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A Brief Introduction to the History of Chemical Kinetics

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Abstract

This chapter begins with a general overview of the content of this work, which explains the structure and mutual relation between discussed topics. The following text provides brief historical background to chemical kinetics, lays the foundation of transition state theory (TST), and reaction thermodynamics from the early Wilhelmy quantitative study of acid-catalyzed conversion of sucrose, through the deduction of mathematical models to explain the rates of chemical reactions, to the transition state theory (absolute rate theory) developed by Eyring, Evans, and Polanyi. The concept of chemical kinetics and equilibrium is then introduced and described in the historical context.

Keywords: kinetics, chemical equilibrium, rate constant, activation energy, frequency factor, Arrhenius equation, Van't Hoff-Le Châtelier's principle, collision theory, transition state theory

1. Introduction

Modern chemical (reaction) kinetics is a science describing and explaining the chemical reaction as we understand it in the present day [1]. It can be defined as the study of rate of chemical process or transformations of reactants into the products, which occurs according to the certain mechanism, i.e., the reaction mechanism [2]. The rate of chemical reaction is expressed as the change in concentration of some species in time [3]. It can also be pointed that chemical reactions are also the subject of study of many other chemical and physicochemical disciplines, such as analytical chemistry, chemical thermodynamics, technology, and so on [2]. The thermodynamics is concerned with the overall energy change between initial and final stage of the process. Since this change can result appear after infinite time, the thermodynamics does not directly deal with the subject of reaction rate [3].

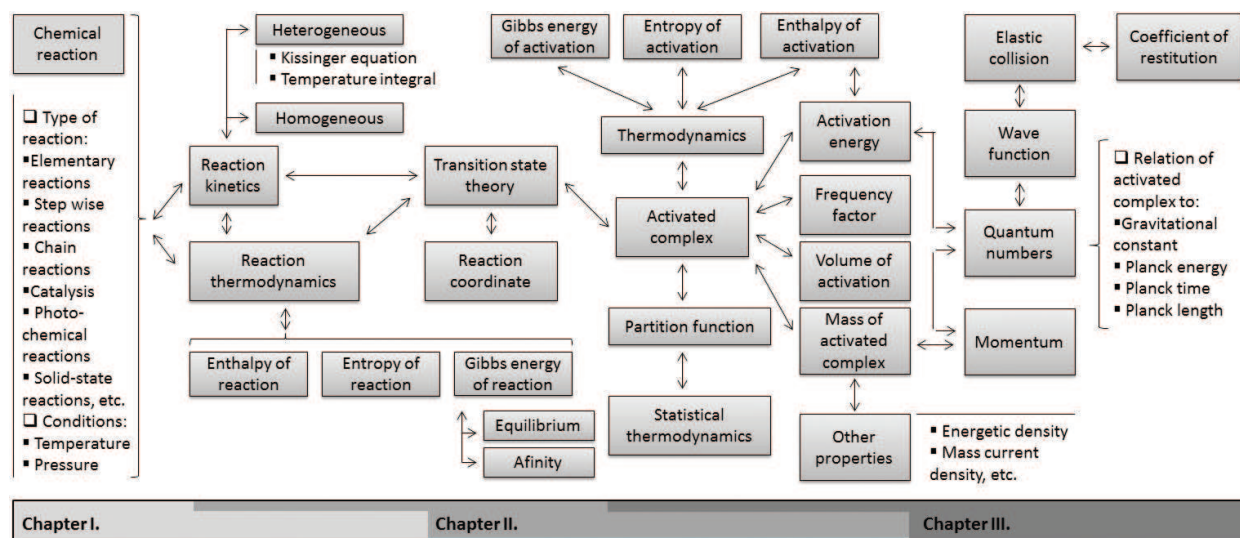


Figure 1. The simplified scheme of the relation between individual topics in this treatise.

The first chapter provides a short insight into the history of understanding of nature, mechanism, kinetics, and thermodynamics of chemical reaction, which results in today widely accepted transition state theory (TST). The second chapter lays the foundations to TST theory including thermodynamic description of activated complex, formulation of partition function and limitation. The last chapter deals with the introduction of a simple approach to the calculation of the change in mass when reactants pass into the activated state. The survey and simplified scheme of the relationship between individual topics, which are described in this chapter, are provided in **Figure 1**.

2. Brief historical background to chemical kinetics

“Chemistry should not only be a science and profession but also an art. And it is only as an artist that the personality of a scientist can survive.” J. von Liebig¹ [4]

The first quantitative study in chemical kinetics has been done by German scientist Ludwig Ferdinand Wilhelmy (1812–1864) in 1850 [5] who used polarimetry to investigate the acid-catalyzed conversion of sucrose. In this early study, Wilhelmy recognized that the reaction rate (dZ/dt) was proportional to the concentration of sucrose (Z) and acid (S) according to the differential equation [5]:

$$-\frac{dZ}{dt} = MZS \Rightarrow \log Z = -MSt + C \quad (1)$$

¹German chemist Justus Freiherr von Liebig (1803–1873) awarded by Alberd Medal of the Royal Society of Arts in 1869. Liebig is well known for the popularization of “Law of the Minimum”, i.e. Liebig’s Law, which was actually found by German botanist Carl Sprenger (1787–1859) in 1828.

where M is the transformation coefficient of sucrose, which is related to the unit of time, i.e., the reaction rate constant and C is the constant of integration.

However, the English chemist Augustus George Vernon Harcourt² (1934–1919, **Figure 2a**) is considered to be the first scientist who made a significant contribution in the field of chemical kinetics³. He was one of the first who planned the experiments to follow the course of a chemical change [6]:

“Every change that we can observe may be regarded as presenting to us two problems, the one relating to the manner or course of the change, and the other to its result. ... In the beginning of chemistry, a quantitative knowledge of the results of chemical changes was deemed sufficient; the advance of science dates from the introduction of exact quantitative ideas. At present such knowledge as we possess of the course of chemical changes, and of their relations to the conditions under which they occur, is merely quantitative.”

In order to measure the velocity of a reaction. Despite Harcourt's lack of skill with mathematics, he had a great respect for it and recognized the importance of applying mathematics to chemical problem⁴ [7–9]. Harcourt himself wrote that [10]:

“...we are occupied in amassing a vast collection of receipts for the preparation of different substances, and facts as to their compositions and properties, which may be of no more service to the generalization of the science, whenever our Newton arises, than were, I conceive, the bulk of the stars to the conception of gravitation.”

Harcourt then played a great part in raising chemistry from its descriptive area into its quantitative one [7]. As early as 1868 he defined chemistry as the science which [11]:

“...investigates the relations of the different kinds matter one to another”.

and which is also concerned with the changes, which occur when substances are placed under different conditions or are placed with one another [7, 11].

The first reaction was investigated by Harcourt in cooperation with British mathematician William Esson⁴ (1838–1916, FRS in 1869) is the process [6, 7, 12]:

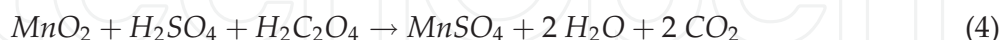


²He was the elder son of Admiral F.E. Vernon Harcourt and of Marcia, sister of the first Lord Tollemache, and grandson of the Archbishop of York [9]. It is easy to discern two important lines of development in chemical kinetics before the First World War. One was centered mainly around the laboratories of van't Hoff and Ostwald, the other was around Harcourt and his students [36].

³Up to this time nearly all chemists, unlike physicists, had been content with purely descriptive and qualitative approaches to their subjects, although there were some notable exceptions, such as Benjamin Collins later Sir B. Brodie (A.G.V. Harcourt^{2,4} was his research assistant [7]).

⁴A.G.V. Harcourt mostly collaborated with mathematicians H. Smith, Ch. Dodgson and W. Esson. One factor that made the collaboration between Harcourt and Esson such an effective one is that Esson had little ambition to do any mathematical research of his own and his entire mathematical interest was in the analysis of Harcourt's kinetic results [7].

This reaction, which occurs in a very dilute aqueous solution, proceeds at a convenient speed at room (constant) temperature and it could be started at a given instant and stopped abruptly by the addition of hydrogen iodide, which liberates iodine. The extent of reaction could be then determined by titrating the amount of iodine with thiosulfate solution. Harcourt also realized that the reaction is accelerated by manganous sulfate being formed, i.e., it occurs in more than one step, and proposed the following reaction sequence [7, 12, 13]:



Esson then tried to find mathematical equations which would interpret the results, on the basis of the hypothesis that:

“...the total amount of change occurring at any moment will be proportional to the quantity of substance then remaining.”

Because of the complexities of reactions Eqs. 2–4 (please also refer to the works of H.F. Launer [14, 15]), Harcourt and Esson only had limited success in interpreting their results. On the other hand, their works [16] are important in containing a clear mathematical treatment of the first-order and the second-order reactions, and of certain types of consecutive reactions. Esson's mathematical procedures are those being used today. He set up appropriate differential equations expressing the relationship between the time derivative of the concentration of reacting substance and the concentration remaining and then obtained the solutions by integration [7].

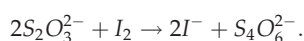
By 1865 Harcourt and Esson had started to work on the kinetically simpler reaction between hydrogen peroxide and hydrogen iodide [6, 7, 17]:



When the solutions of potassium iodide and sodic peroxide are brought in the presence of either an acid or an alkaline bicarbonate, a gradual development of iodine takes place. If sodic hyposulfite (sodium thiosulfate, $Na_2S_2O_3$) is added to the solution, it reconverts (reduces) iodine, as soon as it is formed, into iodide, but appears in no other way to affect the course of reaction. Consequently, if peroxide is present in the excess over the hyposulfite, the whole of the latter is changed by the action of nascent iodine into tetrathionate.⁵ After this conversion, free iodine appears in the solution, and its liberation can be observed with the help of a little starch (indicator, formation of iodine-starch clathrate) previously added to the liquid [17].

Esson found satisfactory equation, which described the results of Harcourt's experiments. Their first paper on this appeared in 1866 [12], and although they continued their work on this

⁵The equation for this quantitative reaction is:



reaction for another 30 years they did not publish any data on this until 1895 when Harcourt and Esson jointly wrote the Bakerian Lecture⁶ [18] delivered at the Royal Society [19].

Much of the work was concerned with the effect of temperature on the rate of reaction [7, 20, 21]:

$$k = A' T^m \quad (6)$$

where k is the rate constant and pre-exponential (prefactor or frequency factor) A' as well as m (ratio dk/k to dT/T [21]) are temperature independent constants.

Previously in 1884 Jacobus Henricus van't Hoff⁷ (1852–1911, **Figure 2b**) had proposed several alternative equations for the temperature dependence [22–24], and one of them was in 1889 adopted by S.A. Arrhenius⁸ (1859–1957, **Figure 2c**) [22]:

$$k = A \exp \left(-\frac{E_a}{RT} \right); \quad (7)$$

where A , E_a , and R are constants, i.e., the frequency factor, the activation energy and universal gas constant ($8.314 \text{ J} \cdot (\text{K} \cdot \text{mol})^{-1}$), respectively. Whereas Eq. 7 provides some insight into the mechanism of the reaction, e.g., the activation energy is the minimum energy required for the reaction to proceed, the Harcourt-Esson equation⁹ (Eq. 6) is theoretically sterile and m is having

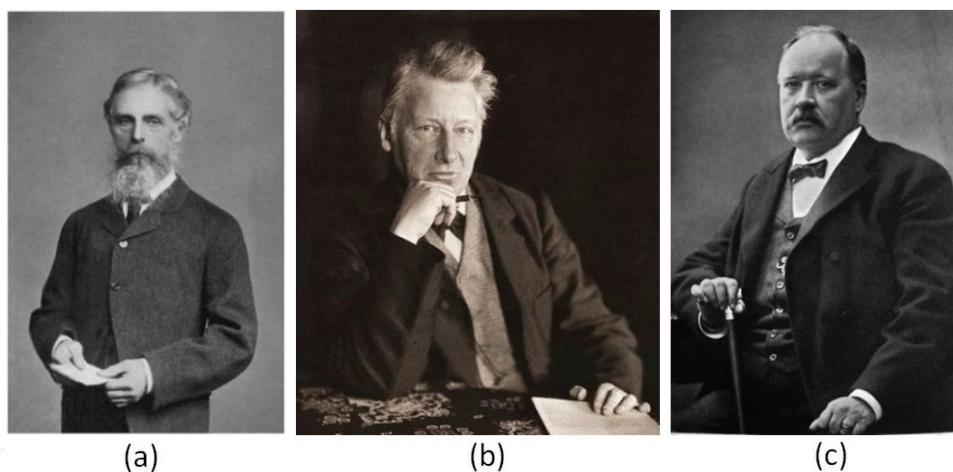


Figure 2. Photographs (all of these pictures belong to free work in the public domain) of A.G.V. Harcourt (a), J.H. van't Hoff by Nicola Perscheid (German photographer (1864–1930) who developed the soft-focus with open depth of field (Perscheid lens) somewhere around 1920) (b), and S.A. Arrhenius (c).

⁶The medal and prize lecture of the Royal Society originated in 1774 (begun in 1775) as a result of the bequest of £100 to the Society by Henry Baker (1698–1774, FRS). The first three Bakerian Lectures were given from 1775 to 1777 by Irish (probably) chemist and mineralogist Peter Woulfe (1927(?)–1803) on the nature of mineral substances [18].

⁷Awarded the first Nobel Prize in chemistry in 1901 for his work on chemical dynamics and on osmotic pressure in solutions [30].

⁸There is a lunar impact crater within Mendel-Rydberg Basin (55.6°N 91.3°W, 40 km) that is named after S.A. Arrhenius.

⁹In the work [21], Harcourt and Esson insisted that their formula (Eq. 6) was superior to any other. On purely empirical grounds they were right, but this fact is of little significance; a double-logarithmic plot is intrinsically more likely to be linear than a single-logarithmic plot [7].

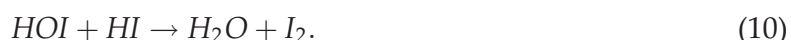
no physical significance [7]. On the other hand, an interesting aspect of their work is that they predicted a “kinetic absolute zero,” at which all reactions would cease. Their value for it was -272.6°C that is in remarkable agreement with the recent value of -273.15°C for the absolute zero [7, 21]. It should also be pointed that Harcourt together with his kinetic work was treated very comprehensively by M. C. King [8, 25, 26] and J. Shorter [27].

For more precise solution for the temperature dependence of reaction rate constant, particularly those covering wide temperature range, it is usual to allow A to be proportional to T^m , so that Eq. 7 leads to the formula [20]:

$$k = A' T^m \exp\left(-\frac{E_a}{RT}\right); \quad (8)$$

where the constant A' is temperature independent (please also refer to Eq. 24).

Van't Hoff also pointed that the first- and the second-order reactions are relatively common while the third order reactions are rare. He provided an example based on the reaction 5, which experimentally behaves as the second-order reaction, despite the fact that there are three reactant molecules. The reaction then most probably proceeds in two steps via the formation of a short-lived reaction intermediate (HOI) as follows [28]:



Even though Dutch scientist J.H. van't Hoff achieved the recognition through organic chemistry¹⁰ for his pioneer works in the field of stereochemistry [23, 29–32]:

¹⁰J.H. van't Hoff work clearly shows that molecular structures of many organic molecules which were studied by leading chemist at that time had indeed a three-dimensional shape and the three-dimensionality was not just a means of conceptualizing molecules. That also includes the statement about the most probable orientation of bonds of carbon atom, i.e. towards the apexes of a tetrahedron, or so called Le Bel – van't Hoff rule: The number of stereoisomers of an organic compound containing no internal planes of symmetry is 2^n , where n represents the number of asymmetric carbon atoms; which was propounded by van't Hoff [31] and in the slightly different form also by his coworker Joseph Achille Le Bel (1847–1930) [32] in 1874. Since the atomic theory was still considered a mere speculation, these ideas came under strong criticism. For example his worst critic, editor of the Journal für praktische Chemie (ISSN 1521–3897), Adolph Wilhelm Hermann Kolbe (1818–1884, Davy medal in 1884, please refer to the e.g. Kolbe electrolysis, synthesis and Kolbe-Schmitt reaction) wrote:

“...two virtually unknown chemists, one of them at a veterinary school and the other at an agricultural institute, pursue and attempt to answer the deepest problems of chemistry which probably will never be resolved (especially the question of the spatial arrangement of atoms), and moreover with an assurance and an impudence which literally astounds the true scientist”.

He also cast doubt on the theories of the structure of benzene by Friedrich August Kekulé von Stradonitz (1829–1896). Ironically, the strong criticism from A.W.H. Kolbe, A. Ladenburg, Mach and others made van't Hoff theory only better known [24], so that it must have overcome all three stages of truth according to the A. Schopenhauer:

“All truth passes through three stages. First, it is ridiculed. Second, it is violently opposed. Third, it is accepted a being self-evident”.

“Thanks to van’t Hoff the chemistry becomes three dimensional”;

by late 1870s, he was no longer chiefly interested in studying organic molecular structures. His focus shifted to molecular transformations and investigation why the chemical reactions proceed at widely different rates. In order to understand the chemical equilibrium and chemical affinity, he began a decade-long research in thermodynamics, chemical equilibrium and kinetics, that is, chemical dynamics¹¹ [33]. In van’t Hoff words [34]:

“...dynamics is devoted to the mutual actions of several substances, i.e. to chemical change, affinity, velocity of reaction and chemical equilibrium.”

The German chemist Friedrich Wilhelm Ostwald¹² (1853–1932, **Figure 3**) defined it similarly as [35]:

“...the theory of the progress of chemical reactions and the theory of chemical equilibrium.”

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 [36].

Among others, the most significant contributions of J.H. van’t Hoff include [23, 36–39]:

1. Deduction of a mathematical model to explain the rates of chemical reactions based on the variation in the concentration of reactants with time.

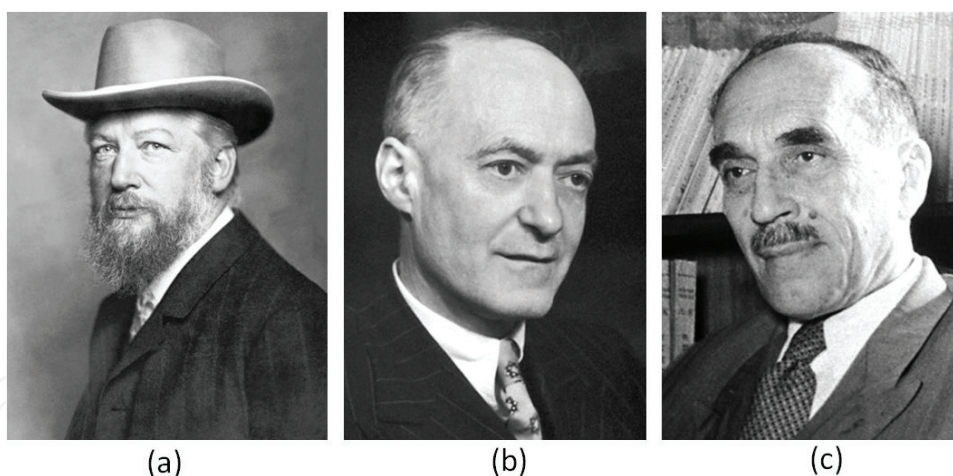


Figure 3. Photographs (all of these pictures belong to free work in the public domain) of W. Ostwald by Nicola Perscheid (German photographer (1864–1930) who developed the soft-focus with open depth of field (Perscheid lens) somewhere around 1920) (a), C.N. Hinshelwood (b), and N.N. Semenov (c).

¹¹ A branch of physical chemistry (closely related to chemical kinetics) that seeks to explain the time-dependent phenomena, such as energy transfer and chemical reactions, in terms of detailed motion of nuclei and electrons which constitute the system [33], i.e. the investigation why chemical reaction proceeds.

¹² Awarded the Nobel Prize in Chemistry in 1909.

2. Derivation of the equation that gave the relation between the heat of reaction and the equilibrium constant¹³, which is widely known as the van't Hoff equation¹⁴:

$$\frac{d \ln K}{dT} = \frac{q}{RT^2}; \quad (11)$$

where K is the equilibrium constant, T is the temperature, R is the universal gas constant and q is the heat required to dissociate a mole of substance in the current notation, the Eq. 11 can be written as:

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2}; \quad (12)$$

where ΔH° is the standard enthalpy change for the reaction.

3. The suggestion of a new method for determining the order (molecularity) of a chemical reaction¹⁵ which involves the measuring of rate (r) at various concentrations (c) of the reactant:

$$r = k c^n; \quad (13)$$

the order of reaction (n) can be then determined from the slope of a plot of $\log r$ against $\log c$.

¹³ Alternatively the relation describes the variation of equilibrium constant with temperature. This equation is commonly known as the van't Hoff isochore [36].

¹⁴ 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. He based his temperature dependence argument on an equation obtained by German chemist August Friedrich Horstmann (1842–1929), who was the first to apply the thermodynamics, particularly the newly formed concept of entropy (R. Clausius (1822–1888) in 1865), to chemical problems. A. Horstmann treated in particular the dissociation pressure (p) of solid substance on the basis of Clausius's principle that at equilibrium the entropy reaches the maximum and deduced the equation [36]:

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

which at given temperature T leads to:

$\ln p + \frac{q}{RT} + const = 0$; The procedure used by van't Hoff for the chemical process at equilibrium was to substitute the equilibrium constant for the pressure:

$$\ln K + \frac{q}{RT} + const = 0;$$

The differentiation of this equation then leads to Eq.11.

¹⁵ This method is still in common use today and is known as „differential method“. The term “order of reaction” was introduced by W. Ostwald [36].

4. The explanation of the effect of temperature on the equilibrium of reaction (Eqs. 11 and 12) H.L. Le Châtelier showed the applicability of this relationship, and this is now known as van't Hoff – Le Châtelier Principle. The law provides an important qualitative discussion of the way in which K is affected by temperature: if the heat evolves when the reaction proceeds 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 .
5. The definition of chemical affinity in terms of maximum external work done in a chemical reaction under constant temperature and pressure as the driving force of reaction. The conclusions of van't Hoff, J. Thomsen, and M. Berthold¹⁶ are used by physicists such as J.W. Gibbs and Helmholtz to extend the thermodynamic principles to chemical systems.

Van't Hoff also pointed that chemical kinetics was different from chemical thermodynamics and German physicist Hermann von Helmholtz had put forth a similar theory in 1882 [23].

Since the ratio of the rate constant for forward (k_1) and reverse (k_{-1}) reactions is equal to the equilibrium constant, the Eqs. 11 or 12 can be treated as follows [36]:

$$\frac{d \ln k_1}{dT} - \frac{d \ln k_{-1}}{dT} = \frac{q}{RT^2}; \quad (14)$$

Van't Hoff argument was that this relationship could be met only if k_1 and k_{-1} vary with temperature in the same manner as does K . Expressed in other words he regarded the heat q as the difference between two energy terms E_1 and E_{-1} :

$$q = E_1 - E_{-1}; \quad (15)$$

so:

$$\frac{d \ln k_1}{dT} - \frac{d \ln k_{-1}}{dT} = \frac{E_1}{RT^2} - \frac{E_{-1}}{RT^2}. \quad (16)$$

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

$$\frac{d \ln k_1}{dT} = \frac{E_1}{RT^2} \quad \text{and} \quad \frac{d \ln k_{-1}}{dT} = \frac{E_{-1}}{RT^2}. \quad (17)$$

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

¹⁶Van't Hoff also expressed the criticism of the so-called "principle of maximum work", which was independently formulated by H.P.J. Thomsen (1826–1909) and French chemist P.E.M. Berthelot (1827–1907). According to this principle, the driving force in a chemical reaction, i.e. chemical affinity, is the evolution of heat. Van't Hoff noted that the principle of maximum work is correct only at the absolute zero temperature, but not at other temperatures, because the sign of q a chemical reaction influences only how the equilibrium constant K (Eq.11) varies with temperature [36, 37, 39].

$$\frac{d \ln k}{dT} = \frac{E}{RT^2}. \quad (18)$$

Van't Hoff then discusses three different possibilities:

(a) The value of E is independent of temperature. In this case, Eq. 18 can be integrated (term

$(E/R) \int dT/T^2 = -(E/RT) + \text{const.}$) to give:

$$\ln k = -\frac{E}{RT} + \text{const.}; \quad (19)$$

or:

$$k = A \exp\left(-\frac{E}{RT}\right); \quad (20)$$

where A is the constant.

(b) There is a parabolic dependence of E on the temperature, i.e., the dependence given by the formula $B + DT^2$, where B and D are the constants. Eq. 18 can be integrated as follows:

$$\ln k = -\frac{B}{RT} + \frac{DT}{R} + \text{const.}; \quad (21)$$

or:

$$k = A \exp\left(-\frac{B - DT^2}{RT}\right). \quad (22)$$

(c) There is a linear relationship between E and temperature, which is given by the term $B + CT$, that leads to the equation:

$$\ln k = -\frac{B}{RT} + \frac{C}{R} \ln T + \text{const.}; \quad (23)$$

or:

$$k = AT^m \exp\left(-\frac{B}{RT}\right); \quad (24)$$

where $m = C/R$ is the constant.¹⁷

The first and simplest of these possibilities (a) that E is independent of temperature was adopted in 1889 by Arrhenius [36, 40], who applied it to a variety of experimental results. He also gave it an interesting interpretation, in terms of equilibrium between reactant molecules and active

¹⁷The detailed survey of relations suggested for the temperature dependence of k is introduced by work of K.J. Laidler [20].

molecules, which were assumed to undergo the reaction very readily. As a result, Eq. 20 is now generally referred to as the Arrhenius equation¹⁸ [36].

In 1893, the German physicist Max Karl Ernst Ludwig Planck (1858–1947, Nobel Prize in 1918 for his “discovery of energy of quanta”), proposed the equation, which solves the relationship of equilibrium constant and pressure (p) [7, 41–43].

$$\frac{d \ln K}{dp} = -\frac{\Delta V}{RT}; \quad (25)$$

where ΔV is the molar change in volume during the reaction. As was pointed by van't Hoff, this equation is analogical to Eqs. 14–17. Since K is k_1/k_{-1} it is possible to introduce so called “possible formula”:

$$\frac{d \ln k}{dp} = -\frac{\Delta V}{RT}; \quad (26)$$

Without any interpretation of ΔV^\ddagger that today means the volume of activation, i.e., the change of volume when the reactants pass into the activated state [7].

Since Harcourt has played a great part in raising the chemistry from its descriptive era into its quantitative one, his teaching influenced many students, such as H.B. Dixon, D.L. Chapman, and N.V. Sidgwick. Harold Baily Dixon (1852–1930) played an important role in the development of physical chemistry in England. Dixon's most important research contributions were dedicated to the investigation of explosive reaction between carbon monoxide and oxygen gas. He made the detonations travel along metal pipes and measured their speeds using a chronometer [36, 44–46].

David Leonard Chapman (1869–1958), his first research was focused on the kinetic theory of gaseous detonations.¹⁹ He used Dixon's results on the velocities of explosion waves in gases for the theoretical treatment of such explosions²⁰ [36, 47]. The region behind the detonation wave is still referred to as the “Chapman-Jouguet layer” or “Chapman-Jouguet condition” [36, 48]. Chapman also worked out an important theory of the distribution of ions at the charged surface [36, 49]. Since related work [50] had been done by French physicist Georges Gouy (1854–1826), the electric double layer considered in their theories is now known as the “Gouy-Chapman layer” [36].

Another gas phase reaction studied by Chapman includes the decomposition of ozone [51, 52], the synthesis of formaldehyde [53], and nitrous oxide [54]. He also made important studies on the thermal and photochemical reactions between hydrogen and chlorine [36, 55, 56] and investigated the allotropic modification [57] and compounds of phosphorus [58, 59]. One very important contribution made by Chapman in 1913 was to apply (for the first time) the steady-

¹⁸The experimental activation energy (Arrhenius activation energy) of the reaction can be then evaluated from the slope of the Arrhenius plot, i.e. the plot of $\ln k$ vs. T^{-1} (please refer to **Figure 2** in the Chapter 2).

¹⁹Chapman's research related to the chemical kinetics of gas reactions was assisted by his wife M.C.C. Chapman who herself carried out a number of independent investigations [36].

²⁰Some of his equations are latterly independently derived by Emile Jouguet [36, 48].

state treatment to a composite mechanism involving intermediates of short lives [60]. This procedure was later used extensively by Max Ernst August Bodenstein (1871–1942) [61], who was able to defend it against its critics [36].

Cyril Norman Hinshelwood²¹ (1897–1967, **Figure 3b**) was English physical chemist:

“Chemistry: that most excellent child of intellect and art”.

He was awarded Nobel Prize in chemistry for 1956 and also made an important contribution to chemical kinetics [62]:

“Nobody, I suppose, could devote many years to the study of chemical kinetics without being deeply conscious of the fascination of time and change: this is something that goes outside science into poetry, but science, subject to the rigid necessity of always seeking closer approximation to the truth, itself contains many poetical elements.”

Among others, Hinshelwood investigated the reaction between hydrogen and oxygen²² [63, 64]:

“According to the generally accepted belief, molecules do not, in most chemical reactions, undergo transformation until they have had imparted to them by some physical agency, such as collision with another molecule, a certain critical amount of energy. This process is commonly called “activation”. ...in exothermic reactions a special mechanism has been shown to be possible, in which the energy set free is communicated by the molecules formed in the reaction to untransformed molecules, and immediately activates them, thereby establishing what is known as a reaction chain.”

The first paper in this series [63] concluded that when the reaction between hydrogen and oxygen occurred in a quartz vessel, two processes proceeded, one on the vessel walls and one in the gas phase (chain reactions²³). The possibility of chain branching has previously been raised by Danish physicist H.A. Kramers (1894–1952) and Russian scientist Nikolay Nikolayevich Semenov²¹ (Semenoff or Semyonov) (1896–1986, **Figure 3c**) [65] who made specific experiments showing the existence of the lowest limit of oxygen pressure during the oxidation of phosphorus [7]. The later work [65] showed that there was a pressure range within which the explosion occurred (“explosion peninsula” [66]) and that there were lower and upper pressure limits beyond which the reaction was slower. Further work was also done on oxidation of phosphine [67] and carbon monoxide [68]. He also participated in the research of Harold Hartley²⁵ (1878–1972) concerned to the thermal decomposition of solids [69–71].

²¹Hinshelwood Nobel prize in chemistry (1956) was shared with N.N. Semenov, who was also awarded by Lomonosov Gold Medal in 1969. There is also a lunar impact crater (89.3°N 46.3°W, diameter 14.2 km) named after C.N. Hinshelwood.

²²Hinshelwood investigated this reaction with his student H.W. Thmopson (1908–1983) [7].

²³In these reactions it is possible that two or more active centers are formed (the second kind of chain) instead of one (the first kind of chain) [7, 64].

A British physical chemist Edmund (“Ted”) John Bowen²⁴ (1898–1980) laid the emphasis on liquids and solids rather than gases. His photochemical work may have been initiated by Hartley’s²⁵ suggestion that it might have been possible to separate the isotopes of chlorine by photochemical means. Since this attempt was not successful Bowen started his photochemical work and the principles of the subject became clearer [7].

It was recognized by that time that in a photochemical processes²⁶, the light behaved as a beam of particles (photons) and that there was a one-to-one correspondence between photons absorbed and molecules put into activated states or dissociated²⁷. In other words, one photon brought about the chemical transformation of one molecule²⁸ as resulted from the investigation of decomposition of chlorine monoxide (Cl₂O) in blue and violet light [7, 72], where he also wrote [72]:

The rarity of such reactions is probably exaggerated, because the most striking photochemical reactions are those of high so-called “light sensitivity.”

The same conclusion also results from the investigation of photochemical decomposition of chlorine dioxide (ClO₂) [73–75] and nitrosyl chloride (NOCl) [76] in tetrachloride solution. The idea of chain reactions and their relation to the principle of photochemical equivalence began to be recognized (W.H. Nernst²⁹ [77], K.F. Bonhoeffer [78]) [7, 79]. Bowen’s paper with H.G. Watts [80] showed that the quantum yields for the photolysis of aldehydes and ketones were much smaller in solution than in the gas phase³⁰ [7].

²⁴ Awarded the Davy Medal (Royal Society of London, named after sir Humphry Davy (1778–1829)) in 1963 and elected FRS (Fellow of University College Oxford) in 1935.

²⁵ Doctoral student of sir John Conroy (1845–1900). Sir H. Hartley was elected FRS in 1926, awarded the Wilhelm Exner Medal (the Austrian Industry Association prize, award dedicated to Wilhelm Exner (1840–1941)) in 1937 and Hoover Medal (the American engineering prize named after Herbert Hoover (1874–1964)) in 1968. He supervised the research of C.N. Hinshelwood and E.J. Bowen.

²⁶ Many notable scientists, such as J.H. Draper²⁷, Arthur Eichengrün (1867–1949), T. Grotthuss²⁷, Selig Hecht (1892–1947), Michael Kasha (1920–2013), Walter Sidney Metcalf (1918–2008), James Pitts (1921–2014), Fritz Weigert (1876–1947), etc., are concerned to investigate the chemical reaction caused by the absorption of light, i.e. photochemistry.

²⁷ The principle, which states that only that light which is absorbed by a system can bring about a photochemical change, is called as the principle of photochemical activation or Grotthuss-Draper law (law was independently proposed by German chemist Freiherr Christian Johann Dietrich Theodor von Grotthuss (1785–1822) in 1817 and English-American scientist John William Draper (1811–1882) in 1842).

²⁸ This fundamental principle, which states that for every quantum of radiation that is absorbed, one molecule of the substance reacts, is known as photochemical equivalence law or Einstein-Stark law (independently formulated by physicists Johannes Stark (1874–1957) and Albert Einstein (1879–1955) between 1908 and 1913).

²⁹ German chemists Walther Hermann Nernst (1864–1941) who is well known for his work in thermodynamics, e.g. the formulation of so called Nernst heat theorem which was used in the development of the third law of thermodynamics. Nernst has an interesting motto:

“Knowledge is the death of research”.

³⁰ His explanation is similar to that of the later suggested “cage effect” where the energy was degraded by the interaction with solvent molecules [7].

Bowen's work on this topic was latterly summarized in the seminal book entitled "The chemical aspects of light" [81, 82].

"Physics and chemistry began with the study of the behaviour of objects of ordinary size, but are now chiefly concerned with the matter on an extremely small scale, so small that normal sense impressions cannot deal with it."

Photochemical reactions usually differ from thermal ones in that the energy of activation is wastefully employed. For example, the thermal decomposition of hydrogen iodide:



where the reaction of two colliding molecules requires the energy of 184.1 kJ. The photochemical process:



requires 283.3 kJ to raise the HI molecule to electronically excited level. This example also illustrates a very common feature of photochemical reactions, i.e., the formation of free atoms or radicals, the subsequent reactions of which give rise to the complexity of measured chemical changes [72, 81].

These secondary processes, e.g., for the reaction mentioned above (Eq. 28), include the reactions:



and³¹



cause that mere observation of a change of pressure or estimation of product concentration by titration is often insufficient to follow the course of reaction and an elaborate analytical procedure at various stages of reaction is usually necessary [81].

Bowen also investigated the chemiluminescence, the emission of radiation as the results of chemical reactions, such as oxidation of phosphorus vapors in oxygen [83]. Together with his students he made also many studies on the kinetics of processes of quenching of fluorescence in solution [84–87], but during his entire research career Bowen wrote much on photochemistry and related topics such as the improvement on photocells and light filters for the mercury lamp [7, 88, 89], the energy transfer between molecules in rigid solvent [90] and the effect of viscosity on the fluorescence yield of solutions [91].

³¹The letter M in Eq.30 is a "third body" to carry away an excess of energy, it can be the wall of photocell.

Ronald (“Ronnie”) Percy Bell³² 1907–1996) was a physician chemist particularly interested in the catalysis by acids and bases, but he also made important contributions to the understanding of solvent effects [7, 92–95] and of quantum-mechanical tunneling³³ [96].

Bell was one of the first to realize that when light hydrogen; but not heavy hydrogen (deuterium³⁴), is transferred in a chemical reaction, there may be a special process, known as “quantum-mechanical tunneling” in which the hydrogen atom passes through the energy barrier rather than over it. In several theoretical papers, he considered the barriers of various shapes and treated the rate at which hydrogen can tunnel through the barrier [7].

Bell was also interested in the problem with which Hinshelwood and Moelwyn-Hughes³⁵ had been concerned [97, 98], i.e., the influence of solvent on the reaction rates:

“Energy among molecules is like money among men. The rich are few, the poor numerous.”³⁶

Hinshelwood and Moelwyn-Hughes proposed the modification of conventional formula (Eq. 20), where the pre-exponential factor was regarded as the frequency of collision calculated from the kinetic theory of gases³⁷, as follows:

$$k = PA \exp \left(-\frac{E_a}{RT} \right); \quad (31)$$

³² Awarded the Gibbs Prize, Meldola Medal (prize of Chemical Society (1921–1979) named after Raphael Meldola (1849–1915)) in 1937 and elected a FRS in 1944.

³³ The quantum mechanical tunneling through the reaction potential energy barrier is usually important only for the reaction of very light atoms which occurs at very low temperatures.

³⁴ Deuterium (D or ²H, i.e. the “heavy hydrogen”) is a hydrogen isotope with one proton and neutron in nucleus, while the core of “light hydrogen” (¹H, protium) contains one proton only. Deuterium was discovered by American physical chemist C. Urey (1893–1981, Nobel Prize for Chemistry in 1934) [4]. Urey contributed to the development of atom bomb and is also well known for so called Miller-Urey experiment that simulated the conditions on early Earth. There is also a lunar impact crater (27.9°N 87.4°E, 38 km), asteroid (4716 Urey) and prize (H.H. Urey Prize for achievement in planetary sciences) named after him.

³⁵ Emyr Alun Moelwyn-Hughes (1905–1978) was Welsh physical chemist.

³⁶ This saying is one of the variations of the “Pareto principle” (or “80–20 rule”), named after the mathematical engineer and physical socioeconomist Vilfredo Federico Damaso Pareto (1848–1923), who postulated that about 80% of a country’s wealth tended to be held by about 20% of the population. According to Jaroslav Šesták (please refer to e.g. Šesták-Berggren equation), the stable economy is modeled by the following power law distribution:

$$y \approx x^{-a};$$

where y is the number of people having an income $\geq x$ and a is an exponent that was estimated to be 1.5 applicable to various conditions and nations.

³⁷ As was proposed by William Cudmore McCullagh Lewis on the basis of collision theory [7]. He was elected FRS in 1926.

where P is so-called “fudge factor,” i.e., an ad hoc quantity, which was intended to express the special conditions,³⁸ which are required for the reaction of molecules after the collision.

Bell relied less on the older collision theory,³⁹ which had been independently developed by Max Trautz (1880–1960) in 1916 [99] and William Lewis (1885–1956) in 1918, and more on transition-state theory as soon as it was formulated in 1935. He quickly realized that, together with Brönsted’s⁴⁰ formulation of rates in terms of activity coefficients, the transition-state theory led to a useful way of interpreting the solvent effects. By making the estimates of activity coefficients for the species in solution, and using the thermodynamic parameters, he was able to relate in a very satisfactory way the rates in solution to those in the gas phase. It had previously been concluded by M.G. Evans⁴¹ and M. Polanyi [7, 100].

Hinshelwood who continued to study the reaction for a number of years became interested in the factors, which influence the value of P and A (Eq. 31), particularly the nature of the reaction, the structure of the reactants and the solvent. He also investigated possible correlations between P and E_a [7]. Shortly before, the work of Henry Eyring⁴² (1901–1981) [101, 102] and Hungarian-British chemist Michael Polanyi (1891–1976) [103] had made an important contribution by constructing a potential-energy surface, which provided a valuable way of envisaging the course of the reaction. In 1977 Eyring wrote [104]:

“This way we got an exciting, if only approximate, potential surface and with it gained entrance into a whole new world of chemistry, experiencing all of the enthusiasm such a vista inspired. We perceived immediately the role of zero point energy in reaction kinetics and our method...made it possible to extend our calculations to all kinds of reactions.”

³⁸The most important is the orientation effect which is related to the need for certain parts of the colliding molecules to come together in order for a collision to be effective [7].

³⁹The rate constant predicted by the collision theory for a bimolecular gas phase reaction is:

$$k(T) = Z_p \rho_{sf} \exp\left(\frac{-E_a}{RT}\right);$$

where Z_p is the size of particle, ρ_{sf} is the steric factor, i.e. the ratio between the preexponential (frequency) factor and collision frequency. The treatment of frequency factor in terms of kinetic theory of gases was developed and supported by many scientists, particularly by Hinshelwood and Moelwyn-Hughes [20].

⁴⁰Johannes Nicolaus Brönsted (1879–1947) was a Danish physical chemist who introduced the protonic theory of acid–base reactions (Brönsted-Lowry theory) in 1923, i.e. in the same year when American physical chemist Gilbert Newton Lewis (1875–1946) proposed his concept of acids and bases, i.e. the Lewis theory of acid–base reactions.

⁴¹British physical chemist Meredith Gwynne Evans (1904–1952) who together with H. Eyring and M. Polanyi is considered the founders of transition state theory together with H. Eyring and M. Polanyi. He was elected a FRS in 1947.

⁴²Awarded Priestley Medal (1975), Elliott Cresson Medal (1969), Irving Langmuir Award (1968), National Medal of Science (1966), Peter Debye Award (1964), Newcomb Cleveland Prize (1932)... H. Eyring was a man who believed that the veracity and simplicity were closely related. Great ideas come from simple people. These are simple ideas that can actually change the world [105].

Later Eyring, Evans, and Polanyi independently developed what has come to be called the transition state theory (absolute rate theory), which provides a way for the calculation of pre-exponential factor for chemical reactions of all kinds [7, 105].

Hinshelwood also published the paper where the correlation effect between P and E_a in terms of potential energy surfaces was discussed [106], and in this work, he also stated that:

“There can be no fundamental difference between the results of a kinetic treatment and those of a thermodynamic treatment. ...the transition state method and the kinetic method of treating reaction velocity problem are very much more similar than they might appear at first sight. The thermodynamic method frequently has the advantage of a greater formal elegance of its equations and a greater generality.”

In this respect, an attempt for the thermodynamic formulation of reaction rates is described in the paper of P. Kohnstamm and F.E.C. Scheffer [107, 108], where they also noted that:

“...not the thermodynamic potential itself, but an exponential function of it would be the function characteristic of the reaction.”

This topic is also deep discussed in the work of M. Pekař [109].

Since the limited space of this chapter does not allow to introduce an immeasurable contribution of many other scientists in the field of reaction kinetics and thermodynamics, it would be suitable to finish this chapter with the quote, that van't Hoff said himself⁴³ [36, 110]:

“A famous name has this peculiarity that it becomes gradually smaller, especially in natural sciences where each succeeding discovery invariably overshadows what precedes.”

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⁴³Van't Hoff had probably on his mind the German chemist A.F. Horstmann (1842–1929) whose important thermodynamic work was eclipsed by that of van't Hoff himself [36].

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