Chemical Kinetics and the Origins
of Physical Chemistry

KEITH J. LAIDLER

Communicated by S. FLÜGGE

Physical chemistry is commonly said to have become established as a recognized field of science in the eighteen-eighties. The year 1887 was indeed of special significance, for it was then that the *Zeitschrift für physikalische Chemie* was founded by OSTWALD and VAN'T HOFF, that ARRHENIUS published his famous theory of electrolytic dissociation,[1] that OSTWALD was appointed professor of physical chemistry at the University of Leipzig, and that the second and final volume of OSTWALD'S *Lehrbuch der allgemeinen Chemie*[2] was published. It is true that OSTWALD was the *second* occupant of the chair of physical chemistry at Leipzig, the first having been the physicist F. WIEDEMANN who had assumed the position in 1871. It is also the case that the expression 'physical chemistry' had been used as early as the eighteenth century[3]. Work in the field prior to 1880 was, however, spasmodic; it was only during that decade that the subject gained momentum and became noticed by workers in other branches of science.

There have been several accounts of the early years of physical chemistry, notably those of ROOT-BERNSTEIN[4] and of HIEBERT[5]. These have emphasized in

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[1] S. ARRHENIUS, Z. physik. Chem., 1, 631–648 (1887).

[2] W. OSTWALD, *Lehrbuch der allgemeinen Chemie*, Akademische Verlagsgesellschaft, Leipzig, 2 vols., 1885–1887. A second and greatly enlarged edition of this, in 2 vols. and 3 parts, but never completed, was published between 1891 to 1902. This work was commonly known as "der grosse OSTWALD", to distinguish it from "der kleine OSTWALD" (Ref. 80). At the time the expressions "allgemeine Chemie" (general chemistry) and "physikalische Chemie" (physical chemistry) were used interchangeably in both German and English.

[3] See J. R. PARTINGTON, *A History of Chemistry*, Macmillan & Co., London, 1961, p. 569.

[4] R. B. ROOT-BERNSTEIN, "The Ionists: Founding Physical Chemistry, 1872–1890", Ph. D. Thesis, Princeton, 1980.

[5] E. N. HIEBERT, "Developments in physical chemistry at the turn of the century", in *Science, Technology, and Society in the Time of Alfred Nobel* (Ed. C. B. BERNHARD, E. CRAWFORD & P. SÖRBOM), Pergamon Press, Oxford, 1982.

particular the important role played by electrochemistry, especially the electrochemistry of solutions, in the early development of the subject. Of comparable importance is the work done in what was then known as 'chemical dynamics'. This topic, which now has a narrower meaning[6], was in the last century concerned with chemical equilibrium and with the rates of chemical reactions. In VAN'T HOFF's words

"[Chemical] dynamics is devoted to the mutual actions of several substances, i.e. to chemical change, affinity, velocity of reaction, and chemical equilibrium".[7]

OSTWALD defined it similarly as

"the theory of the progress of chemical reactions and the theory of chemical equilibrium".[8]

Today the expression 'chemical kinetics' refers to the study of the rates of chemical reactions and not to the properties of chemical systems at equilibrium. The present article deals with some of the early work in chemical kinetics, and relates it in particular to the development of the whole field of physical chemistry, a matter that does not appear to have been treated previously. Although the emphasis will be on the study of chemical reaction rates, there is inevitably some discussion of systems at equilibrium, since the topics are inextricably blended.

Early Work on Chemical Kinetics and Equilibrium

As early as 1777 the German chemist CARL FRIEDRICH WENZEL[9] (1740–1793) described some measurements of the rates of solution of metals in acids, but gave no details, merely saying that the rate increased with increasing concentration of acid. In 1818 the French chemist LOUIS JACQUES THENARD[10] (1777–1857) made an experimental study of the rate of decomposition of hydrogen peroxide, a substance he had discovered in the same year. However, none of these early studies made a quantitative attack on the problem of reaction rates. The chemists of the time were primarily concerned with discovering new compounds, and had

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[6] In the context of modern chemical kinetics, 'dynamics', or more specifically 'molecular dynamics', refers to a branch of kinetics which deals with non-reactive and reactive collisions between molecules, considered in terms of the intermolecular forces. The term 'kinematics' refers only to properties of motion that are independent of the forces.

[7] J. H. VAN'T HOFF, Lectures on Theoretical and Physical Chemistry (translated by R. A. LEHRFELD), Edward Arnold, London, 1899–1900, Vol. 3, p. 9.

[8] W. OSTWALD, "Faraday Lecture: Elements and Compounds", J. Chem. Soc., 85, 506–522 (1904), on p. 508.

[9] C. F. WENZEL, Lehre von der Verwandtschaft der Körper, Dresden, 1777.

[10] L. J. THENARD, Ann. chim. et phys., (2), 9, 314–317 (1818).

not much interest in interpreting chemical behaviour in terms of any kind of concept or theory.

The birth of chemical kinetics is often taken to have occurred in 1850, when the German physicist LUDWIG FERDINAND WILHELMY (1812–1864) studied the rate of inversion of sucrose[11]. WILHELMY was born in Stargard, Pomerania (now Poland), and after operating an apothecary's shop he began in 1843 to study chemistry and physics at the Universities of Berlin, Giessen (now the Justus Liebig University) and Heidelberg. He then studied with the French chemist and physicist HENRI VICTOR REGNAULT (1810–1878) at the Collège de France in Paris. His teaching and research career spanned only five years, from 1849 to 1854 when he retired to private life. During his brief scientific career he worked on a wide variety of problems in physics and chemistry, including capillary action and the equivalence of heat and energy. His kinetic work on the sucrose inversion was of very great importance. He investigated the reaction at various acid concentrations by means of a polarimeter, and found that the instantaneous rate of change of the sugar concentration was proportional to the concentrations of both the sugar and the acid. He set up, for the first time, a differential equation expressing the rate as a function of sucrose concentration; he then integrated the equation and showed that the resulting expression was consistent with his experimental results. He also examined the influence of temperature on the rate of the reaction, and proposed an empirical equation to explain the behaviour; again, this was the first time that this had been attempted. Little notice was taken of WILHELMY's important work until 1884, when OSTWALD[12] called attention to it.

WILHELMY's work was soon followed by investigations by the French chemists PIERRE EUGÈNE MARCELIN BERTHELOT (1827–1907) and LÉON PÉAN DE SAINT-GILLES (1832–1863), who in 1862 published the results of a study of the reaction between ethanol and acetic acid to give ethyl acetate and water[13]. Their work was mainly concerned with the equilibrium that became established after a sufficient period of time had elapsed, but they also obtained some results on the rate of combination of ethanol and acetic acid, finding it to be proportional to the product of the reactant concentrations.

At about the same time the Norwegian chemist PETER WAAGE (1833–1900) and his brother-in-law the mathematician CATO MAXIMILIAN GULDBERG (1836–1902) published the results of investigations which led to what is now usually known, rather unsatisfactorily, as the 'law of mass action'[14]. The true significance

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[11] L. WILHELMY, Poggendorf's Annalen der Physik und Chemie, 81, 413–433, 499–526 (1850). Important excerpts from this paper have been reprinted in H. M. LEICESTER & H. S. KLICKSTEIN, A Source Book in Chemistry, 1400–1900, Harvard Univ. Press, Cambridge, Mass., 1968, pp. 396–400.

[12] F. W. OSTWALD, J. prakt. Chem., 29, 385–408 (1884). OSTWALD also reprinted WILHELMY's paper in his Klassiker, No. 29, "Ueber das Gesetz nach welchem die Einwirkung der Säuren auf den Rohrzucker stattfindet. Herausgegeben von W. Ostwald" Leipzig, 1891.

[13] M. BERTHELOT & L. DE SAINT-GILLES, Ann. Chim. 65, 385–422 (1862) and several later papers.

[14] C. M. GULDBERG & P. WAAGE, Forhandlinger Videnskabs-Selskabet i Christiania, 35–40, 92–94, 111–120 (1864).

of their work is by no means clear-cut, and has been the subject of some contro-
versy[15]. GULDBERG & WAAGE made some rate measurements, but did not study
the dependence of rates on reactant concentrations; instead they incorrectly
assumed that rate equations can be deduced from stoichiometric equations, and
by equating rate equations for a reaction in forward and reserve directions they
arrived at an equilibrium equation. Although their resulting equations were
correct, it is now known that their procedure is not valid, and that chemical equi-
librium must be treated by the methods of thermodynamics (as was first done by
VAN'T HOFF[16]) or statistical mechanics. Thus GULDBERG & WAAGE did not satis-
factorily solve a problem relating to either kinetics or equilibrium; their work was
nevertheless of value in pointing the way to more reliable procedures. GULDBERG
& WAAGE'S first publications[14], in Norwegian, attracted little attention, and not
much more when their work later appeared in French[17] and later again in a re-
vised form in French with the addition of further experimental evidence[18]. Their
work received more notice much later when OSTWALD published a German trans-
lation of their original articles[19].

Another collaboration between a chemist and a mathematician, carried out
at about the same time and quite independently, was much more successful as
far as the field of kinetics is concerned. In the years 1865 to 1867 AUGUSTUS
GEORGE VERNON HARCOURT (1834–1919)[20], then a Student (Fellow) of Christ
Church, Oxford, and later Dr. LEE's Reader in Chemistry, made some very im-
portant studies of reaction rates. Carried out in the Lee's Laboratory at Christ
Church, which HARCOURT himself had established, the experiments were on the
reaction between hydrogen peroxide and hydrogen iodide and that between

[15] See, in particular, E. W. LUND & O. HASSEL, "Guldberg and Waage and the law
of mass action", in *The Law of Mass Action: A Centenary Volume*, Universitatsforlajet,
Oslo, 1964, pp. 37–46; K. J. MYSELS, J. Chem. Educ., **33**, 178, 179 (1956); E. A. GUG-
GENHEIM, J. Chem. Educ., **33**, 544–545 (1956); E. W. LUND, J. Chem. Educ., **42**, 548–550
(1965).

[16] J. H. VAN'T HOFF, Archives néerlandaises des sciences exactes et naturelles, **20**,
239–302 (1885); Königl. Svenska Vetenskaps-Akademiens Handlinger, **21**, No. 17,
3–58 (1886); Z. physikal. Chem., **1**, 481–508 (1887).

[17] C. M. GULDBERG & P. WAAGE, "Etudes sur les affinités chimiques", Brøgger &
Christie, Christiania, 1867.

[18] C. M. GULDBERG & P. WAAGE, J. prakt. Chem., [2], **19**, 69–114 (1879).

[19] W. OSTWALD, *Klassiker*, No. 104: "Untersuchungen über die chemischen Affini-
täten. Abhandlungen aus den Jahren 1864, 1867, 1879, von C. M. GULDBERG und
P. WAAGE. Uebersetzt und herausgegeben von R. Abegg", Leipzig, 1899.

[20] For biographical material see H. B. DIXON, Proc. Roy. Soc., **97**, vii–xi (1920);
J. SHORTER, "A. G. Vernon Harcourt: A founder of chemical kinetics and a friend of
'Lewis Carroll'", J. Chem. Educ., **57**, 411–416 (1980); M. C. KING, "The Chemist in
Allegory: Augustus Vernon Harcourt and the White Knight", J. Chem. Educ., **60**, 177–
180 (1983). The neglect of mathematics in the education of a chemist was in those days
to some extent deliberate; thus Professor C. G. B. DAUBENY, one of HARCOURT's teachers,
published in 1853 a pamphlet which in many respects was an enlightened plea for im-
provements in science teaching, but which included the comment: "It would manifestly
be quite foreign to the purpose, and fatal to the genius, of a School of Physical Science,
to encourage the introduction of any subjects that are treated mathematically".

potassium permanganate and oxalic acid, particular attention being paid to the influence of the reactant concentrations on the rate. HARCOURT'S mathematical knowledge was very slight, as was common among chemists at the time; he knew no calculus, but he enlisted the help of a Scottish colleague, WILLIAM ESSON[21] (1838–1916), who was a Fellow of Merton College, Oxford, and tutor in mathematics; he was later Savilian Professor of Geometry at Oxford. ESSON started with the differential equations for several types of chemical reactions, and by integrating them obtained expressions for the amounts of product formed as a function of time. He dealt in this way with what are now called 'first-order' reactions, in which the rate is proportional to the concentration of a single reacting substance, with 'second order' reactions in which the rate is proportional to the product of two concentrations, and with consecutive reactions in which the product of one first-order reaction undergoes another first-order reaction. By the use of these procedures, which are essentially the same as those commonly used in kinetics today, HARCOURT & ESSON were able to analyze the experimental results that HARCOURT had obtained[22]. They paid no attention to the then very popular, but nebulous and ambiguous, topic of "chemical affinity", and unlike GULDBERG & WAAGE they were not concerned with equilibrium states. HARCOURT and his kinetic work have been treated very comprehensively by CHRISTINE KING[23] and by JOHN SHORTER[24], and there is no doubt that these investigations played a very important role in the development of the field of chemical kinetics.

The Contributions of J. H. van't Hoff

There can be little question that the most outstanding contributions to chemical kinetics in the last century were those of the Dutch chemist JACOBUS HENRICUS VAN'T HOFF[25] (1852–1911). Born in Rotterdam, VAN'T HOFF studied under the German organic chemist FRIEDRICH AUGUST KÉKULÉ (1829–1896) at the University of Bonn, and later under the French chemist CHARLES ADOLPH WURTZ (1817–1884) at the Sorbonne in Paris. He then returned to the University of Utrecht where he obtained his Ph. D. degree in 1874 on the strength of a rather mundane piece of research in organic chemistry. A year before taking his Ph. D.

[21] For biographical material see Proc. Roy. Soc., A, **93**, 44–47 (1917); this article bears the initials "E.B.E.".

[22] A. G. V. HARCOURT & W. ESSON, Proc. Roy. Soc., **14**, 470–474 (1865); **15**, 262–265 (1867); Phil. Trans., **156**, 193–222 (1866); **157**, 117–154 (1867).

[23] M. C. KING, "Experiments with time", Ambix, **28**, 70–82 (1981); **29**, 49–61 (1982), and loc. cit. (Ref. 20); Ambix, **81**, 16–31 (1984).

[24] J. SHORTER, loc. cit. (Ref. 20).

[25] For biographical and scientific information see H. P. M. SNELDERS, in Dictionary of Scientific Biography (Ed. C. C. GILLISPIE), Charles Scribner, New York, 1970–76; F. G. DONNAN, Proc. Roy. Soc., A, **86**, xxxix–xliii (1912); J. WALKER, "Van't Hoff Memorial Lecture", J. Chem. Soc., **103**, 1127–1143 (1913). VAN'T HOFF's scientific work, particularly that relating to ionic dissociation, is treated in detail by R. B. ROOT-BERNSTEIN, Ref. 4, especially pp. 236–350.

degree VAN'T HOFF had published privately a pamphlet[26] that was later to bring him much fame and for which he is still remembered; it was concerned with the 'tetrahedral carbon atom' and its relation to optical and structural isomerism. That VAN'T HOFF failed to include this outstanding work in his Ph. D. dissertation is a tribute to his native shrewdness, since his theory was for some years the object of ridicule; the famous German organic chemist HERMANN KOLBE (1818–1884) made a particularly vitriolic attack on it[27], in terms that have been referred to as "infamous".

For over a year after receiving his Ph. D. degree VAN'T HOFF was unemployed, and his first appointment, in 1875 as a teacher in the State Veterinary College, was unsatisfactory. In 1878, however, he was made professor of chemistry, mineralogy, and geology at the University of Amsterdam. His inaugural address at that university[28], on the role of imagination in science, began with a restrained reply to KOLBE and was an eloquent appeal for the kind of approach to scientific work that he himself achieved so successfully in later years. In 1896 VAN'T HOFF moved to the University of Berlin, where he was freed from the heavy teaching duties that had been required of him in Amsterdam. In 1901 he was awarded the first Nobel prize in chemistry for his work on the theory of solutions.

Aside from his scientific attainments, VAN'T HOFF was a man of unusually fine character and personality. One of his students, the British physical chemist FREDERICK GEORGE DONNAN (1870–1956), said of him:

"To those who had the privilege of working with him he was endeared by the unaffected friendliness of his nature".[29]

He was much interested in poetry, favorite authors being Lord BYRON and ROBERT BURNS; he wrote much verse in his native language and also many Byronic stanzas in English. He was also an excellent pianist, and had a keen appreciation of the beauties of nature.

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[26] J. H. VAN'T HOFF, *Voorstel tot uitbreiding der tegenwoordig in de scheikunde gebruikte structuur-formules in de ruimte; benevens een daarmeê samenhangende opmerking omtrent het verband tusschen optisch actief vermogen en chemische constitutie van organische verbindingen*, (Proposal for the extension of the formulae now in use in chemistry into space; together with a related remark on the relation between the optical rotating power and the chemical constitution of organic compounds), Utrecht, 1874. The pamphlet was translated into French and appeared in Archives néerlandaises des sciences exactes et naturelles, **9**, 445–454 (1874). There later appeared an English translation in *The Foundations of Stereo Chemistry*; *Memoirs by Pasteur, van't Hoff, Le Bel, and Wislicenus*, New York, 1901.

[27] H. KOLBE, J. prakt. Chem., **15**, 473 (1877). VAN'T HOFF was in good company, as KOLBE also attacked the structural efforts of KÉKULÉ, J. F. W. A. VON BAEYER, and EMIL FISCHER. The term 'infamous' is used to describe KOLBE's criticism by, for example, ROOT-BERNSTEIN, Ref. 4, p. 195.

[28] J. H. VAN'T HOFF, "Imagination in Science", speech delivered on 11 October, 1878, at the University of Amsterdam; an English translation was published by Springer-Verlag, New York, in 1967.

[29] F. G. DONNAN, Ref. 25, at p. xliii.

VAN'T HOFF was exceptionally quiet and unassuming; in spite of his friend-
liness he was a man of very few words, and former students have recalled that
in his laboratory silence reigned most of the time[30]. Ever imperturbable, he was
never known to show the slightest irritation, let alone anger. Perhaps his most
striking characteristic was his modesty. At no time did he ever enter into any
controversy as to scientific priority; indeed in his writings he tended to stress
the contributions of others and to deprecate his own. For this reason his work
has never received the recognition it deserves. In chemical thermodynamics,
especially in relation to chemical equilibrium, and in chemical kinetics, he was
responsible for most of the concepts and relationships that are in current use by
scientists today. In spite of this, modern textbooks of physical chemistry, while
making full use of these concepts and equations, usually make little or no reference
to the man in whose mind they originated. It is interesting that VAN'T HOFF should
himself have said:

"A famous name has this peculiarity, that it becomes gradually smaller, espe-
cially in natural sciences where each succeeding discovery invariably over-
shadows what precedes"[31].

In view of VAN'T HOFF's character it is unlikely that he was thinking of himself
when he made this observation; more probably he was thinking of the German
chemist AUGUST FRIEDRICH HORSTMANN (1842–1929) whose important thermo-
dynamic work was eclipsed by that of VAN'T HOFF himself.

VAN'T HOFF's first research subsequent to his Ph. D. degree culminated in
1878–1881 in his first book, *Ansichten über die organische Chemie*[32]. In spite
of its title, this is not a book about organic chemistry, but about structural prob-
lems in chemistry. In it VAN'T HOFF attempted to give an interpretation of what
is now known as the covalent bond. He did so in terms of gravitational attractions
between atoms, assigning different shapes to the various atoms so as to explain
the relative strengths of bonds. This is now known to be completely wrong,
gravitational attraction being too weak by many orders of magnitude. However,
there was no way that this could have been known at the time; it was not until
several decades later that sufficient knowledge of atomic structure allowed the
covalent bond to be explained. VAN'T HOFF's proposals must be judged in the
light of knowledge available when they were put forward, and in that light they
stand as an imaginative approach to a baffling problem. Not surprisingly, how-
ever, his book had little influence on scientific thought.

VAN'T HOFF's second book, *Etudes de dynamique chimique*[33], published in
1884, is in an entirely different category. By all standards this book was ultimately

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[30] H. S. VAN KLOOSTER, "Van't Hoff in retrospect". J. Chem. Educ., **29**, 376–379
(1952); A. F. HOLLEMAN, "My reminiscences of van't Hoff", J. Chem. Educ., **29**, 379–382
(1952).
[31] Quoted by H. S. VAN KLOOSTER, Ref. 30, on p. 376. I do not know the origin of
this comment, which may well have been made in a lecture or private conversation.
[32] J. H. VAN'T HOFF, *Ansichten über die organische Chemie*, Vieweg, Brunswick,
1878–1881.
[33] J. H. VAN'T HOFF, *Études de dynamique chimique*, F. Muller, Amsterdam, 1884.

highly successful and influential, and it still makes for profitable reading a hundred years later. Dealing with both chemical reaction rates and chemical equilibrium, it was the first book ever to have been written on chemical kinetics. Considering the fact that at the time of its appearance fewer than a dozen significant research papers had been published in the field, one can only wonder today that VAN'T HOFF found it possible to draw so many correct, important, and fundamental conclusions from a paucity of experimental data. In addition to already published material, VAN'T HOFF and his assistants had carried out in the Amsterdam laboratories a few very crucial, well-conceived, and well-executed experiments, the results of which were sufficient to allow him to outline the new field in a most sound and comprehensive way. The book is typical of VAN'T HOFF's style in research; his output in experimental work was not large, but everything done by him and his students was of great significance in allowing him to answer fundamental questions of great importance.

Initially, VAN'T HOFF's *Etudes* fell on stony ground. This is by no means surprising since, although today it can be followed with ease by any chemist or physicist, it was much too difficult for the average chemist of the eighteen-eighties; chemists of the time generally had weak mathematical backgrounds, and they were not used to thinking in terms of theoretical concepts. The style of the *Etudes* did not help them, for VAN'T HOFF overestimated the mathematical ability of most of his readers. His derivations, while clear and logical, left out many mathematical steps, which few chemists of the time would have been able to provide for themselves.

It is of interest to note the recollections, in 1913, of the Scottish chemist Sir JAMES WALKER[34] (1863–1935):

> "I remember having read these *Etudes* in 1885 or 1886, and I can well remember the mingled feeling of revelation and bewilderment which the book produced on me ... Here, I thought, was the real thing at last, hard to comprehend, certainly, but something definite. What I understood was excellent. What I did not quite succeed in understanding seemed, somehow, even better"[35].

Coming from one who himself had a distinguished career in physical chemistry, these words are very revealing; WALKER was later professor at Dundee and at Edinburgh, and was the author of *Introduction to Physical Chemistry*[36] (1899), one of the earliest textbooks in the field. If WALKER found the book "hard to comprehend", most chemists would have found it impossible.

It is also of interest that HARCOURT & ESSON, in spite of having done important work in chemical kinetics, apparently failed to recognize the importance of the *Etudes*; in a paper[37] published in 1912 they disussed the temperature dependence

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[34] For biographical information see J. KENDALL, Obituary Notices of Fellows of the Royal Society, **1**, 537–549 (1935).

[35] J. WALKER, Ref. 25, at p. 1138.

[36] J. WALKER, *Introduction to Physical Chemistry*, Macmillan, London, 1899.

[37] A. V. HARCOURT (with a long appendix by W. ESSON), Phil. Trans., A, **212**, 187–204 (1912).

of reaction rates without appreciating VAN'T HOFF's very important contribution to that topic.

It appears that only two reviews of the *Etudes* ever appeared; both were favourable but since they were both written in little-known languages they did little to spread VAN'T HOFF's ideas. One review[38] was written in Dutch by A. C. OUDEMANNS (1831–1895), one of VAN'T HOFF's former teachers. It is tempting to wonder whether OUDEMANNS understood much of the book, since after an initial sentence describing it as an "important work" he contented himself with merely reproducing the table of contents. The other review[39], in Swedish, was of much greater significance, since it was by SVANTE AUGUST ARRHENIUS[40] (1859–1927), who had then just obtained his Ph.D. degree at the University of Uppsala. ARRHENIUS understood and appreciated the book very well, and his detailed review of it brought out some of its main features. At the same time ARRHENIUS offered some sound criticisms, which VAN'T HOFF found to be of help in his later studies. ARRHENIUS sent his review to VAN'T HOFF, whose wife was able to translate it with the aid of a dictionary. This initial exchange of ideas between VAN'T HOFF and ARRHENIUS had many important consequences for both men. ARRHENIUS, who later always referred to VAN'T HOFF in terms of the highest praise[41], later worked in VAN'T HOFF's laboratories, and their association was of great help in leading ARRHENIUS to his theory of electrolytic dissociation[42] and to what is now usually called the "ARRHENIUS equation"; this latter topic is dealt with later in this article.

The *Etudes* is so full of new and important ideas that it is impossible to do justice to it in a brief account; only some of the outstanding features can be mentioned. One of these was VAN'T HOFF's introduction of the symbol[43]

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in the equation of a chemical reaction. At first sight this may seem trivial, but in reality it was important, since it represents VAN'T HOFF's appreciation of the dynamic nature of chemical equilibrium; he used in the *Etudes* (p. 161) the expression 'principle of mobile equilibrium'. Previously chemists had used an 'equals' sign in a chemical equation, but VAN'T HOFF considered that this is useful only in indicating that an equation is balanced. His adoption of the new symbol emphasized his approach in considering the time course of a chemical reaction, and in em-

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[38] A. C. OUDEMANNS, Archives Néerlandaises, 1885.

[39] S. A. ARRHENIUS, Nordisk Revy, 31 March, 1885.

[40] For biographical information see H. A. M. SNELDERS, in *Dictionary of Scientific Biography* (Ed. C. C. GILLISPIE), Charles Scribner, New York, 1970–76; J. WALKER, "Arrhenius memorial lecture", J. Chem. Soc., 1380–1401 (1928).

[41] H. S. TAYLOR, "Fifty years of chemical kineticists", Ann. Rev. Phys. Chem., **13**, 1–18 (1962); on p. 3. TAYLOR remarked that VAN'T HOFF's portrait hung prominently in ARRHENIUS's home.

[42] Ref. 1; for details see ROOT-BERNSTEIN, ref. 4, especially pp. 366–411.

[43] *Etudes*, ref. 33, p. 115; the modified symbol $\rightleftharpoons$ proposed by H. MARSHALL (Proc. Edin. Roy. Soc., **24**, 85 (1902)) is now more commonly used.

phasizing that when a chemical system is at equilibrium, chemical change is taking place at equal rates in the two directions. This idea was not original with VAN'T HOFF, but had been introduced particularly by the British chemist ALEXANDER WILLIAM WILLIAMSON[44] (1824–1904), the German physicist RUDOLPH CLAUSIUS[45] (1822–1888) and the Austrian physicist LEOPOLD PFAUNDLER[46] (1839–1920). Prior to their work it had been thought that chemical equilibrium is reached when the *forces* on the symbol are equal and opposite, and that all reaction then ceases. The realization that this is not the case had important implications for chemical dynamics, and VAN'T HOFF'S new symbol emphasized this point.

Another important innovation in the *Etudes* is VAN'T HOFF'S recognition of what we now call the "order of reaction", although he did not employ that term. (It was introduced in 1887 by OSTWALD[47].) He classified reactions as 'monomolecular' (or 'unimolecular'), by which he meant that their rates were proportional to the first power of the concentration of a reactant. Reactions were called 'bimolecular' if their rates were proportional to the square of a reactant concentration, or to the product of two reactant concentrations. 'Trimolecular' reactions were those involving the product of three concentrations, and so on. Today these terms are used to indicate the number of molecules entering into an individual chemical act, which is not necessarily the same as the power to which the concentration is raised (the 'order' in modern terminology). VAN'T HOFF was quite aware of this distinction, and he referred explicitly to 'the number of molecules entering into reaction' as well as to the 'molecularity' [order].

In the sections of his book dealing with reactions of different molecularities, VAN'T HOFF mentioned a number of examples, giving many experimental results that had not previously been published and that had been obtained by himself and his assistants in the Amsterdam laboratories; during the three years prior to the appearance of the book VAN'T HOFF had published nothing, keeping his results for inclusion in the book. As an example of a unimolecular [first-order] reaction VAN'T HOFF mentioned the decomposition of arsine, for which the balanced equation is

$$2\,AsH_3 = 2\,As + 3\,H_2.$$
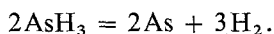
He wrote down the differential equation for this reaction (as had previously been done by HARCOURT & ESSON[22] for a different system), integrated it, and calculated the proportionality constant, which he called the 'velocity constant' (now more often called the 'rate constant'). He recognized that for a 'unimolecular' [first-order] reaction the fraction of the substance disappearing in a given time is independent of the initial amount. In a later section of the book (p. 55) VAN'T HOFF described experiments that proved that the arsine decomposition takes place to some extent on the glass surface of the vessel; he did this by measuring the rate in vessels of different shapes, so that the surface/volume ratio was altered; the

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[44] A. W. WILLIAMSON, Chemical Gazette, **9**, 294 (1851).

[45] R. CLAUSIUS, Ann. Physik, **101**, 338–360 (1857).

[46] L. PFAUNDLER, Ann. Physik **131**, 55–85 (1867), **144**, 428-438 (1872).

[47] F. W. OSTWALD, *Lehrbuch der allgemeinen Chemie*, Akademische Verlagsgesellschaft, Leipzig, 1887, Vol. 2, p. 634.

reaction occurred more rapidly in a vessel in which there was a larger proportion of surface. He also found, for another gas reaction, that coating the walls of the vessel with a substance like vaseline had a marked effect on the influence of the surface. Another unimolecular reaction considered in the *Etudes* (p. 14) was the conversion of dibromsuccinic acid into dibromomaleic acid.

As an example of a 'bimolecular' [second-order] reaction VAN'T HOFF considered the hydrolysis of ethyl acetate by caustic soda, a reaction he represented as

$$NaOH + C_2H_5OOC_2H_3 = CH_3COONa + C_2H_5OH.$$
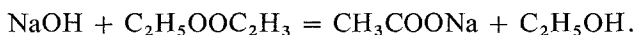
This reaction had been studied by VAN'T HOFF'S assistant L. T. REICHER, who published his results later[48]. Again, VAN'T HOFF set up the differential equation, integrated it, and showed that REICHER'S results gave a satisfactory rate constant. In a similar way, VAN'T HOFF gave the rate equation, in its differential and integrated forms, for a 'polymolecular' reaction, in which the rate is proportional to a concentration to the nth power. However, he was not able to find examples of reactions in which n is greater than two; this is not surprising, since for good reasons reactions with $n \geq 3$ are rare.

Another topic treated very effectively by VAN'T HOFF in the *Etudes* (p. 55) was the influence of various factors, such as the nature of the solvent, on the rates of reactions. He also introduced, on p. 87 of the *Etudes*, a general method, still in common use today and called the 'differential method', for determining the 'molecularity' [order] of a chemical reaction. The method involves measuring rates, v, at various concentrations c of the reactant. Then, if the relationship between the two is of the form

$$v = kc^n \tag{1}$$

the value of n can be determined from the slope of a plot of $\log v$ against $\log c$. This method is much more direct and satisfactory than making an initial guess of the value of n, and then integrating the corresponding rate equation[49]. On p. 89 of the book he applied this method to some results obtained by his assistant L. T. REICHER on the action of bromine on fumaric acid.

Another extremely important matter considered by VAN'T HOFF in the *Etudes* (pp. 114, 116) was the influence of temperature on rate constants and equilibrium constants. In his book he treated rate constants first (on p. 114), but based his argument on the equation for the equilibrium constant given on a later page; here it will be more convenient to treat equilibria first. It is to be noted that in 1884 VAN'T HOFF had not yet given a thermodynamic proof of the condition for equilibrium; that proof he was to give in the following year[16]. He based his temperature-dependence argument on an equation obtained by HORSTMANN, who was the first to apply thermodynamics to chemical problems. HORSTMANN treated in particular

[48] L. T. REICHER, Liebig's Annalen, **228**, 257–287 (1885); **238**, 276–286 (1887).

[49] W. LASH MILLER (Trans. Roy. Soc. Canada, **11**, 245 (1908)) has classified methods of analyzing kinetic data as "the method of systematic exploration" and "the method of guess and try". The differential method of OSTWALD would seem to fall in the first category, the method of integration in the second. LASH MILLER'S own appraisal of the methods, however, is hard to follow.

the dissociation pressure p of a solid substance such as ammonium chloride, and on the basis of CLAUSIUS's principle that at equilibrium the entropy is a maximum he deduced the equation[50]

$$\ln \frac{p_1}{p_2} = \frac{q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{2}$$

where p_1 and p_2 are the pressures at the two temperatures T_1 and T_2, q is the heat required to dissociate a mole of the substance, and R is the gas constant. At a given temperature T this equation becomes

$$\ln p + \frac{q}{RT} + \text{const.} = 0. \tag{3}$$

The procedure used by VAN'T HOFF for a chemical process at equilibrium was to substitute the equilibrium constant K for the pressure, and to regard q as the heat absorbed in the chemical process:

$$\ln K + \frac{q}{RT} + \text{const.} = 0. \tag{4}$$

Differentiation with respect to temperature then gives

$$\frac{d \ln K}{dT} = \frac{q}{RT^2}. \tag{5}$$

His proof was by no means rigourous, but it gave the correct answer. In modern notation this equation is written as

$$\frac{d \ln K}{dT} = \frac{\Delta H^0}{RT^2} \tag{6}$$

where ΔH^0 is the standard enthalpy change for the reaction. This equation is commonly known as the 'VAN'T HOFF isochore', since it applies strictly only to systems at constant volume.

Some of the final section of the *Etudes* is devoted to applying this relationship to various types of chemical reactions. Throughout VAN'T HOFF was aware that the heat q does not necessarily remain unchanged as the temperature is altered. Some of VAN'T HOFF's applications of his equation were to physical processes, such as changes of state.

In his discussion of equation 5 in the *Etudes* (p. 161), VAN'T HOFF presented an important and interesting qualitative discussion of the way in which K is affected by temperature. He pointed out that if heat is evolved when reaction occurs from left to right (q is negative), the equilibrium constant will decrease if the temperature is raised. Conversely, if q is positive, an increase in temperature will increase K. Later in 1884 this generalization was included by the French

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[50] A. F. HORSTMANN, Ber. **4**, 635–639 (1871); Ann. Chem., **170**, 192–210 (1873).

chemist HENRI LOUIS LE CHÂTELIER (1850–1936) in what is generally known today as the "LE CHÂTELIER principle"[51].

The *Etudes* also includes a criticism of the so-called "principle of maximum work", which had previously been formulated independently by the Danish chemist HANS PETER JORGEN THOMSEN (1826–1909) and the French chemist PIERRE EUGÈNE MÁRCELIN BERTHELOT (1827–1907). According to them, the driving force in a chemical reaction is the evolution of heat; in THOMSEN's own words,

> "Every simple or complex change of a purely chemical nature is accompanied by an evolution of heat"[52].

BERTHELOT's formulation[53] is very similar. However, VAN'T HOFF was one of the first to perceive that this generalization cannot be correct. The sign of q in a chemical reaction influences only how the equilibrium constant K varies with temperature; it does not completely control its actual magnitude. At the absolute zero of temperature, VAN'T HOFF noted, the THOMSEN-BERTHELOT principle is correct, but not at other temperatures. At this stage, however, VAN'T HOFF did not introduce the concept of entropy or free energy, which we know now to have important significance in connection with the magnitudes of equilibrium constants.

Another innovation in the *Etudes* (p. 202) is that when an electrochemical cell operates reversibly, the electromotive force produced permits the calculation of what VAN'T HOFF called the "work of affinity" in the chemical reaction that occurs in the cell. This work of affinity is the negative of the GIBBS (free) energy, ΔG, for the reaction; the concept of free energy does not, however, appear in the book.

VAN'T HOFF's treatment of the influence of temperature on equilibrium constants was extended by him, in the *Etudes* (p. 114), to deal with rate constants. His analysis is based on the fact, proved by him in the book, that for forward and reverse reactions the ratio of the rate constants k_1 and k_{-1} is equal to the equilibrium constant K. Equation (6) may therefore be written as

$$\frac{d \ln k_1}{dT} - \frac{d \ln k_{-1}}{dT} = \frac{q}{RT^2}. \tag{7}$$

His argument was that this relationship can be satisfied only if k_1 and k_{-1} vary with temperature in the same manner as does K. Expressed differently, he regarded the heat q as the difference between two energy terms E_1 and E_{-1},

$$q = E_1 - E_{-1} \tag{8}$$

so that

$$\frac{d \ln k_1}{dT} - \frac{d \ln k_{-1}}{dT} = \frac{E_1}{RT^2} - \frac{E_{-1}}{RT^2}. \tag{9}$$

[51] H. L. LE CHÂTELIER, Compt. Rend., **99**, 786–789 (1884); **106**, 355–57 (1888); the expression "LE CHÂTELIER principle" is another manifestation of VAN'T HOFF's lack of interest in priority, since the idea was certainly his.

[52] H. P. J. THOMSEN, Poggendorf's Annalen, **88**, 349–362 (1853); **90**, 261–288 (1853); **91**, 83–104 (1854); **92**, 34–57 (1854).

[53] M. BERTHELOT, Compt. rend. **64**, 413–414 (1867), **71**, 303–314 (1870).

He then argued that the first terms on each side can be equated, as can the second terms:

$$\frac{d \ln k_1}{dT} = \frac{E_1}{RT^2} \quad \text{and} \quad \frac{d \ln k_{-1}}{dT} = \frac{E_{-1}}{RT^2} \tag{10}$$

With the subscript dropped we can thus write, for the influence of the temperature on a rate constant,

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \tag{11}$$

Again, with his usual care and caution VAN'T HOFF did not jump to the conclusion that E in equation (11) was independent of temperature; indeed he decided that this assumption would not be allowable if the equation is applied to considerable intervals of temperature. He discussed, in fact, three different possibilities:

1) That E is independent of temperature; in that case equation (11) can be integrated to give

$$\ln k = -\frac{E}{RT} + \text{const.} \tag{12}$$

or

$$k = Ae^{-E/RT} \tag{13}$$

where A is a constant.

2) That E is of the form $B + DT^2$, where B and D are constants; the equation then integrates to

$$\ln k = -\frac{B}{RT} + \frac{D}{R}T + \text{const.} \tag{14}$$

or

$$k = Ae^{-(B-DT^2)/RT}. \tag{15}$$

3) That E is of the form $B + CT$, which leads to

$$\ln k = -\frac{B}{RT} + \frac{C}{R}\ln T + \text{const.} \tag{16}$$

or

$$k = AT^m e^{-B/RT} \tag{17}$$

where m, equal to C/R, is a constant.

The first and simplest of these possibilities, that E is independent of temperature, was adopted in 1889 by ARRHENIUS[54], who applied it to a variety of experimental results. He also gave it an interesting interpretation, in terms of an equilibrium between reactant molecules and active molecules which were assumed to undergo reaction very readily. As a result, equation (13) is now generally referred

[54] S. ARRHENIUS, Z. physik. Chem., 4, 226–248 (1889); a translation of the four pages in this paper that deal with temperature dependence is included in *Selected Readings in Chemical Kinetics* (Ed. M. H. BACK & K. J. LAIDLER), Pergamon Press, Oxford 1967, pp. 31–35.

to as the 'ARRHENIUS equation', although it was certainly first given by VAN'T HOFF, as ARRHENIUS acknowledges in his paper. The fact that ARRHENIUS is today given credit for the equation is another tribute to VAN'T HOFF'S modesty and lack of interest in claims of priority. In fact, in later writings VAN'T HOFF seems to encourage giving the credit to ARRHENIUS. For example, in his *Lectures on Theoretical and Physical Chemistry*[55], published in 1898, he first gives equation (13), and says that it was 'adopted' by ARRHENIUS, giving a reference without the date. He then says that he himself obtained favourable results with equation (15). Readers would naturally conclude from this presentation that ARRHENIUS gave equation (13) first, and that VAN'T HOFF later considered the more complicated form.

The second possibility suggested by VAN'T HOFF, that E is of the form $B + DT^2$, had already appeared in the inaugural dissertation of L. C. SCHWAB[56], one of VAN'T HOFF'S students at the University of Amsterdam. SCHWAB had investigated the reaction between sodium chloroacetate and caustic soda, at temperatures ranging from $70\,^\circ C$ to $130\,^\circ C$. His analysis of the results showed that they were satisfactorily fitted by equation (14), and this part of the work is summarized in the *Etudes* (p. 112).

The third possibility, that E is of the form $B + CT$, with the result that equation (16) applied, was considered only briefly in the *Etudes*. Ten years later another of VAN'T HOFF'S students, D. M. KOOIJ[57], carried out an investigation of the decompositions of phosphine and arsine, and showed that equation (17) applies to them very satisfactorily.

In spite of the inherent complexity of the whole problem of temperature dependence in chemical kinetics[58], there can be no doubt that VAN'T HOFF had reasoned along exactly the right lines. The procedure generally adopted today in analyses and compilations of kinetic data is first to try the simple equation (13) (the "ARRHENIUS equation"); if that applies satisfactorily, the parameters A and E are listed. If it does not apply, equation (17) is then tried, the parameters m and E being listed. It is almost always possible to interpret data in terms in equation (17).

In assessing the importance of the *Etudes*, it is impossible to disagree with the opinion of Sir JAMES WALKER, who said that VAN'T HOFF had, in the book,

"systematized, exemplified, and applied the principles involved, and in fact left the subject of chemical dynamics much in the state in which we find it today [1912]"[59].

It is, indeed, difficult to think of any important developments in the field that occurred during thirty years or so after the book appeared in 1884; further advances, such as the application of quantum and statistical mechanics to reaction rates, had to wait for a few more years. That VAN'T HOFF could have gained such a deep

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[55] Ref. 7, Vol. 3, p. 232.

[56] L. C. SCHWAB, Inaugural Ph. D. Dissertation, Univ. of Amsterdam, 1883.

[57] D. M. KOOIJ, Z. physik. Chem., **12**, 155–161 (1893).

[58] For a discussion of temperature-dependence in chemical kinetics from a modern point of view see K. J. LAIDLER, J. Chem. Educ., **61**, 494–498(1984).

[59] Ref. 25, at p. 1137.

understanding of the subject in 1884 is all the more remarkable when it is remembered that he had been able to work in kinetics only for a period of six years, and that he had only a small number of assistants and students. Also, during that period at the University of Amsterdam he had been responsible, with the help of only two assistants, for all of the teaching of organic and inorganic chemistry, crystallography, mineralogy, geology, paleontology, animal physiology, and plant physiology; in addition he conducted laboratories in these fields for over 100 science and medical students!

Having made so many innovations in connection with the rates of chemical reactions, VAN'T HOFF could do little more in the next few years than obtain additional experimental evidence in support of his ideas. One new line of investigation he embarked upon was the reaction between phosphorus and dry oxygen, the experimental work on this being done by his British student THOMAS EWAN. In the *Etudes* (p. 50) VAN'T HOFF had already remarked that this reaction is unusual in that under some circumstances a reduction in pressure causes a steady reaction to turn into an explosion. EWAN[60] found that over a certain pressure range the rate is proportional to the square root of the oxygen pressure, and VAN'T HOFF[61] rightly concluded that there is dissociation of oxygen molecules, this dissociation not being a consequence of the reaction, but causing the reaction to occur. However, VAN'T HOFF thought that the oxygen molecules are dissociated into $O^+ + O^-$, which is now known to be incorrect; no doubt his suggestion sprang from his previous work on electrolytic dissociation.

By 1890, when VAN'T HOFF was still under forty, his active research career had essentially ended; he did little of any originality after that year. Having already made such fundamental and comprehensive contributions to thermodynamics, kinetics, and solution theory, he had understandably run out of new ideas. Aside from that, his health was presenting a problem; he was never a robust man, and in his later years he suffered from pulmonary tuberculosis which required him to spend periods in a hospital and which finally ended his life when he was in his fifty-ninth year. During his forties and fifties he did, however, produce several books.

One of these, to the actual writing of which he probably did not contribute a great deal, was a second and revised edition of the *Etudes*. Ten years after the appearance of that book in 1884, he began to realize that it should be brought up to date. Much additional work in kinetics had been done, a good deal of it in VAN'T HOFF's own laboratories, and ARRHENIUS's theory of electrolytic dissociation[1], published in 1887, cast a new light on some of the work on the kinetics of reactions in solution. As he explained in the preface to the revised edition[62], he did not want to introduce many changes, since that would

"take away from the original work its desired documentary character, while to change nothing would be to contribute nothing to making the contents acceptable to the public".

[60] T. EWAN, Phil. Mag. [5], **38**, 505–536 (1894); Z. physik. Chem., **16**, 315–343 (1895).

[61] J. H. VAN'T HOFF, Z. physik. Chem., **16**, 411–416 (1895).

[62] J. H. VAN'T HOFF & E. J. COHEN, *Studien zur chemischen Dynamik*, Frederik Muller & Co., Amsterdam, 1896.

VAN'T HOFF was fortunate at the time to have a very capable assistant, Dr. ERNST JULIUS COHEN[63] (1869–1944), who was prepared to produce a complete revision of the book. This he did very successfully, and it was published in 1896 by the same publisher in Amsterdam, but this time in German, under the title *Studien zur chemischen Dynamik*[62]. The change of language is interesting. The initial choice of French was probably because VAN'T HOFF thought that the great preoccupation of the German chemists with organic chemistry would mean that his book would be better received by the French chemists; his early happy association with WURTZ in Paris probably helped in this decision. By the last decade of the century, however, physical chemistry was beginning to be considered respectable everywhere, and since papers in the *Zeitschrift für physikalische Chemie* were required to be in German, VAN'T HOFF felt that language to be most appropriate for his second edition.

The same year that the German book was published, 1896, an English translation also appeared. The translation was made by VAN'T HOFF'S former student THOMAS EWAN, who had returned to England to become Demonstrator in Chemistry at the Yorkshire College of Science in Leeds (which in 1904 developed into the University of Leeds). This translation, which bears the title *Studies in Chemical Dynamics*[64] and runs to 285 pages, was printed in Amsterdam and published jointly by Frederick Muller & Co. of Amsterdam (which had published the *Etudes* and the *Studien*) and by Williams & Norgate of London.

The revised versions of the book are considerably more extensive than the original *Etudes*, but there are few innovations as far as the fundamental principles of kinetics are concerned. These principles are, however, illustrated and confirmed by additional experimental results, many of which were obtained during the intervening ten years. Also, some of the discussions are brought up to date with reference to the new understanding of the existence of ions in solution.

A few years later VAN'T HOFF published another book which was based on lectures given by him at the University of Berlin. It was entitled *Vorlesungen über theoretische und physikalische Chemie*[65] and appeared in four volumes in 1898 to 1901. An English translation, made by R. A. LEHRFELD, Professor of Chemistry at the East London Technical College, was published at the same time, its title being *Lectures on Theoretical and Physical Chemistry*. One of its three volumes, referred to as *Part I. Chemical Dynamics*, bears some resemblance to the *Studies in Chemical Dynamics*; an important difference is that equilibrium is treated first, followed by kinetics.

There are few innovations in these volumes but one of them, relating to the influence of pressure on reaction rates, is of some importance. In 1893 the German

[63] ERNST JULIUS COHEN succeeded VAN'T HOFF as professor at the University of Amsterdam in 1896, and was the leading physical chemist in Holland for many years. Unhappily, in 1944, at the age of 75, he was a victim of the Nazis at Auschwitz concentration camp.

[64] J. H. VAN'T HOFF & E. J. COHEN, "*Studies in Chemical Dynamics*", translation of Ref. 62 by THOMAS EWAN and published by Frederik Muller & Co., Amsterdam, and Williams and Norgate, London, 1896.

[65] J. H. VAN'T HOFF, *Vorlesungen über theoretische und physikalische Chemie*, 4 vols., Brunswick, 1898–1901; for English translation see Ref. 7.

physicist MAX PLANCK (1858–1947), whose early work was mainly in thermodynamics, deduced the relationship[66]

$$\frac{d \ln K}{dP} = -\frac{\Delta V}{RT} \tag{18}$$

for the influence of the hydrostatic pressure P on the equilibrium constant K for a reaction; ΔV is the molar change in volume during reaction. In the *Vorlesungen* (*Lectures*, pp. 240–241) VAN'T HOFF used an argument that is analogous to the one he used for temperature dependence (equations (7)–(10) above). He again noted that K is k_1/k_{-1}, the ratio of the rate constants for reaction in forward and reverse directions, and he therefore wrote an equation which in modern notation is

$$\frac{d \ln k_1}{dP} - \frac{d \ln k_{-1}}{dP} = -\frac{\Delta V}{RT} = -\frac{\Delta^{\ddagger} V_1}{RT} - \left(-\frac{\Delta^{\ddagger} V_{-1}}{RT} \right). \tag{19}$$

Equating the first terms on each side and dropping subscripts gives

$$\frac{d \ln k}{dP} = -\frac{\Delta^{\ddagger} V}{RT}. \tag{20}$$

VAN'T HOFF referred to it as a "possible formula", and he gave no interpretation of $\Delta^{\ddagger} V$. In terms of modern theory $\Delta^{\ddagger} V$ is the volume change when the reactants pass into an "activated state" where reaction occurs without further difficulty. VAN'T HOFF concluded that the data available to him did not suffice to allow equation (20) to be tested, and this is understandable since pressures of the order of 1 000 atmospheres — not then easily attainable — are usually required to give a significant change in rate. Modern interpretations of pressure effects on reaction rates are commonly based on VAN'T HOFF'S equation (20).

The Contributions of Wilhelm Ostwald

The kinetic work of FRIEDRICH WILHELM OSTWALD[67] (1853–1932) was also of great importance, but it was somewhat less fundamental in character than that of VAN'T HOFF. OSTWALD did not see the subject in as comprehensive a way

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[66] M. PLANCK, Wied. Ann., **32**, 495 (1893); *Vorlesungen über Thermodynamik*, Leipzig, 1897, p. 218.

[67] For biographical and scientific material see J. R. PARTINGTON, *A History of Chemistry*, Macmillan & Co., London, 1964, Vol. 3, pp. 595–612; E. N. HIEBERT & A. G. KÖRBER, in *Dictionary of Scientific Biography* (Ed. C. C. GILLISPIE), Charles Scribner, New York, 1970–76; E. N. HIEBERT, "The energetics controversy and the new thermodynamics", in *Perspectives in the History of Science and Technology* (Ed. D. H. D. ROLLER), Univ. of Oklahoma Press, Norman, 1971; E. N. HIEBERT, "Development of physical chemistry at the turn of the century", in *Science, Technology and Society in the Time of Alfred Nobel* (Ed. C. G. BERNHARD, E. CRAWFORD & D. SÖRBOM), Pergamon Press, Oxford, 1982; R. B. ROOT-BERNSTEIN, "The Ionists: Founding Physical Chemistry, 1872–1890", Ph. D. Thesis, Princeton University, 1980; F. G. DONNAN, "Ostwald Memorial Lecture", J. Chem. Soc., 316–332 (1933).

as did VAN'T HOFF, and his research work, mainly on catalysis in solution, was along narrower lines. OSTWALD did, however, play an outstanding role in the establishment of physical chemistry as a recognized branch of science, and this was as much through his lectures, textbooks, and persuasive personality as through his accomplishments in research.

OSTWALD was born in Riga, Latvia, which was then part of Russia, and his native language was German. Because of his wide interests he was not a good high-school student, taking seven years to complete a course normally covered in five years. He enrolled at the University of Dorpat (now Tartu, Estonia) and first devoted much of his time to literature, music, and painting; however, after some pressure from his father he performed some outstanding research and obtained his doctorate in chemistry in 1878. He then spent three years teaching in a high school, and in 1881 was appointed professor of chemistry at the Riga Polytechnic Institute, where he was at once recognized to be an outstanding teacher. In 1887 he was appointed to the very prestigious position of professor of physical chemistry at the University of Leipzig; at the time this was the only professorship designated for physical chemistry. He remained in Leipzig until 1906 when, after unsuccessfully requesting a lighter teaching load from the university authorities, he resigned and moved to a country estate in Saxony. For the next twenty-four years he remained extremely active, working on a variety of topics including energetics, the history and philosophy of science, pacifism, and colour theory. He received many honours, including the 1909 Nobel Prize in chemistry for his research on catalysis. He worked prodigiously throughout his scientific career, producing 45 books and 500 research papers. He had a large number of research students, many from the U.S., the U.K., and Canada[68]. One of his American students, WILDER D. BANCROFT, said later of him that he was

"loved and admired by more people than any chemist of his time"[69].

There are some similarities in background between VAN'T HOFF and OSTWALD, but their temperaments were very different. They resemble one another in having received their early educations in places that were not in the mainstream of scientific research; this no doubt contributed to their ability to break away from established scientific traditions and to embark on highly original lines of research. Both were extremely hard workers, and both had wide interests in fields other than science. Both had discouraging experiences in their early careers, being unable for a time to find employment in which they had facilities to carry out research; both took advantage of this experience by formulating and developing

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[68] His American students include WILDER D. BANCROFT, HARRY C. JONES, ARTHUR B. LAMB, ARTHUR A. NOYES and THEODORE W. RICHARDS; students from the U.K. include F. G. DONNAN and (Sir) JAMES WALKER; among Canadian students were F. B. KENRICK, J. W. MCBAIN (who later worked mainly in the U.K. and U.S.) and W. LASH MILLER. Not so many of his students came from the continent of Europe, probably because of the emphasis there on organic chemistry.

[69] W. D. BANCROFT, "Wilhelm Ostwald, the great protagonist", J. Chem. Educ., 10, 539–542, 609–613 (1933); on p. 612.

their scientific ideas along highly original lines. Both were initially subjected to a certain amount of ridicule and disdain from other scientists, on account of the unconventional nature of their research; neither let this divert him from the primary purpose of gaining an understanding of chemical processes.

In temperament VAN'T HOFF and OSTWALD were at opposite extremes. VAN'T HOFF was a quiet unassuming man who steadily went about his research work and writing without any concern for priority or recognition. OSTWALD was very different; a man of robust and effervescent charm, he threw himself actively into a variety of controversial issues, and was the most vigourous proponent of the new physical chemistry. Accused of not being a real chemist because he had discovered no new compounds, he characteristically denied the fact; he had discovered minus-one compounds, he said, having identified an alleged new compound with a well-known organic acid! He did not hesitate to express opinions he knew to be unpopular, such as his opposition to the atomic theory — indeed he enjoyed doing so. When proved to be wrong, as he was over the atomic theory, he generously recanted. In spite of their considerable temperamental differences, VAN'T HOFF and OSTWALD remained close friends, having a sincere appreciation of one another's qualities and talents.

In his early research at the University of Dorpat OSTWALD devoted himself to gaining an understanding of chemical affinity, which relates both to the rates with which substances react together, and to the extent of their reaction — that is, to the rate constant and the equilibrium constant for the reaction. Previously JULIUS THOMSEN had employed a thermochemical method for studying affinity, and OSTWALD extended this technique by using other physical methods, such as specific volume, viscosity, refractive index, electric conductivity, optical rotation, and colour. Chemical methods have the disadvantage of disturbing a reaction, but physical methods do not have any such effect. In his Master's dissertation[70] at the University of Dorpat, submitted in 1877, OSTWALD studied the neutralization of acids by bases in aqueous solution by measuring volumes before and after the process had taken place. In his Doctor's dissertation[71] (1878) he extended these investigations by measuring coefficients of refraction. In the course of this work he discovered that when an acid reacts with a series of strong bases, the relative affinities do not depend on the nature of the base. Conversely, for a given base reacting with a strong acid, the nature of the acid did not affect the affinity. This work was done prior to ARRHENIUS's theory of electrolytic dissociation (1887), so that the meaning of OSTWALD's results was not at first clear to him; his later discussions with ARRHENIUS, between 1884 and 1887, contributed greatly to the formulation of that theory. OSTWALD's Ph.D. dissertation research was published in the form of three papers[72] and this work attracted immediate attention in an

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[70] W. OSTWALD, "Volumchemische Studien über Affinität,' Master's dissertation, Univ. of Dorpat, 1877.

[71] W. OSTWALD, "Volumchemische und optisch-chemische Studien", Ph. D. dissertation, Univ. of Dorpat, 1877. Both the master's and the doctoral dissertation were reprinted in OSTWALD's *Klassiker der exakten Wissenschaften*, Leipzig, 1966, No. 250, with an essay on OSTWALD's work by G. HARIG & IRENE STRUBE.

[72] W. OSTWALD, J. prakt. Chem., [2], 16, 385–423 (1877); [2] 18, 328–371 (1878); [2], 22, 305–322 (1880).

important review of chemical affinity[73] written by M. M. PATTISON MUIR (1848–1931), then praelector in chemistry at Gonville and Caius College, Cambridge. PATTISON MUIR described the first two of these papers of OSTWALD, along with the papers of GULDBERG & WAAGE[14], as

"the most important contributions made within recent years towards the final solution of the problem of chemical affinity".

OSTWALD had thus gained much recognition while still well under thirty years of age.

From 1878 to 1881, while teaching in a high school, OSTWALD could carry out little research, but on assuming his position at the Riga Polytechnic Institute he embarked on important investigations, the results of which were published as a series of papers having the general title "Studien zur chemischen Dynamik". In this work OSTWALD departed from the equilibrium studies he had made as a student at Dorpat, and now measured reaction rates. The first paper in the series was concerned with the hydrolysis of acetamide in aqueous solution by a series of acids[74]; an important feature of this paper was its description of a very simple but effective thermostat which later was very widely used. A second paper described a similar study of the acid hydrolysis of methyl acetate[75], and there were several other papers in the series[76]. OSTWALD's main object in carrying out these investigations was not to verify equations of chemical kinetics but rather to compare the affinities of different acids by comparing the rates of their reactions with various other substances. He observed a marked parallelism between his equilibrium and kinetic measurements, again finding that the affinity of a strong acid, as measured by the kinetic method, was independent of the nature of the anion. A few years later OSTWALD returned again to this type of problem, which was essentially a study of the catalytic action of acids.

A certain day in June, 1884, was an important one for OSTWALD, for he received a copy of the Ph.D. dissertation of SVANTE ARRHENIUS, of whom he had not previously heard. This incident and its results have been well documented by ROOT-BERNSTEIN[5], and can here be summarized very briefly. ARRHENIUS's dissertation, which described electrolytic conductivity measurements but did not provide a satisfactory interpretation of them, received a poor rating by the examiners at the University of Uppsala; ARRHENIUS, much discouraged, sent copies of the dissertation to VAN'T HOFF, OSTWALD, and others. OSTWALD had already made measurements of the electrical conductivities of solutions of a number of acids, and had also made kinetic measurements of their catalytic activities. On receiving ARRHENIUS's dissertation in June, 1884, OSTWALD at once prepared a short paper[77] in which he described his own results. This paper, which is dated

[73] M. M. PATTISON MUIR, Phil. Mag., [5], **8**, 181–203 (1879).

[74] W. OSTWALD, J. prakt. Chem., [2], **27**, 1–29 (1883).

[75] W. OSTWALD, J. prakt. Chem., [2], **28**, 449–495 (1883).

[76] For example, W. OSTWALD, J. prakt. Chem., [2], **29**, 385–408 (1884); [2], **31**, 307–317 (1885); **35**, 112–121 (1887); Z. physik. Chem., **2**, 127–147 (1888).

[77] W. OSTWALD, J. prakt. Chem., [2], **30**, 93–95 (1884).

July, 1884, and appeared later in the year, made full acknowledgement of the importance of ARRHENIUS'S results.

Shortly after submitting his paper OSTWALD travelled to Uppsala to discuss with ARRHENIUS the interpretation of their two sets of results. He also offered ARRHENIUS an appointment at the University of Riga, but for personal reasons ARRHENIUS was unable to accept it. This offer of OSTWALD led to a somewhat Gilbertian situation. ARRHENIUS, never a man to suffer fools gladly, had made no attempt to conceal his contempt for his examiners at the University of Uppsala, and had been particularly obnoxious to the chemist PER THEODOR CLEVE (1840–1905) and the physicist THOBIAS ROBERT THALÉN (1827–1905); both these men were competent in their narrow fields but quite incapable of appreciating the new physico-chemical ideas. The action taken by OSTWALD, who although still in his early thirties was already a respected figure in the scientific world, caused some consternation; perhaps ARRHENIUS might one day achieve distinction, in which case failure to offer him a position in his own country would prove embarrassing. The solution the authorities reached has a touch of genius about it. They first offered ARRHENIUS, late in 1885, a junior appointment (privatdocent) at the University of Uppsala, and very shortly afterwards awarded him a travelling fellowship that would keep him out of the country, and therefore in no position to cause them much annoyance, for most of the next five years. After all, much can happen in five years – the man might electrocute himself.

ARRHENIUS made a most profitable use of his travelling fellowship. He first worked for some months in 1886 with OSTWALD in Riga; later that year and early in 1887 he worked in Würzburg with the German physicist FRIEDRICH KOHLRAUSCH (1840–1910), who himself had done important work on the conductivities of solutions of electrolytes. Later in 1887 ARRHENIUS joined the Austrian physicist LUDWIG BOLTZMANN (1844–1906) at the University of Graz. Early in 1888 he moved to Amsterdam where he had a very profitable collaboration with VAN'T HOFF, and later he went to work again with OSTWALD, who by that time had moved to Leipzig.

By 1887 ARRHENIUS had been able to formulate his important theory of electrolytic dissociation; his paper on this appeared in the June, 1887, issue of the *Zeitschrift für physikalische Chemie*[1], a journal which OSTWALD and VAN'T HOFF had just founded and which first appeared in that year.

There can be little doubt that OSTWALD's correspondence and collaboration with ARRHENIUS, beginning in 1884, was of great help in the formulation of the theory of electrolytic dissociation. There is also little doubt that the main credit for the theory is due to ARRHENIUS; OSTWALD, in fact, required a few months to be convinced of it. When he was, he accepted the theory with great enthusiasm, and in the following year he published an important paper[78] on what is now called the "OSTWALD dilution law"; in it he showed for a number of weak acids that the variation of conductivity with concentration is in very close agreement with ARRHENIUS's theory. Later, ARRHENIUS himself carried out some kinetic studies[79] which related the catalytic activities of acids to their electrical conductivities

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[78] W. OSTWALD, Z. physik. Chem., **2**, 36–37 (1888).

[79] S. ARRHENIUS, Z. physik. Chem., **4**, 226–248 (1889); **28**, 317–335 (1899).

and, in the light of the theory of electrolytic dissociation, to the concentrations of hydrogen ions.

During approximately the same period that VAN'T HOFF was preparing his *Etudes*, OSTWALD was also working on an important book, his *Lehrbuch der allgemeinen Chemie*[2], which appeared in two volumes, the first being published in 1885 and the second in 1887. This book, which was a textbook of what today we would call physical chemistry, covers a much wider field than the *Etudes*. Unlike the *Etudes*, which was prepared with the meticulous care that was characteristic of VAN'T HOFF, the *Lehrbuch* shows some signs of hasty writing, not surprising in view of OSTWALD's prodigious literary output. The book later appeared in parts from 1891 to 1902 as a second edition, which was never completed. A shorter version, *Grundriss der allgemeinen Chemie*[80] was published in 1889; this was translated by OSTWALD's Scottish student (Sir) JAMES WALTER and appeared in 1890 with the title *Outlines of General Chemistry*[81].

The appearance of the *Lehrbuch* was a very important event in the history of physical chemistry, for it can be regarded as the first textbook in that field. Its approach was very different from that of any previous book on chemistry, and naturally it reflects the new approach that OSTWALD was taking, of trying to interpret the results of chemical experiments in the light of the principles of physics. In 1886 OSTWALD studied VAN'T HOFF's *Etudes*, and the second volume of the *Lehrbuch* pays generous tribute to VAN'T HOFF's book and shows evidence of its influence.

One important kinetic innovation in that second volume, and one that affects kinetics today, was OSTWALD's definition of the "order of reaction"[82]. In the *Etudes* VAN'T HOFF had spoken of "monomolecular" and "bimolecular" reactions, these expressions relating not necessarily to the number of molecules entering into reaction, but to the power of the concentration that appeared in the empirical rate equation. OSTWALD's proposal was to refer to this power as the "order" of the reaction; a reaction is of the first order if the rate is proportional to the first power of a single reactant concentration; it is of the second order if the rate is proportional to a concentration squared, or to the product of two concentrations. This useful terminology is helpful in avoiding any confusion with the number of molecules entering into reaction. VAN'T HOFF, however, seems never to have adopted this convention.

In the second edition of the *Lehrbuch*, which came out in parts from 1891 to 1902 and was never completed, OSTWALD also dealt with other kinetic problems of fundamental importance. In one of the issues, which appeared in 1893, he considered successive reactions[83], in which the product of one reaction undergoes a second reaction, which may undergo a further reaction, and so forth. According to what was later called "OSTWALD's law of successive reactions", the first inter-

[80] W. OSTWALD, *Grundriss der allgemeinen Chemie*, Leipzig, 1889; this was commonly known as "der kleine OSTWALD".

[81] W. OSTWALD, *Outlines of General Chemistry* (Ref. 80, translated by JAMES WALKER), London, 1890.

[82] W. OSTWALD, *Lehrbuch*, Vol. 2, p. 634 (1887).

[83] W. OSTWALD, *Lehrbuch*, 2nd edition, Vol. 2, Part 1, p. 574 (1893).

mediate to be formed will be the one which involves the smallest loss of free energy; the next will be the one that involves the next smallest loss of free energy, and so on. In Part 2 of the same volume, which appeared in 1902, he gave his now famous definition of a catalyst as

> "a substance that changes the velocity of a reaction without itself being changed by the process"[84].

Another important innovation in that same issue was his "method of isolation"[85]. His suggestion was that if the rate of a reaction depends upon the concentrations of two reacting substances, the concentration of one of them can be held at a high value so that it does not change during the process; the order with respect to the other reactant can then be obtained.

OSTWALD also proposed a number of very important kinetic principles and methods in various scientific publications, particularly in the *Zeitschrift für physikalische Chemie*. In 1888, for example, he introduced the idea of the half life of a reaction[86], which is the time for half of a reactant to be consumed, and he showed how it can be used to determine the order of the reaction. The method depends on the fact that the half life $t_{\frac{1}{2}}$ is inversely proportional to the initial concentration c of a reactant raised to the power of $n - 1$, where n is the order:

$$t_{\frac{1}{2}} \propto \frac{1}{c^{n-1}}. \tag{21}$$

If two experiments are carried out at initial concentrations c_1 and c_2, it follows that the half lives are related by
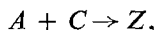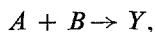
$$\frac{(t_{\frac{1}{2}})_1}{(t_{\frac{1}{2}})_2} = \left(\frac{c_2}{c_1}\right)^{n-1}. \tag{22}$$

Then

$$n = 1 + \frac{\ln\left[(t_{\frac{1}{2}})_1/(t_{\frac{1}{2}})_2\right]}{\ln(c_2/c_1)} \tag{23}$$

which allows n to be calculated from the ratio of the half lives at the two concentrations.

Another kinetic phenomenon noted and discussed by OSTWALD was that of "coupled reactions"[87]. He and others had observed that when two reactions involving a common reactant are occurring in the same vessel, for example

$$A + B \rightarrow Y,$$

$$A + C \rightarrow Z,$$

[84] W. OSTWALD, *Lehrbuch*, 2nd edition, Vol. 2, Part 2, pp. 248, 262 (1902).

[85] W. OSTWALD, *Lehrbuch*, 2nd edition, Vol. 2, Part 2, p. 238 (1902); the method had previously been mentioned by ESSON, in an Appendix to A. G. V. HARCOURT & W. ESSON, Phil. Trans., **157**, 117–154 (1867).

[86] W. OSTWALD, Z. physik. Chem., **2**, 127–147 (1888).

[87] W. OSTWALD, Z. physik. Chem., **34**, 248–252 (1900).

one reaction is sometimes accelerated by the other. OSTWALD was not, however, able to find any satisfactory explanation for this effect; this is not surprising, since hardly anything was known at the time of the detailed mechanisms of the reactions that showed this effect.

From about 1888 until the turn of the century OSTWALD's main research efforts were devoted to the study of catalysis, a subject that up to that time was in a somewhat confused state. It had been known from the eighteenth century that reactions could be accelerated by the addition of certain substances, and in 1836 the Swedish chemist JÖNS JAKOB BERZELIUS (1779–1848)[88] introduced the word "catalysis" to describe this effect. He believed, however, as did most scientists of his day, that catalytic action is due to a special kind of force exerted by the catalyst on the reaction. Throughout the nineteenth century many examples of catalysis had been reported and classified, but until OSTWALD's work there was no understanding of the nature of the effect.

One of OSTWALD's early investigations on this topic was concerned with what he himself called 'autocatalysis'[89]; this term applies to reactions catalyzed by the reaction products, and which are therefore accelerated as the reaction proceeds. For example, the hydrolysis of an ester is catalyzed by acids, and an acid is formed in the reaction; in the initial absence of acid the hydrolysis is therefore at first slow, but it accelerates as the acid product of the reaction accumulates in the system.

During his extensive experimental studies on this and other types of catalysis, OSTWALD suggested several definitions of the effect. One of these is that a catalyst is

"any substance that alters the velocity of a chemical reaction without modification of the energy factors of the reaction"[90].

A later definition suggested by him has been widely quoted, and is:

"A catalyst is any substance that alters the velocity of a chemical reaction without appearing in the end product of the reaction"[91].

A third definition, which appeared in his revised *Lehrbuch*, has already been quoted[84]. All of these definitions are quite acceptable, and are consistent with the definition approved in 1981 by the International Union of Pure and Applied Chemistry:

"A catalyst is a substance that increases the rate of reaction without modifying the overall standard Gibbs energy change in the reaction; the process is called

[88] J. J. BERZELIUS, Jahresber. Chem., **15**, 237–245 (1836).

[89] W. OSTWALD, Berichte über die Verhandlungen der Sächsischen Akademie der Wissenschaften zu Leipzig, **41**, 189–191 (1890).

[90] W. OSTWALD, Chem. Betrachtungen, Aula No. 1, 1895.

[91] W. OSTWALD, Physik. Z., **3**, 313–322 (1902).

catalysis, and a reaction in which a catalyst is involved is known as a *catalyzed reaction*"[92].

In 1901 OSTWALD suggested for the first time a classification of catalytic reactions, as follows:[93]

1. *Crystallization from supersaturated solutions.* For example, crystallization from such solutions is often brought about by a particle of dust or a crystal.

2. *Catalysis in homogeneous systems.* For instance, acids catalyze the hydrolysis of esters and of sucrose.

3. *Catalysis in heterogeneous systems.* The reaction between oxygen and sulphur dioxide, for example, is catalyzed by platinum metal.

4. *Catalysis by enzymes, the biological catalysts.* The hydrolysis of amygdalin catalyzed by the enzyme emulsion provides an example.

OSTWALD himself did little work on heterogeneous catalysis (unlike VAN'T HOFF), but worked extensively on the other types of catalysis.

OSTWALD summarized his work on catalysis in a review paper[94] in 1901 and later in 1909 on receiving the Nobel prize for his work in that field[95]. It must be said that in spite of his important and valuable work OSTWALD never succeeded in developing a satisfactory theory of catalysis. He did, however, recognize[93] that a catalyzed reaction proceeds by some kind of an alternative pathway made possible by the introduction of the catalyst. From this he drew the correct conclusion that a substance that lowers the rate of a reaction (now known as an inhibitor) cannot do so by introducing a more difficult pathway, for the reaction would continue to occur at the original rate by following the path for the uncatalyzed process. Again, he was unable to offer any satisfactory explanation for the retardation of reactions by added substances.

These failures to provide explanations were inevitable, because at the turn of the century very little had been discovered about the individual reaction steps that occur in overall reactions. This was due in part to the lack of experimental techniques for detecting and identifying intermediate reaction species, which frequently have very short lives. It is now known that inhibiting substances often exert their action by removing active intermediates such as free radicals, but there was no way that OSTWALD could have been aware of such processes. With the advent of new techniques, particularly after the First World War, there was much progress in the detailed understanding of the mechanisms of catalyzed reactions,

[92] *Manual of Symbols and Terminology for Physicochemical Quantities and Units. Appendix V. Symbolism and Terminology in Chemical Kinetics*; report prepared by K. J. LAIDLER and published in Pure & Appl. Chem., **53**, 753–771 (1981); the quotation is on p. 762.

[93] W. OSTWALD, Z. Elektrochem., **7**, 995–1006 (1901); Nature, **65**, 522–526 (1902).

[94] W. OSTWALD, "Über Katalyse", Verhandlungen der Gesellschaft deutscher Naturforscher und Ärzte, **73**, 184–201 (1901); this was later published as a separate pamphlet in 1902 and in Physikal. Zeit., **3**, 312–323 (1902). A condensed and translated version appeared in Nature, **65**, 522–526 (1902).

[95] W. OSTWALD, "Über Katalyse. Nobelpreisvortrag, gehalten in Stockholm am 12. Dezember 1909", in *Les Prix Nobel en 1909*, Stockholm, 1910, pp. 63–88.

and there can be no doubt that OSTWALD's pioneering studies paved the way for these advances.

One characteristic aspect of OSTWALD's work on catalysis was that he was fond of making unverifiable statements of the kind that would not today be considered useful or relevant. Examples of such statements are

(a) Every reaction is capable of being catalyzed.

(b) Every substance can act as a catalyst for some reaction.

(c) Every catalyzed reaction can also proceed without a catalyst.

From the modern point of view every balanced reaction is capable of occurring, but its rate may be so low that no detectable product may be formed in millions of years; at ordinary temperatures, for example, the reaction between hydrogen and oxygen has a half life greater than the age of the solar system!

No account of OSTWALD's kinetic work would be complete without some reference to his attempts to employ the principles of chemical dynamics to support his anti-atomic views. Long after the formulation in 1803 of the atomic theory by the English chemist JOHN DALTON (1766–1844), many scientists remained sceptical about the real existence of atoms. Notable among those who rejected the theory was the Austrian physicist and philosopher ERNST MACH (1836–1916). His and OSTWALD's reasons, however, were different; OSTWALD based his rejection on various energetic arguments, with which MACH did not agree.

OSTWALD expressed his objections to the atomic theory – which he referred to as a "mere hypothesis" – in several forms, one of which he presented in London in 1904 in his Faraday Lecture to the Chemical Society[96]; he admitted to some temerity in doing so as the Chemical Society had the previous year been holding centenary celebrations in honour of the birth of DALTON's atomic theory.

In this lecture OSTWALD asked a rhetorical question,

"What are the most important achievements of the chemistry of our day?"[97]

He then said:

"I do not hesitate to answer: *chemical dynamics*, or the theory of the progress of chemical reactions and the theory of chemical equilibrium"[97].

He went on to make a statement which he admitted "sounds most remarkable", namely that

"*It is possible to deduce from the principles of chemical dynamics all the stoichiometrical laws; the law of constant proportions, the law of multiple proportions and the law of combining weights*"[97] [his italics].

He then argued in some detail that the phase rule, together with dynamical principles, lead to the stoichiometric laws without any need to invoke the atomic hypothesis. The weakness of his argument, which had previously been pointed

[96] W. OSTWALD, Ref. 8; the expression "mere hypothesis" is on p. 509.

[97] Ref. 96, p. 508.

out to him by LUDWIG BOLTZMANN[98], was that the results of chemical dynamics and the phase rule themselves require the atomic hypothesis. Also, his arguments would not apply to a process occurring in a single phase; when the elements hydrogen and iodine react together in the gas phase to form hydrogen iodide, the hydrogen iodide always has the same composition, and phase-rule arguments have no relevance.

In 1909 OSTWALD became finally convinced of the real existence of atoms by the experiments of the British physicist JOHN JOSEPH THOMSON (1856–1940) and of the French physical chemist JEAN BAPTISTE PERRIN (1870–1942). He apparently continued to believe, however, that the stoichiometric laws do not require the atomic theory, but can be arrived at by dynamical arguments.

Other Early Kinetic Contributions

Although VAN'T HOFF and OSTWALD undoubtedly made the outstanding contributions to chemical kinetics in the last century, mention should also be made of several others who played an important role.

One of these was WALTHER NERNST[99] (1864–1941), whose interest in kinetics was inspired by OSTWALD, whom he joined as an assistant in 1887 when OSTWALD was appointed to the University of Leipzig. Born in Brieson, West Prussia (now Wabrzezno, Poland), NERNST attended the University of Würzburg where he worked under FRIEDRICH KOHLRAUSCH. In 1891 he became professor of physical chemistry at the University of Göttingen, and in 1905 was appointed professor of physical chemistry and director of the Institut für physikalische Chemie at the University of Berlin. NERNST's main research was in thermodynamics and electrochemistry, and his greatest achievement, the NERNST heat theorem or the third law of thermodynamics, gained him the Nobel Prize in chemistry in 1920.

In 1898 NERNST did some work on the role of diffusion processes in influencing the rates of chemical reactions[100]. His most important contribution to kinetics, however, came later, when in 1918 he explained[101] the photochemical combination of hydrogen and chlorine in terms of a mechanism in which chlorine atoms

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[98] For a detailed account of the energetics controversy, including BOLTZMANN's attack on OSTWALD's views in Lübeck in 1895, see E. H. HIEBERT, "The energetics controversy and the new thermodynamics", in *Perspectives in the History of Science and Technology* (Ed. D. H. D. ROLLER), University of Oklahoma Press, Norman, 1971, pp. 67–86.

[99] For biographical and scientific information see E. N. HIEBERT in *Dictionary of Scientific Biography* (Ed. C. C. GILLESPIE), Charles Scribner, New York, 1970–76; E. N. HIEBERT, Ref. 5; E. N. HIEBERT, "Nernst and electrochemistry", in *Selected Topics in the History of Electrochemistry* (Ed. G. DUBPERNELL & J. H. WESTBROOK), The Electrochemistry Society, Princeton, N.J., 1978; E. N. HIEBERT, "Walther Nernst and the application of physics to chemistry", in *Springs of Scientific Creativity* (Ed. R. ARIS, H. T. DAVIS & R. H. STUEWER), Univ. of Minneapolis Press, 1983; K. MENDELSSOHN, *The World of Walther Nernst*, Macmillan, London, 1973.

[100] W. NERNST, Z. physik. Chem., **47**, 52–55 (1904).

[101] W. NERNST, Z. Electrochem., **24**, 335–356 (1918).

with hydrogen molecules to give HCl and a hydrogen atom, and in which hydrogen atoms react with chlorine molecules:

$$Cl + H_2 \rightarrow HCl + H,$$

$$H + Cl_2 \rightarrow HCl + Cl.$$
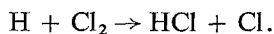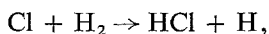
In this pair of reactions, product molecules are formed without any loss of chlorine atoms, and a process having this type of feature has come to be known as a "chain reaction". NERNST'S mechanism for the hydrogen-chlorine reaction later had to be modified in certain details, but it led to important developments in chemical kinetics, many other reactions being found to occur by chain mechanisms.

Significant contributions to chemical kinetics were also made by another former collaborator of OSTWALD, MAX BODENSTEIN (1871–1942). Born in Magdeburg, BODENSTEIN attended the University of Heidelberg where his research was directed by VIKTOR MEYER (1848–1897). After working with OSTWALD he held various university appointments and finally succeeded NERNST in 1923 as director of the Institut für physikalische Chemie in Berlin, a position he held until 1936.

BODENSTEIN was an extremely skillful experimentalist, and his investigations were mainly on the kinetics of thermal and photochemical gas-phase reactions and on reactions on surfaces. Prior to the turn of the century he worked extensively on the thermal and photochemical reaction between hydrogen and iodine, on the reverse decomposition of hydrogen iodide, and on the equilibrium established between these substances[102]. Beginning in about 1906, BODENSTEIN and his co-workers investigated the thermal and photochemical reactions between hydrogen and bromine[103] and between hydrogen and chlorine[104]. In 1913 he and W. DUX[105] obtained very high quantum yields for the photochemical hydrogen-chlorine reaction; under some conditions they found that one quantum (photon) of radiation brought about the transformation of over a million molecules of reactants. To explain this surprising result they proposed for the first time the idea of chain reactions in which active intermediates not only give rise to products of reaction but also regenerate themselves. They originally suggested that the active intermediates were ions[105], and later that they were excited chlorine molecules[106]. NERNST'S correct suggestion[101] that it is atoms that are involved was later accepted by BODENSTEIN, who in 1931 commented:

"For the hydrogen-chlorine reaction I assumed – in 1913 – that the primary act is an ionisation of the chlorine molecule

$$Cl_2 + E = Cl_2^+ + \theta$$
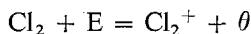
[102] M. BODENSTEIN, Z. physik. Chem., **13**, 56–127 (1894); **22**, 1–22, 23–33 (1897); **29**, 295–314 (1899).

[103] M. BODENSTEIN & S. C. LIND, Z. physik. Chem., **57**, 168–192 (1907); M. BODENSTEIN, Z. Elektrochem., **22**, 327–329 (1916).

[104] M. BODENSTEIN & W. DUX, Z. physik. Chem., **85**, 297–328 (1913); M. BODENSTEIN, Z. physik. Chem., **85**, 329–397 (1913); M. BODENSTEIN & W. UNGER, Z. physik. Chem., **B. 11**, 253–278 (1930).

[105] M. BODENSTEIN & W. DUX, Ref. 104.

[106] M. BODENSTEIN & W. DUX, Z. Elektrochem., **22**, 53–61 (1916).

I ought to have known even then that this was impossible—I did not. Later, in 1916, I suggested an excited molecule of chlorine, $Cl_2 + E = Cl*_2$"[107].

Two students of VERNON HARCOURT at Christ Church, Oxford, H. B. DIXON and D. L. CHAPMAN, also made very important early contributions to kinetics, and played an important role in establishing the new discipline of physical chemistry, especially in the United Kingdom. HAROLD BAILY DIXON[108] (1852–1930) was born in London in the same year as VAN'T HOFF, and died two years before OSTWALD. He went to Christ Church with the intention of taking a degree in classics, but his studies in that field were unsatisfactory, and VERNON HARCOURT rescued him from academic oblivion by arousing in him an interest in chemistry, in which DIXON was most successful. In 1875 he was elected a Fellow of Trinity College, Oxford, and in 1879 he transferred to a similar post in adjoining Balliol College. In 1887 he was appointed professor of chemistry at Owens College, Manchester, which in 1903 became the University of Manchester. DIXON played an important role in the development of physical chemistry in England, particularly as a result of his wide knowledge of the subject and through his meticulously prepared lectures, which proved extremely popular—so much so that women wished to attend them. In 1884 the Oxford University authorities allowed women to do so "but only by special permission in each case and with the accompaniment of some elderly person"[109]. In the next academic year three women did attend DIXON's lectures; however, it was not until 1904 that women were allowed to work in the Oxford laboratories, and only in 1920 were they granted degrees. (Cambridge, it might be added, was much more backward, and did not grant degrees to women until 1947.)

DIXON's most important research contributions were concerned with certain gas reactions, such as the reaction between carbon monoxide and oxygen, which give rise to explosions or detonations. He caused these detonations to travel along metal pipes, and measured their speeds by means of a chronometer. Some of these experiments were carried out in a makeshift laboratory established beneath what is now Staircase 16 (the Salvin Building) of Balliol College; this laboratory had been established by Sir BENJAMIN COLLINS BRODIE (1817–1880) and was often known as the Brodie Laboratory[109]. When DIXON wanted the detonations to traverse greater distances he set up longer tubes in a passage under the Dining Hall of Balliol. HARTLEY[110] has stated that some of the experiments

[107] M. BODENSTEIN, Trans. Faraday Soc., 27, 413–424 (1931).

[108] For biographical and scientific information see H. B. BAKER & W. A. BONE, "Harold Baily Dixon, 1852–1930", J. Chem. Soc., 3349–3368 (1931); Proc. Roy. Soc., A, 134, i–xvii (1931–32).

[109] E. J. BOWEN, "The Balliol-Trinity Laboratories, Oxford", Notes and Records of the Royal Society, 25, 227–236 (1970); T. W. M. SMITH, "The Balliol-Trinity Laboratories", Part II, Thesis in chemistry, Oxford University, 1979.

[110] For accounts of early work in the Balliol-Trinity Laboratories at Oxford see Sir HAROLD HARTLEY, "Schools of Chemistry of Great Britain and Ireland. XVI The University of Oxford", J. Royal Inst. of Chem., 79, 116–127, 176–184 (1955); "The contributions of the College Laboratories", Chem. in Britain, 1, 521–524 (1965); Studies in the History of Chemistry, Clarendon Press, Oxford, 1971; E. J. BOWEN, Ref. 109; T. W. M. SMITH, Ref. 109.

were carried out *in* Balliol Hall; if so, it was presumably not at meal times. The results of DIXON's experiments were described in three long papers[111] which together constitute a valuable monograph on detonations. These contributions of DIXON were described in VAN'T HOFF'S *Studien*[62] and *Studies*[64], and more extensively in his *Vorlesungen*[65] and *Lectures*[7].

DIXON also carried out investigations on the influence of water vapour on explosions and other reactions in the gas phase, and these were much extended by his student HERBERT BRERETON BAKER[112] (1862–1935). Born in Blackburn, Lancashire, BAKER went to Balliol College, Oxford, where he became an assistant to DIXON. After some years as a schoolmaster, at Dulwich College, he later succeeded VERNON HARCOURT as Dr. LEE's Reader in Chemistry at Oxford. From 1912 to 1932 he was professor of chemistry at Imperial College, London.

BAKER is best known for his work on the effect of moisture on chemical change. The elaborate procedures he used for removing water have become known as 'BAKERian drying', and he himself was referred to as 'Dry Reaction BAKER' or as 'Dry BAKER'. He discovered, for example, that in the complete absence of moisture phosphorus and sulphur may be distilled in oxygen without any reaction taking place. He also found that completely dry ammonia and hydrogen chloride do not combine, and that dry ammonium chloride does not decompose[113]. BAKER's work was also of much interest to VAN'T HOFF, who discussed it in the *Vorlesungen*[65].

The other student of VERNON HARCOURT at Christ Church who made important kinetic contributions was DAVID LEONARD CHAPMAN[114] (1869–1958). Born in Wells, Norfolk, CHAPMAN studied both physics and chemistry at Oxford, and compared with most chemists of his time he was unusually proficient in both physics and mathematics as well as in chemistry. After a period of teaching at Giggleswick School in Yorkshire he joined H. B. DIXON in 1897 at Owens College, Manchester. In 1907 he was appointed a Fellow of Jesus College, Oxford, where he had the responsibility of directing the College chemistry laboratories, known as the Sir LEOLINE JENKINS Laboratories. CHAPMAN distinguished himself in his earlier days as an excellent teacher, and his research has never received the recognition it deserves, probably because of his very unassuming nature.

CHAPMAN's first research was on the theory of gaseous detonations; DIXON's results on the velocities of explosions waves in gases were used by CHAPMAN as the basis of the first sound theoretical treatment of such explosions[115]. Some of his equations were later arrived at independently by EMILE JOUGUET[116], and the region immediately behind a detonation wave is still referred to as the "CHAP-

[111] H. B. DIXON, Phil. Trans., **175**, 617–684 (1884); **184**, 97–188 (1893); **200**, 315–352 (1903).

[112] For biographical information see J. C. PHILIP, J. Chem. Soc., 1893–1896 (1935); J. F. THORPE, Obituary Notices. F.R.S., **1**, 523–526 (1935).

[113] H. B. BAKER, J. Chem. Soc., **65**, 611–624 (1894).

[114] For biographical and scientific information see E. J. BOWEN, Biog. Mem. F.R.S., **4**, 35–44 (1958).

[115] D. L. CHAPMAN, Phil. Mag., [5], **47**, 90–104 (1899).

[116] E. JOUGUET, Compt. Rend., **138**, 1685–1688 (1904); **139**, 121–124 (1904); **144**, 415–417, 560–563 (1907).

MAN-JOUGUET layer". CHAPMAN also worked out an important theory of the distribution of ions at a charged surface[117]; related work had been done by the French physicist GEORGES GOUY[118] (1854–1926), and the electric double layer considered in their theories is now known as the "GOUY-CHAPMAN layer".

Most of CHAPMAN's research was on the chemical kinetics of gas reactions, and in it he was ably assisted by his wife MURIEL C. C. CHAPMAN who herself carried out a number of independent investigations. One reaction studied in some detail by CHAPMAN was the ozone decomposition, and by varying the surface/volume ratio (an idea suggested by VAN'T HOFF in the *Etudes*[33]), he determined the relative importance of the surface reaction[119]. The CHAPMANS also made important studies on the thermal and photochemical reactions between hydrogen and chlorine[120].

One very important contribution made by CHAPMAN in 1913 was to apply, for the first time, the steady-state treatment to a composite mechanism involving intermediates of short lives[121]. This procedure was later used extensively by BODENSTEIN[122], who ably defended it against its critics. CHAPMAN was also the first to develop the rotating-sector technique for measuring the mean lives of these intermediates of short lives[123]; this procedure has since been used very widely in kinetic investigations.

Concluding Remarks

It is easy to discern two important lines of development of research in chemical kinetics before the First World War; one was on the continent of Europe and centred mainly around the laboratories of VAN'T HOFF and OSTWALD; the other, of less importance but nevertheless highly significant, centred mainly around VERNON HARCOURT and his students. The rise of physical chemistry undoubtedly owes much not only to the research in kinetics and in other fields carried out by these workers, but also to the importance all of them placed on excellence in teaching. A considerable number of distinguished kineticists of a later period can trace their scientific ancestries back to either OSTWALD or HAARCOURT[124]; not so many are descended from VAN'T HOFF.

[117] D. L. CHAPMAN, Phil. Mag., **25**, 475–481 (1913).

[118] G. GOUY, J. Physique, [4], **9**, 457–467 (1910).

[119] D. L. CHAPMAN & H. E. JONES, Trans. Chem. Soc., 2463–2477 (1910); 1811–1819 (1911).

[120] C. H. BURGESS & D. L. CHAPMAN, J. Chem. Soc., **89**, 1399–1434 (1906); D. L. CHAPMAN & P. S. MACMAHON, J. Chem. Soc., **95**, 959–964 (1909).

[121] D. L. CHAPMAN & L. K. UNDERHILL, J. Chem. Soc., 496–508 (1913).

[122] M. BODENSTEIN, Ann. Physik., **82**, 836–840 (1927).

[123] F. BRIERS, D. L. CHAPMAN, & E. WALTERS, J. Chem. Soc., 562–569 (1926).

[124] Scientific descendantes of OSTWALD include I. LANGMUIR (through NERNST), H. S. TAYLOR (through BODENSTEIN), and W. C. McC. LEWIS (through DONNAN). Scientific descendants of HARCOURT include C. N. HINSHELWOOD, R. P. BELL, and E. J. BOWEN (all through DIXON, BAKER, and H. B. HARTLEY). There are few scientific descendants of VAN'T HOFF; one who worked with him was H. A. DAWSON, later Professor of Chemistry at Leeds University, who did important work on general acid-base catalysis. Dr. JOHN SHORTER (see also Ref. 20) has informed the author that a survey of kineticists

An interesting difference between the Continental and British workers is that the latter worked somewhat in isolation. OSTWALD and VAN'T HOFF both kept in close touch with research done elsewhere, including the kinetic work done in England; VAN'T HOFF's book, for example, had much to say about the work of HARCOURT, DIXON, and BAKER. As CHRISTINE KING[125] has pointed out, however, VERNON HARCOURT seems to have remained quite unaware of the work of GULD-BERG & WAAGE[14], and in their later work on temperature dependence of reaction rates HARCOURT & ESSON[37] either ignored or disparaged the work of VAN'T HOFF and ARRHENIUS on the same topic. Similarly, the experiments of DIXON and BAKER bore very little relation to other work in kinetics. The somewhat later work of CHAPMAN, on the other hand, showed much more awareness of what was being done elsewhere. The influence of the early British kineticists would undoubtedly have been even greater if they had worked less in isolation.

By the beginning of the present century physical chemistry had established itself as a recognized branch of chemistry. Already a number of textbooks in physical chemistry had appeared subsequent to OSTWALD's *Lehrbuch*: WOLFENDEN[126] has listed nine that were published in English between 1890 and 1902, and this is ample testimony to the vigour of the new field.

In 1904 an important book on chemical kinetics appeared, the first since the *Etudes*[33] and its successors, the *Studien*[62] and the *Studies*[64]; this was *Chemical Statics and Dynamics*[127], by JOSEPH WILLIAM MELLOR (1869–1938). Born in Huddersfield, MELLOR was a student of H. B. DIXON at Owen's College, Manchester, and later became director of research in the Ceramic Institute at Stoke on Trent. He was also the author of a monumental sixteen-volume *Comprehensive Treatise on Inorganic and Physical Chemistry*. His *Chemical Statics and Dynamics* gave a masterly review of the work done in the field, on the continent of Europe as well as in England, and it exerted an important influence for many years on progress in chemical kinetics. From reading it one gains a very clear impression of the important role played by chemical kinetics in the development of the field of physical chemistry, and indeed of chemistry as a whole.

and physical organic chemists at the University of Hull showed that they were nearly all descendants of HARCOURT, and the same may well be true of other universities in the U.K.

[125] M. C. KING, Ambix, **28**, 70–82 (1981); **29**, 49–61 (1982); **31**, 16–31 (1984).

[126] J. H. WOLFENDEN, "The earliest textbooks of physical chemistry in English", J. Chem. Educ., **50**, 532 (1973).

[127] J. W. MELLOR, *Chemical Statics and Dynamics*, Longmans, Green & Co., London, 1904; this book was dedicated to MELLOR's teacher H. B. DIXON.