYNAL TO SARRAUT

**RAYNAL, GUILLAUME THOMAS** (1713–1796), French writer and propagandist, widely read and very influential in his day, was an important precursor of the French Revolution. Born at Saint-Geniès in the Aveyron, April 12, 1713, he was educated at the Jesuit college at Rodez, and himself became a Jesuit. He taught at Pézenas, Clermont and Toulouse, left the Society of Jesus at about the age of 34 and went to Paris; he exercised minor ecclesiastical functions at Saint-Sulpice. Meanwhile he entered the world of letters and from 1747 to about 1752 was literary correspondent to the duchess Dorotea of Saxe-Gotha to whom he addressed his *Nouvelles littéraires*. His first major publications were *Histoire du stadthoudérat* (1747) and *Histoire du Parlement d'Angleterre* (1748), both hack work. In the first he appeared as an opponent of despotism; in the second, as an advocate of absolute monarchy, a discrepancy to be explained by the different orientation of French foreign policy in relation to Holland and to Great Britain. From 1750 to 1754 he edited the *Mercure de France*. This literary activity won for him a place in French society and he became a guest at the tables of Helvétius and D'Holbach and a friend of Montesquieu.

His most celebrated work was *Histoire philosophique et politique des établissements et du commerce des Européens dans les deux Indes*, first published in 1770 in six volumes, revised in 1774 and again, with changes of an outspoken and audacious character, in 1780. This was not his unaided work. Diderot, in particular, contributed extensively to it and Alexandre Deleyre, a disciple of Montesquieu, is reputedly responsible for the 19th book, which contains a general statement of political philosophy and is of more lasting interest than the rest. The whole work is a compendium of information and ideas on history, economics and politics, with an advanced anticlerical bias. Reprints were extremely numerous. The book fell foul of the Holy See in 1774, when it was placed on the Index, and of the *parlement* of Paris in 1781, when it was sentenced to be burned and the author was sent into exile. Raynal thereupon went first into Belgium, where he was the subject of many hostile lampoons, then into Prussia, where his reception at the hands of Frederick II was less cordial than he expected, and finally into Switzerland. In 1784 he was permitted to return to France, though not to Paris. He settled first at Toulon, then at Marseilles, where he entertained the youthful Napoleon, who read

*Histoire philosophique*. His banishment from Paris was rescinded in 1790; he returned to the metropolis and engaged cautiously in political activity. He died at Chaillot on March 6, 1796.

See A. Feugère, *Un précurseur de la Revolution: l'abbé Raynal* (1922) and *Bibliographie critique de l'Abbé Raynal* (1922); H. Wolpe, *Raynal et sa machine de guerre* (1957). (Rt. S.)

**RAYNALD OF CHÂTILLON** (d. 1187), a knight in the service of Constance, princess of Antioch, whom she chose for her husband in 1153, four years after the death of her first husband, Raymund (*q.v.*). One of Raynald's first acts was a brutal assault on the patriarch of Antioch; while two years later he made an unjustifiable attack on Cyprus, in the course of which the island was ravaged. The act brought its punishment in 1159, when he had to humiliate himself before the emperor Manuel, doing homage and promising to accept a Greek patriarch; and when Manuel came to Antioch in the same year, and was visited there by Baldwin III, Raynald led his horse into the city. Later in the year he was captured by the Mohammedans and held for 17 years. Released in 1176, he married Stephanie, the widow of Humphrey of Toron, and heiress of Krak and Mont Royal, to the southeast of the Dead Sea—fortresses which controlled the trade routes between Egypt and Damascus, and gave him access to the Red sea. In Nov. 1177, at the head of the army of the kingdom, he won a victory over Saladin, who only escaped with difficulty from the pursuit. But in 1181 the temptation of the caravans which passed by his fortress proved too strong, and in spite of a truce between Saladin and Baldwin IV, he began to plunder. Saladin demanded reparations from Baldwin IV. Baldwin could only reply that he was unable to coerce his unruly vassal. The result was a new outbreak of war between Saladin and the Latin kingdom (1182). In the course of the hostilities Raynald launched ships on the Red sea, partly for buccaneering, partly, it seems, with the design of attacking Mecca, and of challenging Mohammedanism in its own holy place. His ships were captured by one of Saladin's officers; and at the end of the year Saladin himself attacked Raynald in his fortress of Krak, at a time when a number of guests were assembled to celebrate the marriage of his stepson, Humphrey of Toron. The siege was raised, however, by Count Raymund of Tripoli; and until 1186 Raynald was quiet. In that year he espoused the cause of Sibylla and Guy de Lusignan against Count Raymund, and his influence contributed to the recognition of Guy as king of Jeru-

salem. His policy at this crisis was not conceived in the best interests of the kingdom; and a step which he took at the end of the year was positively fatal. Hearing of a rich caravan, in which the sister of Saladin was traveling, he swooped down from his fortress upon it. Thus, for the second time, he broke a truce between the kingdom and Saladin. Guy could not extort from him the satisfaction which Saladin demanded: Raynald replied that he was lord in his lands, and that he had no peace with Saladin to respect. Saladin swore that Raynald should perish if ever he took him prisoner; and next year he was able to fulfill his oath. He invaded the kingdom, and, at the battle of Hittin, Raynald along with King Guy and many others fell into his hands. Saladin, after rebuking Raynald strongly for his treachery, offered him his life if he would become a Mohammedan. He refused, and Saladin slew him with his own hands or caused him to be slain.

**RAYNAUD'S DISEASE**, first described by P. Edouard Raynaud in 1862, is characterized by a reaction in a susceptible person following exposure to cold or emotional disturbance such as anger or fear. Typically there are three stages. During the first, the affected parts, most commonly the fingers or toes, less commonly the nose, cheeks or ears, become blanched or waxen and cold. They are relatively bloodless and if cut bleed little. This is caused by a spasm in the arterioles, the smallest arteries through which blood normally flows to the capillaries. In some patients the local colour changes to slate gray (the second stage). This persists while the stimulating factor continues and is associated with numbness, tingling and sometimes pain. Return to a warm environment or release from tension results in the relaxation of the arterioles and a flush of blood into the area together with a throbbing sensation, increased local warmth and intense redness, after which the part returns gradually to normal. The symptoms of this disease may occur frequently for years, with no evidence of serious damage; gangrene is extremely rare. The underlying cause is unknown. The onset usually occurs between the ages of 15 and 35 years; 90% of the cases are in females.

A similar phenomenon, Raynaud's syndrome, is known to be present in some patients in the early stages of arteriosclerosis and thromboangiitis obliterans, two diseases affecting the arteries of the extremities (see **ARTERIES, DISEASES OF**). The syndrome may also develop following repeated blows to a hand, as in the use of a pneumatic hammer or in the playing of handball, and has occurred in concert pianists and typists. Since it does not occur in all who are exposed, individual susceptibility must be assumed. Raynaud's syndrome is also associated with other diseases, such as scleroderma, a condition producing a hardening of the skin and sometimes the deeper tissues, and with some blood diseases such as cryoglobulinemia, in which the blood solidifies if reduced much below the usual body temperature.

Treatment for the classical Raynaud's disease is not specific. The patient should try to avoid exposure to stimulating factors. A warm climate is beneficial and it is advisable for the patient to wear warm gloves and socks and to avoid winter sports. Neurologic surgery has been widely used; it is more successful for Raynaud's disease of the feet than of the hands. Many drugs have been tried without much effect.

Treatment of Raynaud's syndrome secondary to some other condition must depend on the primary condition. If repetitive injury is responsible, the only recourse is to discontinue the activity causing it. The primary diseases mentioned above must be treated. In addition cold, being an aggravating factor, must be avoided.

See I. S. Wright, *Vascular Disease in Clinical Practice*, 2nd ed. (1954). (I. S. W.)

**RAYNOUARD, FRANÇOIS JUSTE MARIE** (1761–1836), French dramatist and Romance philologist who also played some part in the politics of the Revolutionary and Napoleonic period, was born at Brignoles in Provence, Sept. 18, 1761, and educated for a legal career. Sent as deputy to the legislative assembly in Paris (1791), he was imprisoned on the fall of the Girondins (1793) but released in the Thermidorian reaction (1794). His first play *Caton d'Utique* was then published. After practising as a lawyer at Draguignan, he returned to Paris in 1803.

His second play, *Les Templiers* (1805), was a great success in the theatre. He was made a member of the Corps Législatif (1806) and of the Académie Française (1807). His next play, *Les États de Blois, ou la mort du duc de Guise* (1810), offended Napoleon and was banned; his later tragedies attracted little notice. After Waterloo, Raynouard abandoned politics, despite the protests of constituents in the Var *département*, and devoted himself to the study of the language and literature of the troubadours. His major works were *Choix des poésies originales des troubadours*, 6 vol. (1816–21; vol. 6 was also published separately as *Grammaire comparée des langues de l'Europe latine dans leurs rapports avec la langue des troubadours*, 1822) and the posthumous *Lexique roman*, 6 vol. (1838–44). He was a member of the Académie des Inscriptions from 1816.

Raynouard died at Passy on Oct. 27, 1836.

**RAYON**: see **FIBRE, MAN-MADE**.

**RAYONNANT STYLE**, in architecture, the fully developed French Gothic style (see **GOTHIC ARCHITECTURE**) of the latter half of the 13th and the first three-quarters of the 14th centuries. It is characterized by a complete mastery of the structural ideas of the Gothic vaulted church; great skill in stone-cutting; the elimination of wall surface; the reduction in area of all supports to the minimum; thorough development and lavish use of bar tracery (*q.v.*) based on geometric forms; reduction in size and importance of the triforium gallery; and a general attempt to accent all vertical lines. In carved ornament the spherical crocket of the earlier Gothic was replaced by a fully opened, upturned leaf and naturalistic foliage-decorated capitals, string courses and the like.

"Rayonnant" pertains to the radiating tracery of the rose windows, a single, although characteristic, detail; the term has been nearly abandoned, even in France. Marcel Aubert in Robert de Lasteyrie's posthumous work, *L'Architecture Religieuse en France à l'Époque Gothique*, vol. ii, p. 5, calls the style from 1140 to 1200 *le gothique primitif* and that of the years 1200 to 1400 *simply gothique*.

Characteristic examples are: Sainte Chapelle, Paris (1243–48); the choir of Amiens cathedral (1258–69); additions to the transepts of Notre Dame in Paris (1258–1315); St. Urbain in Troyes (1262–76); Portail des Libraires at Rouen cathedral (1280); and the choir of the abbey church of St. Ouen at Rouen (1318). Chronologically, this phase of French Gothic corresponds to the Decorated period (*q.v.*) in England and the High Gothic style in Germany. In France it was followed by the Flamboyant style (*q.v.*). (P. F.)

**RAYY**, one of the great cities of Iran, the ancient Ragha, Latin *Rhages*. The expedition of the Boston and Pennsylvania museums disclosed a prehistoric settlement on the site dating from the third millennium B.C. Rayy is mentioned in the Avesta as a sacred place and is also mentioned in the Apocrypha. In the 9th century, the Caliph Al-Mahdi became governor and there his son, Haroun-al-Rashid, was born. Under Al-Mahdi's rule the city rapidly became a magnificent metropolis, rivaled in western Asia only by Damascus and Baghdad. It covered at least 25 sq.mi., and according to Mustawfi it contained 20,000 mosques, 2,750 minarets, innumerable baths and colleges. It continued to be a city of political, commercial and artistic importance through Seljuk times. In the 12th century it was tormented and greatly weakened by the fury of rival religious sects, was overcome by the Mongols in 1220 and, according to some probably much exaggerated reports, completely destroyed and the inhabitants massacred. Mongol occupation, however, terminated the dominance of Rayy. It was famous for its decorated silks of an unsurpassed *finesse* and artistic perfection. Rayy has been wrongly credited with the bulk of the luxurious type of Persian pottery of the 12th and 13th centuries. (See **POTTERY AND PORCELAIN: Persia and the Near East**.) Only one architectural monument, the tower of Toghrul (1137) survives. The centre of Rayy was situated about 6 mi. S. of modern Tehran.

**RAZI, AL-** (FAKHR AL-DIN ABU ABDALLAH MOHAMMED IBN UMAR IBN AL-HUSAIN AL-RAZI) (1149–1209), Moslem theologian and scholar, was born the son of a preacher at Rayy (Rhagae),



near the modern Tehran. After devoting himself to alchemy in his youth, he studied theology and philosophy at Ray and Maragha. In law he followed the school of Shāfi'i (q.v.), on whose merits he composed a celebrated book; in theology that of Ash'ari (q.v.). Although he could not come to terms with the anti-intellectualism of the mystics, he was recognized as an authority on the mystic life as well as on scholastic theology and the law. As a student of tradition, however, he was considered weak. His contemporaries saw in him above all the defender of orthodoxy against dissenters and heretics. During an extensive journey to Khwārizm and Transoxiana he preached (in Arabic and Persian) against the local sectarians and more particularly against the philosophical school of the Mu'tazilites, who, in the end, compelled him to withdraw to his birthplace. Subsequently, he found honour at the court of Shihāb ad-Dīn Ghūrī (d. 1205) and especially in the entourage of the Khwārizmshāh 'Alā' ad-Dīn Mohammed (1199-1220), whom he followed to Khurasan. Later he settled in Herāt, where he died, as some would have it, poisoned by one of the sects which he had combated.

His greatest work, *Mafātīḥ al-Ghaib* ("Keys of the Hidden"), an extensive commentary on the Koran, has been printed at various times in Cairo and Istanbul. Razi studied the Koran also from the point of view of its style and examined the rare expressions in the holy book. Some of his dogmatic and legal writings continue to enjoy a high reputation, as do his contributions to philosophy. His dogmatic position was analyzed by Schmolders in his *Essai sur les écoles philosophiques chez les Arabes* (1842). His disputations with the Mu'tazilites were studied by P. Kraus in *Islamic Culture* (1938) and the *Bulletin de l'Institut Egyptien* (1939).

For a list of Razi's works see C. Brockelmann, *Geschichte der arabischen Literatur*, 2nd ed., vol. i, pp. 666-669 (1943-49); and M. Schreiner, *Zeitschrift d. deutschen morgenlaend. Gesellschaft* vol. lii. The most extensive source for his biography is Tāj ad-Dīn Subkī (d. 1370), *Ṭabaqāt ash-Shāfi'iyya al-kubrā* (1323-24 and 1905-06).

(G. E. V. G.)

**RAZIN, STENKA** (STEPHEN TIMOFEEVICH) (d. 1671), Cossack hetman and rebel, whose parentage and date and place of birth are unknown. We first hear of him in 1661 in a diplomatic mission from the Don Cossacks to the Kalmuck Tatars, and in the same year we meet him on a pilgrimage of 1,000 miles to the great Solovetsky monastery on the White Sea "for the benefit of his soul." After that all trace of him is lost for six years, when he reappears as the leader of a robber community established at Panshinskoe, among the marshes between the rivers Tishina and Ilovlya, from whence he levied blackmail on all vessels passing up and down the Volga. His first considerable exploit was to destroy the "great water caravan" consisting of the treasury barges and the barges of the patriarch and the wealthy merchants of Moscow. He then sailed down the Volga with a fleet of 35 galleys, capturing the more important forts on his way and devastating the country. At the beginning of 1668 he defeated the voivode Jakov Bezobrazov, sent against him from Astrakhan, and in the spring embarked on a predatory expedition into Persia which lasted for 18 months. Sailing into the Caspian, he ravaged the Persian coasts from Derbend to Baku, massacred the inhabitants of Resht, and in the spring of 1669 established himself on the isle of Suina, off which, in July, he annihilated a Persian fleet sent against him. Stenka, as he was generally called, had now become a potentate with whom princes did not disdain to treat. In Aug. 1669 he reappeared at Astrakhan, and accepted a fresh offer of pardon from the tsar there. In 1670 Razin rebelled against the government, captured Cherkask, Tsaritsyn and other places, and on June 24 burst into Astrakhan. After massacring all who opposed him, and giving the rich bazaars of the city over to pillage, he converted Astrakhan into a Cossack republic. After a three weeks' carnival of blood and debauchery Razin quitted Astrakhan with 200 barges full of troops to establish the Cossack republic along the whole length of the Volga, as a preliminary step toward advancing against Moscow. But his forces were stayed by the resistance of Simbirsk, and after two bloody encounters close at hand on the banks of the Sviyaga (Oct. 1st and 4th), Razin was ultimately routed and fled down the

Volga.

But the rebellion was by no means over. The emissaries of Razin, armed with inflammatory proclamations, had stirred up the inhabitants of the modern governments of Nizhny-Novgorod, Tambov and Penza, and penetrated even so far as Moscow and Great Novgorod. It was difficult to rouse the oppressed population by the promise of deliverance from their oppressors. Razin proclaimed that his object was to root out the boyars and all officials, to level all ranks and dignities, and establish cossackdom, with its corollary of absolute equality, throughout Muscovy. Even at the beginning of 1671 the issue of the struggle was doubtful. Eight battles had been fought before the insurrection showed signs of weakening, and it continued for six months after Razin had received his quietus. At Simbirsk his prestige had been shattered. Even his own settlements at Saratov and Samara refused to open their gates to him, and the Don Cossacks, hearing that the patriarch of Moscow had anathematized Stenka, also declared against him. In 1671 he was captured at Kagalnik, his last fortress, and carried to Moscow, where, on June 6, after bravely enduring unspeakable torments, he was quartered alive.

See N. I. Kostomarov, *The Rebellion of Stenka Razin*, 2nd ed. (1859); S. M. Solovov, *History of Russia*, vol. ii (1895); R. N. Bain, *The First Romanovs* (1905). (R. N. B.)

**RAZOR.** The razor is an instrument used for shaving. The early razor of modern times was made of steel which had a wedge-shaped section, with straight sides tapering to a sharp edge, and although simple in form it was a good and durable instrument for its purpose. Early in the 19th century, the practice was introduced of hollowing out the sides of the blade by grinding, to facilitate sharpening the blade, and improve fineness of the cutting edge. At first the degree of hollowness, or concavity of the sides of the blade was small, but with great skill, hollow-grinding has been carried considerably further, increasing the lightness and flexibility of the blade. The full hollow blade is thinner in the centre than nearer the cutting edge.

**Safety Razor.**—The razor is naturally considered a dangerous instrument, and many attempts have been made to make it safe. Not until the introduction of the "Gillette" type of razor, at the beginning of the 20th century, was a satisfactory solution found. The principle of the "safety" razor is to place a guard between skin and cutting edge of the razor blade, so that the guard permits the edge to pass over the uneven surface of the part to be shaved, removing the hair without cutting the skin. In some cases devices are provided to enable the user to strop or resharpen the blades. Other safety devices are based on the desire to retain the general form of the ordinary razor, while rendering it safe in use. These take the form of fitting a suitable guard to the blade of the ordinary razor, or the substitution of a holder, carrying an adjustable blade of the strip-steel type.

**Electric Razor.**—With the invention of the Schick Dry Shaver by Jacob Schick, an entirely new technique was introduced to the art of shaving. This dry shaver consists of a shearing head mounted on a powerful little motor encased in an insulated handle. The shearing head includes an outer and an inner member—the outer member having a very thin shear plate with openings or slots in it to rest against the skin, while the inner member has teeth which co-operate with the nether edges of the walls of the shear plate slots or openings in a shearing action. The toothed inner member is held up tightly against the inside surface of the shear plate by means of springs or other appropriate means and is made to reciprocate very rapidly underneath the shear plate by the motor. The hairs of the face which penetrate the openings or slots in the shear plate are thus sheared off by the reciprocating motion of the inner member in co-operation with the nether edges of the slot walls of the stationary shear plate.

The electric dry shaver operates without the use of sharp blades, soaps, brushes, creams and lotions.

**RAZOR-BILLED AUK** (RAZORBILL), *Alca torda*, a member of the auk family (Alcidae), known also as marrot, murre, scout, tinker or willock; some of these names it shares with guillemot (q.v.) and puffin (q.v.). It is a common sea bird of the North Atlantic, resorting in vast numbers to rocky cliffs for



breeding, and returning to the open sea for the rest of the year. It is in many respects intermediate between the guillemot and the great auk (*q.v.*). In habits the razorbill agrees with guillemots, laying its single egg on ledges of cliffs. It breeds on both sides of the north Atlantic, wandering as far south as the Mediterranean on the east and Long Island on the west in winter. It feeds on fish.

**RAZZIA** (an adaptation of the Algerian Arabic *ghāziah*, from *ghasw*, to make war), a foray or raid made by African Moslems. As used by the Arabs, the word denotes a military expedition against rebels or infidels, and razzias were made largely for punishment of hostile tribes or for the capture of slaves. English writers in the early years of the 19th century used the form *ghrazzie*, and Dixon Denham in his *Travels* (1826) styles the raiding force itself the *ghrazzie*. The modern English form is copied from the French, while the Portuguese variant is *gazia*, *gaziva*.

**RÉ, ÎLE DE**, an island  $1\frac{1}{2}$  mi. off the port of La Pallice in the southwestern part of France. The island, with a northwest-southeast length of 15 mi. and an average width of  $2\frac{1}{4}$  mi., is separated from the coast of Vendée to the north by a shallow bay, the Pertuis Breton, 6 mi. broad, and from the island of Oléron to the south by another, the Pertuis d'Antioche,  $7\frac{1}{2}$  mi. broad. The Atlantic coast is reef-fringed, but there are small-craft harbours on the landward side. The most important of these is La Flotte. The largest shore indentation on the east coast, the Fier d'Ars, nearly divides the island, leaving an isthmus only 230 ft. wide to maintain the island's continuity. Dunes and salt marshes cover a large part of the northern end of the island. Many salt pans for the collection of salt by evaporation have been built along the landward shore. Industries are fishing, oyster cultivation, and the collection of seaweed for fertilizer. The island has some cropland which is in vineyards or in early spring vegetables. Île de Ré is included in the *département* of Charente-Maritime. Population of the island (1954) 9,315.

**REA, SAMUEL** (1855–1929), U.S. railroad official, was born at Hollidaysburg, Pa., on Sept. 21, 1855. In 1871 he entered the service of the Pennsylvania railroad as chainman and rodman. From 1875 to 1877 he was assistant engineer on construction of the Monongahela river bridge at Pittsburgh. He was next appointed assistant engineer for the Pittsburgh and Lake Erie railroad and returned to the Pennsylvania lines in 1879 in a similar capacity. In 1888 he was appointed assistant to the second vice-president of the Pennsylvania railroad, which position he retained until 1889 when he was made chief engineer on construction of the belt line tunnel under Baltimore for the Baltimore and Ohio railroad.

In 1892 he again returned to the Pennsylvania railroad as assistant to the president, and became first vice-president in 1911. In 1913 he was elected president. He was in charge of the construction of the Pennsylvania station in New York city (completed in 1910), the connecting tunnels under the Hudson and East rivers, the New York Connecting railroad and Hell Gate bridge over the East river (opened in 1917). In 1917 he became a member of the executive committee on national defense of the American Railway association, known as the Railroads War Board. He retired from the presidency of the Pennsylvania railroad on Sept. 30, 1925. He died at Gladwyne, Pa., on March 24, 1929. He wrote *The Railways Terminating in London* (1888).

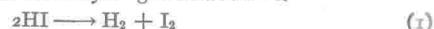
**REACTION KINETICS** is that branch of physical science which deals with the determination and interpretation of the rates of chemical change. The subject includes the consideration of the rates both of everyday but complicated reactions such as hard-boiling an egg (an example of protein coagulation) and of simpler but less commonplace reactions such as the one between hydrogen and chlorine. Rates have been measured for slow reactions (*e.g.*, the disintegration of ordinary uranium, only half of which will decompose in 5,000,000,000 years) and for fast reactions (*e.g.*, the dissociation of oxygen from haemoglobin, which is almost complete in a tenth of a second). An attempt is made in each case to show quantitatively the effect of changes in the experimental conditions upon the reaction velocity, and to describe in as much detail as possible the behaviour of the molecules at the moment of their reaction.

Many familiar processes involve chemical reactions which proceed at measurable rates. For example, the rusting of iron, the fermentation of sugar, the "drying" of paint, the hardening of plaster of Paris, the baking of bread and the growth of plants, all involve chemical reactions of greater or lesser complexity, and for each example there is considerable interest in the rate of reaction. In general, these familiar processes are very complex, partly because many of the materials are not single pure compounds, but mixtures. It is well known, however, that the rusting (oxidation) of iron requires both air and water, and that the reaction proceeds much more rapidly near the ocean (where salt is deposited on the iron) than it does elsewhere. The rate of rusting also depends upon the composition of the metal (pure iron and stainless steel corrode less rapidly than do cast iron and mild steel) and on temperature (corrosion is rapid in a stream of steam and air). (See CORROSION AND OXIDATION OF METALS.)

Scientists have been largely concerned with measuring the rates of reactions such as the decomposition of ozone, the oxidation of sulphur dioxide and the nitration of hydrocarbons; they assume that an understanding of these and similar reactions of pure chemicals will eventually lead to an understanding of more complex (if more familiar) reactions.

Studies of reaction velocity have not only played a fundamental role in the growth of theoretical chemistry; the concepts developed in these studies have also been highly fruitful in industry, especially in the field of catalysis (*q.v.*). A case in point is the Haber process for the manufacture of ammonia (*q.v.*), which is based in part on studies of reaction kinetics. Both theoretical and practical research in the field of reaction kinetics was by mid-century under way in hundreds of laboratories.

A specific example of a rate study is the work on the decomposition of hydrogen iodide to form hydrogen and iodine.



This reaction proceeds at a rate convenient for measurement in the neighbourhood of 320° C., at which temperature not only the hydrogen and hydrogen iodide but even the iodine is gaseous. (This reaction is a reversible one; however, for the moment, it is better to postpone discussion of this complication and to consider only the reaction as written.) The rate of decomposition of hydrogen iodide increases as the quantity of hydrogen iodide per unit volume is increased; quantitatively, the rate is proportional to the square of the concentration of hydrogen iodide. The rate increases by a factor of 1.9 when the temperature is increased from 320° C. to 330° C. The reaction occurs within the body of the gas, and not on the glass walls of the vessel in which the experiment is performed.

The facts just cited have been interpreted to indicate that when two molecules of hydrogen iodide collide, a chemical change occurs only if the velocity of one of them with respect to the other exceeds 2.4 km./sec. (about 5,000 m.p.h.). The average diameter (so far as collision is concerned) of these hydrogen iodide molecules can also be calculated from the kinetic data; it is of an order of magnitude ( $0.8 \times 10^{-8}$  cm.), roughly consistent with the results of other measurements of the sizes of molecules. The effective collisions (*i.e.*, those which lead to reaction) result in a simple interchange of atoms; here the hydrogen and iodine atoms in each of the two colliding molecules of hydrogen iodide separate; simultaneously, the two hydrogen atoms combine to form a hydrogen molecule, and the two iodine atoms combine to form an iodine molecule.

For the discussion of even the simple example of the decomposition of hydrogen iodide, it has been necessary to employ the elementary concepts of chemistry (*q.v.*) and of the kinetic theory (*q.v.*) of matter. For the more detailed treatment of reaction kinetics which follows, a somewhat more extensive knowledge of these subjects is assumed. In the last sections of this article, a precise presentation is attempted.

**History.**—Gross differences in the rates of chemical reactions have long been recognized. By the beginning of the 19th century, several instances were known where the rate of a chemical change could be greatly increased by adding to the reacting system a small quantity of some apparently inert material. For example, it was discovered in 1796 that the dehydrogenation of alcohols pro-

ceeds much more rapidly in the presence of metals than it does in their absence. In 1836, Jöns Jakob Berzelius grouped together many reactions of this type and gave the name "catalysts" to the materials which accelerate chemical change. (The modern definition of catalysts is given below.) Although the qualitative concept of reaction rate was by that time well established, the first quantitative measurement and mathematical formulation of reaction velocity is generally credited to L. F. Wilhelmy, who, in 1850, measured the rate of "inversion" (hydrolysis) of cane sugar.

**Definitions.**—Chemical reactions can be classified as homogeneous or heterogeneous. Homogeneous reactions are those (like the decomposition of hydrogen iodide) which occur completely within one phase (gaseous, liquid or solid). Heterogeneous reactions are those (like the reaction between a metal and an acid) where the reactants are components of two or more phases (solid and gas, solid and liquid, two mutually immiscible liquids, etc.) or where one or more reactants undergo chemical change at an interface; *i.e.*, on the surface of a solid catalyst.

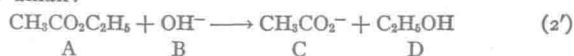
Reactions may also be classified as "reversible" or "irreversible." An irreversible reaction is one in which the reactants, if mixed in the proper proportions, are almost completely converted to the reaction products; a reversible reaction is one in which appreciable quantities of all the reactants and of all the reaction products are present in the system no matter how long the reaction is allowed to proceed. The mixture eventually formed in such a reversible reaction is called the equilibrium mixture; the same equilibrium mixture may be prepared from suitable amounts of either the reactants or the reaction products. For example, the same equilibrium mixture of hydrogen, iodine and hydrogen iodide (at definite temperature and pressure) can be prepared by starting either with equivalent quantities of hydrogen and iodine or with pure hydrogen iodide. If the definition of equilibrium is that adopted in thermodynamics (*q.v.*), then every reaction is, in principle, reversible. There are reactions, however, where the extent of the reverse reaction is too small to be detected by any experimental means at present known; such reactions are usually regarded, for the purposes of kinetics, as irreversible.

**"Order" of Reaction.**—The fundamental law of reaction kinetics was developed by C. M. Guldberg and P. Waage around 1867 (an independent and similar formulation was made by Jacobus Henricus van't Hoff). These authors assumed that, at constant temperature, the rate of any simple chemical reaction is proportional to the product of the concentrations of the various reacting substances. They showed in a general way that their law of chemical change is consistent with the kinetic molecular theory of matter, and that the data for many chemical reactions could be formulated quantitatively in terms of their theory. Since 1870, the concepts of Guldberg and Waage have been extended and modified, but most of reaction kinetics is still based upon their work.

Consider the simple homogeneous, irreversible reaction between two compounds, A and B (the reactants), to form C and D (the reaction products).



An example of this sort of reaction is the saponification of ethyl acetate by alkali:



Equations (2) and (2') as written represent the stoichiometry of the chemical change; *i.e.*, the equations show the relationship between the weights of the initial reactants and those of the final products. The reaction rate may be proportional to the concentrations of the reactants which appear in the stoichiometric equation; if, however, the reaction occurs in several consecutive chemical steps, or requires a catalyst, the kinetics may be more complicated

(see below) than those which could be implied from the stoichiometry. The treatment for a simple case follows.

At the beginning of the reaction, the compounds A and B are present in definite concentrations, say  $a_0$  and  $b_0$  moles per litre respectively<sup>1</sup>; the concentrations of C and D are zero. As the reaction proceeds, the concentrations of A and B decrease, whereas the concentrations of C and D increase. If the concentrations of A and B at any instant are represented by the symbols (A) and (B), then the law of Guldberg and Waage states that wherever equation (2) represents the true kinetic course of the reaction, the reaction velocity,  $v$ , is proportional to (A) and to (B). This statement in mathematical form is

$$v = k(A)(B) \quad (3)$$

where  $k$ , the proportionality factor, is called the rate constant. Note that the rate of reaction,  $v$ , and the rate constant,  $k$ , are not the same, but are connected by an equation of the form of (3).

An equation such as (3) may accurately describe the rate of a chemical reaction. Unfortunately, however, a good experimental method for directly measuring the rate,  $v$ , of a reaction is usually not to be found. The quantities which can usually be determined experimentally are the time and the concentrations of the reactants or reaction products. An equation such as (3) can be transformed by the methods of calculus (*q.v.*) into an equation expressing a relationship between these concentrations and time. Although the details of this transformation are in no way necessary for the succeeding argument, they are nevertheless presented here for the sake of continuity.

If the concentration of C at any instant is represented by  $x$ , then the rate,  $v$ , of formation of C is  $dx/dt$ , the derivative of  $x$  with respect to time; and equation (3) can be replaced by (3').

$$v = \frac{dx}{dt} = k(A)(B) = k(a_0 - x)(b_0 - x) \quad (3')$$

The integrated form of equation (3) is

$$\log_e \frac{b_0(a_0 - x)}{a_0(b_0 - x)} = kt(a_0 - b_0) \quad (4)$$

where  $t$  is the time measured from the beginning of the reaction; the other symbols have been previously defined. In principle, it should be possible to obtain for every reaction an equation, analogous to (4), from which the concentrations of the various reactants and products at any moment may be calculated.

One method of testing experimentally whether equations (3) and (4) adequately describe the rate of any particular reaction is to measure  $x$  (the concentration of C) at several different times,  $t$ . An attempt is then made to choose a single value for the rate constant  $k$  such that all the sets of corresponding values of  $x$  and  $t$  satisfy equation (4). If this attempt is successful, the experiment is then repeated at the same temperature but with different initial concentrations ( $a_0$  and  $b_0$ ) of A and B. If and only if these new data also satisfy equation (4) with the rate constant  $k$  unchanged, the demonstration that the reaction obeys the rate equations (3) and (4) is complete. The constant,  $k$ , is thus independent of the initial concentrations of A and B; it is, however, a function of the temperature and it depends of course

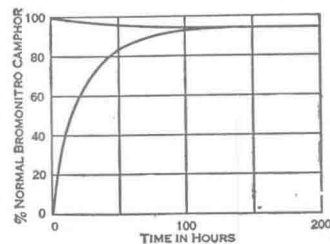


FIG. 2.—RATES AT WHICH EQUILIBRIUM IS ESTABLISHED BETWEEN THE TWO FORMS OF BROMONITROCAMPHOR

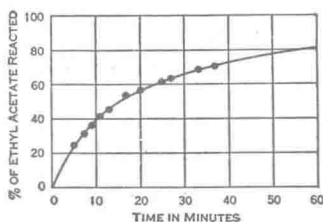


FIG. 1.—SAPONIFICATION OF 0.01M ETHYL ACETATE WITH 0.01M NaOH AT 25° C. CIRCLES, EXPERIMENTAL POINTS, LINE, THEORETICAL FOR  $k = 6.5 \text{ MIN}^{-1} (\text{M/l})^{-1}$

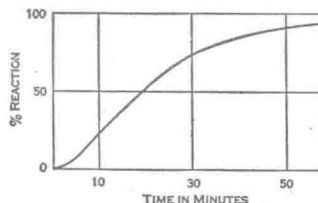


FIG. 3.—SUCCESSIVE FIRST ORDER REACTIONS, WHERE THE RATE CONSTANT OF THE SECOND IS FOUR TIMES AS GREAT AS THAT OF THE FIRST (DIAZOTIZATION OF PHENYL MERCURIC NITRATE IN 20% HNO<sub>3</sub> WITH 0.16 M/l HNO<sub>2</sub>)

<sup>1</sup> For reactions in the gas phase, the partial pressure of each gas is used as a measure of its concentration.

<sup>2</sup> Where  $a_0 = b_0$ , the corresponding equation is  $\frac{x}{a_0(a_0 - x)} = kt \quad (4')$

upon the chemical nature of the reactants A and B. Fig. 1 is a graphical representation of equation (4) for the saponification of ethyl acetate.

If the equations for various chemical reactions are treated as was equation (3) for reaction (2'), then these reactions fall into a number of different classes. A reaction, the rate of which may be described by an equation of the form

$$v = k(A) \quad (5)$$

is called a first order reaction; one described by an equation of the form

$$v = k(A)^2 \quad \text{or} \quad v = k(A)(B) \quad (6) \text{ or } (6')$$

is called a second order reaction, etc. In general, a reaction the rate of which may be described by the equation

$$v = k(A)^m(B)^n(C)^p(D)^q \dots \quad (7)$$

is called a reaction of order  $r$ , where  $r = m + n + p + q + \dots$ . Such a reaction is said to be of order  $m$  with respect to A, of order  $n$  with respect to B, etc. (Some reactions may be of nonintegral order; e.g., half-order. The majority of known reactions are of first or second order.)

In certain reactions, such as the inversion of cane sugar,



the rate is proportional to the concentration of some substance (in this instance, the hydronium ion of the acid) (see ACIDS AND BASES), which does not appear among either the reactants or the reaction products in the chemical equation; the reaction cited (equation [8]) is said to be catalyzed by hydronium ion  $H_3O^+$ , or hydrated hydrogen ion.

$$v = k(C_{12}H_{22}O_{11})(H_3O^+) \quad (9)$$

If the catalyst is one of the reaction products, the reaction is said to be autocatalyzed.

**Reversible Reactions.**—The reactions hitherto described have been assumed to be irreversible, in the sense defined above. If the reaction between the compounds A and B, on the one hand, and C and D, on the other, is reversible, then equation (2) must be rewritten.



Wherever equation (2'') represents the true kinetic course of the reactions, the rates  $v_f$  of the "forward" and  $v_r$  of the "reverse" reactions are given by equations (10) and (10').

$$v_f = k_f(A)(B) \quad (10)$$

$$v_r = k_r(C)(D) \quad (10')$$

If the reaction is begun by mixing A and B (either pure or in solution), the initial concentrations of C and D are each zero; hence the rate,  $v_r$ , of the reverse reaction is also zero. However, as A and B react to form C and D, these products in turn react to regenerate A and B. The net rate at which C and D are formed is therefore the difference between  $v_f$  and  $v_r$ .

$$v = v_f - v_r = k_f(A)(B) - k_r(C)(D) \quad (11)$$

The net rates of the forward and reverse reactions for a particular case are shown graphically in fig. 2. In the reaction in question, a mixture of the two tautomers (see TAUTOMERISM) of bromonitrocaphor is formed both from the normal (N) and from the pseudo (P) isomer.

The rate at which the equilibrium mixture is formed from pure N is shown in the upper curve; the rate at which the equilibrium mixture is formed from pure P is shown in the lower curve.

As the latter reaction proceeds, P is converted into N; hence, the forward rate decreases and the reverse rate increases. Eventually, the two rates become equal, and the net rate,  $v$ , is zero; thus, a dynamic equilibrium is achieved. This state of dynamic equilibrium is not a condition in which no reaction occurs, but is

one in which the rates of the forward and reverse reactions are equal. This kinetic concept of dynamic equilibrium has been experimentally verified by the use of radioactive tracers (see ISOTOPE).

When, for a reaction which follows equation (2''), the forward and reverse reactions proceed at equal rates, it is seen that

$$v_f = v_r = k_f(A)(B) = k_r(C)(D) \quad (12)$$

From equation (12) it follows that

$$\frac{(C)(D)}{(A)(B)} = \frac{k_f}{k_r} = K_e \quad (13)$$

where  $K_e$ , the ratio of the rate constants for the forward and reverse reactions, is called the equilibrium constant. Equation (13) gives the relative concentrations of the compounds A, B, C, and D at equilibrium; these concentrations need not be even approximately equal, for in general the rate constants of the forward and reverse reactions differ considerably from one another.

An equation analogous to (13) but more general is obtained by a parallel treatment of a reaction (7). Although this more general expression is correct as a first approximation, it nevertheless disagrees with the precise thermodynamic definition of equilibrium. Consideration of this and similar difficulties is postponed to the sections on collision theory and on activated-complex theory.

**Complex Reactions.**—The reactions so far considered are of simple types; all sorts of combinations of these types are possible. For example, reactions sometimes occur in several steps.



Here the rate of formation of B is proportional to the concentration of A, and the rate of formation of C is proportional to the concentration of B. Since, initially, the concentration of B is zero, the initial rate of formation of C is zero. Fig. 3 shows graphically the concentration of C at any time,  $t$ , in a system where the rate constants for the two consecutive reaction steps are of comparable magnitude. Other cases of interest are those in which one of the successive reactions is reversible, or of second order, etc. Considerable complexity is not only possible but common.

What has already been said makes it evident that the kinetic equation for a reaction cannot be inferred from the chemical equation, which gives only the relationship between the weights of reactants which will combine with one another and the weights of the final products (i.e., the stoichiometric relations). The kinetic expression, it is true, must account for the stoichiometric findings, but it should do more than that. Usually more than one reaction path between the initial reactants and the final products is conceivable. Under favourable conditions kinetic considerations permit the selection of just one of these reaction paths, and kinetic measurements demonstrate that the path selected, and no other, is the one which the reaction takes. Under less favourable conditions, kinetic considerations are insufficient to eliminate all reaction paths but one. Even here, however, they serve to rule out many of those paths which from mere stoichiometric considerations might be considered possible.

A simple example will illustrate the ideas just expressed. A chemist might investigate an irreversible reaction, the stoichiometric expression for which is  $A \rightarrow C$ . This expression means that each molecule of the reactant A is converted (eventually) into one molecule of the product, C. It does not tell whether each molecule of A is converted directly into a molecule of C or whether each molecule of A is converted first into a molecule of an intermediate, B, which is in turn converted into a molecule of C. In the former instance, the proper kinetic expression for the reaction  $A \rightarrow C$  may coincide with the stoichiometric expression. In the latter instance, the proper kinetic expression is  $A \rightarrow B \rightarrow C$ . Measurements of the extent of the reaction at various stages in its course are often sufficient to decide questions of the kind here raised. In the particular instance cited, if the reaction followed a curve of the sort shown in fig. 3, that fact would show that the kinetic expression for the reaction was  $A \rightarrow B \rightarrow C$ . If, on the other hand, the reaction followed a curve predicted from equation (5), and somewhat resembling the one shown in fig. 1, that fact would show that the kinetic expression for the reaction was  $A \rightarrow C$ , coinciding with the stoichiometric expression.

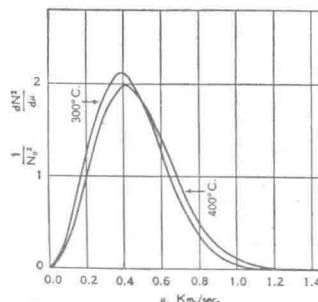


FIG. 4A.—MAXWELL-BOLTZMANN DISTRIBUTION OF PAIRS OF MOLECULES OF HYDROGEN IODIDE (AT 300° C. AND AT 400° C.). THE VELOCITY OF ONE MEMBER OF ANY PAIR RELATIVE TO THE OTHER MEMBER OF THE PAIR IS  $\mu$



This fact alone would not rule out compound B as an intermediate, but it could be an intermediate in the reaction only under certain special circumstances (*i.e.*, the reaction  $B \rightarrow C$  would have to be very fast as compared with the reaction  $A \rightarrow B$ ).

If any individual reaction is to be thoroughly understood, its reaction kinetics must be investigated. The object in view is to determine by inference from the kinetic measurements whether the reaction proceeds in one or more stages, to determine the order of each reaction stage with respect to each one of the reactants, and to determine for each particular stage whether or not it is catalyzed by some substance (possibly an ion) which does not appear in the stoichiometric expression for the over-all reaction. It should, however, be stated that kinetic considerations by themselves, although they greatly aid in the treatment of the problem stated, are often insufficient for its solution in all details.

If a kinetic study shows that two molecules (of the same or of different compounds) react with one another directly, then the reaction is said to be bimolecular. In a many-stage reaction, some individual step may be bimolecular, although the over-all reaction is not of second order and may indeed (like [14]) be of no definite order. It is likewise possible for a reaction to be of the second order, but to contain no single step which is truly bimolecular. The interpretation of the reaction kinetics for any individual reaction is thus a difficult matter, and for many important reactions the conclusions are still tentative.

**Application of the Kinetic Molecular Theory.**—Guldberg and Waage assumed that the rate of any reaction is proportional to the product of the concentrations of the reactants (equation [7]); they interpreted this hypothesis in terms of the kinetic molecular theory. The number of collisions between the molecules of compound A and the molecules of compound B is proportional to the product  $A(B)$  of their concentrations; Guldberg and Waage's law amounts then to a statement that molecules react only if they collide, and that the rate at which they react is proportional to the number of collisions per second.

But although reaction between two molecules cannot occur unless these molecules collide, it does not follow that reaction must occur every time two molecules collide, even though these are molecules of substances which can react chemically one with another. For most reactions, it has been fully determined that the vast majority of collisions are "elastic"; *i.e.*, that the molecules rebound from one another without chemical reaction. It is possible by means of the kinetic molecular theory to compute the number of collisions per second between the molecules of two compounds which are present in a solution or a gas in known concentrations. For example, the number of collisions between pairs of molecules of hydrogen iodide at a temperature of  $320^\circ \text{C}$ . and a total pressure of one atmosphere is approximately  $10^{28}$  per cubic centimetre per second. Under the conditions stated, there are only about  $10^{19}$  molecules of hydrogen iodide in a cubic centimetre of gas. Hence, if every collision between two molecules of hydrogen iodide led to chemical change, the reaction would be over in a small fraction of a second, too short a time indeed to measure. It has been computed that in the system described, only one collision in about  $10^{15}$  leads to chemical change.

**Temperature Coefficients of Reaction Rates.**—Another (and historically older) consideration leading to the conclusion that not all collisions cause reaction is based on the increase of reaction rates with increase in temperature. According to kinetic-molecular theory, the number of collisions between molecules of two compounds present at definite concentrations increases as the square root of the absolute temperature. For example, the number of collisions at  $25^\circ \text{C}$ . ( $298^\circ$  absolute) is only about 1.5% greater than the number at  $15^\circ \text{C}$ . ( $288^\circ$  absolute). But the rates

of most reactions increase by a factor of two or more when the temperature is raised by  $10^\circ \text{C}$ .; as much material may react in an hour at  $100^\circ \text{C}$ . as in a year at  $0^\circ \text{C}$ . In some instances, such as the denaturation of egg albumin, the reaction rate increases one hundredfold when the temperature is raised  $10^\circ \text{C}$ .

However, the assumption that only those molecules which collide with high energy of impact react with one another not only furnishes an explanation for the high temperature coefficients of reaction rates, but also accounts for the fact that collisions effective in bringing about chemical change are usually rare. To bring out the connection between the assumption and the conclusions, it is necessary to consider the velocity of one molecule relative to another. This relative velocity is not the same for all colliding pairs, but there is a determinable probability that for any one particular pair the relative velocity will lie close to any chosen value,  $u$ , of the relative velocity. This probability is calculated from the Maxwell-Boltzmann distribution curve (*see* KINETIC THEORY OF MATTER) shown in figs. 4a and 4b for hydrogen iodide at  $300^\circ \text{C}$ . and  $400^\circ \text{C}$ . The horizontal co-ordinate represents the velocity,  $\mu$ , in km./sec., of one molecule of hydrogen iodide relative to the one with which it collides; the vertical co-ordinate represents the probability that the relative velocity is  $\mu$ . (More precisely, the ordinate is equal to  $1/N_0^2 d(N^2)/d\mu$ , where  $N_0$  is the total number of molecules under consideration, and  $d(N^2)$  is the number of pairs of molecules with velocity lying between  $\mu$  and  $\mu + d\mu$ .) Fig. 4b is an enlargement in vertical scale of part of fig. 4a. Figs. 4a and 4b indicate (1) that only a minute number of molecular pairs have relative velocities in excess of the 2.4 km./sec. required for reaction (*see* above), and (2) that, although the average value of the relative velocity is not greatly increased by raising the temperature from  $300^\circ \text{C}$ . ( $573^\circ$  absolute) to  $400^\circ \text{C}$ . ( $673^\circ$  absolute), the number of molecular pairs with high relative velocities is increased by a large factor. Thus the assumption that reaction is limited to molecular pairs with high relative velocities at the moment of collision qualitatively explains both the fact that few collisions are "effective" in producing reaction and the fact that the rates of most chemical reactions increase sharply with increase in temperature.

The complete equation (24) for the reaction rate derived from the kinetic collision theory is given in the next to last section of this article. Here it is sufficient to say that this complete equation is consistent (within experimental error) with an empirical equation (15) advanced by Svante August Arrhenius in 1889 which has proved useful.

$$\log_e \frac{k_2}{k_1} = \frac{Q}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (15)$$

In equation (15)  $k_1$  and  $k_2$  are the rate constants at the absolute temperatures  $T_1$  and  $T_2$  respectively,  $Q$  is a constant called the activation energy, and  $R$  is the gas constant (1.98 cal./mole degree) ( $\log_e$  refers to natural logarithms). The larger the value of  $Q$ , the more sensitive is the reaction rate to changes in temperature. Reactions with values of  $Q$  varying from less than 500 up to about 100,000 cal./mole have been discovered.  $Q$  divided by the number of molecules in a mole (Avagadro's number) is (roughly) equal to the relative kinetic energy of a molecular pair which is just sufficient to make the members of the pair react upon collision.

**Reaction Mechanism.**—In this section, it will be shown how reaction kinetics may be used to determine the path or mechanism of a somewhat puzzling reaction. The example chosen is the reaction in aqueous solution between acetone and bromine. Here the stoichiometric



expression (16) is of the same form as equation (2). In 1904, however, A. Lapworth discovered that the rate of this reaction is proportional to the concentration of the acetone and of the hydrogen bromide (one of the reaction products) but independent of the concentration of the bromine and of all other substances known to be present in the system. The kinetic equation, therefore, is

$$v = k(\text{CH}_3\text{COCH}_3)(\text{HBr}) \quad (17)$$

These facts suggest the hypothesis that the acetone is slowly converted into some reactive intermediate by the action of the acid;

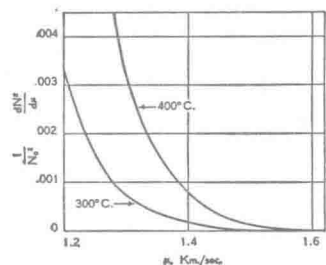
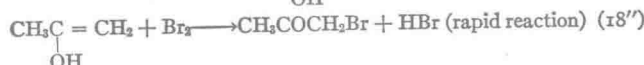
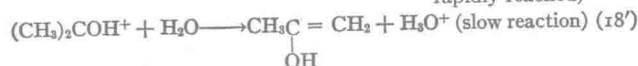


FIG. 4B.—EXPANDED SCALE DRAWING OF HIGH-VELOCITY END OF FIG. 4A

this reactive intermediate then combines rapidly with bromine. The hypothesis has more recently been elaborated as follows:



The proposed reaction between the catalyst and the acetone results in the transformation of the acetone into a reactive intermediate (the "enolic" modification of acetone; see TAUTOMERISM), which subsequently reacts rapidly with bromine. The rate,  $v$ , of the entire reaction is equal to that for the slowest step in the process, namely reaction (18'). The kinetic equation for this step is

$$v = k'((\text{CH}_3)_2\text{COH}^+) \quad (19)$$

The concentration of water is essentially constant and does not enter into equation (19); its concentration can be included in the rate constant,  $k'$ . The ion  $(\text{CH}_3)_2\text{COH}^+$  would be in equilibrium with the acetone and acid present in the solution if it were not for the reactions (18') and (18'') which slowly but essentially irreversibly remove some of this ion.

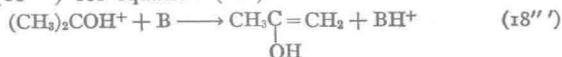
The ion  $(\text{CH}_3)_2\text{COH}^+$  is described as in pseudoequilibrium with acetone and acid, or as in a "steady state." The "steady state" concentration of the ion is given to a good approximation by the equilibrium expression

$$\frac{[(\text{CH}_3)_2\text{COH}^+]}{[(\text{CH}_3)_2\text{CO}][\text{H}_3\text{O}^+]} = K \quad (19')$$

When the theoretical equations (19) and (19') are combined, the experimentally verified kinetic equation (17) for the bromination of acetone is obtained; the rate constant  $k$  is the product of  $k'$  and  $K$ .

Not only does the mechanism presented in equations (18), (18') and (18'') agree with equation (17), but it will further explain many other facts. It is consistent, for example, with the observation that acetone reacts with chlorine, or with iodine at the same rate as it does with bromine. This is in accord with the proposed mechanism, since equation (18'), which does not involve the halogen at all, is postulated as the rate-determining step in the halogenation.

A more detailed investigation of the reaction has revealed that it is catalyzed not only by hydronium ion but also by molecules of un-ionized acids; it is also catalyzed by bases. The catalysis by un-ionized acid molecules can be accounted for by substituting equation (18'') for equation (18')



where B represents a molecule of any base. (The detailed mathematical analysis needed to prove the above statement, although beyond the scope of this article, is treated by L. P. Hammett in *Physical Organic Chemistry*.)

The proposed mechanism is thus consistent with a large and varied selection of quantitative kinetic evidence. This is a necessary condition, but not a sufficient one to establish the mechanism; it does, however, make the proposed mechanism quite probable.

**Catalysis.**—A catalyst is defined as a substance which increases the rate of a chemical reaction, but which can be recovered quantitatively and unchanged at the end of the reaction. There are many substances which (for specified reactions) approach this definition closely. Typical examples of homogeneous catalysis are the action of acids to increase the rate of hydrolysis ("inversion") of cane sugar, the action of bases to increase the rate of polymerization in the preparation of bakelite, the action of oxides of nitrogen in the chamber process for manufacturing sulphuric acid. Typical examples of heterogeneous catalysis are the action of finely divided iron to increase the rate at which nitrogen and hydrogen combine to form ammonia, the action of vanadium pentoxide to increase the rate at which sulphur dioxide and oxygen combine to form sulphur trioxide in the contact process for manufacturing sulphuric acid, and the action of finely divided nickel to

increase the rate at which hydrogen combines with vegetable oils to form solid fats (e.g., "Crisco"). (For a discussion of theory, manufacture and use of catalysts see CATALYSIS.)

Catalysts accelerate chemical reactions in various different ways. The bromination of acetone (cited above) illustrates one of the most common modes of action. Here the acid which in this case is the catalyst combines with one of the reactants (acetone) to form an intermediate chemical compound. Then, in a later step of the complex reaction, the catalyst is regenerated and so becomes available for further reaction. In this way the catalyst goes through a complete cycle, and a trace of catalyst increases the rate at which a large amount of material reacts.

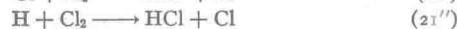
It is interesting to note that a catalyst can increase the rate of a chemical reaction but cannot change its point of equilibrium. If this statement were not correct, it would be possible to construct a perpetual motion machine. Since perpetual motion is an impossibility (see THERMODYNAMICS), it follows that in a reversible reaction the catalyst must accelerate both the forward and the reverse rate and in the same proportion.

**Photochemical Reactions.**—Reactions which take place in the presence of light but not in the dark are called photochemical reactions; their rate depends upon the amount of light absorbed. This subject is treated fully in the article on PHOTOCHEMISTRY. The principles here needed are the following: (1) Only the light which is absorbed by the system is effective in promoting chemical change; (2) radiant energy (light) is available only in units called quanta (see LIGHT); (3) a molecule which absorbs light and is thereby activated (i.e., enters into a reaction with light) absorbs one and only one light quantum (A. Einstein). Subsequently, the activated molecule may enter into other, more complicated chemical reactions.

**Chain Reactions.**—Hydrogen gas reacts with chlorine at room temperature provided that the mixture is illuminated; the reaction (except under special circumstances, see below) does not occur in the dark. The form of the equation for the chemical reaction



resembles that of the reaction for the formation of hydrogen iodide (reverse of equation 1); the kinetics of the two reactions are, however, quite different. The reaction between hydrogen and chlorine proceeds when visible light is used. Since light of this wave length is absorbed by chlorine, but not by hydrogen, it follows that chlorine is the reactant affected by the light. Measurements have shown that as many as 1,000,000 molecules of hydrogen chloride are produced for every light quantum absorbed. Evidently a very special mechanism must be postulated to account for this fact. It has been assumed (W. Nernst, M. Bodenstein) that, as an indirect or direct result of the illumination, the molecules of  $\text{Cl}_2$  which absorb light quanta are dissociated into chlorine atoms (21). These atoms then react as shown in equations (21') and (21'').



Each chlorine atom obtained by the illumination reacts with a molecule of hydrogen to produce a molecule of hydrogen chloride and an atom of hydrogen (21'); the latter in turn reacts with a molecule of chlorine to produce another molecule of hydrogen chloride and to regenerate an atom of chlorine (21''). The cycle is then repeated. Reactions characterized by such cycles are called chain reactions. If there were no side reactions to destroy the intermediate hydrogen and chlorine atoms, then, in principle, one chlorine atom could convert all the hydrogen and chlorine in the system to hydrogen chloride. In fact, the chain length varies from a few units to a million, depending upon the experimental conditions. The chains are broken (or terminated) when the chlorine or hydrogen atoms are removed. There are several means of removing these reactive atoms. For example, oxygen combines with either chlorine or hydrogen atoms, and traces of oxygen are effective in decreasing the rate of the reaction in question. In this reaction then, oxygen acts as a negative catalyst, or an inhibitor, or a chain breaker. (These terms are not, however, exactly synonymous.) Another means of breaking the chain is

the combination of hydrogen atoms and chlorine atoms present in the gas mixture to form hydrogen chloride. Such combination occurs on the walls of the vessel, or when a hydrogen atom and a chlorine atom, in what is called a three-body collision, collide simultaneously with some third particle (such as a chlorine molecule); interestingly, the combination does not occur when only a hydrogen and a chlorine atom collide. Such a combination independent of the wall or of any third particle would violate either the law of the conservation of momentum or the law of the conservation of energy, or both. (See MECHANICS.) The fact that no such combination is observed simply means that the molecular system in question obeys the laws of mechanics, as do the molecular systems in all similar reactions which have been carefully studied.

The validity of the proposed chain mechanism for the reaction between hydrogen and chlorine is supported (1) by the high photochemical yield of the reaction (*i.e.*, the large amount of hydrogen chloride produced per quantum of light absorbed), (2) by the fact that kinetic equations based upon the chain mechanism adequately describe the reaction velocity and (3) by experiments showing that the reaction can be initiated in the dark by the introduction into the reaction mixture of hydrogen or chlorine atoms from some outside source. There is good reason to believe that hydrogen atoms are produced by an electric arc discharge in hydrogen gas, and that chlorine atoms are produced in the reaction between sodium vapour and chlorine. If the products from either of these reactions are rapidly introduced into a mixture of hydrogen and chlorine, the formation of hydrogen chloride is initiated.

Reaction kinetics has provided much evidence to show that many reactions either in the gas phase or in solution proceed by chain mechanisms.

**Heterogeneous Reactions.**—Heterogeneous reactions include the solution of solids in solvents, and the reverse process, the crystallization of solids from solution. The reaction of metals with acids and problems of corrosion are part of the subject of heterogeneous reactions. However, by far the majority of the research on heterogeneous reactions is devoted to heterogeneous catalysis (*e.g.*, reactions between gases or liquids catalyzed by solids, etc.). For example, finely divided iron greatly accelerates the rate at which nitrogen and hydrogen unite to form ammonia. Recent studies have shown that iron adsorbs nitrogen in such a fashion as to activate it (by a reaction analogous to the formation of iron nitride); the hydrogen subsequently reacts with the adsorbed nitrogen. Although heterogeneous reactions of this sort are of considerable theoretical and practical interest (see ADSORPTION; CATALYSIS) the present article is devoted largely to a consideration of homogeneous reactions.

**Enzymes.**—Almost the earliest chemical reactions known are the fermentations by which sugar is converted to alcohol or vinegar (fermentation) or lactic acid (souring of milk). These and similar reactions occur in the presence of living organisms, such as yeasts, fungi, etc. In 1897 E. Buchner discovered that, in the fermentation of sugar, the function of the living yeast is to produce a catalyst for the reaction. He destroyed the yeast cells by grinding them with sand. The filtered juice, although it contained no living organisms, nevertheless rapidly converted sugar to alcohol. The complex organic catalysts produced by living cells are called enzymes; those so far investigated in detail have proved to be protein complexes.

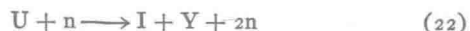
The extensive investigation, largely by methods of reaction kinetics, of the fermentation of sugar has revealed the fact that the reaction is a complex one in which many enzymes take part. Active research is at present under way to elucidate the path of many enzymatic processes, and to determine if possible the detailed mechanisms by which enzymes function as catalysts.

There are enzymatic systems which convert starch into sugar and sugar into alcohol; others hydrolyze proteins into a mixture of amino acids; still others synthesize proteins in the body; such systems are responsible for the conversion (by a form of combustion) of sugar to carbon dioxide and water, with the liberation of energy. The accelerating effect of some of these enzyme systems is enormous. For example, one part of beef catalase can be de-

tected in 25,000,000 parts of water by the acceleration it produces in the decomposition of hydrogen peroxide. Since the mechanism of enzyme action is unknown, and since the kinetics of enzyme action differs considerably from the kinetics of reactions accelerated by ordinary catalysts, direct comparisons are difficult and likely to be inaccurate. As a rough first approximation, however, catalase is about 10,000 times as active a catalyst as is an equal weight of ferrous ion in catalyzing the decomposition of hydrogen peroxide, and urease is about 10,000 times as active (at 20° C. and in neutral solution) as is an equal weight of sodium hydroxide in accelerating the hydrolysis of urea.

**Explosions.**—Chemical explosions are rapid reactions which are strongly exothermic; that is to say, these reactions are very rapid ones which evolve large quantities of heat. The hot gases formed in the chemical reaction, or the air heated by the energy released, produce a region of high pressure near the site of the explosion. This region of high pressure travels outward through the air in the form of an explosion wave which usually causes much of the destruction resulting from the explosion (see COMBUSTION; EXPLOSIVES). It is of interest to inquire what are the necessary conditions, and what are the possible mechanisms for a reaction which consumes many pounds of material in (say) 10<sup>-5</sup> seconds. There are two well-known types of mechanism for explosions: the chain branching mechanism and the thermal mechanism. The latter type was suggested by Van't Hoff, the former by N. N. Semionoff; examples of both types have been discovered.

The theory of the chain-branching mechanism is that, during the early stages of a chain reaction, more chains are initiated per unit time than are terminated. The most spectacular example of an explosion caused by chain branching is the fission of atomic nuclei, such as occurs in atomic bombs. Here the disintegration of a particular sort of uranium, U<sup>235</sup> (or of plutonium) is initiated by neutrons, but, in the disintegration, neutrons are also produced. (See ATOMIC ENERGY; ISOTOPE; NUCLEUS.) If exactly one neutron were produced from each disintegrating nucleus of U<sup>235</sup>, a chain reaction analogous to the reaction between hydrogen and chlorine would result. In fact, however, more than one neutron is produced by each nuclear disintegration; the average number is probably about two. An equation for the atomic disintegration is



where U, n, I and Y are the symbols for uranium, the neutron, iodine, and yttrium, respectively. (Other elements besides iodine and yttrium are also produced in the disintegration; the principles involved are, however, the same.) The faster the reaction proceeds, the more rapidly are neutrons produced and the more rapidly does the reaction rate increase. Since the disintegration of the uranium is accompanied by a large evolution of energy, the reaction is an explosion.

The second type of explosion mechanism is the thermal one. Most chemical reactions are carried out under conditions such that the heat evolved (or absorbed) by the reaction is taken away (or supplied) by the surrounding medium. If, however, a highly exothermic reaction is carried out under conditions such that the heat is not carried away by the surroundings, the reaction mixture must become hotter. At the more elevated temperature, the rate of the reaction is much greater; the rate of heat evolution, therefore, becomes much greater also, and the reaction mixture rapidly becomes still hotter. Such a reaction must necessarily lead to an explosion. The question whether a particular exothermic reaction will lead to an explosion is thus largely a question of the conditions under which the reaction is carried out. If the reaction can be made to proceed at such a rate that the heat lost to the surroundings per unit time is small compared with the heat input caused by the chemical reaction during the same interval, a thermal explosion ensues.

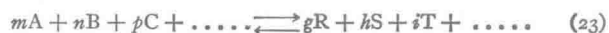
**Reactions of Isotopes.**—In general, the reaction rates of compounds which differ only in that they contain different isotopes of the same element are identical within experimental error. When, however, one of the lighter elements is involved, this need not be the fact. A compound which contains atoms of C<sup>14</sup> (radioactive carbon) may react at a rate which differs appreciably (*e.g.*,



by 10%) from that of a compound identical except that it contains only normal carbon atoms. The rate of the reactions of compounds containing deuterium (heavy hydrogen) may, in certain cases, differ from those of the corresponding compounds of light hydrogen by a factor as large as eight. These large differences in rate, which may occur when a bond to a hydrogen atom is formed or broken, arise from an effect (zero-point vibrational energy) predicted by quantum mechanics (*q.v.*). Although a discussion of the theory of this effect is out of place here, the phenomenon is proving a most useful tool in investigations of reaction mechanisms.

**The Collision Theory.**—In the theory of reaction kinetics as so far presented, several difficulties have been noted. The present section is devoted to a discussion of these difficulties and the methods of avoiding them; a knowledge of physical chemistry on the part of the reader is assumed.

The ratio of the rates of a forward and of the corresponding reverse reactions gives an approximate expression for the equilibrium constant of the reaction in question, as shown for a special case by equation (13). In the more general case, an analogous treatment of the reaction



leads to equation (24).

$$\frac{(R)^g(S)^h(T)^i \dots}{(A)^m(B)^n(C)^p \dots} = K_e \quad (24)$$

The ratio of concentrations on the left side of equation (24) is obtained even if the kinetic equation for the reaction is a complex one. For example, if the reaction is catalyzed, the catalyst concentration appears in the expression for the rate of both the forward and the reverse reaction; it thus cancels out in equation (24). Careful inspection shows that other possible complexities are likewise of no effect on  $K_e$ . But equation (24) is nevertheless not precisely correct. The true equilibrium expression (*see* THERMODYNAMICS) is defined in terms of the "activities," not the concentrations, of the reactants and reaction products. Although in dilute solutions the concentration of any substance closely approaches its activity, the two functions are by no means identical. (An analogous statement applies to gases at low pressure.) It is therefore clear that the law of Guldberg and Waage, although approximately correct, is not and cannot be uniformly valid.

The difficulty noted cannot be avoided by the assumption that reaction rates are proportional to activities rather than to concentrations; this assumption has been proved false by investigations of the rates of ionic reactions. The ratio of the activity of any substance to its concentration defines its activity coefficient. The activity coefficients of ions depend upon the ionic strength of the solution in which they occur (*see* SOLUTIONS, *Solutions of Electrolytes*). This ionic strength is a function of the concentrations and of the charges on all the ions present; in dilute solutions the activity coefficients of all ions decrease with increasing ionic strength. But the rates of reactions between two ions of like charge increase with increase of ionic strength; only for reactions between ions of opposite charge do the rates (like the activity coefficients) decrease with increasing ionic strength. Thus the rate of a reaction is not proportional to the "activities" of the reactants; it has already been shown that only as a first approximation is this rate proportional to the ionic concentrations.

The difficulty, at least insofar as ionic reactions are concerned, has been resolved by the assumption that reaction rates are proportional not to concentrations or activities, but to the number of collisions per second between the reacting ions. The number of collisions between charged particles should not be strictly proportional to the product of their concentrations. Let  $W$  be the ratio between the number of collisions among the reacting ions and the product of the ionic concentrations. Then, because of interionic effects,  $W$  should increase with increasing ionic strength for reactions between ions of like charge, and decrease with increasing ionic strength for reactions between ions of unlike charge. This predicted behaviour is in qualitative agreement with the anomaly in ionic reaction rates already cited.

J. A. Christiansen's calculation (1924) based on the theory of P. Debye and E. Hückel, accounts quantitatively for the observed

rates of ionic reactions in dilute solution. Further, although the forward and reverse rates, taken separately, are not proportional to the activities of the reactants and reaction products, the expression obtained by setting equal the rates of the forward and reverse reactions (corrected to account for interionic effects) yields the thermodynamic equilibrium expression in terms of activities, not concentrations. How this happens is made clearer in the consideration (*see* below) of the activated-complex theory of reaction velocity. In general, it has been assumed that consideration of the actual number of collisions always leads to corrections for the law of Guldberg and Waage, such that the dynamic and thermodynamic equilibrium constants become equal.

It should be pointed out that interionic and other forces not only affect the change in the number of collisions with change in concentration; they also affect the actual number of collisions per unit time. Thus, in a reaction between two positively charged ions, forces of electrostatic repulsion lower the number of collisions far below that computed from the kinetic molecular theory. Furthermore, it is not true that every collision between reactant particles moving, relative to one another, with a velocity greater than the critical one,  $u_0$ , leads to chemical change. There must also be a definite orientation of the molecules with respect to one another at the moment of collision. This consideration holds especially for complex molecules, which may be capable of reacting only at one end. The collision theory is thus considerably less precise than may at first have appeared.

Application of kinetic molecular theory to a simple bimolecular reaction (*e.g.*, the decomposition of hydrogen iodide) leads to equation (25), which relates the rate constant,  $k$ , with  $u_0$  the minimal velocity at collision, necessary for reaction.

$$k = \frac{4N^2d^2}{c^2} \sqrt{\frac{\pi kT}{m}} \left(1 + \frac{mu_0^2}{2kT}\right) e^{-mu_0^2/2kT} \quad (25)^*$$

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \quad (26)$$

Here  $N$  molecules of effective diameter  $d$  and weight  $m$  are present at a concentration of  $c$  moles per litre and at an absolute temperature  $T$ . The symbol  $e$  is the base of the system of natural logarithms, and  $k$  is Boltzmann's constant,  $1.38 \times 10^{-16}$  ergs/degree. If the values of  $k$  are experimentally determined for a series of temperatures, the values of both  $u_0$  (the minimal velocity of one molecule relative to another required for effective collisions) and of  $d$  (the effective diameter of the particles) can be determined. The difficulties previously discussed then appear as anomalously large or small values of  $d^2$ . That is to say, when the reacting particles attract each other, the cross sections of the molecules (proportional to  $d^2$ ) which are "effective" for collisions, will be large compared to these cross sections as determined by other methods; conversely, when the particles repel one another, or when a preferred orientation is necessary for reaction, the "effective" cross section will be small. The latter condition holds (although not to a marked degree) for the hydrogen iodide reaction.

An alternative description of the reaction process may be obtained by computing a collision number on the basis of the best available estimates for molecular cross sections and by replacing equation (25) by (27), to which it is approximately equivalent.

$$k = PZe^{-Q/RT} \quad (27)$$

Here  $Z$  is the "normal" collision factor,  $P$  is the "probability" factor defined by equation (27), and  $Q$  is the activation energy which does not differ greatly from  $\frac{1}{2}Mu_0^2$ , where  $M$  is the molecular weight of the substance in question. The difficulties of the collision theory are then contained in the factor  $P$ , and the problem of obtaining precise agreement between theory and experiment is reduced to that of computing  $P$  correctly.

One additional aspect of collision theory deserves attention. Some reactions (as previously stated) are of the first order. Such reactions would seem to be independent of collisions. In what way can these reactions be correlated with collision theory? Some first-order reactions probably cannot be so correlated. The disintegration of radium is strictly of the first order; the rate of the

\* If the two molecules which react are not identical, this expression must be somewhat modified. Among other modifications, the reduced mass  $\mu$  replaces  $m$ . If the masses of the two molecules in question are  $m_1$  and  $m_2$ , then the reduced mass  $\mu$  is defined by equation (26).



reaction depends upon changes in the radium nucleus, which are unaffected by collisions of the molecule as a whole. But in ordinary chemical, as opposed to nuclear, reactions, the energy necessary for reaction is probably acquired by the decomposing molecule through previous collisions.

**The Activated-Complex Theory.**—An alternative general theory of reaction kinetics is formulated in terms of the so-called "activated complex." (S. A. Arrhenius, J. N. Brönsted, N. Bjerrum, H. Eyring). In this theory, it is assumed that all the reactants are in pseudoequilibrium with an activated complex, X,



which in turn decomposes to give the reaction products. The activated complex X is not a true molecule; it is merely a stage in the process by which the reactants become the reaction products. Hence, the activated complex is not in true equilibrium with the reactants. The activated-complex theory, however, is founded on the assumption that the concentration of the activated complex may be computed just as if it were a real, stable chemical compound. The rate of reaction is then the product of the concentration of X multiplied by the rate at which it decomposes. This rate can be computed by the general methods of quantum mechanics (*q.v.*); it is the same for all activated complexes, regardless of the materials out of which they have been formed. For a reaction such as (23), the activated-complex theory leads to equation (29)

$$v = \kappa \frac{kT}{h} K^* (A)^m (B)^n (C)^p \dots \frac{\gamma_A^m \gamma_B^n \gamma_C^p}{\gamma_X} \quad (29)$$

where  $k$  is the Boltzmann constant,  $h$  is Planck's constant,  $K^*$  is the equilibrium constant for the formation of the activated complex (its decomposition into the reaction products being disregarded), and  $\gamma_A, \gamma_B, \gamma_C, \dots, \gamma_X$  are respectively the activity coefficients of the reactants and of the activated complex. The constant  $\kappa$  is called the transmission coefficient; it is usually nearly unity. When the activated-complex theory is used to describe a reversible reaction, a distinction must be drawn between the activated complex formed from the reactants and that formed from the reaction products. The two complexes, although structurally the same, differ with respect to the materials from which they have been formed and into which they are decomposing. Unless the distinction in question is made, the theory is self-contradictory.

Equation (29) contains  $\gamma_X$ , the activity coefficient for the activated complex. Although this coefficient cannot be measured (since the activated complex is not a stable entity) it can be estimated for the complexes which occur in ionic reactions. The charge on the activated complex must be the sum of the charges on the reactants; furthermore, the charge on an ion, as a first approximation, determines its activity coefficient. Equation (29) correctly predicts the rates of ionic reactions; it leads to results identical with those obtained by Christiansen. Although in particular instances the collision theory may be more convenient to apply than is the activated complex theory, or vice versa, the two always lead to the same results; they are, in essence, two different languages in which the same phenomena may be described.

At equilibrium, the rates of the forward and reverse reactions are equal. When two rate expressions analogous to (29) are used, an equation (30) is obtained from which the activity coefficient of the activated complex and the transmission coefficients have been eliminated.

$$\frac{(R)^r (S)^s (T)^t \dots (\gamma_R)^r (\gamma_S)^s (\gamma_T)^t \dots}{(A)^m (B)^n (C)^p \dots (\gamma_A)^m (\gamma_B)^n (\gamma_C)^p \dots} = K \quad (30)$$

Here  $K$  is the true thermodynamic equilibrium constant, expressed in terms of activities (concentrations multiplied by activity coefficients).

The pseudoequilibrium constant,  $K^*$ , of equation (29) is related to the free energy of activation,  $\Delta F^*$ , the heat of activation  $\Delta H^*$ , and the entropy of activation  $\Delta S^*$ , by equation (31).

$$-RT \log_e K^* = \Delta F^* = \Delta H^* - T \Delta S^* \quad (31)$$

The heat of activation,  $\Delta H^*$ , corresponds roughly with the energy of activation,  $Q$ , of the collision theory; the entropy of activation,  $\Delta S^*$ , may be roughly related to the logarithm of the "probability"

factor,  $P$ , of equation (27).

The thermodynamic concept of entropy has been interpreted, through statistical mechanics, in terms of molecular vibrations. Likewise, entropy of activation can often be interpreted in terms of the geometry and of the estimated vibrational frequencies of the activated complex.

The application of the activated-complex theory depends upon the computation of the pseudoequilibrium constant,  $K^*$ . Thus, the kinetic problem is replaced by a thermodynamic one, and all the powerful tools of thermodynamics and of statistical mechanics become immediately available for its solution. It is possible in principle (always) and in practice (occasionally) to calculate the rate of a chemical reaction without the use of any experimentally determined kinetic data. The difficulties reside principally in the selection of appropriate constants for the activated complex. For the reaction between a hydrogen atom and a hydrogen molecule (which has been investigated by the use of ortho- and parahydrogen and of deuterium), the absolute reaction rate has been computed by methods related to the activated-complex theory (E. Wigner). Most reactions are, however, too complex for complete mathematical solution by methods now known.

**BIBLIOGRAPHY.**—H. S. Taylor and S. Glasstone, *Treatise on Physical Chemistry* (1942); L. P. Hammett, *Physical Organic Chemistry* (1940); J. B. Sumner and G. F. Somers, *Chemistry and Methods of Enzymes* (1943); N. N. Semenov, *Chemical Kinetics and Chain Reactions* (Oxford, 1935); H. D. Smyth, *Atomic Energy for Military Purposes* (1945); C. N. Hinshelwood, *Kinetics of Chemical Change in Gaseous Systems* (Oxford, 1940); S. Glasstone, K. J. Laidler and H. Eyring, *The Theory of Rate Processes* (1941). (F. H. W.R.)

**READE, CHARLES** (1814–1884), English novelist and dramatist, the son of an Oxfordshire squire, was born at Ipsden, Oxfordshire, on June 8, 1814. He entered Magdalen college, Oxford, proceeded B.A. in 1835, and became a fellow of his college. He was subsequently dean of arts, and vice-president of Magdalen college, taking his degree of D.C.L. in 1847. His name was entered at Lincoln's Inn in 1836; he was elected Vinerian fellow in 1842, and was called to the bar in 1843. He kept his fellowship at Magdalen all his life, but after taking his degree he spent the greater part of his time in London. He began as a dramatist, and it was his own wish that "dramatist" should stand first in the description on his tombstone.

His first comedy, *The Ladies' Battle*, appeared at the Olympic theatre in May 1851. It was followed by *Angelo* (1851), *A Village Tale* (1852), *The Lost Husband* (1852) and *Gold* (1853). But Reade's reputation was made by the two-act comedy, *Masks and Faces*, in which he collaborated with Tom Taylor. It was produced in Nov. 1852, and later was expanded into three acts. By the advice of the actress, Laura Seymour, he turned the play into a prose story which appeared in 1853 as *Peg Woffington* as did also *Christie Johnstone*, a study of Scottish fisher folk. In 1854 he produced, with Tom Taylor, *Two Loves and a Life* and *The King's Rival*; and, unaided, *The Courier of Lyons*—well known under its later title, *The Lyons Mail*—and *Peregrine Pickle*. In 1855 appeared *Art*, afterward known as *Nance Oldfield*.

He made his name as a novelist in 1856, when he published *It's Never Too Late to Mend*, a novel written with the purpose of reforming abuses in prison discipline and the treatment of criminals. Five minor novels followed in quick succession—*The Course of True Love Never Did Run Smooth* (1857), *Jack of All Trades* (1858), *The Autobiography of a Thief* (1858), *Love Me Little, Love Me Long* (1859), and *White Lies* (1860), dramatized as *The Double Marriage*. In 1861 his masterpiece, *The Cloister and the Hearth*, appeared, relating the adventures of the father of Erasmus. It is one of the finest historical novels in existence. Returning from the 15th century to modern English life, he produced another novel with a purpose, *Hard Cash* (1863), in which he directed attention to the abuses of private lunatic asylums. Three other novels "with a purpose" were *Foul Play* (1869), in which he exposed the iniquities of ship-knackers, and paved the way for the labours of Samuel Plimsoll; *Put Yourself in His Place* (1870), in which he grappled with the trade unions; and *A Woman-Hater* (1877), on the degrading conditions of village life. *The Wandering Heir* (1875), of which he also wrote a version for the stage, was suggested by the Tichborne trial.

Outside the line of these moral and occasional works Reade produced three elaborate studies of character—*Griffith Gaunt* (1866), *A Terrible Temptation* (1871), *A Simpleton* (1873). The first of these was in his own opinion the best of his novels. His greatest success as a dramatist attended his last attempt—*Drink*—an adaptation of Zola's *L'Assommoir*, produced in 1879. In that year his friend Laura Seymour, who had kept house for him since 1854, died. Reade's health failed from that time, and he died on April 11, 1884, leaving behind him a completed novel, *A Perilous Secret*, which showed no falling off in the arts of weaving a complicated plot and devising thrilling situations. Reade was an amateur of the violin, and among his works is an essay on Cremona violins with the title, *A Lost Art Revived*.

**BIBLIOGRAPHY.**—Charles L. Reade and Compton Reade, *Charles Reade, a Memoir*, 2 vol. (1887); A. C. Swinburne, *Miscellanies* (1886); John Coleman, *Charles Reade as I Knew Him* (1903); Walter C. Phillips, *Dickens, Reade and Collins, Sensation Novelists* (1919); M. Elwin, *Charles Reade* (London, 1931); J. F. Quinn, *Charles Reade: Social Crusader* (1946).

**READING, RUFUS DANIEL ISAACS**, 1ST MARQUESS OF (1860–1935), British statesman, was born on Oct. 10, 1860, in London, the second son of Joseph Isaacs, merchant. He was educated at University College school, London, and abroad. At the age of 16 he went to sea, his parents believing that the discipline would be good for him. A subsequent venture on the stock exchange was a failure. He then read for the bar and was called in 1887; his legal career was unbroken and successful. He entered parliament as a Liberal Imperialist, winning a seat for his party at Reading in 1904, which he retained until he went to the house of lords. He became attorney general in 1910, and in 1912 was given a seat in the cabinet, which no attorney general had held before. On Oct. 22, 1913, he was made lord chief justice, and in Jan. 1914 was created Baron Reading of Erleigh. In this office he distinguished himself by humanity in the conduct of criminal cases and by the establishment of the principle that the court of criminal appeal should act as a real court of revision, upsetting verdicts or reducing sentences even of the individual high court judges.

After the outbreak of the war in Aug. 1914, he assisted in the drafting and the administration of those measures which saved England from financial ruin. In 1915 he was president of the Anglo-French Loan commission to the United States, where he succeeded in floating a great war loan. In 1917 he was appointed high commissioner and special envoy to the United States, and in November of that year was created an earl. In 1918 he was appointed high commissioner and special ambassador at Washington.

Lord Reading's term as viceroy of India began in 1921. At that time he was faced immediately by four acute problems. First, the dyarchy system of the Montagu-Chelmsford Government of India act, devised as a step in advance toward complete self-government, was definitely rejected by the leaders of the united Hindu and Mohammedan educated population, who in the movement known as *Swaraj* had resolved to make it unworkable. The second was the influence of Mahatma Gandhi, one of the most remarkable men of all time, who had inflamed millions of Indians to a boycott of the west by the east and a kind of gigantic movement of passive resistance, in which both British products and British government were to be alike rejected. The third was that the national temper of India had been aroused by prohibitions and indignities put upon Indians in other parts of the empire. The fourth, the story of the Punjab rebellion and the slaughter at Amritsar in 1919, with the support of Gen. Reginald Dyer's action there by the governing classes in England, had excited a feeling of such fierce resentment through the length and breadth of the peninsula as might have caused a general uprising. In dealing with the revolt against the dyarchy, he was compelled to imprison the two Mohammedan leaders, the brothers Ali. And although he was able to establish some kind of self-government in most of the local provinces and even something like friendly co-operation in the central legislative council, the constitution broke down in the Central Provinces and had to be suspended in Bengal, with a return to complete autocratic government. In the case of the boycott of the west the viceroy, after attempts at reconciliation with Gandhi, authorized his prosecution for inciting to mass civil disobedience.

Upon Lord Reading's return to England in April 1926 he was created a marquess, the first commoner to be so created since the duke of Wellington. He was secretary of state for foreign affairs, Aug.–Nov. 1931, in Ramsay MacDonald's national government. He died Dec. 30, 1935. (See INDIA: History.)

**READING**, a county and parliamentary borough and the county town of Berkshire, Eng., 38 mi. W. of London by road. Pop. (1961) 119,870. Area 14.2 sq.mi. Reading is an important junction of railways running west from London and south from the midlands, and the Kennet and Avon canal, to Bath and Bristol, and the Thames afford it connections by water. It lies on the Kennet river near where it joins the Thames. All the ancient churches are restored: Greyfriars church, formerly monastic, was completed early in the 14th century and after the dissolution of the monasteries served successively as a town hall, a workhouse and a jail, being restored to its proper use in 1864; St. Mary's was rebuilt in 1551 from the remains of a nunnery founded by Aelfthryth in expiation of the murder of her stepson Edward the Martyr; St. Laurence's is a Perpendicular building with Norman and Early English features; St. Giles's was much damaged during the siege of 1643 by the parliamentary forces and is almost wholly rebuilt. Public gardens occupy most of the site of the Benedictine abbey.

A University college was opened in 1892 and affiliated to Oxford; its success led to the gathering of an endowment fund and it became an independent university with a charter in 1926. Its researches into agriculture, horticulture and dairying are of special importance. The National Institute of Research in Dairying, established in 1912, is part of the university. At the grammar school, founded in 1485 and now occupying modern buildings, Archbishop Laud (a native of Reading) was educated. There is also a bluecoat school (1656) now just outside the borough at Sonning. The municipal museum, besides an art gallery and other exhibits, includes Roman relics from Silchester (*q.v.*) and finds from the Thames.

Reading early became a place of importance. In 871 the Danes encamped there, and in 1006 it was burned by Sweyn. It consisted of only 30 houses at the time of the Domesday survey. It is thought that a fortification existed there before the Conquest, and Stephen built a masonry castle which Henry II destroyed. On the foundation of a Benedictine abbey in 1121, the town, hitherto demesne of the crown, was granted to the abbey by Henry I. Henry VIII converted the abbey, whose church was among the largest in the country, into a palace and it was destroyed during the Civil War. From the 12th until the 16th century, Reading's history was that of the struggle as to rights and privileges between the abbey and the merchants' guild. A 16th-century account of the merchants' guild shows that many trades were then carried on, but John Leland says the town "chiefly stoneth by clothing." By the 17th century the trade had begun to decline; the bequest of the clothier John Kendrick (d. 1624) did little to revive it, and it was greatly injured by the Civil War. In the 18th century the chief trade was in malt.

The first town charter is that of Henry III (1253), confirmed and amplified by succeeding sovereigns. The governing charter until 1835 was that of Charles I (1639), incorporating the town under the title of the mayor, aldermen and burgesses. The market, chiefly held on Saturday, can be traced to the reign of Henry III; four fairs granted by the charter of 1562 are still held.

Reading is an agricultural centre with famous nursery gardens. Its biggest and best-known industry is biscuit manufacture, but there is much business in printing, iron foundries, engineering works, malting and brewing. The sale of corn, cattle and flour is carried on extensively, and there are pottery and brick works, together with riverside boatbuilding yards. The parliamentary borough, which used to return two members before the Reform act of 1885, regained that privilege in 1948.

**READING**, a city of southeastern Pennsylvania, U.S., the seat of Berks county, is located on the Schuylkill river, 58 mi. N.W. of Philadelphia.

The population in 1950 was 109,320 and decreased by 10.2% in 1960 to 98,177. However, the population of the Reading standard metropolitan statistical area comprising Berks county increased from 255,740 in 1950 to 275,414 in 1960.