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Introducing the Effective Mass of Activated Complex and the Discussion on the Wave Function of this Instanton

Authored by Petr Ptáček,
Tomáš Opravil and František Šoukal

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Edited by **Petr Ptáček, Tomáš Opravil**
and **František Šoukal**

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Meet the authors

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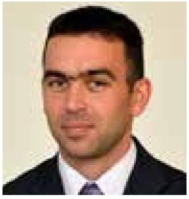
Tomáš Opravil was born in 1978 in Olomouc, Czech Republic. He received his PhD degree in Inorganic Materials Science and Technology from Brno University of Technology, Faculty of Chemistry, in 2009. Since 2009 till now, he has been working at the Institute of Materials Chemistry as an assistant professor and since 2010 at the Materials Research Centre of Brno University of Technology as a senior researcher. Since 2015 till now, he is the head of the Inorganic Materials Group. His current teaching and research activities include chemistry, materials structure and chemistry, heat treatment of silicates, ceramics, refractory materials, special inorganic cements and binders, geopolymers, secondary energy products, etc. Opravil has published over 100 scientific articles, including full-length articles, book chapters and contributions to international conferences; he has registered over 15 national patents and 2 international patents and participated in the development of applied industrial technologies.



František Šoukal was born in 1981 in Trebic, Czech Republic. He received his PhD degree in Inorganic Materials Science and Technology from Brno University of Technology, Faculty of Chemistry, in 2007. Since 2007 till now, he has been working at the Institute of Materials Chemistry as an assistant professor and since 2015 as an associated professor. Since 2010, he has also been working at the Materials Research Centre of Brno University of Technology as a senior researcher and till 2015 has led the Inorganic Materials Group. His current teaching and research activities include chemistry, materials structure and chemistry, heat treatment of silicates, ceramics, refractory materials, special inorganic cements and binders, geopolymers, secondary energy products, etc. Soukal has published over 100 scientific articles, including full-length articles, book chapters and contributions to international conferences; he has registered over 15 national patents and 2 international patents and participated in the development of applied industrial technologies.

Contents

Preface

This short monograph establishes the concept of effective (reduced) mass and effective rate (velocity) of activated complex.

The formulation of these properties, which leans on the results from kinetic approach, which was suggested and described in the previous work (Ceramics International 42 (15); 2016: 16969–16980), enables the calculation of many other properties, such as the most probable speed of activated complex, momentum, energetic density, mass flux, etc., and the definition of two quantum numbers of activated state, i.e., the activation energy and momentum. These two numbers allow to characterize the motion of activated molecule alongside the reaction coordinate as well as the formulation of wave function of pertaining instanton (pseudoparticle). The formulation of these parameters and the wave function for oscillation of activated complex instanton around the equilibrium, but not stable position, i.e., the peak of the energetic barrier, is demonstrated on the example of the process of thermal decomposition of calcite and aragonite. Furthermore, modified expression of Kissinger equation and experimental solution of approximation parameter in the Doyle equation for temperature integral was suggested in this work.

The monograph is organized into three chapters. The first of them deals with a short historical background, which introduces the beginning of chemical kinetics and the formulation of its cardinal rules in the historical context. The readers can get acquainted with the early beginning of chemical kinetics through the works of A.V.G Harcourt, W. Esson, J. Van´t Hoff, H. Dixon, C. Hinshelwood, Moelwin-Hughes, Eyring, Evans, Polanyi, etc. The chapter ends with the invention of transition state (absolute rate) theory, which is briefly described in the next chapter of this monograph.

As was mentioned above, the second chapter is dedicated to the introduction to transition state theory, including the formulation of partition function, the calculation of reaction rate and the frequency factor. Furthermore, the limitation of transition state theory and kinetic isotope effect is also discussed. The last chapter explains the concept of effective mass and effective rate of activated state as well as derived properties mentioned in the first paragraph above.

On behalf of all the authors, I hope that this publication holds your interest. If you, readers, find the published information useful or in some manner inspirational for your work, it will be the nicest reward for us.

Special Thanks

I wish to thank all the readers who spend their time to read this work. Moreover, I wish to thank Halina Szklorzová for the language and grammar correction of this work.

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Chapter 1

A Brief Introduction to the History of Chemical Kinetics

Petr Ptáček, Tomáš Opravil and František Šoukal

Additional information is available at the end of the chapter

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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].

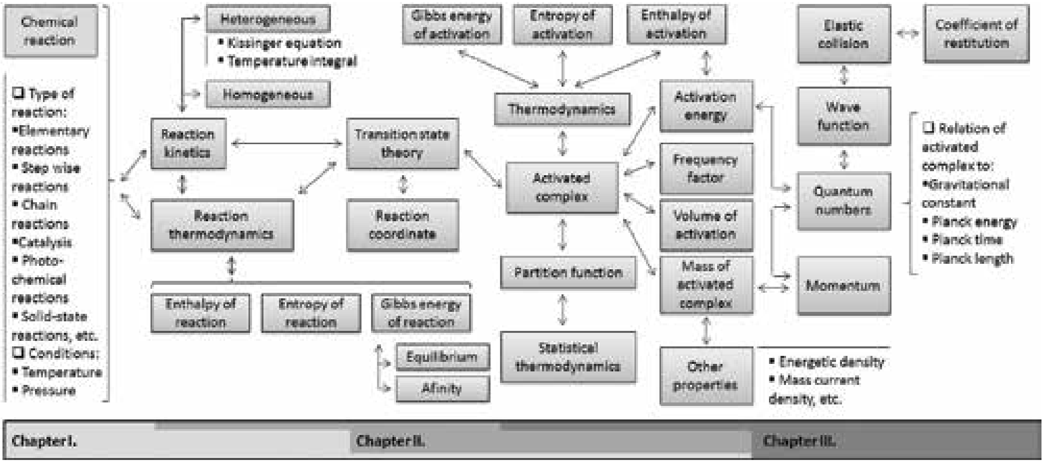

Figure 1. The simplified scheme of the relation between individual topics in this treatise.

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 Liebeg*[1] [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]:

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

---

[1] German 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 Harcourt[2] (1934–1919, **Figure 2a**) is considered to be the first scientist who made a significant contribution in the field of chemical kinetics[3]. 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 problem[4] [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 Esson[4] (1838–1916, FRS in 1869) is the process [6, 7, 12]:

$$K_2Mn_2O_8 + 3\,H_2SO_4 + 5\,H_2C_2O_4 \rightarrow K_2SO_4 + 2\,MnSO_4 + 10\,CO_2 + 8\,H_2O \tag{2}$$

---

[2] He 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].

[3] Up 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]).

[4] A.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]:

$$K_2Mn_2O_8 + 3\,MnSO_4 + 2\,H_2O \rightarrow K_2SO_4 + 2\,H_2SO_4 + 5\,MnO \tag{3}$$

$$MnO_2 + H_2SO_4 + H_2C_2O_4 \rightarrow MnSO_4 + 2\,H_2O + 2\,CO_2 \tag{4}$$

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]:

$$H_2O_2 + 2\,HI \rightarrow 2\,H_2O + I_2. \tag{5}$$

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

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[5] The equation for this quantitative reaction is:

$$2S_2O_3^{2-} + I_2 \rightarrow 2I^- + S_4O_6^{2-}.$$

reaction for another 30 years they did not publish any data on this until 1895 when Harcourt and Esson jointly wrote the Bakerian Lecture[6] [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]:

$$k = A^{'}T^{m} \tag{6}$$

where $\boldsymbol{k}$ is the rate constant and pre-exponential (prefactor or frequency factor) $\boldsymbol{A'}$ as well as $\mathbf{m}$ (ratio $\mathrm{d}\boldsymbol{k}/\boldsymbol{k}$ to $\mathrm{d}\boldsymbol{T}/\boldsymbol{T}$ [21]) are temperature independent constants.

Previously in 1884 Jacobus Henricus van't Hoff[7] (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. Arrhenius[8] (1859–1957, **Figure 2c**) [22]:

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

where $\boldsymbol{A}$, $\boldsymbol{E}_a$, and $\boldsymbol{R}$ are constants, i.e., the frequency factor, the activation energy and universal gas constant (8.314 $\mathrm{J\cdot(K\cdot mol)^{-1}}$), 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 equation[9] (Eq. 6) is theoretically sterile and $\boldsymbol{m}$ is having

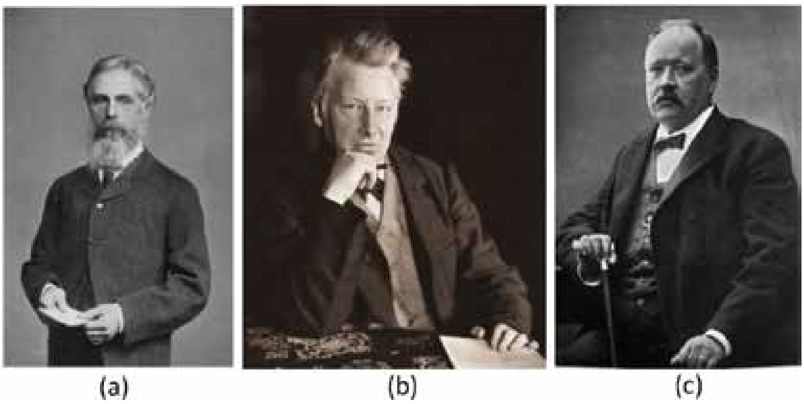

Figure 2. Photographs (all of these pictures belong to free work in the public domain) of A.G.V. Harcourt (a), J.H. van't Hoff by Nicola Perscheid (German photographer (1864–1930) who developed the soft-focus with open depth of field (Perscheid lens) somewhere around 1920) (b), and S.A. Arrhenius (c).

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[6] The medal and prize lecture of the Royal Society originated in 1774 (begun in 1775) as a results 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].

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

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

[9] In 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 $\boldsymbol{A}$ to be proportional to $\boldsymbol{T}^{\mathrm{m}}$, so that Eq. 7 leads to the formula [20]:

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

where the constant $\boldsymbol{A}'$ 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]:

$$H_2O_2 + HI \rightarrow HOI + H_2O; \tag{9}$$

$$HOI + HI \rightarrow H_2O + I_2. \tag{10}$$

Even though Dutch scientist J.H. van't Hoff achieved the recognition through organic chemistry[10] for his pioneer works in the field of stereochemistry [23, 29–32]:

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[10] J.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 an 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 dynamics[11] [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 Ostwald[12] (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.

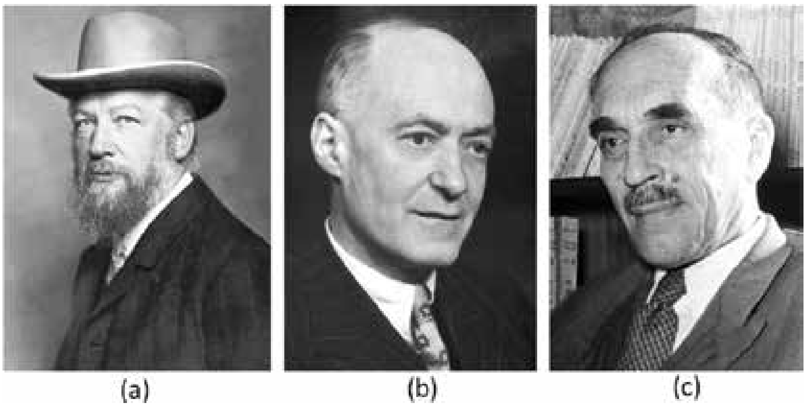

Figure 3. Photographs (all of these pictures belong to free work in the public domain) of W. Ostwald by Nicola Perscheid (German photographer (1864–1930) who developed the soft-focus with open depth of field (Perscheid lens) somewhere around 1920) (a), C.N. Hinshelwood (b), and N.N. Semenov (c).

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[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 constant[13], which is widely known as the van't Hoff equation[14]:

$$\frac{d \ln K}{d\mathrm{T}} = \frac{q}{RT^2}; \tag{11}$$

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

$$\frac{d \ln K}{d\mathrm{T}} = \frac{\Delta H^\circ}{RT^2}; \tag{12}$$

where $\Delta \boldsymbol{H}^\circ$ is the standard enthalpy change for the reaction.

3. The suggestion of a new method for determining the order (molecularity) of a chemical reaction[15] which involves the measuring of rate (r) at various concentrations (c) of the reactant:

$$r = k\, c^n; \tag{13}$$

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

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

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

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 $\boldsymbol{K}$ is affected by temperature: if the heat evolves when the reaction proceeds from left to right ($\boldsymbol{q}$ is negative), the equilibrium constant will decrease if the temperature is raised. Conversely, if $\boldsymbol{q}$ is positive, an increase in temperature will increase $\boldsymbol{K}$.
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. Berthold[16] 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 ($\boldsymbol{k}_1$) and reverse ($\boldsymbol{k}_{-1}$) reactions is equal to the equilibrium constant, the Eqs. 11 or 12 can be treated as follows [36]:

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

Van't Hoff argument was that this relationship could be met only if $\boldsymbol{k}_1$ and $\boldsymbol{k}_{-1}$ vary with temperature in the same manner as does $\boldsymbol{K}$. Expressed in other words he regarded the heat $\boldsymbol{q}$ as the difference between two energy terms $\boldsymbol{E}_1$ and $\boldsymbol{E}_{-1}$:

$$q = E_1 - E_{-1}; \tag{15}$$

so:

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

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

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

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

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[16] Van'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 $\boldsymbol{K}$ (Eq.11) varies with temperature [36, 37, 39].

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

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

$$\ln k = -\frac{E}{RT} + const.; \tag{19}$$

or:

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

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 + D$\boldsymbol{T}^2$, where B and D are the constants. Eq. 18 can be integrated as follows:

$$\ln k = -\frac{B}{RT} + \frac{DT}{R} + const.; \tag{21}$$

or:

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

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

$$\ln k = -\frac{B}{RT} + \frac{C}{R} \ln T + const.; \tag{23}$$

or:

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

where ***m*** = C/***R*** is the constant.[17]

The first and simplest of these possibilities (a) that ***E*** is independent of temperate 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

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[17] The 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 equation[18] [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 ($\boldsymbol{p}$) [7, 41–43].

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

where $\Delta \boldsymbol{V}$ 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 $\boldsymbol{K}$ is $\boldsymbol{k}_1/\boldsymbol{k}_{-1}$ it is possible to introduce so called "possible formula":

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

Without any interpretation of $\Delta \boldsymbol{V}^{\#}$ 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. Sidgwik. 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 explosions[20] [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-

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[18] The 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 $ln\ \boldsymbol{k}$ vs. $\boldsymbol{T}^{-1}$ (please refer to **Figure 2** in the Chapter 2).

[19] Chapman'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].

[20] Some 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 Hinshelwood[21] (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 oxygen[22] [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 reactions[23]). The possibility of chain branching has previously been raised by Danish physicist H.A. Kramers (1894–1952) and Russian scientist Nikolay Nikolayevich Semenov[21] (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 Hartley[25] (1878–1772) concerned to the thermal decomposition of solids [69–71].

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[21] Hinshelwood 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.

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

[23] In 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 Bowen[24] (1898–1980) laid the emphasis on liquids and solids rather than gases. His photochemical work may have been initiated by Hartley's[25] 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 processes[26], 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 dissociated[27]. In other words, one photon brought about the chemical transformation of one molecule[28] as resulted from the investigation of decomposition of chlorine monoxide (Cl_2O) 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 (ClO_2) [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. Nernst[29] [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 phase[30] [7].

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[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. Draper[27], Arthur Eichengrün (1867–1949), T. Grotthuss[27], 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:

$$2\,HI \rightarrow H_2 + I; \tag{27}$$

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

$$HI + hv \rightarrow H + I; \tag{28}$$

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:

$$H + HI \rightarrow H_2 + I; \tag{29}$$

and[31]

$$I + I(+M) \rightarrow I_2(+M); \tag{30}$$

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].

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[31] The 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 Bell[32] 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 tunneling[33] [96].

Bell was one of the first to realize that when light hydrogen; but not heavy hydrogen (deuterium[34]), 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-Hughes[35] 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 gases[37], as follows:

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

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[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 ^{2}H, i.e. the "heavy hydrogen") is a hydrogen isotope with one proton and neutron in nucleus, while the core of "light hydrogen" (^{1}H, 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 $\boldsymbol{P}$ 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's[40] 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. Evans[41] 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 $\boldsymbol{P}$ and $\boldsymbol{A}$ (Eq. 31), particularly the nature of the reaction, the structure of the reactants and the solvent. He also investigated possible correlations between $\boldsymbol{P}$ and $\boldsymbol{E}_\mathrm{a}$ [7]. Shortly before, the work of Henry Eyring[42] (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."*

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[38] The 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].

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

$$\boldsymbol{k}(\boldsymbol{T}) = \boldsymbol{Z}_p \boldsymbol{\rho}_{sf} exp\left(\frac{-\boldsymbol{E}_a}{\boldsymbol{RT}}\right);$$

where $\boldsymbol{Z}_\mathrm{p}$ 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].

[40] Johannes 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.

[41] British 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.

[42] Awarded 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 $\boldsymbol{P}$ and $\boldsymbol{E}_{\mathrm{a}}$ 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 himself[43] [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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Chapter 2

Introduction to the Transition State Theory

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Additional information is available at the end of the chapter

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Abstract

The transition state theory (TST), which is also known as theory of absolute reaction rates (ART) and the theory of activated state (complex), is essentially a refined version of crude collision theory, which treats the reacting molecules as the rigid spheres without any internal degree of freedom. The theory explains the rate of chemical reaction assuming a special type of chemical equilibrium (quasi-equilibrium) between the reactants and activated state (transition state complex). This special molecule decomposes to form the products of reaction. The rate of this reaction is then equal to the rate of decomposition of activated complex. This chapter also explains the limitation of TST theory and deals with the kinetics isotope effect.

Keywords: transition state theory, theory of absolute reaction rates, activated complex, equilibrium constant, reaction rate, kinetics, activation energy, frequency factor, partition function, thermodynamics of activated state, kinetics isotope effect

1. Introduction

> *"Two major findings have, however, stood the test of time. First, there was the unmistakable evidence that molecular collisions play the all-important role in communicating the activation energy to the molecules which are to be transformed and, second, there was the recognition of the activation energy (derivable for the Arrhenius Law of the temperature dependence) as a dominant, though by no means the sole, factor determining reactivity in general."—C.N. Hinshelwood* [1]

The transition state method in chemical kinetics dates back to the important article of French physical chemist René Marcelin (1885–1914) [2, 3] who laid the foundation of the concept of potential energy surface (PES). The transition state theory (TST), which is widely accepted today, describes the rates of elementary reactions[1] on molecular scale. The theory was formulated by Erying and Polanyi in 1935 (The calculation of absolute reaction rates [4]) in order to explain bimolecular reactions based on the relationship between kinetics and thermodynamics [5, 6]. Based on their original assumption that the reaction rates can be calculated absolutely, the theory is also called as the theory of absolute reaction rates (ART) [7].

> *"I showed that rates could be calculated using quantum mechanics for the potential surface, the theory of small vibrations to calculate the normal modes, and statistical mechanics to calculate the concentration and rate of crossing the potential energy barrier. This procedure provides the detail picture of the way for reactions that still dominates the field"* [8].

In other words, TST (ART) theory states that [9]:

> *"Atoms and molecules can collide and combine to form an unstable, high energy complex. When the molecules fall out of this high energy state, they may do so as new and different molecules, or in their original states. The energy required to reach the activated state must be available if the molecules are to change into something new."*

As was introduced in the previous chapter, the term "transition state" was suggested by M. Polanyi and M.G. Evans, who also made a significant contribution to this theory. Today, the TST theory becomes the paradigm for interpretation of the rates of chemical processes[2] as well as their dependence on temperature, medium, structure, and other parameters [10].

The basic assumption of STS theory is the existence of activated state (activated complex[3]), which is formed via the activation of reactants, i.e. the collision between reactant molecules does not form the product of reaction directly. Eyring wrote [4]:

> *"The activated state is because of its definition always a saddle point with positive curvature in all degrees of freedom except the one which corresponds to crossing the barrier for which it is of course negative."*

Since the kinetic energy of colliding molecules[4], possessing sufficient energy and having proper orientation, is transformed into potential energy the energetic state of activated complex is characterized by positive molar Gibbs energy. The standard Gibbs energy of activation (standard free energy of activation) is the difference between the transition state of a reaction and the ground state of reactants [5, 7, 11, 12].

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[1] Single step reactions, which proceed without intermediates, that is, an elementary reaction is assumed to pass through a single transition state [11].

[2] Despite the fact that the formation of transition state was originally developed for chemical reactions, the theory of thermally activated processes is the key factor for any transport phenomena, for example, the thermally activated jump of atom from one interstitial position to another.

[3] From this reason the TST is also known and more appropriately termed as the activated complex theory (ACT) [6].

[4] Hinshelwood [12] shows that the molecular collisions could both activate and deactivate the reactant molecule.

Activated state is then formed as highly energized and then unstable intermediate[5], which has transient existence and decomposes to form the products of reaction. The rate of reaction is given by the definite rate of decomposition of activated complex [5]. The other most important assumption of STS theory is the existence of chemical equilibrium[6] [6, 13] (quasi-equilibrium) between reactants and activated state (complex) [6]. Despite the fact that this equilibrium is different from classical chemical equilibrium, it can be described by the same thermodynamic treatment [14]. It can be then summarized that TST theory assumes that chemical reaction (or any other activated process[2] proceeds as two-stage process:

1. Formation of activated complex;
2. Decomposition of activated complex into the products of reaction;

as is shown in example in **Figure 1**. (Notes: The representation of energetic pathway derived from the intersection of the PES associated with the reaction.) (Since the catalysts provide an alternative reaction mechanism with lower $\boldsymbol{E}_\mathrm{a}$ (**Figure 1(d)**), the rate of reaction increases (Eq. 7 in Chapter 1). This demonstration of significant effect of mechanism on the value of activation energy emphasizes the necessity to know the whole kinetic triplet ($\boldsymbol{E}_\mathrm{a}$, $\boldsymbol{A}$ and $\boldsymbol{n}$) to complete the characterization of reaction kinetics.)

A general stoichiometric equation for the chemical reaction between $\boldsymbol{R}_\mathrm{i}$ chemical species (individuals, that is, atoms, molecules, ions, etc.) in the state marked by the appending (*f*)[7]:

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[5] Activated state is then less stable state than any other occurring during the reaction [6].

[6] Chemical equilibrium is the state in which both, reactants and products are present in the concentrations which have further tendency to change with time [13]. The concept of chemical equilibrium was developed after French chemist Claude Louis Berthollet (1748–1822, elected FRS in 1789) found that some chemical reactions are reversible. Josiah Willard Gibbs (1839–1903) suggested that the equilibrium is attained when the Gibbs free energy of the reaction system under constant temperature and pressure reaches its minimum value (the rate of process in both directions is identical):

$$\Delta_r \boldsymbol{G} = \Delta_r \boldsymbol{G}^\circ + \boldsymbol{RT}\ln \boldsymbol{K} = 0. \tag{a}$$

The relation between the standard Gibbs free energy and the equilibrium constant is given by the equation:

$$\Delta_r \boldsymbol{G}^\circ = -\boldsymbol{RT}\ln \boldsymbol{K}; \tag{b}$$

(please refer also to Eq. 26), at the equilibrium of reaction $\Delta_\mathrm{r}G^\circ = 0$, that is, $\boldsymbol{K} = 1$. The idea regarding the behavior of an equilibrium system when the changes to its reaction conditions occur is given by "Le Châtelier's principle" (Henry Louis Le Châtelier, 1850–1936), which is also known as "The equilibrium law." The equilibrium constant for the process of formation of activated state cannot be measured experimentally [6].

[7] This appending usually refers to solid (*s*), liquid (*ℓ*), gas (*g*) or kind of solvent, the most aqueous solution (*aq*). An example to the general formula Eq. 1, that is, the reaction of formation of carbon monoxide is presented below:

$$\boldsymbol{C}(s) + \frac{1}{2}\boldsymbol{O}_2(a) \Longleftrightarrow \boldsymbol{CO}(g) \Longrightarrow 0 = \boldsymbol{CO}(g) - \boldsymbol{C}(s) - \frac{1}{2}\boldsymbol{O}_2(g) \Longrightarrow \sum_i \boldsymbol{v}_i \boldsymbol{R}_i(f) = 0.$$

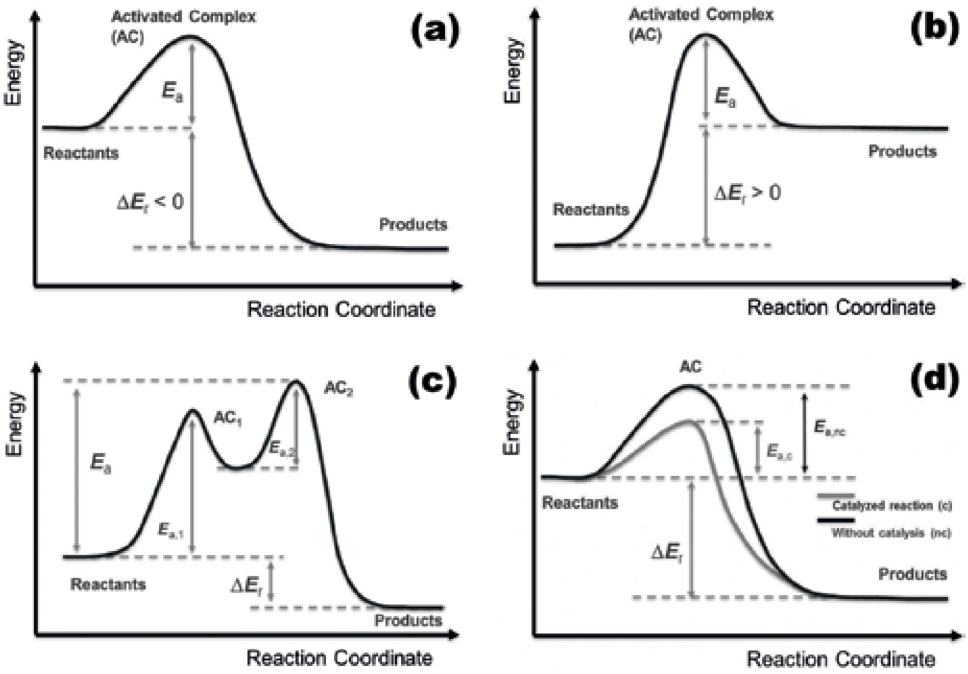

Figure 1. Potential energy diagram (potential energy profile or reaction coordinate diagram for exothermic (a) endothermic (b) multistep process (c) and catalyzed reaction (d).

$$\sum_i \nu_i R_i(f) = 0 \quad \Rightarrow \quad aA(f) + bB(f) + \ldots \Leftrightarrow sS(f) + tT(f) + \ldots \tag{1}$$

where A, B… and S, T… are reactants and products (reaction products), respectively. Integers[8] ν_i = a, b, s, t… are the stoichiometric coefficients[9], i.e. the degree to which a chemical species participates in a reaction, that is conventionally negative for reactants and positive for products.

For the selected case of the three-atom bimolecular reaction of the type:

$$AB + C \leftrightarrow A + BC. \tag{2}$$

It is possible to write:

$$AB + C \leftrightarrow A \ldots B \ldots C \rightarrow A + BC; \tag{3}$$

where $A \cdots B \cdots C$ is an activated complex. The energy difference between the energy of activated complex and reactants is termed as the activation energy ($\boldsymbol{E_a}$).

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[8] From the Latin word “integer” that means “whole.”

[9] The term stoichiometry, which was first used in 1792 by German chemist Jeremias Benjamin Richter (1762–1807), is derived from Greek words “stoicheion” and “metron”, that is, “element” and “measure,” respectively.

Since the equilibrium of activated complex with reactant is assumed, it is possible to define the equilibrium constant of activation:

$$AB + C \leftrightarrow A\ldots B\ldots C; \tag{4}$$

as follows:

$$K^{\#} = \frac{[C^{\#}]}{[AB]\ [C]} = \frac{[C^{\#}]}{\prod_i [C_i]^{\nu_i}}; \tag{5}$$

where $[C^{\#}] = \boldsymbol{K}^{\#}[AB][C]$ denotes the concentrations of activated complexes. The rate of the reaction is then given by the activated complex decomposition rate, i.e.:

$$A\ldots B\ldots C \rightarrow A + BC; \tag{6}$$

which is proportional to $[\boldsymbol{C}^{\#}]$, so that the relation can be written:

$$r = \nu^{\#}[C^{\#}] = \nu^{\#}K^{\#}[AB][C]; \tag{7}$$

where $\boldsymbol{\nu}^{\#}$ is the activated complex decomposition frequency.

According to the statistical thermodynamics, the value of equilibrium constant (Eq. 5) in the reaction 3 is given by the formula:

$$K^{\#} = \frac{Q_0^{\#}}{Q_{AB}\,Q_C}\exp\left(-\frac{E_0}{RT}\right); \tag{8}$$

where $\boldsymbol{E}_0$ is an energetic difference between the energy of activated state (product) and reactants that is given as relative to the energy of atoms in gaseous state at the temperature of 0 K. So in this particular case the value of $\boldsymbol{E}_0 = \boldsymbol{E}_a$. The quantities $\boldsymbol{Q}_0^{\#}$, $\boldsymbol{Q}_{\mathrm{AB}}$, and $\boldsymbol{Q}_{\mathrm{C}}$ are the partition functions of activated state and reactant molecules.

2. Formulation of partition function

The partition function of molecule $\boldsymbol{Q}$, which consists of multiple quantum microstates $\boldsymbol{j}$ (index for the microstate of the system[10]) [15] which share the same energy ε_j, i.e. the energy levels of the system, which are degenerated, can be expressed by the following formula:

---

[10] In statistical mechanics, a microstate is a specific microscopic configuration of a thermodynamic system that the system may occupy with a certain probability in the course of its thermal fluctuation. In contrast, the macrostate of the system refers to its macroscopic properties, such as its temperature and pressure. A macrostate is characterized by a probability distribution of possible states across a certain statistical ensemble of all microstates [15].

$$Q = \sum_j g_j \ \exp\left(-\frac{\varepsilon_j}{k_B T}\right) = \sum_j g_j \ \exp\left(-\beta\,\varepsilon_j\right); \tag{9}$$

where g_j is the number of allowed equimolar quantum microstates (degeneracy factor) and $\boldsymbol{k}_B$ is the Boltzmann constant[11]. The value of thermodynamic beta is defined as:

$$\beta = \frac{1}{k_B T} = \frac{1}{\tau} = \frac{1}{k_B}\frac{dS}{dE} = \frac{\partial \ \ln g_j}{\partial \ \varepsilon_j}; \tag{10}$$

and the exponential factor exp $(-\boldsymbol{\beta}\boldsymbol{\varepsilon}_j)$ is known as the Boltzmann factor, $\boldsymbol{S}$ is the entropy and $\boldsymbol{E}$ is the energy. $\boldsymbol{\tau}$ in Eq. 10 is termed as the fundamental temperature that has a unit of energy, i.e. the joule ($J = kg{\cdot}m^2/s^2$). The denominator $\boldsymbol{k}_B\boldsymbol{T}$, i.e. the product of the Boltzmann's constant and thermodynamic temperature, that expresses an energy on molecular scale, is also termed as the constant of distribution.

The partition function is then the summation of terms $exp\left(-\boldsymbol{\varepsilon}_j/\boldsymbol{k}_B\boldsymbol{T}\right)$ for all allowed quantum states (*j*) of the system, which can be considered for the sum of energy of independent moves, such as [16]:

• Translation: the translational energy for one-dimensional motion is usually given by the following equation:

$$Q_{trans} = \frac{1}{2} m \overline{v}^2 = \frac{\overline{p}^2}{2m}; \tag{11}$$

where $\boldsymbol{m}$ is the mass and $\overline{\boldsymbol{p}}$ is the momentum of particle.

• Rotation: the rotational (angular) kinetic energy around the axis of rotation is given by the formula:

$$Q_{rot} = \frac{1}{2} I \omega^2; \tag{12}$$

where $\boldsymbol{\omega}$ is the angular velocity and $\boldsymbol{I}$ is the moment of inertia around the axis of rotation. The comparison of Eqs. (11) and (12) shows that the moment of inertia in rotating system is the parameter analogical to mass and the angular velocity is a quantity, which is analogical to the velocity.

• Vibration: the reactants, e.g, the species AB, C in Eqs. 2–4, have 3 N-6 or 3 N-5 vibrational degrees of freedom ($\boldsymbol{n}_{\mathrm{VDF}}$, please refer also to footnote 16) as they are non-linear or linear, respectively. The same can also be extended to the activated complex ($A{\cdots}B{\cdots}C$) that possesses

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[11] Heat (energy), which is required to increase the temperature by 1 K for one gas particle, i.e. $\boldsymbol{k}_B = \boldsymbol{R}/\boldsymbol{N}_A$ = (1.380648 52 ± 0000000 79)·10^{-23} J·K^{-1}, where N_A = (6.022140857 ± 0000000 074)·10^{23} mol^{-1} is Avogadro constant (Lorenzo Romano Amedeo Carlo Avogadro, 1776–1856). The constant was named after Austrian physicist Ludwig Eduard Boltzmann (1844–1906).

$3{\cdot}(\boldsymbol{N}_{AB} + \boldsymbol{N}_C) - 6$ or $3{\cdot}(N_{AB} + N_C) - 5$ vibrational degrees of freedom if it is non-linear or linear, respectively.

- Energy of the electron states.

So it is possible to write the formula:

$$Q = Q_{trans}\ Q_{rot}\ Q_{vibr}\ Q_{el}. \tag{13}$$

The calculation of this energy then requires the information about allowed energetic levels and their degeneration in the molecule, which can be determined via the methods of quantum mechanics from the structure of this molecule, i.e., the molecular parameters.

As was already mentioned, the activated complex moving along one-dimensional reaction pathway, which is known as the reaction coordinate (collective variable), is decomposed to the product of the reaction. That enables to split the partition function into two parts:

1. Contribution (one particular degree of freedom) that corresponds to the shift (vibration) along the reaction coordinate ($\boldsymbol{Q}_{\mathrm{rk}}$), which leads to the decomposition of activated complex;

2. Contribution corresponding to another molecular degree of freedom ($\boldsymbol{Q}_{\mathrm{oth}}$); so it can be written:

$$Q^{\#} = Q_{rk}\ Q_{oth}. \tag{14}$$

The allowed energetic state for quantum oscillator vibrating along the reaction coordinate results from the solution of Schrödinger equation:

$$\varepsilon_n = \frac{nh\nu}{k_B T}; \tag{15}$$

where $\boldsymbol{n} = 0, 1, \dots \infty$, $\boldsymbol{\nu}$ is the oscillator frequency and $\boldsymbol{h}$ is the Planck constant. The $\boldsymbol{Q}_{\mathrm{rk}}$ partition function can be then expressed by the formula:

$$Q_{rk} = \sum_{n=0}^{\infty} \exp\left(-\frac{nh\nu}{k_B T}\right). \tag{16}$$

Using the following substitution:

$$\frac{nh\nu}{k_B T} = x; \tag{17}$$

in order to solve this geometric series (Eq. 16), the relation can be written:

$$Q_{rk} = \frac{1}{1 - \exp\left(-\frac{h\nu}{k_B T}\right)}. \tag{18}$$

A small value of $\boldsymbol{\nu}$ means that the product $\boldsymbol{h\nu} \gg \boldsymbol{k_B T}$ and the denominator in Eq. 18 should be developed in every convergent Taylor[12] (Maclaurin[13]) series (expansion or polynomial):

$$\begin{aligned} \exp\left(-\frac{h\nu}{k_B T}\right) &= 1 - \frac{h\nu}{k_B T} + \frac{1}{2}\left(\frac{h\nu}{k_B T}\right)^2 - \frac{1}{6}\left(\frac{h\nu}{k_B T}\right)^3 + \frac{1}{24}\left(\frac{h\nu}{k_B T}\right)^4 - \cdots \\ &= 1 - \frac{h\nu}{k_B T} \end{aligned}. \tag{19}$$

It is then possible to write that[14]:

$$Q_{rk} \cong \frac{1}{1 - 1 + \frac{h\nu}{k_B T}} = \frac{k_B T}{h\nu}. \tag{20}$$

---

[12] The power series of infinite sum of term calculated from the values of the function's derivatives at a single point (p):

$$f(x) = \sum_{n=0}^{\infty} f^{(n)}(p) \frac{(x-p)^n}{n!}.$$

[13] The Maclaurin series (polynomial), that is, the Taylor series[14] expansion of a function $f(x)$ around $x = 0$, is an infinite sum:

$$f(x) = \sum_{n=0}^{\infty} f^{(n)}(x) \frac{x^n}{n!} = f(0)\frac{x^0}{0!} + f'(0)\frac{x^1}{1!} + f''(0)\frac{x^2}{2!} + f'''(0)\frac{x^3}{3!} + f^{(4)}(0)\frac{x^4}{4!} + \cdots \tag{a}$$

Since:

$$f(x) = \exp(-x) \Longrightarrow f(0) = 1. \tag{b}$$

$$f'(x) = -\exp(-x) \Longrightarrow f'(0) = -1. \tag{c}$$

$$f''(x) = \exp(-x) \Longrightarrow f''(0) = 1. \tag{d}$$

$$f'''(x) = -\exp(-x) \Longrightarrow f'''(0) = -1, etc.; \tag{e}$$

The series (a) is then expanded:

$$e^{-x} = 1 - x + \frac{x^2}{2} - \frac{x^3}{6} + \frac{x^4}{24} - \frac{x^5}{120} + \frac{x^6}{720} \cdots; \tag{f}$$

That is, the series that is equal to Eq. 19. The series is named after Scottish mathematician Colin Maclaurin (1698–1746).

[14] This particular vibrational degree of freedom, which corresponds to the vibration along the reaction coordinate ($\boldsymbol{Q}_{\text{rk}}$ contribution to the partition function), disappears, when the activated complex becomes dissociated into products (Eq. 6), so:

$$Q_{rk} = \lim_{n_{VDF}^{rk}} \frac{1}{1 - \exp\left(-\frac{h\nu}{k_B T}\right)} = \frac{1}{1 - \left(1 - \frac{h\nu}{k_B T}\right)} = \frac{\boldsymbol{k_B T}}{\boldsymbol{h\nu}}$$

Since the frequency of this vibration means the frequency of decomposition of activated state into the product ($\boldsymbol{\nu}^{\#}$), the combination with Eq. 5 and substitution to Eq. 7 enable to formulate the rate of reaction as follows:

$$\begin{aligned} r = \nu^{\#}\left[C^{\#}\right] = \nu^{\#}K^{\#}\,[AB][C] = \\ \nu^{\#}\frac{kT}{h\nu^{\#}}\frac{Q_{oth}}{Q_{AB}\,Q_{C}}\exp\left(-\frac{E_a}{RT}\right)[AB][C]^{;} \end{aligned} \tag{21}$$

and then:

$$r = \frac{k_B T}{h}\frac{Q_{oth}}{Q_{AB}\,Q_{C}}\exp\left(-\frac{E_a}{RT}\right)[AB][C]. \tag{22}$$

3. Calculation of the reaction rate

Since the kinetic equation for the reaction 2 can be written as follows[15]:

$$r = k\ \ [AB]\,[C]; \tag{23}$$

where $\boldsymbol{k}$ is the rate constant, the combination of Eqs. (8) and (22) then leads to the formula:

$$k = \frac{k_B T}{h}\frac{Q_{oth}}{Q_{AB}\,Q_{C}}\exp\ \left(-\frac{E_a}{RT}\right); \tag{24}$$

which enables to calculate the reaction rate from the properties of activated complex and reactants. Unfortunately, the evaluation of partition function of the activated state is usually difficult due to the lack of information about its structure. Therefore, the following formula is often used:

$$k = \frac{k_B T}{h}K^{+}; \tag{25}$$

where $\boldsymbol{K}^{+}$ is the equilibrium constant of activation (Eq. 4), which does not include particular part of partition function that corresponds to the vibration along the reaction coordinate. Assuming the parity $\boldsymbol{K}^{+} = \boldsymbol{K}^{\#}$, the following relation can be written:

$$-RT\ \ \ln K^{\#} = \Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \tag{26}$$

---

[15] Eq. 23 expresses a fundamental approach of empirical kinetics, which is based on experimental experiences with reactions, which occur in homogenous phase. The rate of reaction is the product of two functions:

$$\boldsymbol{r} = \boldsymbol{k}(\boldsymbol{T})\boldsymbol{f}(\boldsymbol{c}_i)$$

One of them is the function of temperature only ($\boldsymbol{k}(\boldsymbol{T})$, Eq. 20 in Chapter 1) and the second depends on concentrations of reactants in the reaction (Eq. 1).

The combination of above introduced Eqs. 24–26 then leads to the expression of general form of so-called Eyring-Polanyi equation[16]:

$$k = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\#}}{R}\right) \exp\left(-\frac{\Delta H^{\#}}{RT}\right) = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^{\#}}{RT}\right) = \nu^{\#} K^{\#}; \tag{27}$$

where term $\boldsymbol{\nu}^{\#} = \boldsymbol{k_B T/h}$ is known as the universal frequency (frequency factor). The combination of Eq. 27 with universal frequency of activated complex ($\boldsymbol{\nu}^{\#}_{AC}$, please refer to Eq. 115 in Chapter 3) enables to solve the relation between the Arrhenius (Eq. 20 in Chapter 1) and Eyring (Eq. 27) rate constants as follows:

$$\boldsymbol{k}_{Arrhenius} = \boldsymbol{A} \cdot exp\left(-\boldsymbol{E}_a/\boldsymbol{RT}\right) = \boldsymbol{k}_{Eyring}/\boldsymbol{e} = \left(\boldsymbol{\nu}^{\#}\boldsymbol{K}^{\#}\right)/\boldsymbol{e} \Longrightarrow \boldsymbol{k}_{Arrhenius}/\boldsymbol{k}_{Eyring} = 1/\boldsymbol{e}.$$

Since every vibration does not necessarily result in the decomposition of activated complex into the products, the proportionality constant (transmission coefficient) $\boldsymbol{\kappa}$ can be introduced into the Eyring equation (Eq. 27) to get the relation[17] [17, 18]:

$$\begin{aligned} k = \kappa \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\#}}{R}\right) \exp\left(-\frac{\Delta H^{\#}}{RT}\right) = \\ \kappa \frac{k_B T}{h} \exp\left(-\frac{\Delta G^{\#}}{RT}\right) = \kappa \nu^{\#} K^{\#} = k^{\#} K^{\#} \end{aligned}; \tag{28}$$

where $\boldsymbol{k}$ is assumed to be directly proportional to the frequency of the vibrational mode, which is responsible for the decomposition of the activated complex into products. Furthermore, the transmission coefficient ($\boldsymbol{\kappa}$) is in most cases considered to be close to unity, so Eq. 28 comes to Eq. 27. Since $\boldsymbol{k}^{\#} \geq \boldsymbol{k}$ the value of transmission coefficient is then $0 \leq \boldsymbol{\kappa} \leq 1$.

The temperature dependence of the rate constant k is then given by the Arrhenius law (Eq. 20) introduced in Chapter 1. The comparison of this equation (Eq. 27) to Arrhenius enables to derive that for the processes occurring in the condensed phases $\boldsymbol{E}_a \approx \Delta \boldsymbol{H}^{\#}$[18] [6, 19]:

$$\Delta H^{\#} = E_a - RT; \tag{29}$$

and the frequency factor can be considered as independent on temperature. The entropy of activation can be calculated from the relation:

$$\Delta S^{\#} = R \ln\left(\frac{hA}{k_B T}\right); \tag{30}$$

and:

---

[16] The formulation of this equation resembles the van't Hoff-Arrhenius Equation (Eq. 7 in Chapter 1).

[17] The term $\boldsymbol{\kappa}(\boldsymbol{k_B T/h})$ in Eq. 28 is close to 10^{12} s^{-1} for many bond vibrations [17].

[18] The term is usually not to be higher than 10 kJ·mol^{-1}, while the activation energy is mostly higher than 100 kJ·mol^{-1}. Therefore, the final difference should be below 10%.

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}. \tag{31}$$

The linearized (logarithmic) form of Eq. 27, which can be written as follows:

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^{\#}}{R}\frac{1}{T} + \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\#}}{R}; \tag{32}$$

enables to determine the enthalpy ($\Delta \boldsymbol{H}$) and the entropy of activation ($\Delta \boldsymbol{S}^{\#}$) from the investigation of reaction rate (kinetics) of reaction at different temperatures. The plot (so-called Eyring plot) of *ln* ($\boldsymbol{k}/\boldsymbol{T}$) versus reciprocal temperature ($1/\boldsymbol{T}$) provides straight line with the slope of $-\Delta \boldsymbol{H}^{\#}/\boldsymbol{R}$ and the intercept $ln\,(\boldsymbol{k}_B/\boldsymbol{h}) + \Delta \boldsymbol{S}^{\#}/\boldsymbol{R}$.

The examples of Arrhenius (a) and Eyring plot (b) for the process of thermal decomposition of calcite[19], i.e. the trigonal polymorph of $CaCO_3$, in an inert atmosphere of N_2:

$$CaCO_3(s_1) \overset{T}{\leftrightarrow} CaO(s_2) + CO_2(g); \tag{33}$$

are introduced in **Figure 2**.

The slope of Arrhenius plot (($-\boldsymbol{E}_a/\boldsymbol{R}$), please refer to Eq. 20 in Chapter 1) is used to write the relation for the activation energy (Arrhenius activation energy) as follows:

$$E_a = -R\left(\frac{\partial \ln k(T)}{\partial(1/T)}\right)_p = -p\left(\frac{\partial \ln k(T)}{\partial(1/V_m(T))}\right)_p; \tag{34}$$

where $V(T)$ is the volume of ideal gas at temperature $\boldsymbol{T}$. That means that:

$$\ln\ k(T) = \ln\ A - \frac{E_a}{pV_m(T)} \quad \Rightarrow \quad k(T) = A\ \exp\left(-\frac{E_a}{pV_m(T)}\right). \tag{35}$$

The isobaric character of the process means that the relation between Eqs. 20, 34 and 35 is given by the Charles's Law[20] [20]:

$$\frac{V_m}{T} = \text{const.} = \frac{\text{R}}{\text{p}}; \tag{36}$$

which is also known as the law of volumes.

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[19] This example uses the data of original thermogravimetric (TGA, please refer to Footnote^2 in Chapter 3) kinetic experiments (TG-DTA analyzer, SDT Q600, Thermal Instruments) performed for the purpose of this book with transparent variety of calcite, that is, optical calcite or "Iceland Spar," from Leping, China. Please compare also the slope of both plots in **Figure 2** with respect to the discussion on Eq. 29, that is, the fact that $\boldsymbol{E}_a \approx \Delta \boldsymbol{H}^{\#}$. Furthermore, the plot $\Delta \boldsymbol{H}^{\#}$ vs. $\boldsymbol{T}$ is straight line with the slope-$\boldsymbol{R}$ and the intercept $\boldsymbol{E}_a$.

[20] French inventor and scientist Jacques Alexandre César Charles (1746–1823). The law was formulated by Joseph Louis Gay-Lussac (1778–1850) in 1802 [20], who gave credit to unpublished work by J. Charles.

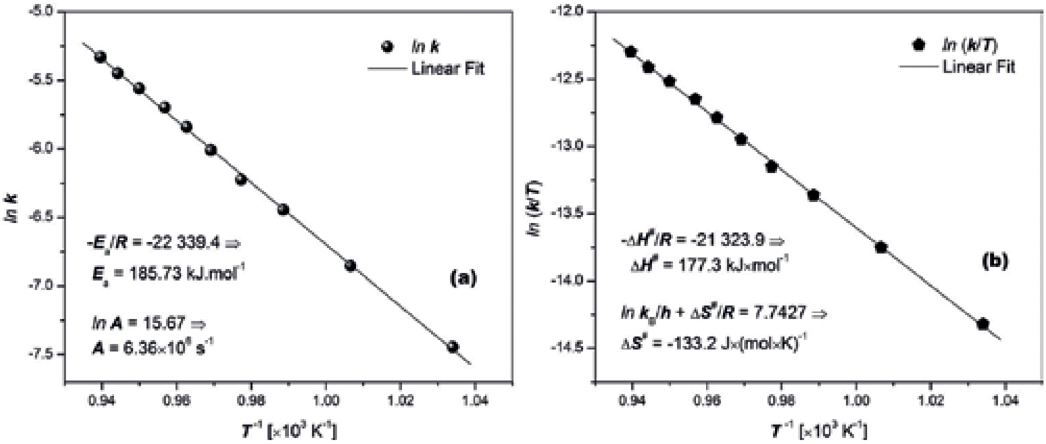

Figure 2. An example of calculation of enthalpy and entropy of activation for the process of thermal decomposition of calcite: the temperature dependence of the rate constant presented in the form of Arrhenius plot (a) and Eyring plot (b).

4. Frequency factor as the function of temperature

The temperature dependence for experimental (marked by subscript *exp*), i.e. usual form of the Arrhenius equation (Eq. 20 in Chapter 1), and theoretically calculated (*th*) reaction rate constants can be written as follows:

$$k_{\exp} = A_{\exp} \ \exp\left(-\frac{E_{a,\exp}}{RT}\right); \tag{37}$$

and

$$k_{th} = B(T) \ \exp\left(-\frac{W}{RT}\right); \tag{38}$$

where the pre-exponential factor ***B***(***T***) is the function of temperature and ***W*** is the difference between energy of reactants and activated complex in the basic state. According to the transition state theory, the value of ***B***(***T***) is approximately proportional to the temperature.

The equations for the experimental and calculated (theoretical) activation energy can be then written as follows:

$$E_{a,\exp} = RT^2 \frac{d \ln k_{\exp}}{dT}; \tag{39}$$

and:

$$E_{a,th} = RT^2 \frac{d \ln k_{th}}{dT} = RT^2 \frac{d \ln B(T)}{dT} + W = \Theta \ RT + W; \tag{40}$$

where:

$$\Theta = T\ \frac{d\ln\ B(T)}{dT}. \tag{41}$$

The substitution to Eq. 38 then leads to the formula:

$$k_{th} = B(T)\ \exp(\Theta)\exp\left(-\frac{E_{th}}{RT}\right). \tag{42}$$

In the case that:

$$B(T) = CT; \tag{43}$$

where **C** is a constant, it can be written that:

$$\Theta = T\frac{d\ln B(T)}{dT} = 1; \tag{44}$$

and then:

$$k_{th} = B(T)\exp\left(-\frac{E_{th}}{RT}\right). \tag{45}$$

That also means the parity:

$$E_{th} = E_{\exp}; \tag{46}$$

and:

$$A_{th} = B(T) = CT. \tag{47}$$

Since the value of **Θ** is close to one, the pre-exponential (frequency) factor can be considered as independent of temperature[21].

5. Limitations of transition state theory (TST)

As was mentioned above, the universality of the transition state theory provides a conceptual foundation for understanding the course and rate of elementary reaction on molecular scale. On the other hand, the TST theory can fail in some cases, for example [21, 22]:

1. If applied to each elementary step of multistep reactions (**Figure 1c**).

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[21] Please refer also to the discussion on Eq. 8 in Chapter 1. This equation considers the frequency factor as proportional to **T^m**.

2. When the intermediates are very short-living, so that the Boltzmann distribution[22] of energies is not reached before the process continues to the next step.

3. The transition state theory also fails for some reactions at high temperatures due to the more complex motions of molecules or at very low temperatures due to the quantum tunneling.

Furthermore, the TST is also based on the assumption that atomic nuclei behave according to the classic mechanics. It is assumed that unless atoms or molecules collide with enough energy to form the transition structure (activated complex), the reaction does not occur. However, according to the quantum mechanics, for any barrier with a finite amount of energy, there is a possibility that particles can still tunnel across the barrier [21].

6. Kinetic isotope effect

The discovery of isotopes[23] [23, 24] of the elements resulted from a thorough study of the properties of radioactive substances during the first years of the twentieth century.

> *"The word isotope signifies 'the same place' in allusion to isotopes occupying the same place in the Periodic Table"* [24].

The conclusion that certain species of atom have identical chemical properties but different radioactive properties comes from chemical studies, which accompanied the study of radioactivity. The fundamental theory of the chemical isotope effect was established in 1947 by Urey [25] and Bigeleisen and Mayer who stated [26]:

> *"It is pointed out that the possibility of chemical separation of isotopes is a quantum effect. This permits a direct calculation of the difference in the free energies of two isotopic molecules."*

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[22] The Boltzmann distribution (*F*), which is also called the Gibbs distribution, is a probability distribution which expresses the probability that the system is in a certain state for given energy and temperature of the system. The ratio of Boltzmann distribution for two energetic states is known as the Boltzmann factor that depends on the energy difference between these states:

$$\frac{\boldsymbol{F}(state\ 2)}{\boldsymbol{F}(state\ 1)} = \exp\left(\frac{\boldsymbol{E}_1 - \boldsymbol{E}_2}{\boldsymbol{kT}}\right).$$

[23] The history of isotopes fittingly commences with the discovery of radiothorium, a new product in the thorium disintegration series, by Sir William Ramsay (1852–1916) and Otto Hahn (1879–1968) in 1905 [24]. The isotopes were discovered and proved by English radiochemist Frederick Soddy (1877–1956, Nobel Prize for chemistry in 1921) and physical chemist Kasimir Fajans (1887–1975). Together with Ernest Rutherford (1871–1937), F. Soddy provided the base towards the understanding of radioactivity:

"…radioactive substances were transformed from one element to another."

The word isotope was first suggested by Scottish doctor Margaret Todd (1859–1918) in 1913, a family friend of F. Soddy. The experimental method that first revealed the existence of isotopes among the successive products of radioactive change had been applied in 1907.

The kinetic isotope effect (KIE) is the effect of isotopic substitution on the reaction rate[24]. Early research on the effect of the difference in mass between isotopes upon the rate of chemical transformation has been limited entirely to the very lightest elements, especially hydrogen; although the effect of isotopic mass upon the rate of many physical properties has been extend throughout the periodic table [3, 27, 28]. The heavy atom kinetic isotope effect studies became possible after the Second World War with the availability of radioactive isotopes and mass spectrometers for the measurement of stable isotope ratios [29].

The origin of all isotope effects lies in the differences of various vibrational modes of a molecule which arise when one isotope is substituted with another [17]. There are two kinds of KIE recognized [30, 31]:

1. Primary kinetics isotope effect, i.e. the effect of isotopic substitution on the rate constant of transformation of isotopologues. Isotopologues are molecules which differ only in their isotopic composition (the number of isotopic substitutions or also isotopic identities), for example, protium containing water (H_2O[25]) and deuterium (please refer to Footnote[36] in Chapter 1) **bearing semiheavy (HDO) or heavy water (D_2O)**. Other examples are CH_4 and CH_3D, or $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, and $^{12}C^{18}O^{16}O$, and so on.

For the multiple isotopic substitution (two or more rare isotopes) in isotopologues, the name "clumped" isotopologues are used. If isomers have the same number of each isotopic atoms but they occupy different symmetrically non-equivalent positions, e.g. $^{14}N^{15}N^{16}O$ and $^{15}N^{14}N^{16}O$, they are termed as isotopomers, i.e. isotopic isomers [30, 31].

For heavy atoms (heavy atoms isotope effects), the maximum reaction rate constant ration is proportional to the square root of inverse isotopic masses:

$$\frac{k_x}{k_y} = \sqrt{\frac{M_y}{M_x}}. \tag{48}$$

2. Secondary kinetics isotope effect (steric isotope effect), which is attributed to different vibrational amplitudes of isotopologues, e.g. the mean-square of amplitudes of vibration of C-H bonds is greater than that of C-D bonds

One of the other early studies of KIE was the work of Beeck et al. [32] and the ^{14}C effect in the decarboxylation of malonic acid (propanedioic acid, $CH_2(COOH)_2$) and bromomalonic acid by Yankwich and Calvin [28]. The effect of isotopic mass on certain chemical equilibria was used to separate the isotopes. From this point of view, the classic theory (formulated in 1947 [25, 26]), i.e. the mass-dependent theory, assumes that at a constant temperature, the isotope enrichment factor is proportional to the isotopic mass difference and inversely proportional to the product of masses of two isotopes. For as long as four decades after the formulation of the mass-dependent theory, a failure of the isotope effect in chemical exchange equilibria to follow

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[24] It should also be pointed that isotopic composition of material contains a lot of information regarding its origin and history [25, 31].

[25] With regard to oxygen, there are isotopologues $H_2{}^{18}O$ and $H_2{}^{16}O$.

the theory has not been reported [33]. The mass-independent isotope fractionations were first observed for O and S in 1983 [34].

Also, the course of crystallization could be affected by isotopic composition hence rapidly grown crystals could have a disequilibrium elemental and isotopic concentrations, which result from the diffusion limitation and diffusivity differences in the growth medium [35]. The isotopic composition is also affected by the presence of simple organic molecules and could be a crystal-face-dependent [36]. The variations in oxygen ($^{18}O/^{16}O$) and hydrogen ($^{2}H/^{1}H$) isotope ratios of water and ice are powerful tools in hydrology and ice core studies [37]. The fractionation of Cu, Fe, and Zn isotopes during the oxidative weathering of sulfide-rich rocks could also have an impact on the distributions of stable Fe, Cu, and Zn isotopes in natural waters [38].

Historically, the isotope techniques came into use in catalysis in 1960s with the investigation of oxygen and other molecules reactivity [39]. The study of dynamics of isotope transfer under steady-state reaction conditions, the so-called Steady-State Isotopic Transient **Kinetic** Analysis (SSITKA), is successfully employed in the investigation of mechanism of heterogeneous catalytic reactions [40, 42–45] and to estimate the surface concentrations of intermediates and reaction rate coefficients [40].

SSITKA method was initially developed by Happel [41, 46], Bennett [47], and Biloen [42, 48].

> *"…proper understanding of heterogeneous catalysis is linked to understanding of transient effects. The interpretation requires a model based on elementary steps, and various steps may be rate-determining as the conversion and temperature vary."* [47].

The basic idea of the isotope dynamic experiment is as follows. When the reaction under study achieves the steady state, the initial feed gas flow is stepwise replaced by another flow differing in the isotope composition, but absolutely identical in a chemical one. The composition of feed gas and reaction products is continuously measured using a quadrupole mass spectrometer [40, 45].

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Chapter 3

Introducing an Approach to Effective Mass of Activated Complex

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Additional information is available at the end of the chapter

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Abstract

This chapter provides the information about the concept of effective mass and effective velocity of the activated complex and its connection to the transition state theory. Therefore, these parameters are of essential importance for the field of homogenous as well as heterogeneous kinetics. They also prove to be useful for the calculation of many other properties of activated state, such as momentum, energetic density, mass flux, etc., as will be demonstrated on the example of thermal decomposition of calcite and aragonite. Since the activation energy and the momentum of activated state enable to complete the characterization of motion of this instanton (pseudoparticle) alongside the reaction coordinate, these parameters can be then considered as two quantum numbers of activated complex. The quantum numbers of activated state, that is, the activation energy and momentum, also explain the relation of activated complex to Planck energy, length and time, as well as to the Gravitational constant. This idea was also applied to derive the wave function of activated complex pseudoparticle, which is affected by the isotopic composition of the sample and polymorphism as well. Furthermore, the findings introduced in this chapter enable to derive and propose the modified Kissinger equation and experimental solution for the approximation parameter in the Doyle equation of temperature integral.

Keywords: activated complex, activated state, effective mass, effective velocity, mean lifetime, half-life, group velocity, phase velocity, momentum, kinetics, transition state theory, activation energy, quantum numbers, Schrödinger equation, instanton, pseudoparticle, wave function, modified Kissinger equation, temperature integral, approximation parameter, thermal decomposition of solids

1. Chapter introduction and basic assumptions

> *"Transition state theory has a long history and bright future"*—Truhlar et al [1].

The definition of effective or reduced mass of activated complex ($\boldsymbol{M}^{\#}$) is one of the basic assumptions of new kinetic approach to the calculation of activation energy, which was suggested and described in previous work in detail [2]. In its simplest form, the formula of this approach can be written as follows:

$$E_a = const.'' T_{m,\Theta 1}^2 M^{\#} = \left(const.''' T_{m,\Theta 1}\right)^2 M^{\#} = RT_{m,\Theta 1}^2 \frac{\partial \ln Q^{\#}}{\partial T} \tag{1}$$

where $\boldsymbol{T}_{m,\Theta 1}$ is the thermodynamic (absolute Kelvin scale) temperature of peak measured by thermal analysis (TA [3–7], such as DTA[1], DTG[2], DSC[3]…) with the heating rate (**Θ**) of 1 K·min^{-1} or extrapolated to this heating rate (please refer to Eq. 12 and **Figure 2(b)**), $\boldsymbol{Q}^{\#}$ is the partition function of activated molecule (please refer to discussion of Eq. 24 and Eqs. 8 and 14 in Chapter 2), and:

$$\begin{aligned} const.'' &= \frac{R}{M^{\#}}\frac{\partial \ln Q^{\#}}{\partial T} = \frac{k_B}{m_{(1)}^{\#}}\frac{\partial \ln Q^{\#}}{\partial T} = const.'''^{2} \\ &\approx \operatorname{csch}(e) + 1 = 1 + \frac{1}{\sinh(e)} = 1 + \frac{2}{e^e - e^{-e}} = 1.1326\ldots \end{aligned} \tag{2}$$

is the square of temperature-rate kinetic coefficient[4] (***const.'''*** = 1.0642… m·K^{-1}·s^{-1})[5], which can be e.g. also represented by the following series:

$$\boldsymbol{const.''} \approx 1 + 2\boldsymbol{e}^{-\boldsymbol{e}} \sum_{k=0}^{\infty} \boldsymbol{e}^{-2\boldsymbol{e}k} \tag{3}$$

where $\boldsymbol{m}_{(1)}^{\#} = \boldsymbol{M}^{\#}/\boldsymbol{N}_A$ is the mass of activated molecule and the constant ***e*** = 2.71828… is the base of natural logarithms, that is the Euler's number[6], which is also known as the Napier's

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[1] Differential thermal analysis (DTA) is the TA method where the difference between heat flow rates into a sample and inert reference material (usually alumina) is measured [3]. The calibration of DTA and DSC[3] instruments uses melting and phase transition of temperature standard reference materials such as pure metals (In, Sn, Zn, Ag, Au…) or salts KNO_3, $KClO_4$, Ag_2SO_4, K_2CrO_4, quartz, K_2SO_4, $BaCO_3$ and $SrCO_3$. A comprehensive effort related to standardization and nomenclature of TA methods was launched in 1965 by the International Confederation for Thermal Analysis (ICTA) [4, 6]. In 1992, the name was changed to International Confederation for Thermal Analysis and Calorimetry (ICTAC) in order to reflect close relationship between TA and calorimetry.

[2] DTG, where adjective derivative "D" is pertaining 1st derivative (mathematical) of TG (thermogravimetric) or TGA (Thermogravimetric Analysis) curve (thermoanalytical or ICTAC discouraged collocation thermal curve) [3].

[3] Differential scanning calorimetry (DSC) is the TA method where the heat flow rate difference between sample and reference material is measured [3].

[4] The numerical value of ***const.***″ to 20 decimal places is 1.13255326439210664113… The decimal approximation for ***const.*** (Eq.2) is then 1.06421485818988011399…

[5] In order to avoid the confusion with the rate constant of reaction, this work uses the abbreviation "***const.***", instead of letter "***k***".

constant[7]. This infinite sum will converge very rapidly. The value of ***const.″*** is reached even for the first two members of this series.

More general expression for Eq. 1 is given by the following formula:

$$E_a \Theta^{\frac{(2-d)\,RT_{m,\Theta 1}}{E_a}} = const.'' \;\; T^2_{m,\Theta} M^{\#} \tag{4}$$

where $\boldsymbol{d} = ln\left(\boldsymbol{T}_{m,\Theta\neq 1}/\boldsymbol{T}_{m,\Theta 1}\right)/\,ln\,\boldsymbol{\Theta}$ is the constant exponent (power) of power function (please refer to Eq. 12) with the scaling factor $\boldsymbol{T}_{m,\Theta 1}$:

$$T_{m,\Theta} = T_{m,\Theta 1}\,\Theta^d \quad \Rightarrow \quad \Theta = \left(\frac{T_{m,\Theta}}{T_{m,\Theta 1}}\right)^{\frac{1}{d}}. \tag{5}$$

Since the value of power in Eq. 5 is $\boldsymbol{d} \ll 1$, the relation 4 can also be written in the following form [2]:

$$E_a \Theta^{\frac{2\,RT_{m,\Theta 1}}{E_a}} \approx const.'' \;\; T^2_{m,\Theta} M^{\#}. \tag{6}$$

For example, the DTG peak (numerical derivation of thermogravimetric experiment) for the thermal decomposition of calcite (Eq. 33 in Chapter 2) heated with the rate of 1 K·min^{-1} under inert atmosphere of nitrogen is shown in **Figure 1**.

Since the activation energy of this reaction (Eq. 33 in Chapter 2) is already known (please refer to **Figure 2(a)** in Chapter 2), it is possible to calculate the mechanism of the process using the formula[8] of Augis and Bennett [8]:

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[7] The constant (irrational transcendental number) was actually discovered by the Swiss mathematician Jacob Bernoulli (1655–1654), who solved (1683) the value of the formula:

$$\lim_{n\to\infty}\left(1+\frac{1}{n}\right)^n = e. \tag{a}$$

Bernoulli is the most known for the solution (1696) of the Bernoulli differential equation:

$$y' + P(x)y = Q(x)y^n; \tag{b}$$

where $\boldsymbol{n}$ can be any real number ($\boldsymbol{R}$) but $\boldsymbol{n} \neq 0$ and 1.

[8] With the exception of possible change in the reaction mechanism of the process, which may take place with increasing temperature (please refer to discussion of **Figure 10**), the value of kinetic coefficient should stay constant over the given interval of temperature (please refer to Footnote 9). Within the same interval it should be also insensitive to the shift of peak temperature with heating rate (Eqs.8 and 12). In the case that the average value of FWHM over the investigated interval of heating rate is applied for the calculation of kinetic exponent, the obtained dependence can be accurately approximated by the power law. Despite of the fact, that coefficient of variation is usually lower than 10%, the non-zero value of skewness and kurtosis of data means that results are not normally distributed. Therefore, the calculation of kinetic exponent with the average value of FWHM over the investigated interval of heating rate cannot be recommended.

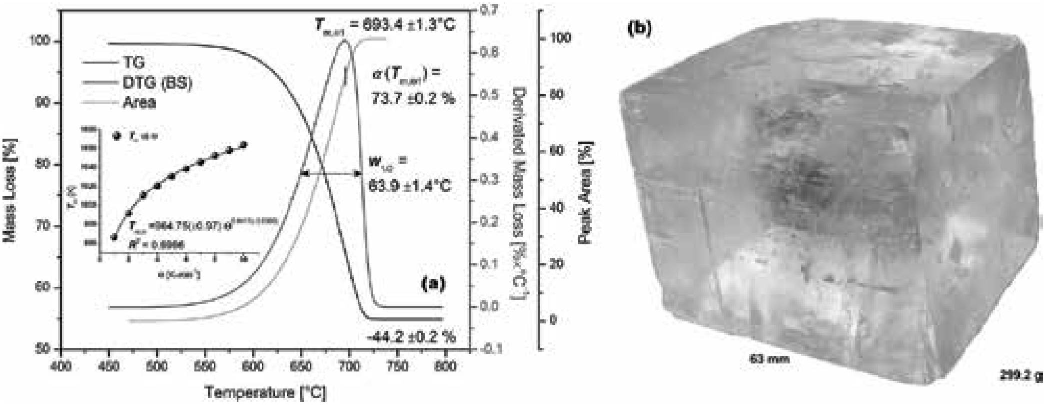

Figure 1. Thermal decomposition of calcite (20 mg) heated with the rate of 1 K·min^{-1} under inert (N_2) atmosphere (a) (Since the kinetics of the process was evaluated from DTG only, the thermogram (DTA curve) is not plotted in this graph.). DTG peak was subtracted to baseline (BS). The plot of T_m vs. Θ is shown in detail. The photograph (photography from author's mineralogical collection) of analyzed calcite specimen in the variety of well-developed transparent rhomb of Iceland spar (b).

$$n = \frac{2.5\ RT_m^2}{w_{1/2}\ E_a} \tag{7}$$

where R is the universal gas constant (8.314 J·K^{-1}·mol^{-1}), n is a dimensionless exponent of Avrami equation (kinetic coefficient)[9] [9–12], which is related to the mechanism of the process also known as the kinetic exponent) and $w_{1/2}$ is the full width at half maximum of peak (FWHM). According to Christian [13], this particular value of n = 1.64 corresponds to the zero or decreasing nucleation rate where the growth of new phase is controlled by the diffusion.

Before we continue, it is also interesting to solve the nature of apparent change of kinetic coefficient with heating rate. This behavior results from the effect of heating rate on the peak temperature and full width at half maximum of peak (Eq. 7), while the value of activation energy stays constant (please check this assumption with regard to the discussion of Eqs. 19–24 in Chapter 1 and Footnote 44). Both dependencies can be accurately approximated by the power law:

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[9] Together with the activation energy and the frequency factor, the kinetic coefficient is the part of so-called kinetic triplet. There is no clear physical interpretation for this constant (n, reaction "order", nucleation rate, growth morphology, etc.), as well as for so-called effective overall reaction rate constant or temperature-dependent factor (k, which depends on the nucleation as well as on the growth rate) in the Avrami equation:

$$\alpha = 1 - exp\left(-[kt]^n\right);$$

where t is the time and α is the degree of conversion (fractional conversion, formed (crystalized) volume fraction). The Arrhenius type of equation (Eq. 7 in Chapter 1) is usually assumed for the temperature dependence of $k(T)$. It should also be pointed out that the equation was independently developed several times. Therefore, it is also known as the Johnson and Mehl [12] - Avrami [9, 10] - Kolmogorov [11] (KJMA) equation.

$$T^2_{m,\Theta} = T^2_{m,\Theta 1} \quad \Theta^a = \frac{n\, w_{1/2,\Theta 1} E_a}{2.5R} \quad \Theta^a \tag{8}$$

and:

$$w_{1/2,\Theta} = w_{1/2,\Theta 1} \quad \Theta^b = \frac{2.5R}{n\, const.'' M^\#} \quad \Theta^b = \frac{18.352}{n M^\#} \quad \Theta^b. \tag{9}$$

where $\boldsymbol{T^2_{m,\Theta 1}}$ and $\boldsymbol{w_{1/2,\Theta 1}}$ are the scale factors (coefficients) and $\boldsymbol{a}$ an $\boldsymbol{b}$ are the scaling exponents for argument $\boldsymbol{\Theta}$, respectively.

With regard to introducing the approach to the compensation of the effect of heating rate on calculated value of kinetic exponent, Eqs. 7–9 can be combined and further treated as follows:

$$n = \frac{2.5 \ \ RT^2_{m,\Theta 1}}{w_{1/2,\Theta 1} \ \ E_a} = \frac{2.5 \ \ RT^2_{m,\Theta}}{w_{1/2,\Theta} \ \ E_a} \quad \Theta^{b-a} \tag{10}$$

where the kinetic coefficient, the fraction ($2.5\, \boldsymbol{RT^2_{m,\Theta}}/\boldsymbol{w_{1/2,\Theta}E_a}$) as well as the correction term $\boldsymbol{\Theta^{b-a}}$ are all dimensionless and $\boldsymbol{T^2_{m,\Theta 1}}/\boldsymbol{T^2_{m,\Theta}} = \left(\boldsymbol{w_{1/2,\Theta 1}}/\boldsymbol{w_{1/2,\Theta}}\right)\boldsymbol{\Theta^{b-a}}$. It can also be derived, that the activation energy is:

$$E_a = \frac{2.5 \ \ RT^2_{m,\Theta 1}}{w_{1/2,\Theta 1} \ \ n} = \frac{2.5 \ \ RT^2_{m,\Theta}}{w_{1/2,\Theta} \ \ n} \quad \Theta^{a-b}. \tag{11}$$

Using the experimental data for the abovementioned example of the process of thermal decomposition of calcite, the dependence of $\boldsymbol{T^2_{m,\Theta}}$, $\boldsymbol{w_{1/2,\Theta}}$ and $\boldsymbol{\Theta^{b-a}}$ on heating rate is shown in **Figure 2(a)**.

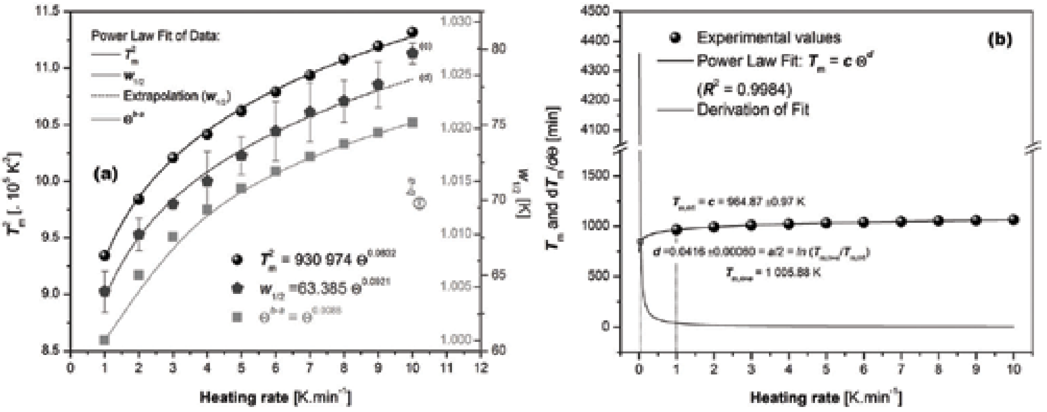

Figure 2. Change of T^2_m, $w_{1/2}$ and Θ^{b-a} with heating rate (a) and dependence of peak temperature on heating rate (b). Excluding the last outlying value (c), the fit was extrapolated to the heating rate of 10°C·min^{-1} (d).

It is obvious that the power dependence of the peak temperature (**T_m**) on heating rate (**Θ,** please refer also to previous work [2]) is:

$$T_{m,\Theta} = c\ \Theta^{d} = T_{m,\Theta 1}\ \Theta^{\frac{a}{2}} \tag{12}$$

where $\boldsymbol{c} = \boldsymbol{T}_{m,\Theta 1}$ (Eq. 5). In contrast to the scale factor, the nature of scale coefficient $\boldsymbol{d}$ is much more puzzling. The first derivation of Eq. 12 according to the heating rate gives an equation:

$$\frac{\partial T_{m,\Theta}}{\partial\ \Theta} = cd\ \Theta^{d-1} = T_{m,\Theta 1}\ \ln\left(\frac{T_{m,\Theta=e}}{T_{m,\Theta 1}}\right)\Theta^{\frac{a}{2}-1}. \tag{13}$$

Figure 2(b) shows the function (Eq. 12) and its derivation (Eq. 13) with the intersection point for $\boldsymbol{\Theta} = \boldsymbol{d}$.[10]. It can also be written that:

$$d = \ln\left(\frac{T_{m,\Theta=e}}{c}\right)\Big/\ln\left(e\right) = \ln\left(\frac{T_{m,\Theta=e}}{T_{m,\Theta 1}}\right) = a - \ln\left(\frac{T_{m,\Theta=e}}{T_{m,\Theta 1}}\right) = \frac{a}{2} \tag{14}$$

where $\boldsymbol{T}_{m,\Theta=e}$ is the peak temperature calculated (Eq. 12) for the heating rate equal to the Euler number.

Since the formula obtained by the first derivation of Eq. 9 according to the heating rate is analogical to Eq. 13:

$$\frac{\partial w_{1/2,\Theta}}{\partial\ \Theta} = b\,w_{1/2,\Theta 1}\ \Theta^{b-1} \tag{15}$$

it can be treated with similar manner. Analogically to Eq. 14, it can be written:

$$b = \ln\left(\frac{w_{1/2,\Theta=e}}{w_{1/2,\Theta 1}}\right). \tag{16}$$

Eqs. 8, 12, 14 and 17 then provide the set of important parameters, which can have interesting utilization in many branches of heterogeneous kinetics. For example, it enables to eliminate the constant term from Kissinger Equation [14, 15]:

$$\ln\left(\frac{\Theta}{T_m^2}\right) = -\frac{E_a}{RT_m} + \mathrm{C}. \tag{17}$$

The formulation of $\boldsymbol{C}$ for $\boldsymbol{\Theta} = 1$ and $\boldsymbol{e} = (\boldsymbol{T}_{m,\Theta=e}/\boldsymbol{T}_{m,\Theta 1})^{\boldsymbol{1/d}}\,{}^\circ C{\cdot}min^{-1}$ (Eqs. 5 and 12) enables to write the following relations:

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[10] The ratio of derivation (Eq. 13) to its function (Eq. 12) is:

$$\frac{\boldsymbol{cd}\ \boldsymbol{\Theta}^{\boldsymbol{d}-1}}{\boldsymbol{c}\ \boldsymbol{\Theta}^{\boldsymbol{d}}} = \frac{\boldsymbol{d}}{\boldsymbol{\Theta}} \tag{a}$$

so $\boldsymbol{d}/\boldsymbol{\Theta} = 1$ if $\boldsymbol{d} = \boldsymbol{\Theta}$.

$$\begin{array}{l} \ln\left(\dfrac{1}{T^2_{m,\Theta 1}}\right) = -\dfrac{E_a}{RT_{m,\Theta 1}} + C \quad \Rightarrow \quad C = \dfrac{E_a}{RT_{m,\Theta 1}} - \ln\left(T^2_{m,\Theta 1}\right) \quad [\Theta = 1] \\ 1 - \ln\left(T^2_{m,\Theta=e}\right) = -\dfrac{E_a}{RT_{m,\Theta=e}} + C \quad \Rightarrow C = \dfrac{E_a}{RT_{m,\Theta=e}} - \ln\left(T^2_{m,\Theta=e}\right) + 1 \quad [\Theta = e] \end{array} . \qquad (18)$$

The substitution from Eqs. (8) and (18) to Eq. 17 then leads to the following relation for the effective mass of activated complex[11]:

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[11] It is then possible to write the relation:

$$\frac{\boldsymbol{E_a}}{\boldsymbol{RT}_{m,\Theta 1}} - 2\ln \boldsymbol{T}_{m,\Theta 1} = \frac{\boldsymbol{E_a}}{\boldsymbol{RT}_{m,\Theta=e}} - 2\ln \boldsymbol{T}_{m,\Theta=e} + 1 \qquad \text{(a)}$$

which can be further treated as follows:

$$\ln\frac{\boldsymbol{T}^2_{m,\Theta=e}}{\boldsymbol{T}^2_{m,\Theta 1}} = \boldsymbol{a}\ln \boldsymbol{e} = \boldsymbol{a} = \frac{\boldsymbol{E_a}}{\boldsymbol{R}}\left(\frac{1}{\boldsymbol{T}_{m,\Theta=e}} - \frac{1}{\boldsymbol{T}_{m,\Theta 1}}\right) + 1. \qquad \text{(b)}$$

The combination of (b) with Eq. 1 and further treatment leads to the relation:

$$\boldsymbol{E_a} = const.'' \; T^2_{m,\Theta 1}M^{\#} = \frac{\boldsymbol{R}\,(a-1)}{\frac{1}{T_{m,\Theta=e}} - \frac{1}{T_{m,\Theta 1}}} \Longrightarrow \boldsymbol{M}^{\#} = \frac{\boldsymbol{R}\,(a-1)}{const.''\left(\frac{\boldsymbol{T}^2_{m,\Theta 1}}{\boldsymbol{T}_{m,\Theta=e}} - \boldsymbol{T}_{m,\Theta 1}\right)}. \qquad \text{(c)}$$

Using the general solution of Eq. 18:

$$\boldsymbol{C} = \frac{1}{\boldsymbol{a}}\ln\left(\frac{\boldsymbol{T}^2_{m,\Theta}}{\boldsymbol{T}^2_{m,\Theta 1}}\right) - \ln \boldsymbol{T}^2_{m,\Theta} + \frac{\boldsymbol{E_a}}{\boldsymbol{RT}_{m,\Theta}}. \qquad \text{(d)}$$

A modified Kissinger equation can be derived:

$$\frac{2\,(\boldsymbol{a}-1)\ln\frac{T_{m,\Theta 1}}{T_{m,\Theta}}}{\boldsymbol{a}} = (1-\boldsymbol{a})\ln\boldsymbol{\Theta} = -\frac{\boldsymbol{E_a}}{\boldsymbol{R}}\left(\frac{1}{\boldsymbol{T}_{m,\Theta}} - \frac{1}{\boldsymbol{T}_{m,\Theta 1}}\right); \qquad \text{(e)}$$

where the plot of $(1-\boldsymbol{a})\ln\boldsymbol{\Theta}$ versus $(1/\boldsymbol{T}_{m,\Theta} - 1/\boldsymbol{T}_{m,\Theta 1})$ is the straight line with the slope (gradient) of $-\boldsymbol{E_a}/\boldsymbol{R}$ (please refer also to Eqs. 8 and 14). The value of **C** can be then calculated from Eq.18 or Eq. (d).
It is also obvious that:

$$\frac{\boldsymbol{T}^2_{m.\Theta=e}}{\boldsymbol{T}^2_{m,\Theta 1}} = \boldsymbol{e}^a \Rightarrow \frac{\boldsymbol{T}_{m,\Theta=e}}{\boldsymbol{T}_{m,\Theta 1}} = \sqrt{\boldsymbol{e}^a} = \boldsymbol{e}^d \text{ and } \ln\left(\frac{\boldsymbol{T}^2_{m,\Theta=e}}{\boldsymbol{T}^2_{m.\Theta 1}}\right) = \boldsymbol{a}. \qquad \text{(f)}$$

That means that the dependence of peak temperature on the heating rate (Eq. 8) can be ascertained from only two measurements carried out with the heating rate $\boldsymbol{\Theta} = 1$ and $\boldsymbol{e}$ (please refer to the Footnote 7). The same data can also be used for direct calculation of effective mass of activated complex (Eq. 19) and then for the activation energy (Eq. 1). The frequency factor can then be directly calculated as follows:

$$\boldsymbol{A} = \frac{2.5\exp\left(\frac{\boldsymbol{E_a}}{\boldsymbol{RT}_{m,\Theta 1}}\right)}{60\,\boldsymbol{w}_{1/2,\Theta 1}}; \qquad \text{(g)}$$

where the denominator expresses the peak's FWHM ($60\,\boldsymbol{w}_{1/2,\Theta 1}/\boldsymbol{\Theta}\ \left[s^{-1}\right]$) measured with the heating rate $\boldsymbol{\Theta} = 1\ K{\cdot}min^{-1}$, while the numerator is dimensionless (please refer also to Eq. 54). Since the kinetic exponent can be calculated from Eq. 7, whole kinetic triplet (please refer to Footnote 9) can be determined by this method.

$$M^{\#} = \frac{R\left(\ln\frac{T^2_{m,\Theta=e}}{T^2_{m,\Theta 1}} - 1\right)}{const.''\left(\frac{T^2_{m,\Theta 1}}{T_{m,\Theta=e}} - T_{m,\Theta 1}\right)} = \frac{R\ (a-1)}{const.''\left(\frac{T^2_{m,\Theta 1}}{T_{m,\Theta=e}} - T_{m,\Theta 1}\right)}. \tag{19}$$

This relation provides an easy experimental way for the determination of effective mass of activated complex from only two TA[1] experiments. Furthermore, the modified Kissinger equation can be derived by similar way (please refer to Eq. (e) in Footnote 11).

Another example is the application of Eq. 16 in the experimental solution of approximation parameter $\boldsymbol{B(x)}$ in the empirical Doyle equation for temperature integral $\boldsymbol{p(x)}$ [16]:

$$\mathrm{p(x)} = 7.03 \cdot 10^{-3} \exp\left(x\,B(x)\right) \tag{20}$$

in the following form[12]:

$$\mathrm{p(x)} = 7.03 \cdot 10^{-3} \exp\left(x\,\frac{T_{m,\Theta=e}}{T_{m,\Theta 1}}\right) = 7.03 \cdot 10^{-3}\ \ \exp\left(x\sqrt{e^a}\right) \tag{21}$$

where the quantity of $\boldsymbol{x} = \boldsymbol{E_a/RT}$. The published value for the term $\boldsymbol{B(x)}$ ranges from 1.195 to 1.034 with the average value of 1.052 [17, 18]. Suggested Eq. 21 then provides a reasonable experimental solution for the parameter $\boldsymbol{B(x)}$ in particular reaction system, for example, $\boldsymbol{B(x)} = 1.043$ for the process of thermal decomposition of calcite[13].

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[12] In further work, we dealt with the most important formulation of modified equation, where the approach of compensation of the mutual influence between the transport of heat and the transport of mass was applied.

[13] The processes of thermal decomposition of calcite (**Figure 1**) and aragonite (**Figure 11**) show $\boldsymbol{B(x)}$ = 1.043 and 1.040 (please refer also to the footnote 51). When using the experimental data from previous work focused on the kinetics of thermal decomposition of strontium carbonate [39]:

$$SrCO_3 \longleftrightarrow SrO + CO_2(g); \tag{a}$$

the value of $\boldsymbol{B(x)}$ is 1.036 for α-(orthorhombic) and 1.045 for β-$SrCO_3$ (hexagonal) polymorph. Presently studied process of thermal decomposition of barium carbonate:

$$BaCO_3 \longleftrightarrow BaO + CO_2(g); \tag{b}$$

$\boldsymbol{B(x)}$ = 1.003. Therefore, the value of $\boldsymbol{B(x)}$ decreases in the following order:

$$CaCO_3 - SrCO_3 - BaCO_3; \tag{c}$$

that is, with increasing relative atomic mass of Alkaline Earth Element (AEE) atom, and the value is also lower for high-temperature (hexagonal) phase than for low-temperature polymorph of carbonate. It was also recognized that the value of $\boldsymbol{B(x)}$ is not affected by the size of crystallites in the sample.

Another example could be the dehydroxylation step during the process of thermal decomposition (400–700°C) of kaolinite [15]:

$$Al_2O_3{\cdot}2\ SiO_2{\cdot}2\ H_2O \longrightarrow Al_2O_3{\cdot}2\ SiO_2 + 2\ H_2O(g); \tag{d}$$

In which the parameter $\boldsymbol{B(x)}$ = 1.031.

Since the average value of $\boldsymbol{B}(\boldsymbol{x})$ is then very close to the temperature-rate kinetic coefficient (***const.'''*** = 1.064… $\mathrm{mK^{-1}s^{-1}}$), there is also another experimental proof for previously suggested approximation of the average value of parameter $\boldsymbol{B}_{av}(\boldsymbol{x})$ [2]:

$$\mathrm{B_{av}}\,(\mathrm{x}) = const.''' = \sqrt{const.''} = \sqrt{\operatorname{csch}(e) + 1}. \tag{22}$$

A deeper information about the approximation of the temperature integral term $\boldsymbol{p}(x)$[14] can be found in the following literature [17, 19–25].

2. Effective mass and derived properties of activated complex

The relation between Augis and Bennett equation (Eq. 7), ***const.''*** and $\boldsymbol{M}^{\#}$ was already solved in the previous work as follows [2]:

$$const.'' = \frac{2.5\ R}{nM^{\#}w_{1/2,\Theta 1}} \Rightarrow M^{\#} = \frac{2.5\ R}{const.''\,n\,w_{1/2,\Theta 1}} = \frac{E_a}{const.''\,T^2_{m,\Theta 1}}. \tag{23}$$

Since Eq. 23 contains three constants, it is also possible to write:

$$\begin{aligned} M^{\#} &= \frac{2.5\ R}{const.''}\frac{1}{n\,w_{1/2,\Theta 1}} = 18.352\ \frac{1}{n\,w_{1/2,\Theta 1}} = \frac{R}{const.''}\frac{\partial \ln Q^{\#}}{\partial T} \quad \Rightarrow \\ \frac{\partial \ln Q^{\#}}{\partial T} &= \frac{const.''}{R}M^{\#} = \frac{2.5}{n\,w_{1/2,\Theta 1}} = \frac{E_a}{RT^2_{m,\Theta 1}} = \frac{T'}{T^2_{m,\Theta 1}} = \alpha_{Q^{\#}} \quad \left[K^{-1}\right] \end{aligned} \tag{24}$$

where $\boldsymbol{T}' = \boldsymbol{E}_a/\boldsymbol{R}$ (please refer to Eq. 39) and $\boldsymbol{\alpha}_{Q^{\#}}$ is the coefficient that describes how the partition function of the object changes with the change in temperature. Eq. 24 also means that the term $\partial\, ln\, \boldsymbol{Q}^{\#}/\partial\, \boldsymbol{T}$ is coded directly in the shape of peak of thermoanalytical curve. Since the unit of this term corresponds to the reciprocal temperature, for example, for applied example of the process of thermal decomposition of calcite, it is possible to calculate:

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[14] Well known approximations of $\boldsymbol{p}(\boldsymbol{x})$ are provided by, e.g. Doyle [23]:

$$p(x) \cong \frac{1}{x}; \tag{a}$$

Coats and Redfern [20]:

$$p(x) \cong \left(1 - \frac{2}{x}\right)/x; \tag{b}$$

and Gorbatchev [25]:

$$p(x) \cong \frac{1}{x+2}. \tag{c}$$

$$\frac{\partial ln\, \boldsymbol{Q}^{\#}}{\partial \boldsymbol{T}} = \boldsymbol{\alpha}_{Q^{\#}} = 2.391{\cdot}10^{-2}K^{-1};$$

and to derive the temperature dependence of partition function on the temperature as follows:

$$\boldsymbol{Q}^{\#}(T_2) = \boldsymbol{Q}^{\#}(T_1)\, exp\left(\boldsymbol{\alpha}_{Q^{\#}}[\boldsymbol{T}_2 - \boldsymbol{T}_1]\right).$$

Furthermore, for $\boldsymbol{n} = 1$, that is, for the first (Eqs. 28–30) and pseudo-first order reactions[15], the value of parameter $\boldsymbol{M}^{\#}$ is given by the equation:

$$M^{\#} = \frac{18.352}{w_{1/2,\Theta 1}} \Rightarrow \frac{\partial \ln Q^{\#}}{\partial T} = \frac{2.5}{w_{1/2,\Theta 1}}[n = 1]. \tag{25}$$

For the example of thermal decomposition of calcite (Eq. 33 in Chapter 2) mentioned above, it is possible to calculate that $\boldsymbol{M}^{\#} = 0.1755$ kJ·mol^{-1} (**Table 1**)[16]. Furthermore, Eq. 24 means that:

$$M^{\#} \propto \frac{1}{n}. \tag{26}$$

Parameter of activated complex	E_a [kJ·mol^{-1}]	$\boldsymbol{A}$ [10^6 s^{-1}]	$\boldsymbol{n}$	$\boldsymbol{T}'$ [K]	$\boldsymbol{M}^{\#}$ [kg·mol^{-1}]	$\boldsymbol{V}^{\#}$ [m^3·mol^{-1}]
	185.73	6.36	1.64	22339.4	0.1755	1.833
	$\boldsymbol{\rho}^{\#}$ [kg·m^3]	$\overline{v}_x$ [m·s^{-1}]	$\boldsymbol{\delta}$ [m]	$\boldsymbol{t}_\delta$ [s]	$\overline{\boldsymbol{j}}^{\#}$ [kg·m^{-2}·s^{-1}]	$\overline{\boldsymbol{p}}^{\#}$ [kg·m·s^{-1}·mol^{-1}]
	$9.576{\cdot}10^{-2}$	1028.6	$1.86{\cdot}10^{-4}$	$1.57{\cdot}10^{-7}$	98.504	255.35

The value needs to be divided by Avogadro constant (Footnote 11 in Chapter 2) to calculate the momentum of single activated molecule, that is, $\overline{\boldsymbol{p}}^{\#}_{(1)} = 4.24{\cdot}10^{-22}$ for calcite.

Table 1. Kinetic triplet and parameters of activated complex for the process of thermal decomposition of calcite (Eq. 33 in Chapter 2).

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[15] The concertation of one reactant in the second-order reaction of the type:

$$A + B \longrightarrow Products; \tag{a}$$

could be considered to be constant, that is, if $\boldsymbol{B}$ is in a great excess with respect to $\boldsymbol{A}$, so its concentration remains almost unchanged during the reaction. Therefore, it can be written:

$$-\frac{d[A]}{dt} = \boldsymbol{k}[A][B] = \boldsymbol{k}'[A]; \tag{b}$$

where $\boldsymbol{k}'$ is the pseudo-first rate constant of the reaction.

[16] The substitution of data from **Figure 1(a)** and **Table 1** to Eq. 1 enables to calculate the activation energy:

$$E_a = 1.1326{\cdot}966.55^2{\cdot}0.1755 = 185.73{\cdot}10^3 J{\cdot}mol^{-1};$$

where $\boldsymbol{T}_{\mathrm{m},\Theta 1} = 693.4 + 273{,}15 = 966.55$ K (please refer to **Figure 2(a)**).

The effective mass of activated state is then indirectly proportional to the reaction mechanism, the value of which is also affected by the values of $\boldsymbol{T}_{\mathrm{m}}$ and $\boldsymbol{w}_{1/2}$[17] (please refer to Eq. 7). For the case of two different samples of the same species, such as two samples of calcite but of different crystallinity (1 and 2), the denominator of Eq. 25 should be very much the same value:

$$\frac{n_{(1)}}{n_{(2)}} \cong \frac{w_{1/2,\,(2)}}{w_{1/2,\,(1)}}. \tag{27}$$

This relation then introduces the law, which enables to keep the change in mass when the reactants pass into an activated state. Small observed differences are most probably caused by the combination of different isotopic compositions (please refer to Section 6 in Chapter 2), different content of admixtures in the sample and an experimental error.

The value of $\boldsymbol{M}^{\#}$ depends on the reaction mechanism, which is technically speaking often more complicated than simply written form of chemical equation for the process. For example, Eq. 33 in Chapter 2 is formally classified as the first-order reaction of the type [26]:

$$A \to \text{Products} \quad \Rightarrow \quad -\frac{\mathrm{d[A]}}{\mathrm{dt}} = k[A] \tag{28}$$

which means that the rate of the process is a linear function of the concentration of reactant [$\boldsymbol{A}$], that is, there is a linear dependence of the plot *ln* [$\boldsymbol{A}$] vs. time ($\boldsymbol{t}$). The separation of variables in Eq. 28 and their integration leads to the formula:

$$\int_{[A]_0}^{[A]_t} \frac{\mathrm{d[A]}}{[A]} = -\int_0^t k\,dt \quad \Rightarrow \quad \ln\frac{[A]_t}{[A]_0} = -kt \tag{29}$$

so:

$$[A]_t = [A]_0 \exp\,(-kt). \tag{30}$$

However, the experimental value of $\boldsymbol{n}$ shows that real course of the process of thermal decomposition of calcite could be much more complicated, which is demonstrated below. It can be then concluded that the value of effective mass of activated state is affected by the mechanism of reaction. Therefore, there may not always be the direct relation to the stoichiometry of usual transcript of the reaction. It should be pointed out that scientific literate contains tremendous number of works dealing with the topic of thermal decomposition of $CaCO_3$, for example [27–32], etc.

Eq. 1 can also be combined with Eq. 34 in Chapter 2 to provide the relation:

---

[17] For example, using calcite with higher sizes of crystallites leads to the increase of $\boldsymbol{T}_{\mathrm{m}}$ and $w_{1/2}$ as well. Therefore, the nature of applied sample, its treatment (purification, intensive milling process, etc.) and applied conditions of analysis may also affect the mechanism of the investigated process, that is, the value of parameter $\boldsymbol{M}^{\#}$ as well.

$$M^{\#} = \frac{-R\left(\frac{\partial \ln k}{\partial \frac{1}{T}}\right)_p}{const.''\, T^2_{m,\Theta 1}}. \tag{31}$$

From that it can be derived that:

$$M^{\#} = -\frac{R}{const.''\, T^2_{m,\Theta 1}} \frac{\ln\left(\frac{k_2}{k_1}\right)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \tag{32}$$

and:

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{const.''\, T^2_{m,\Theta 1} M^{\#}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right). \tag{33}$$

For the small difference between $\boldsymbol{T}_1$ and $\boldsymbol{T}_2$, the approximation can also be written[18]:

$$\begin{gathered}
\ln\left(\frac{k_2}{k_1}\right) \approx \frac{const.''\, T^2_{m,\Theta 1} M^{\#}}{R}\left(\frac{T_2 - T_1}{T_1^2}\right) \quad \Rightarrow \\
\ln\left(\frac{k_2}{k_{\left(T_{m,\Theta 1}\right)}}\right) = \frac{const.''\, M^{\#}}{R}\left(T_2 - T_{m,\Theta 1}\right) \quad \left[T_1 = T_{m,\Theta 1}\right].
\end{gathered} \tag{34}$$

This equation can next be transformed to the formula:

$$M^{\#} \approx \frac{23}{\pi \Delta T} \ln\left(\frac{k_2}{k_1}\right). \tag{35}$$

This equation has an important implication that:

$$23\, const.'' \approx R\pi = \frac{pV^{\#}}{T'}\pi. \tag{36}$$

The combination of Eqs. (23) and (36) leads to the formula:

---

[18] The solution of the limit (refer to the right side of Eq.33):

$$\lim_{T_2 \to T_1}\left(\frac{1}{\boldsymbol{T}_2} - \frac{1}{\boldsymbol{T}_1}\right) = 0 = -\frac{T_2 - T_1}{T_1^2} + \frac{(T_2 - T_1)^2}{T_1^3} - \frac{(T_2 - T_1)^3}{T_1^4} + \frac{(T_2 - T_1)^4}{T_1^5} \cdots;$$

can be approximated by the first term of Taylor expansion series (refer to the right side of Eq.34). The accuracy of this approximation increases as $\Delta \boldsymbol{T} \to 0$, i.e. with decreasing difference between $\boldsymbol{T}_1$ and $\boldsymbol{T}_2$.

$$const.'' \approx \frac{2.5 \cdot 23}{\pi n M^{\#} w_{1/2}} = \frac{18.064}{n M^{\#} w_{1/2}} = \\ \frac{2.875}{C_{PA}} \frac{1}{n M^{\#} w_{1/2}} = \frac{2.875}{C_{PT}} \frac{1}{n M^{\#} w_{1/2}} \tag{37}$$

where C_{PA} is the Plouffe's constants and C_{PT} is the Pythagorean triple constant for the hypotenuses[19]. As an alternative to Eq. 33, it is also possible to write:

$$\ln\left(\frac{k_2}{k(T_{m,\Theta 1})}\right) = -\frac{const.'' \, T_{m,\Theta 1}^2 M^{\#}}{R}\left(\frac{1}{T_2} - \frac{1}{T_{m,\Theta 1}}\right). \tag{38}$$

These relations enable to describe $\boldsymbol{M}$ as the slope of plot $ln\,(\boldsymbol{k}_2/\boldsymbol{k}_1)$ vs. $(1/\boldsymbol{T}_2 - 1/\boldsymbol{T}_1)$ as $ln\,\boldsymbol{k}_2/\boldsymbol{k}(\boldsymbol{T}_{m,\Theta 1})$ versus $(1/\boldsymbol{T}_2 - 1/T_{m,\Theta 1})$ (**Figure 3**). The right side numerator of the last two equations is equal to $\boldsymbol{E}_{\mathrm{a}}$ (Eq. 1). Eq. 33 can be applied to the isothermal as well as nonisothermal kinetic experiment, while Eq. 38 is suitable for nonisothermal experiment only.

Since the dimension of term:

$$\frac{E_a}{R} = T' = -\left(\frac{\partial \ln k}{\partial \frac{1}{T}}\right)_p, \quad i.e. \quad \left[\frac{\frac{J}{mol}}{\frac{J}{mol\ K}} = K\right] \tag{39}$$

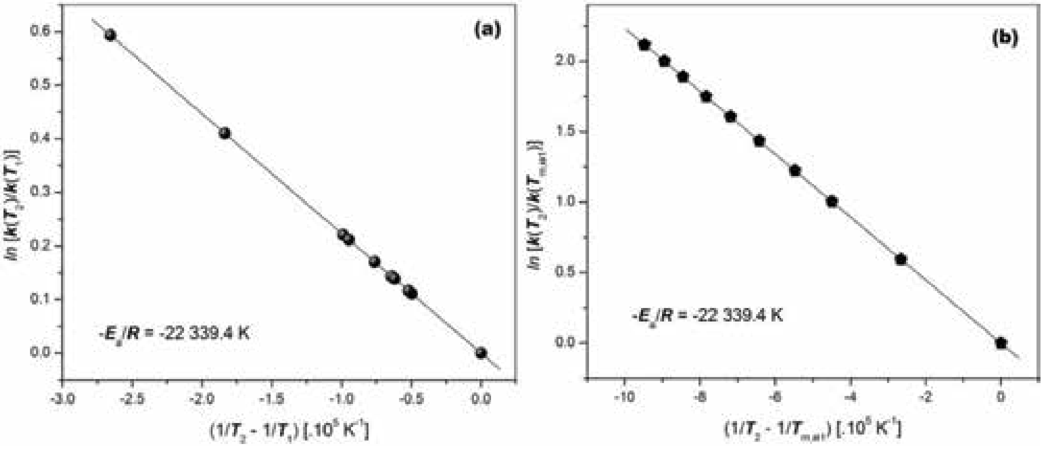

Figure 3. Graphs of $ln\,(\boldsymbol{k}_2/\boldsymbol{k}_1)$ vs. $\left(\boldsymbol{T}_2^{-1} - \boldsymbol{T}_1^{-1}\right)$ (a) and $ln\,\left(\boldsymbol{k}_2/\boldsymbol{k}_{T_{m,\Theta 1}}\right)$ vs. $\left(\boldsymbol{T}_2^{-1} - \boldsymbol{T}_{m,\Theta 1}^{-1}\right)$ (b).

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[19] An interesting consequence of these relations is to be solved in the next article.

is equal to the temperature (temperature term of activated complex, please refer to Eqs. (80) and (81)), it is also possible to easily calculate the volume of activated state ($\boldsymbol{V}^{\#}$) as follows:

$$V^{\#} = \frac{RT'}{p} = \frac{E_a}{p} = 8.205 \cdot 10^{-5} T'. \tag{40}$$

The combination with Eq. 36 in Chapter 2 then leads to the condition:

$$\frac{T'}{V^{\#}} = \frac{T}{V_m(T)} = \frac{R}{p} \tag{41}$$

where $\boldsymbol{T'}/\boldsymbol{V}^{\#} = f(\boldsymbol{T})$, so the temperature of the reaction affects the thermodynamics (stability) of activated complex, that is, the reaction rate which is given by its decomposition, (Eq. 7 in Chapter 2), but the temperature does not alter the value of activation energy. It can be further derived that:

$$\frac{V^{\#}}{V_m(T)} = \frac{T'}{T} = \frac{E_a}{RT}. \tag{42}$$

The density of activated state could be solved to:

$$\rho^{\#} = \frac{M^{\#}}{V^{\#}} = \frac{M^{\#} p}{RT'} = \frac{p}{r^{\#} T'} \tag{43}$$

where $\boldsymbol{r}^{\#} = \boldsymbol{R}/\boldsymbol{M}^{\#}$ is the specific gas constant and $\boldsymbol{p}/\boldsymbol{T'} = \boldsymbol{R}/\boldsymbol{V}^{\#}$ (please refer to Eq. 80 and the discussion thereof). Since:

$$M^{\#} = \rho^{\#} V^{\#} = \rho^{\#} \frac{RT'}{p} = \frac{4}{3} \pi {r_{AC}^{\#}}^{3} \rho^{\#}. \tag{44}$$

The effective diameter of activated complex can be calculated as follows:

$$r_{AC}^{\#} = \sqrt[3]{\frac{3\ M^{\#}}{\pi \rho^{\#} N_A}} = \sqrt[3]{\frac{3\ m_{(1)}^{\#}}{\pi \rho^{\#}}}. \tag{45}$$

If we consider that the velocity of activated state is equal to the term [2]:

$$\overline{v}_x = \sqrt{\frac{E_a}{M^{\#}}}\ ,\ i.e.\ \left[\sqrt{\frac{\frac{J}{mol}}{\frac{kg}{mol}}} = \frac{m}{s} \right] \tag{46}$$

and:

$$2\overline{v}_x^2 = \overline{v}^2. \tag{47}$$

Assuming the parity that for the peak of energetic barrier it is $-\overline{v}_x = \overline{v}_x$ [20], it is also possible to derive that:

$$\rho^{\#}\overline{v}_x^2 = \frac{\rho^{\#}\overline{v}^2}{2} = p, \quad i.e. \quad \left[\frac{kg}{m^3}\left(\frac{m}{s}\right)^2 = \frac{kg}{m\,s} = Pa\right] \tag{48}$$

and then:

$$\frac{\rho^{\#}\overline{v}^2}{2} - p = 0. \tag{49}$$

Since the energetic density in activated volume is equal to the pressure:

$$p = \frac{E_a}{V^{\#}}, \quad i.e. \quad \left[\frac{\frac{J}{mol}}{\frac{m^3}{mol}} = Pa\right] \tag{50}$$

more general form of Eq. 49 can be predicted:

$$\frac{\rho^{\#}\overline{v}^2}{2} + \rho^{\#}\phi - p = 0 \tag{51}$$

which was first introduced in the previous work [2]. This equation predicts the way, how the energetic density of activated state could be affected via the potential force field (ϕ).

It is possible to derive the mass velocity (mass current density or mass flux) of activated complex ($\overline{j}^{\#}$) in solution from the dimension of the following term:

$$\frac{E_a}{V^{\#}\overline{v}_x} = \left[\frac{\frac{J}{mol}}{\frac{m^3}{mol}\frac{m}{s}} = \frac{kg}{m^2 s}\right] = \overline{j}^{\#} = \frac{p}{\overline{v}_x} = \frac{101325}{\overline{v}_x} = \rho^{\#}\overline{v}_x. \tag{52}$$

Since the activation energy of the process is considered to be constant, the velocity vector of activated state does not vary with time either:

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[20] The details can be found in the previous work [2].

$$\frac{\partial \bar{v}_x}{\partial t_\delta} = 0 \quad \Rightarrow \quad \nabla \bar{v} = 0. \tag{53}$$

That means that the divergence of velocity vector is zero and the net total flux through the surface of activated complex must be equal to zero.

Since the dimension of term:

$$\delta = \frac{\bar{v}_x}{A} = \frac{\sqrt{\frac{E_a}{M^\#}}}{A} = 24\ \bar{v}_x w_{1/2,\Theta 1}\ \exp\left(-\frac{E_a}{RT_{m,\Theta 1}}\right)\ [m] \tag{54}$$

has a physical meaning of length, it is possible to calculate the length of energetic barrier ($\boldsymbol{\delta}$) from this relationship. From the combination of Eq. 54 with the Arrhenius equitation, it can also be derived that $\boldsymbol{w}_{1/2,\Theta 1}\boldsymbol{k}(\boldsymbol{T}_{m,\Theta 1}) = 1/24$. Therefore, the rate constant for the peak temperature $\boldsymbol{T}_{m,\Theta 1}$ can be directly calculated $\left(\boldsymbol{k}(\boldsymbol{T}_{m,\Theta 1}) = 1/\left(24\, \boldsymbol{w}_{1/2,\Theta 1}\right)\right)$ using full width at half maximum of peak measured with the heating rate $\Theta = 1\ K{\cdot}min^{-1}$.

The mean lifetime of activated complex ($\boldsymbol{t}_\delta$), that is, the time, which is required to overcome the energetic barrier is then equal to:

$$t_\delta = \frac{\delta}{\bar{v}_x} = A^{-1} = \frac{\exp\left(-\frac{E_a}{RT}\right)}{k(T)} = 1.443\, t_{1/2} \quad \Rightarrow \quad A = \frac{1}{t_\delta} = \frac{1}{\delta}\sqrt{\frac{E_a}{M^\#}} \tag{55}$$

where $\boldsymbol{t}_{1/2} = ln\, 2/\boldsymbol{A} = \boldsymbol{t}_\delta\, ln\, \mathbf{2}$ is the half-life of activated complex. That means that the concentration of activated complex can be written in terms of the exponential decay equation (please refer also to Eq. 7 in Chapter 2):

$$\left[\boldsymbol{C}^\#\right]_t = \left[\boldsymbol{C}^\#\right]_0 exp\,(-\boldsymbol{At});$$

where term $\boldsymbol{At} = \boldsymbol{t}/\boldsymbol{t}_\delta$ ($\boldsymbol{At}_\delta = 1$) and $\left[\boldsymbol{C}^\#\right]_t$ and $\left[\boldsymbol{C}^\#\right]_0$ are the concentrations of activated complexes at time $\boldsymbol{t}$ and $\boldsymbol{t} = 0$, that is, the initial quantity. This formula then enables to write:

$$\boldsymbol{k}(\boldsymbol{T}) = -\frac{1}{\boldsymbol{t}} \ln \frac{\left[\boldsymbol{C}^\#\right]_t}{\left[\boldsymbol{C}^\#\right]_0} \exp\left(-\frac{\boldsymbol{E}_a}{\boldsymbol{RT}}\right) \Longrightarrow \boldsymbol{k}(\boldsymbol{T}) = \frac{\ln \boldsymbol{e}}{\boldsymbol{t}_\delta} \exp\left(-\frac{\boldsymbol{E}_a}{\boldsymbol{RT}}\right) \Longrightarrow \ln \boldsymbol{k}(\boldsymbol{T})$$

$$= \ln \frac{1}{\boldsymbol{t}_\delta} - \frac{\boldsymbol{E}_a}{\boldsymbol{RT}} \left[\boldsymbol{t} = \boldsymbol{t}_\delta \Rightarrow \left[\boldsymbol{C}^\#\right]_t = \frac{\left[\boldsymbol{C}^\#\right]_0}{\boldsymbol{e}}\right];$$

(please refer also to Eq. 20 in Chapter 1 and to discussion of Eq. 27 in Chapter 2). The effective rate of activated complex[21] can be then formulated as follows:

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[21] It is also interesting to apply the Albert Einstein's (1879–1955) special theory of relativity (STR), where it is possible to calculate the invariant mass of activated state as follows:

$$m^{\#,0}_{(1)} = m^{\#}_{(1)}\sqrt{1-\frac{\overline{v}^2}{c^2}}; \tag{a}$$

which is, e.g. for calcite $2.915 \cdot 10^{-25}$ kg. Since activated on the peak of energetic barrier, it has the kinetic energy only (please refer to the discussion of Eqs. 79 and 82 in Section 4), it can further be written:

$$\frac{E_a}{N_A} = E_{(1)} = E_{k(1)} = m^{\#}_{(1)}c^2 - m^{\#,0}_{(1)}c^2 = \left(\frac{1}{\sqrt{1-\frac{\overline{v}^2}{c^2}}}-1\right)m^{\#,0}_{(1)}c^2 = (\gamma-1)\,m^{\#,0}_{(1)}c^2; \tag{b}$$

where the subscript (1) denotes the value pertinent to one activated molecule, i.e. the molar value divided by the Avogadro constant (Footnote 11 in Chapter 2), c is the speed of light in vacuum and the term:

$$\left(\frac{1}{\sqrt{1-\frac{\overline{v}^2}{c^2}}}\right) = \frac{1}{\sqrt{1-\beta_v^2}} = \gamma;\ \text{where}\ \beta_v = \frac{\overline{v}}{c}; \tag{c}$$

is known as the Lorentz factor (Lorentz term), which was named after Dutch physicist Hendrik Antoon Lorentz (1853–1928, awarded by Nobel prize for Physics in 1902). Since the dimensionless rate ratio of activated complex to the speed of light β_v is very low the value of $\gamma \to 1$, e.g. 1.00000000001177 for calcite. It can be then verified that:

$$E_a = E_{(1)}N_A = E_{k(1)}N_A = (\gamma-1)\,m^{\#,0}_{(1)}c^2 = \tag{d}$$

$$= (1.00000000001177 - 1) \cdot 2.915 \cdot 10^{-25} \cdot 299792458^2 \cdot 6.022 \cdot 10^{23} = 185.73 \cdot 10^3\ J \cdot mol^{-1}.$$

Please compare this value to data in **Table 1**. Using special theory of relativity, the energy of activated state can be expressed as follows:

$$E \approx m^{\#,0}_{(1)}c^2 + E_{(1)} = m^{\#,0}_{(1)}c^2 + \frac{1}{2}m^{\#}_{(1)}\overline{v}^2; \tag{e}$$

i.e. as the sum of Einstein's mass-energy equivalence formula ($E = mc^2$) and kinetic (activation) energy. That enables to formulate the energy ratio:

$$o = \frac{E_{(1)}}{m^{\#,0}_{(1)}c^2}. \tag{f}$$

The value of this ratio is $1.177 \cdot 10^{-11}$ and $1.2 \cdot 10^{-11}$ for in this book investigated samples of calcite and aragonite, respectively. The relation between o and β_v is given by the formula:

$$1-\beta_v^2 = \frac{1}{(1+o)^2}. \tag{g}$$

For the effective mass (h), the velocity (ch) and the momentum (i) of activated complex, the relations can be then written:

$$m^{\#}_{(1)} = m^{\#,0}_{(1)}\,(1+o) = \frac{m^{\#,0}_{(1)}}{\sqrt{1-\beta_v^2}}; \tag{h}$$

$$\overline{v} = c\,\frac{\sqrt{(1+o)^2-1}}{1+o}; \tag{i}$$

and:

$$\overline{p}^{\#}_{(1)} = m^{\#,0}_{(1)}\,c\,\sqrt{(1+o)^2-1}. \tag{j}$$

$$\overline{v}_x = \frac{\delta}{t_\delta} = \sqrt{\frac{E_a}{M^\#}} \quad \Rightarrow \quad E_a = M^\# \overline{v}_x^2 = \frac{1}{2} M^\# \overline{v}^2 = E_k \tag{56}$$

for the peak of energetic barrier.

The effective rate of activated complex (Eqs. 46, 47 and 56) can also be formulated using the relation for the speed of sound in ideal gas as follows:

$$\overline{v}_x = \sqrt{\frac{p}{\rho^\#}} \tag{57}$$

and:

$$\overline{v} = \sqrt{\gamma \frac{p}{\rho^\#}} = \sqrt{2 \frac{p}{\rho^\#}} \tag{58}$$

where γ is the value of adiabatic index, that is, the isentropic expansion factor. The value of this index is given by the ratio:

$$\lambda = \frac{c_{pm}}{c_{vm}} = \frac{2R}{R} = 2 = \frac{\Delta H^\#}{\Delta U^\#} \tag{59}$$

where $\Delta \boldsymbol{U}^\#$ is the internal energy of activation. From Eq. 58, it can be further derived that:

$$\overline{v} = \sqrt{2 \frac{p}{\rho^\#}} = \sqrt{2 \frac{RT'}{M^\#}} = \sqrt{2 \frac{E_a}{M^\#}} = \sqrt{2 \frac{kT'}{m^\#_{(1)}}}. \tag{60}$$

Since:

$$\overline{v} = \sqrt{\frac{K_B}{\rho^\#}} \tag{61}$$

the bulk modulus of activated complex can also be calculated as follows:

$$K_B = \rho^\# \overline{v}^2 = 2p. \tag{62}$$

The nature of velocities $\overline{\boldsymbol{v}}_x$ and $\overline{\boldsymbol{v}}$ can also be easily solved from the statistic probability function known as the Maxwell-Boltzmann distribution:

$$F(\overline{v}^2) = \sqrt{\frac{2}{\pi}}\, n_P \left(\frac{m}{k_B T}\right)^{3/2} \exp\left(\frac{-m \overline{v}_P^2}{2 k_B T}\right) \overline{v}_P^2 \tag{63}$$

where $\boldsymbol{n}_P$ is the number of particles with the velocity $\overline{v}_P$. With regard to the translation energy (Eq. 56) and two degrees of freedom [2] of activated state, it can then be written:

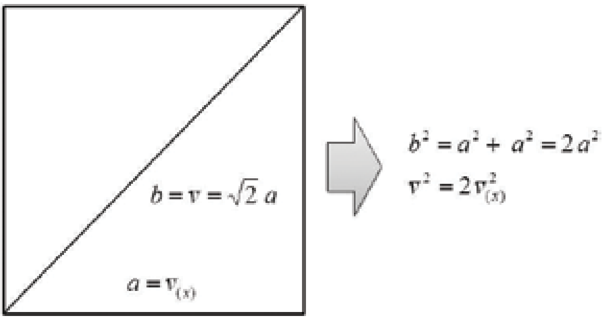

Figure 4. The relation between $\overline{v}_x$ and $\overline{v}$. Please refer to Eqs.47 and 68.

$$F\left(\overline{v}^2\right) = \sqrt{\frac{2}{\pi}}\left(\frac{M^{\#}}{RT'}\right)\exp\left(-\frac{M^{\#}\,\overline{v}^2}{2RT'}\right)\overline{v}^2. \tag{64}$$

This relation can be further transformed to the following formula:

$$F\left(\overline{v}^2\right) = \frac{\sqrt{\frac{2}{\pi}}}{\overline{v}_x^2}\,\frac{\overline{v}^2}{e} = \frac{\sqrt{\frac{2}{\pi}}}{a^2}\,\frac{b^2}{e} \tag{65}$$

where the scale parameter of Maxwell–Boltzmann distribution (***a***) is:

$$a = \overline{v}_x = \sqrt{\frac{RT'}{M^{\#}}} \quad \Rightarrow \quad \frac{1}{a^2} = \frac{M^{\#}}{RT'} = \frac{1}{\overline{v}_x{}^2} = \frac{1}{const.''T^2_{m,\Theta 1}} \tag{66}$$

and the mode of Maxwell-Boltzmann distribution (***b***) is:

$$b = \overline{v} = a\sqrt{2} \tag{67}$$

that is, the diagonal of the square with the side length equal to $\boldsymbol{a} = \overline{\boldsymbol{v}}_x$ (**Figure 4**).

These equations Eqs. 64–66 also define the role of ***const."*** (Eq. 1) in the Maxwell–Boltzmann distribution. Furthermore, Eq. 65 can be solved as follows:

$$0.58705\ldots = \frac{2\sqrt{\frac{2}{\pi}}}{e} = \sqrt{\frac{2}{\pi}}\,\frac{\overline{v}^2}{e\overline{v}_x^2} \quad \Rightarrow \quad \frac{\overline{v}^2}{\overline{v}_x^2} = 2. \tag{68}$$

Eq. 68 then also provides an important proof for the validity of Eq. 47. From this point of view, the velocities $\overline{v}_x$ and $\overline{v}$ are the scale factor and the mode, that is, the most probable speed, in Maxwell-Boltzmann distribution, respectively. Furthermore, it can also be written that:

$$M^{\#} = \frac{-2E_a\ln\left(\frac{1}{e}\right)}{\overline{v}^2} = \frac{2E_a\ln(e)}{b^2} = \frac{E_a}{\overline{v}^2_{(x)}}. \tag{69}$$

Eq. 67 means that all activated complexes have constant values of the ratio:

$$\frac{\overline{v}}{\overline{v}_x} = 1.4142\ldots = \sqrt{2} = M_a \tag{70}$$

where $\boldsymbol{M}_{\mathrm{a}}$ is the Mach number, which is defined as the dimensionless ratio of velocity of object and of speed of sound in given medium, that is in this particular case it is the ratio of $\overline{\boldsymbol{v}}$ and $\overline{\boldsymbol{v}}_x$ (Eqs. 47 and 68), respectively. With regard to the most probable rate of activated complex (mode of the Maxwell-Boltzmann distribution, Eq. 64), the translation of activated molecule along the reaction coordinate is always supersonic.

The combination of Eq. 70 with Eqs. (1) and (56) then leads to the formula:

$$E_a = \frac{{M_a}^2}{2}\ M^{\#}\overline{v}_x^2 = M^{\#}\overline{v}_x^2. \tag{71}$$

Furthermore, the combination of Eqs. (56) and (71) leads to the relation between both $\overline{\boldsymbol{v}}$ and $\overline{\boldsymbol{v}}_x$, that is, to Eq. 47.

The values of $\overline{\boldsymbol{v}}$ and $\overline{\boldsymbol{v}}_x$ are also related to the velocity of De Broglie's "phase wave" (phase velocity $\overline{\boldsymbol{v}}_p = \boldsymbol{E}_a/\overline{\boldsymbol{p}}^{\#} = \boldsymbol{\lambda}^{\#}/\boldsymbol{T}^{\#} = \boldsymbol{\omega}^{\#}/\overline{\boldsymbol{k}} \Rightarrow \boldsymbol{E}_a = \left(\boldsymbol{\omega}^{\#}\overline{\boldsymbol{p}}^{\#}\right)/\overline{\boldsymbol{k}}$), which should occur in the phase with intrinsic particle periodic phenomenon [33]. The relation between these velocities can then be expressed by the formula:

$$\overline{v} = \sqrt{2}\ \overline{v}_x = 2\ \overline{v}_p = 2\ \frac{E_a}{\overline{p}^{\#}} = 2\ \lambda^{\#}\nu^{\#} = \frac{\overline{p}^{\#}_{(1)}\, c^2}{\sqrt{c^2\overline{p}^{\#2}_{(1)} + m^{\#,0^2}_{(1)}\, c^4}} \tag{72}$$

where $\boldsymbol{m}^{\#,0}_{(1)}$ is the invariant mass of activated complex (please refer to Eq. (a) in Footnote 21). Therefore, the ratio of $\overline{\boldsymbol{v}} : \overline{\boldsymbol{v}}_x$ (Eq. 70) has exactly the same value as the ratio of $\overline{\boldsymbol{v}}_x : \overline{\boldsymbol{v}}_p$:

$$\frac{\overline{v}}{\overline{v}_x} = \frac{\overline{v}_x}{\overline{v}_p} = \sqrt{2} = 1.4142\ldots \tag{73}$$

so:

$$\overline{v}_x = \sqrt{2}\ \overline{v}_p. \tag{74}$$

It is then obvious that $\overline{\boldsymbol{v}}_x$ is the diagonal of the square with the side length equal to $\overline{\boldsymbol{v}}_p$. Since the ratio:

$$\overline{v}^2 : {\overline{v}_{(x)}}^2 : {\overline{v}_{(p)}}^2 = 1 : 2 : 4 \tag{75}$$

the squares of these velocities ($\overline{\boldsymbol{v}}^2$, ${\overline{\boldsymbol{v}}_x}^2$ and ${\overline{\boldsymbol{v}}_p}^2$) then form a geometric sequence (**Figure 5**) with common ratio = 2 (Eq. 68).

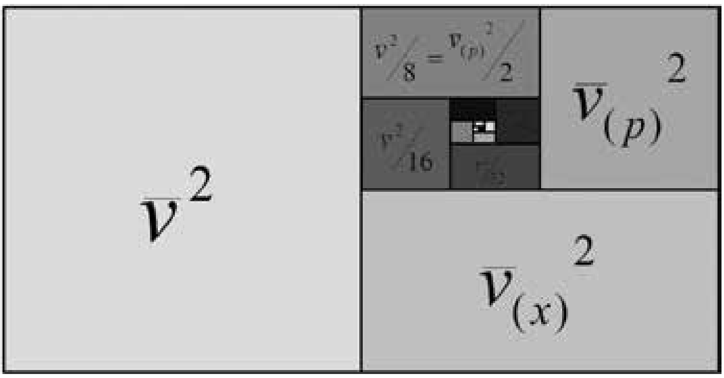

Figure 5. The diagram showing the geometric series of $\overline{v}^2$, $\overline{v}_x{}^2$ and $\overline{v}_p{}^2$.

The values of $\overline{v}^2$, $\overline{v}_x{}^2$ and $\overline{v}_p{}^2$ for the example of thermal decomposition of calcite and aragonite applied in this book are:

529045.43: 1058090.86: 2116181.72;

and

539291.80: 1078583.61: 2157167.22;

respectively. That also enables to express the value of v_x^2 as the geometric ratio of $\overline{v}^2$ and $\overline{v}_p{}^2$:

$$\overline{v}_x{}^2 = \sqrt{\overline{v}^2\,\overline{v}_p{}^2}. \tag{76}$$

Therefore, the quantum numbers of activated complex, that is, the activation energy and the momentum of activated complex, enable to express the following three velocities, that is:

1. The group velocity of a supersonic activation wave, which is equal to the most probable velocity (mode) resulting from the Maxwell-Boltzmann distribution ($\overline{v}$).
2. Sonic dissipation (shock) wave, which corresponds to the velocity of sound. This velocity (scale parameter of Maxwell-Boltzmann distribution) is termed in this work as the effective speed of activated complex ($\overline{v}_x$).
3. Phase velocity, that is the subsonic De Broglie "phase wave" ($\overline{v}_p$), which is equal to the speed at which the phase of the wave propagates in given medium.

That behavior makes it possible to suggest the theory that the formation of activated complex (reversible process, please refer to Chapter 2) also generates the irreversible dissipative wave (shock wave). This discontinuity in the pressure, temperature and density preserves the energy, but increases the system entropy. That means that the formation of activated state (activated

Parameter of Activated complex	E_a [kJ·mol^{-1}]	A [10^7 s^{-1}]	n	T' [K]	$M^{\#}$ [kg·mol^{-1}]	$V^{\#}$ [m^3·mol^{-1}]
	199.38	3.86	1.86	23981.8	0.1849	1.968
	$\boldsymbol{\rho}^{\#}$ [kg·m^3]	$\overline{v}_x$ [m·s^{-1}]	δ [m]	t_δ [s]	$\overline{j}^{\#}$ [kg·m^{-2}·s^{-1}]	$\overline{p}^{\#}$ [kg·m·s^{-1}·mol^{-1}]
	$9.394 \cdot 10^{-2}$	1038.5	$3.39 \cdot 10^{-4}$	$2.59 \cdot 10^{-8}$	97.564	271.51

The value needs to be divided by Avogadro constant (Footnote 11 in Chapter 2) to calculate the momentum of single activated molecule, that is, $\overline{\boldsymbol{p}}^{\#}_{(1)} = 4.53 \cdot 10^{-22}\ kg \cdot m \cdot s^{-1}$ for aragonite.

Table 2. Kinetic triplet and parameters of activated complex for the process of thermal decomposition of aragonite (Eq. 33 in chapter 2).

molecule and shock wave) causes increasing entropy of the system, even in the case, that activated complex decomposes back to the reactants.

Also, there is really interesting fact that $\overline{v}$ which relates to the process of thermal decomposition of calcite (**Table 1**) and aragonite (**Table 2**), is of the magnitude, which corresponds to the rate of sound or ultrasound in liquids (please refer also to the discussion of Eq. 56), for example, 1497 m·s^{-1} in distilled water at 25°C. Since only the longitudinal wave[22] can be propagated in liquids and gases (fluids in general), the activated complex can oscillate (transfer energy) along the direction of the reaction coordinate only. It can be then derived:

$$\overline{v}_x{}^2 = \frac{p}{\rho^{\#}} = \frac{E_a}{M^{\#}} = \frac{\overline{v}^2}{2} = const.''\, T^2_{m,\Theta 1} \tag{77}$$

and then:

$$\begin{aligned} \overline{v}^2 &= 2\,const.''T_{m,\Theta 1}2 \quad \Rightarrow \\ \overline{v} &= \sqrt{2\,const.''}\,T_{m,\Theta 1} = 1.505\ldots\ T_{m,\Theta 1}\ \approx\ \sqrt{\frac{5e}{6}}\ T_{m,\Theta 1}\ . \end{aligned} \tag{78}$$

Then there is direct proportionality between $\overline{\boldsymbol{v}}$ and $\boldsymbol{T}_{m,\Theta 1}$, where the value of proportionality constant is $\sqrt{2\,\boldsymbol{const}''}$. From this, it can be calculated that the most probable rate of activated complex is equal to the speed of sound in air (346.3 m·s^{-1}, dry air at 25°C) and water (1497 m·s^{-1}) for $\boldsymbol{T}_{m,\Theta 1}$ equal to 230.1 and 994.7 K, respectively.

Since further increasing of temperature increases the rate of activated complex as well, so it becomes comparable with the speed of sound in the solids, it can then also be deduced that increasing the temperature of the process ($\boldsymbol{T}_{m,\Theta 1}$) increases the probability of oscillation in the direction perpendicular to the reaction coordinate, that is, the activated state can get additional

---

[22] On the contrary, the longitudinal as well as transversal waves (oscillate perpendicular to the direction of energy transfer) can propagate in the solids.

degrees of freedom. The energy which is stored in those additional degrees of freedom then increases the energetic density of activated complex, which is on the contrary reduced by the value of $\boldsymbol{V}^{\#}$ which increases with temperature (Eq. 81).

Therefore, there is a possibility to formally divide the reactions according to the behavior of activated state described above, as follows:

1. Reaction with most probable (group) velocity of activated state in fluid region, that is the value of $\overline{v}$ is comparable to the speed of sound in gases and liquids. It can be potentially divided to the subregion of gases and liquids.
2. Reaction with most probable velocity of activated state in solid region, that is the value of $\overline{v}$ is comparable to the speed of sound in solids.

3. Introducing the quantum numbers of activated complex

Since the effective mass and the velocity of activated state are known, it is also possible to calculate the momentum per mol of activated states[23] as follows[24]:

$$\overline{p}^{\#} = M^{\#}\overline{v} = \overline{p}^{\#}_{(1)} N_A = N_A \hbar \overline{k} = \frac{N_A h}{\lambda^{\#}} \tag{79}$$

and to formulate the activation energy using the constitutive equation of the state of activated complex:

$$f\left(p, V^{\#}, T'\right) = 0 \tag{80}$$

that is:

$$RT' = pV^{\#} \quad \Rightarrow \quad \frac{V^{\#}}{V} = \frac{T'}{T} = \frac{E_a}{RT} = \frac{E_a}{pV} \tag{81}$$

as follows:

$$E_a = \frac{\overline{p}^{\#2}}{2\ M^{\#}} = \frac{N_A^2\, \hbar^2 \overline{k}^2}{2M^{\#}} = N_A\, h\, \nu^{\#}_{AC} = RT' = pV^{\#} \tag{82}$$

---

[23] The calculation of momentum per particle then requires to divide Eq. 79 by $\boldsymbol{N}_{\mathrm{A}}$ (Footnote 11 in Chapter 2).

[24] Eq. 79 then corresponds to the de Broglie matter waves (Louis Victor Pierre Raymond de Broglie, 1892–1987, Nobel Prize in Physics in 1929).

where $\boldsymbol{\hbar}$ is reduced Planck (Dirac[25]) constant[26], $\bar{k}$ is the wave vector, $\boldsymbol{\lambda}^{\#} = \boldsymbol{h}/\boldsymbol{p}^{\#}_{(1)}$ is the de Broglie wavelength[27] and $\boldsymbol{\nu}^{\#}_{AC} = (\boldsymbol{k}_B\boldsymbol{T})/\boldsymbol{h}$ (please refer to Eq. 115 and Eq. 27 in Chapter 2) is the universal frequency of activated complex. Eq. 81 also means that the pressure can affect the temperature and the rate constant of process, but the value of activation energy should be independent of the pressure. The combination of Eq. 29 in Chapter 2 with Eq. 81 then leads to the formula[28]:

$$E_a = p \int_{V_m(T)}^{V^{\#}} dV + RT = p\ \left(V^{\#} - V_m(T)\right) + RT = R\ \left(T' - T\right) + RT \tag{83}$$

that is the effect of reaction temperature on enthalpy of activation (corresponds to the work of isobaric process) lays in the reduction of $\Delta H^{\#}$ for reversible isobaric work $-\boldsymbol{p}\cdot[\boldsymbol{V}_m(\boldsymbol{T}_2) - \boldsymbol{V}_m(\boldsymbol{T}_1)] = -\boldsymbol{R}\Delta\boldsymbol{T}$ (**Figure 6**), and then:

$$\frac{E_a}{RT} = \frac{p}{RT} \int_{V_m(T)}^{V^{\#}} dV + 1 = \frac{\Delta V}{V_m(T)} + 1 = \frac{T'}{T} \tag{84}$$

where $\varDelta\boldsymbol{V} = \boldsymbol{V}^{\#} - \boldsymbol{V}_m(\boldsymbol{T})$. Eq. 84 could be further treated as follows:

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[25] Named after English physicist Paul Dirac (1902–1984). Dirac was awarded the Nobel Prize in Physics in 1933.

[26] Reduced Planck constant is the ratio:

$$\hbar = \frac{h}{2\pi} = 1.054571800 \cdot 10^{-34}\ J \cdot s \cdot rad^{-1}; \tag{a}$$

or the product:

$$\hbar = E_p t_p = \frac{E_p L_p}{c} \Rightarrow h = 2\pi\, E_p t_p = \frac{2\pi\, E_p L_p}{c}; \tag{b}$$

where E_{p} is the Planck energy (the derived Planck unit):

$$E_p = \sqrt{\frac{\hbar c^5}{G}} = \frac{\hbar}{t_p} \approx 1.956 \cdot 10^9\ J; \tag{c}$$

t_{p} is the Planck time (the basic Planck unit):

$$t_p = \sqrt{\frac{\hbar G}{c^5}} = \frac{\hbar}{E_p} \approx 5.391\ 16 \cdot 10^{-44}\ s; \tag{d}$$

c = 299,792,458 m·s^{-1} is the speed of light in a vacuum and G is the Gravitational (Universal or Newton's) constant (6.67408·10^{-11} m^3·kg^{-1}·s^{-2}). The other four basic Planck units are the Planck length:

$$L_p = \sqrt{\frac{\hbar G}{c^3}} \approx 1.616\ 229 \cdot 10^{-35}\ m; \tag{e}$$

The Planck mass, the Planck electric charge and the Planck temperature.

[27] Please refer also to Eq. 11 in Chapter 2.

[28] For example, the molar volume of ideal gas at the temperature of 966.55 K (according to **Figure 1** and **Figure 2(b)** this temperature corresponds to thermal decomposition of calcite at the heating rate of 1 K·min^{-1}) is $V_m = \boldsymbol{RT}/\boldsymbol{p} =$ 7.931·10^{-2} $m^3 \cdot mol^{-1}$, so Eq. 83 provides the value E_{a} = −101,325·(7.931·10^{-2} - 1.833) + 8.314·966.55 = 185.73·10^3 kJ·mol^{-1}. Please compare to the value in **Table 1**.

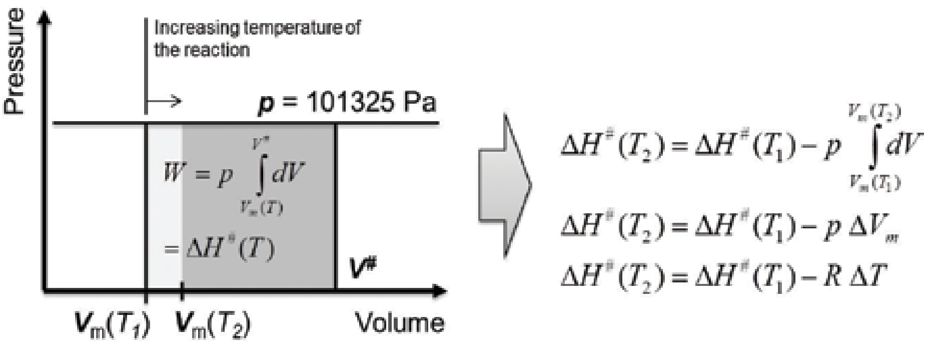

Figure 6. The influence of temperature on the enthalpy of activation. This topic as well as the temperature dependence of $\Delta S^\#$ is also described in previous work [2].

$$\frac{E_a}{RT} - 1 = \frac{1}{V_m(T)} \int_{V_m(T)}^{V^\#} dV = \frac{V^\#}{V_m(T)} - 1 \tag{85}$$

so:

$$\frac{E_a}{RT} = \frac{V^\#}{V_m(T)} \quad \Rightarrow \quad E_a V_m(T) = RT V^\#. \tag{86}$$

From Eq. 86 it can then be easily verified that $\boldsymbol{E_a} = \boldsymbol{pV^\#} = \boldsymbol{RT'}$ (Eq. 82). Therefore, if $\boldsymbol{E_a} > 0$ (activated processes) the value of $\boldsymbol{V^\#} > \boldsymbol{V_m(T)} \Rightarrow \boldsymbol{\Delta V} > 0$ (the activated complex does a positive work), so $\boldsymbol{E_a} > \boldsymbol{RT}$.

Before we continue with quantum numbers of activated complex, it is interesting to mention that Eqs. (79) and (82) allow to solve the relation of these numbers (the activation energy and the momentum) to the Gravitational constant (***G***), for example, as follows:

$$\overline{p}^\# = N_A \frac{L_p^2 c^3}{G} \overline{k} \tag{87}$$

and:

$$E_a = \frac{N_A^2 L_p^4 c^6 \overline{k}^2}{2\ M^\# G^2} = \frac{1}{2} M^\# \overline{v}^2. \tag{88}$$

As results from footnote 29, there are other equations analogical to the Planck energy[26] ($\boldsymbol{E}_\mathrm{p}$, Eq. (c)):

$$\overline{p}^\# = N_A \frac{E_p^2 G}{c^5} \overline{k} \tag{89}$$

and:

$$E_a = \frac{N_A^2\, E_p^4\, G^2\, \bar{k}^2}{2\ M^{\#}\, c^{10}} \tag{90}$$

or to the Planck time[26] ($\boldsymbol{t}_{\mathrm{p}}$, Eq. (e)):

$$\bar{p}^{\#} = N_A \frac{t_p^2\, c^5}{G} \bar{k} = \frac{N_A\, Y \bar{k}}{G} = N_A \hbar \bar{k} \tag{91}$$

and then the relation:

$$E_a = \frac{N_A^2\, t_p^4\, c^{10}\, \bar{k}^2}{2\ M^{\#}\, G^2} = \frac{N_A^2\, Y^2\, \bar{k}^2}{2\ M^{\#}\, G^2} = \frac{N_A^2\, \hbar^2\, \bar{k}^2}{2\ M^{\#}} \tag{92}$$

can be easily formulated. It can also be clearly seen that:

$$\begin{aligned} L_p^2\, c^3 = t_p^2\, c^5 = \frac{E_p^2\ G^2}{c^5} = \frac{\bar{p}^{\#}\, G}{N_A \bar{k}} = \frac{2\ E_a\, M^{\#}\, c^5}{N_A^2\, \bar{k}^2\, E_p^2} \\ = Y \approx 7.0383 \cdot 10^{-45} = \frac{1.866 \cdot 10^{-26} c^2 \bar{p}^{\#}_{(1)}}{8\, \pi\, \bar{k}} \end{aligned} \tag{93}$$

where $1.866 \cdot 10^{-26}\ m \cdot kg^{-1} = (8\, \boldsymbol{\pi G})/c^2$ is the Einstein's constant (the coupling constant in the Einstein field equation), which is directly proportional to the gravitational constant, constant term $\boldsymbol{Y}$ and activation energy as well (Eq. 93). The dimension of this constant term $\boldsymbol{Y}$ can be derived, for example, from Eq. 93 as follows:

$$\frac{2\ E_a\, M^{\#}\, c^5}{N_A^2\, \bar{k}^2\, E_p^2} \quad \Rightarrow \quad \left[\frac{\frac{J}{mol} \frac{kg}{mol} \left(\frac{m}{s}\right)^5}{\left(\frac{1}{mol}\right)^2 \left(\frac{1}{m}\right)^2 J^2} = \frac{kg\, m^7}{J\, s^5} = \frac{m^5}{s^3} \right]. \tag{94}$$

All abovementioned equations for the calculation of momentum and activation energy (Eqs. 87–92) contain this term ($\boldsymbol{Y}$) in the numerator. It can then be written that:

$$G = \frac{N_A Y \bar{k}}{\bar{p}^{\#}} = \frac{Y \bar{k}^{\#}}{\bar{p}_{\ (1)}}\ . \tag{95}$$

Using, for example Eq. 91, the relation can further be derived:

$$\frac{\bar{p}^{\#}}{\bar{k}} = \frac{N_A\, Y}{G} = N_A \hbar \tag{96}$$

and Eq. 92:

$$\frac{2M^{\#}E_a}{\overline{k}^2} = \left(\frac{N_A Y}{G}\right)^2 = {N_A}^2\hbar^2. \tag{97}$$

It can also be verified that:

$$\overline{p}^{\#} = \sqrt{2M^{\#}E_a} = M^{\#}\overline{v} \tag{98}$$

and:

$$\overline{v}^2 = \frac{2E_a}{M^{\#}} \quad \Rightarrow \quad E_a = \frac{1}{2}M^{\#}\overline{v}^2. \tag{99}$$

The motion of activated complex can then be fully characterized by two numbers, that is the activation energy and the momentum, which are directly proportional to physical action $\boldsymbol{Y}/\boldsymbol{G} = \hbar$. Therefore, these two numbers can be considered as the quantum numbers of activated complex.

4. Formulation of wave function, reduced mass and relative velocity of activated complex

Using the momentum, the mass activation energy, etc., for one molecule of activated complex[20,23], the Avogadro constant is left out from these relations. Furthermore, the quantum numbers of activated state and its mass can then be defined in terms of universal physical constants, for example, the Gravitational constant, reduced Planck constant and the speed of light in the vacuum.

The important consequences of relations 79 and 82 are the following:

1. The activated complex at the peak of energetic barrier, which represent the equilibrium, but not a stable state, has the kinetic energy (momentum) only.
2. The complete characterization of the motion of activated complex alongside the reaction coordinate requires the knowledge of two its quantum numbers:
    - **a.** Activation (kinetic) energy, it is obvious that activated processes have $\boldsymbol{E_a} > 0$;
    - **b.** Momentum of activated complex.
3. There is not any quantization either for the energy or for the momentum of activated state.
4. The shift from the equilibrium position (the peak of energetic barrier and the bottom of potential well at the same time) decreases the kinetic energy and increases the potential energy of activated complex.

The expression of $\boldsymbol{M}^{\#}$ from Eq. 82 leads to the formula:

$$M^{\#} = \frac{1}{E_a}\frac{\left(\hbar\bar{k}N_A\right)^2}{2} = 2.017\cdot 10^{-21}\frac{\bar{k}^2}{E_a}. \tag{100}$$

The substitution for $\boldsymbol{E}_{\mathrm{a}}$ (Eq. 1) in this formula then enables to write:

$$const.^{\#} = \frac{1}{2}\left(\frac{\hbar\bar{k}N_A}{T_{m,\Theta 1}M^{\#}}\right)^2 \tag{101}$$

and:

$$p = \frac{\left(N_A\hbar\bar{k}\right)^2}{2M^{\#}V^{\#}} = \frac{\rho^{\#}\bar{v}^2}{2} \tag{102}$$

where:

$$\bar{v} = \frac{2E_a}{\bar{p}^{\#}} = \frac{2E_a}{\bar{p}_{(1)}N_A}. \tag{103}$$

From the discussion above, it can then be concluded, that the definition of change in mass when the reactants pass into the activated state, enables to calculate many important parameters of activated complex. It is then feasible to use the Schrödinger equation[29] for the description of its behavior, but the solution is in the same form as for classical physics:

$$E_a = \frac{\left(N_A\hbar\bar{k}\right)^2}{2M^{\#}} = N_A\hbar\omega^{\#} \tag{104}$$

where:

$$\omega^{\#} = \frac{E_a}{N_A\hbar} = \frac{N_A\hbar\bar{k}^2}{2\ M^{\#}} \tag{105}$$

is an angular frequency which is related to the "ordinary" universal frequency of activated complex $\boldsymbol{\nu}^{\#}_{AC}$ ($\boldsymbol{\nu}^{\#}_{AC}/\boldsymbol{\nu}^{\#} = (\boldsymbol{E}_a/\boldsymbol{RT}) = \ln \boldsymbol{A}/\boldsymbol{k} + 1/\boldsymbol{e}$, please refer to Eq. 27 in Chapter 2 ⇒ the reaction rate constant ratio $\boldsymbol{k}_{Arhenius}/\boldsymbol{k}_{Eyring} = 1/\boldsymbol{e} \approx 1/2.71828 = 0.36788$) via the relation:

---

[29] Erwin Rudolf Josef Alexander Schrödinger (1887–1961). The Schrödinger's equation describes the behavior (evolution with time) of a physical system in which the quantum effects, such as the particle-wave duality take place:

$$i\hbar\frac{\partial\psi(\bar{r},t)}{\partial t} = \hat{H}\psi(\bar{r},t); \tag{a}$$

where i is the imaginary unit, $\hbar = h/2\pi$ is reduced Planck constant, ψ is the wave function (*psi*), $\bar{r}$ is the position vector, t is the time. The Hamiltonian (evolutional) operator:

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar}{2m}\nabla^2 + V(\bar{r},t); \tag{b}$$

where $\hat{T}$ is the kinetic and $\hat{V}$ is the potential energy operator, characterizes the total energy of wave function. This operator was named after Irish physicist, astronomer and mathematician William Rowan Hamilton (1805–1865) who was awarded the Royal Medal (The King's (Queen's) Medal) in 1835.

$$\omega^{\#} = 2\pi \nu^{\#}_{AC} = 2\pi \frac{E_a}{hN_A}. \tag{106}$$

It is obvious that the activated complex behaves as the pseudoparticle (instanton) that corresponds to one dimensional, that is the reaction coordinate (***r***), plane wave with the equation:

$$\psi(r,t) = e^{\left(E_{(1)}t-\overline{p}^{\#}_{(1)}r\right)/(i\hbar)} \tag{107}$$

where ***r*** (please refer to the discussion of Eq. 113) is the shift of activated complex from equilibrium position (the peak of energetic barrier) and the value of $\boldsymbol{E}_{(1)} = \boldsymbol{E}_a/\boldsymbol{N}_A$ and the Hamiltonian[31] is equal to the kinetic energy operator:

$$\widehat{H} = \widehat{T} = \frac{\widehat{p}^2}{2m^{\#}_{(1)}} = \frac{(-i\hbar\nabla)^2}{2m^{\#}_{(1)}} = \frac{(-i\hbar)^2}{2m^{\#}_{(1)}}\Delta = -\frac{\hbar^2}{2m^{\#}_{(1)}}\frac{\partial^2}{\partial r^2} \tag{108}$$

where ∇ is the nabla (del) operator[30] and $\varDelta = \nabla^2 = \nabla\cdot\nabla$ is the Laplace operator[31] (Laplacian). The pertinent kinetic energy of activated complex is then given by the formula:

$$E_{(1)} = \frac{\overline{p}^{\#}_{(1)}2}{2m^{\#}_{(1)}} = \frac{\overline{p}^{\#2}}{2M^{\#}N_A} = k_B T^2_{m,\Theta 1}\frac{\partial \ln Q^{\#}}{\partial T} = \frac{E_a}{N_A} \tag{109}$$

where $\boldsymbol{m}^{\#}_{(1)} = \boldsymbol{M}^{\#}/\boldsymbol{N}_A$ and the operator:

$$\widehat{p} = -i\hbar\nabla = -i\hbar\frac{\partial}{\partial r} \tag{110}$$

has the momentum:

$$\overline{p}^{\#}_{(1)} = \pm\hbar\overline{k} = \pm\sqrt{2m^{\#}_{(1)}E_{(1)}} = \pm\frac{\overline{p}^{\#}}{N_A}. \tag{111}$$

The commutation of operators $\widehat{T}$ and $\widehat{p}$ then means that:

---

[30] The vector differential operator "*nabla*" in three dimensional coordinate system with the basis vectors $\overline{i}, \overline{j}$ and $\overline{k}$ and is written as:

$$\nabla = \overline{i}\frac{\partial}{\partial x} + \overline{j}\frac{\partial}{\partial y} + \overline{k}\frac{\partial}{\partial z}.$$

[31] The differential operator given by the divergence of gradient of a function in Euclidian space:

$$\varDelta = \nabla\cdot\nabla = \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2};$$

which was named after the mathematician Euclid of Alexandria. The formulation of del or Laplacian depends on the coordinate system applied, that is, Cartesian, cylindrical and spherical coordinate.

$$\left[\widehat{T},\widehat{p}\right] = 0. \tag{112}$$

The solution of motion of activated complex (state) mentioned above enables to consider it and treat it as an instanton, that is a pseudoparticle. The pertinent wave function can be then used to describe its motion or to calculate the probability of tunneling through the energetic barrier, e.g. by means of the WKB (Wentzel-Kramers-Brillouin) approximation.

This behavior enables to use the following idea about the nature of activated complex (**Figure 7(a)**[32]). The activated complex is in equilibrium with products ($\boldsymbol{K}^{\#}$, please refer to the discussion of Eq. 5 in Chapter 2). The projection of this equilibrium is the linear spring, where the activated complex oscillates ($\pm \boldsymbol{r}$) around the equilibrium position (please refer to note (4) and the discussion of Eq. 82). This oscillation is the characteristics symptom of negative feedback of activated complex to the products. Furthermore, the shift from the equilibrium position reduces the kinetic energy and increases the potential energy of activated complex.

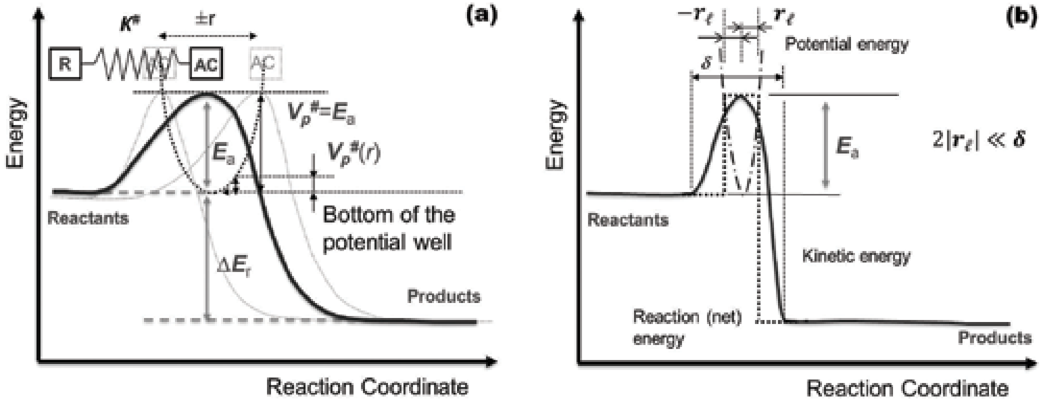

Figure 7. Simplified scheme of energy diagram (general exothermic reaction, please refer to **Figure 1(a)** in Chapter 2) showing increasing potential energy of activated complex (AC) caused by its oscillation around the peak of energetic barrier. The equilibrium of activated complex with reactants (***R***) was approximated by Hooke's spring (a). The scheme of energy diagram that includes the oscillation of activated state around the equilibrium position (b).

---

[32] For the peak of energetic barrier, it can then be written:

$$\boldsymbol{E}_r = \Delta E_r + \boldsymbol{E}_a = \Delta E_r + \frac{\hbar^2 \overline{\boldsymbol{k}}^2}{2\,\boldsymbol{m}^{\#}_{(1)}}; \tag{a}$$

that is, the relation which is analogical to the highest energies of the valence band and the lowest energies of the conduction band in many semiconductors:

$$\boldsymbol{E}(\overline{k}) = \boldsymbol{E}_0 + \frac{\hbar^2 \overline{\boldsymbol{k}}^2}{2\,\boldsymbol{m}^*}; \tag{b}$$

where $\boldsymbol{E}(\overline{k})$ is the energy of electron with the wave vector $\overline{k}$, $\boldsymbol{E}_0$ is the edge of energy of band and $\boldsymbol{m}^*$ is the effective mass of electron.

This behavior of activated state attached by spring to the product can be approximated by the Hooke's law[33] [34, 35], where the force ***F***, which shifts the activated complex from the peak of energetic barrier[34] is given by the Newton's second law[40]:

$$F = -k_s^{\#} r = m_{(1)}^{\#} \frac{\partial^2 r}{\partial t^2} = m_{(1)}^{\#} a^{\#} \tag{113}$$

where $\boldsymbol{a}^{\#}$ is the acceleration of activated molecule (Eq. 116) and $\boldsymbol{k}_s^{\#}$ is the positive constant of the spring, which can be calculated from its angular frequency:

$$\omega^{\#} = \sqrt{\frac{k_s^{\#}}{m_{(1)}^{\#}}} \quad \Rightarrow \quad \omega^{\#2} = \frac{k_s^{\#}}{m_{(1)}^{\#}}. \tag{114}$$

That also means that the universal frequency of activated state ($\boldsymbol{\nu}_{AC}^{\#}$) is independent of $\boldsymbol{r}$[35], that is it depends on the mass of activated complex only:

$$\begin{aligned} \nu_{AC}^{\#} &= \frac{k_B T'}{h} = \frac{E_{(1)}}{h} = \frac{1}{2\pi}\sqrt{\frac{k_s^{\#}}{m_{(1)}^{\#}}} = \frac{1}{2\pi}\ \omega^{\#} \quad \Rightarrow \\ E_{(1)} &= \frac{h}{2\pi}\omega^{\#} = \hbar\omega^{\#} = k_B T' \end{aligned}. \tag{115}$$

The acceleration of activated molecule during this oscillation is then given by the formula:

$$a^{\#} = -\omega^{\#^2} r = -4\pi^2 \nu_{AC}^{\#}{}^2 r. \tag{116}$$

The potential energy, which is stored in the spring (activated complex) during the oscillation, is given by the relation:

$$V_{p,1}^{\#}(r,t) = \frac{1}{2} k_s^{\#} r^2. \tag{117}$$

This behavior is in agreement with previous conclusions derived from Eq. 82. Since the change in the potential energy is of constant rate, the relation can also be written:

$$\frac{\partial^2 V_{p,1}^{\#}(r,t)}{\partial r^2} = k_s^{\#}. \tag{118}$$

The increase of energy (Eq. 117) then leads to the decrease of the momentum of activated complex (Eq. 111):

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[33] English natural philosopher, architect and polymath Robert Hooke (1635–1703).

[34] The other end of spring, that is, the reactants, is considered for the fixed position.

[35] The net energy of the activated complex is constant during the time.

$$\overline{p}^{\#}_{(1)}(r,t) = \pm\sqrt{2m^{\#}_{(1)}\left(E_{(1)} - V^{\#}_{p,1}(r,t)\right)} = \pm\sqrt{2m^{\#}_{(1)}\left(T^{\#}_{(1)}(r,t)\right)} \tag{119}$$

where $\boldsymbol{T}^{\#}_{(1)}(r,t)$ is the kinetic energy of activated complex during its oscillation around the energetic peak, so:

$$E_{(1)} = \frac{\overline{p}^{\#}_{(1)}(r,t)^2}{2m^{\#}_{(1)}} + V^{\#}_{p,1}(r,t). \tag{120}$$

Therefore, the momentum of activated complex is equal to zero when $\boldsymbol{E}_{(1)} = \boldsymbol{V}^{\#}_{p,1}$ (**Figure 7(b)**), that is for two spring limits, that is in amplitude positions:

$$r_{\ell} = \sqrt{\frac{2E_{(1)}}{k^{\#}_{s}}} = \frac{\lambda^{\#}}{\pi} = A_p \tag{121}$$

where $\boldsymbol{\lambda}^{\#}/\boldsymbol{r}_{\ell} = \boldsymbol{\pi}$. Since there are no losses in the energy (the activated complex is an adiabatic system[36]), the activation energy has a constant value of:

$$E_{(1)} = \frac{1}{2}k^{\#}_{s}r_{\ell} = \frac{1}{2}m^{\#}_{(1)}\overline{v}^2. \tag{122}$$

Furthermore the value of $2\,|\boldsymbol{r}_{\ell}| \ll \boldsymbol{\delta}$ is very small in comparison to the length of potential barrier (Eq. 54). In other words, the length of energetic barrier is much longer than the section which belongs to the oscillation of activated complex. The pertinent wave can then be described by the equation for the simple harmonic motion:

$$r(t) = A_p \ \cos\left(2\pi\nu^{\#}_{AC}t\right) \tag{123}$$

where $\boldsymbol{A}_p = \boldsymbol{r}_{\ell}$ (Eq. 121) is the amplitude and $\boldsymbol{\nu}^{\#}_{AC}$ is the universal frequency of activated complex (Eq. 115). Further treatment of Eq. 123 then leads to the formula of the wave function[37]:

$$r(t) = \sqrt{\frac{2E_{(1)}}{k^{\#}_{s}}} \ \cos\left(\sqrt{\frac{k^{\#}_{s}}{m^{\#}_{(1)}}}t\right) = \frac{\lambda^{\#}}{\pi} \ \cos\left(\sqrt{\frac{k^{\#}_{s}}{m^{\#}_{(1)}}}t\right) \tag{124}$$

and then:

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[36] The "walls" of this system do not allow the transport of matter and heat.

[37] The formula is the solution of an ordinary differential equation (ODE):

$$\boldsymbol{m}^{\#}_{(1)}\frac{\partial^2\boldsymbol{r}}{\partial\boldsymbol{t}^2} + \boldsymbol{k}^{\#}_{s}\boldsymbol{r} = 0 \Longrightarrow \boldsymbol{m}^{\#}_{(1)}\frac{\partial^2\boldsymbol{r}}{\partial\boldsymbol{t}^2} = -\boldsymbol{k}^{\#}_{s}\boldsymbol{r}.$$

Please refer also to Eq. 13 in Chapter 2.

$$\begin{aligned} r(t) &= \frac{\lambda^{\#}}{\pi} \cos\left(\sqrt{\frac{k_s^{\#}}{m_{(1)}^{\#}}}t\right) = \frac{\lambda^{\#}}{\cos^{-1}(-1)} \cos\left(\sqrt{\frac{k_s^{\#}}{m_{(1)}^{\#}}}t\right) \\ &\cong \frac{\lambda^{\#}}{0.31831} \cos\left(\sqrt{\frac{k_s^{\#}}{m_{(1)}^{\#}}}t\right) \end{aligned}. \tag{125}$$

Since the magnitude of this function starts with the value $\boldsymbol{r}(0) = \boldsymbol{r}_{\ell}$, it is possible to shift the beginning of wave function (negative phase shift about $-\pi/2 = -1.570796$ radians[38])[39] to the peak of energetic barrier, where $\boldsymbol{r}(0) = 0$, then the wave function can be written:

$$r(t) = \sqrt{\frac{2E_{(1)}}{k_s^{\#}}} \cos\left(\left(\sqrt{\frac{k_s^{\#}}{m_{(1)}^{\#}}}t\right) - \frac{\pi}{2}\right) = \frac{\lambda^{\#}}{\pi} \sin\left(\sqrt{\frac{k_s^{\#}}{m_{(1)}^{\#}}}t\right). \tag{126}$$

The period of this equation is given by the relation:

$$T^{\#} = 2\pi\sqrt{\frac{m_{(1)}^{\#}}{k_s^{\#}}}. \tag{127}$$

This solution also provides an important insight to the nature of the mass and the velocity vector of activated state, which can be actually characterized as follows:

- Reduced (effective[32]) mass of activated state ($\boldsymbol{m}_{(1)}^{\#}$);
- Relative velocity of the bodies before the collision ($\overline{\boldsymbol{v}}$).

The activation can then be characterized as the change in kinetic energy during the perfectly elastic collision. Since there is no dissipation, if the kinetic energy is dissipated (the formation of activated state is a reversible process), the change of energy for this kind of collisions is:

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[38] Like $\boldsymbol{e}$ and π, the $\pi/2$ is the transcendental number. This value corresponds to 90°, i.e. to 1 quadrant. The positive phase shift about $3\pi/2 = 4.712388\ldots$ radians, i.e. 270° (3 quadrants), which leads to the equation:

$$\boldsymbol{r}(\boldsymbol{t}) = \sqrt{\frac{2\boldsymbol{E}_{(1)}}{\boldsymbol{k}_s^{\#}}}\, cos\left(\left(\sqrt{\frac{\boldsymbol{k}_s^{\#}}{\boldsymbol{m}_{(1)}^{\#}}}\boldsymbol{t}\right) + \frac{3\pi}{2}\right) = \frac{\boldsymbol{\lambda}^{\#}}{\pi}\, sin\left(\sqrt{\frac{\boldsymbol{k}_s^{\#}}{\boldsymbol{m}_{(1)}^{\#}}}\boldsymbol{t}\right); \tag{a}$$

has the same effect, because:

$$\cos\left(x - \frac{\pi}{2}\right) = \cos\left(x + \frac{3\pi}{2}\right) = \sin(x). \tag{b}$$

[39] There is a very important fact that this phase shift corresponds to complete elliptic integral of the second kind:

$$\frac{\pi}{2} = \boldsymbol{E}(0);$$

especially for the investigation of kinetics of thermal decomposition of solids by TA methods[1], but we will deal with the details of this topic in future article.

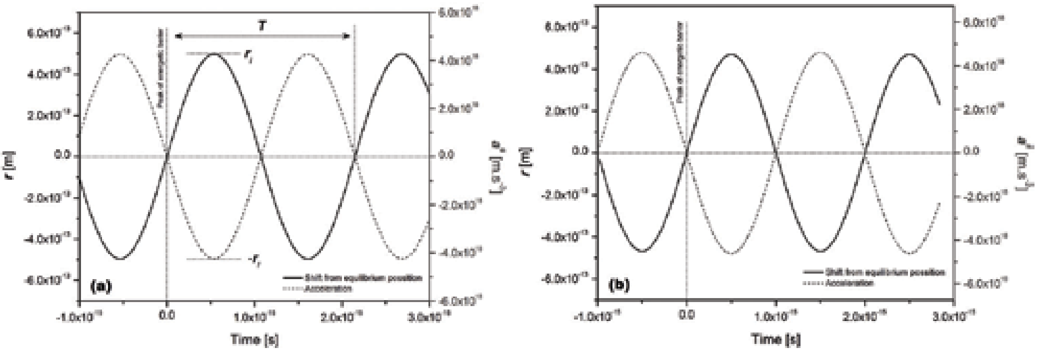

Figure 8. The wave function (Eq. 115) of activated state for the thermal decomposition of calcite (a) and aragonite (b).

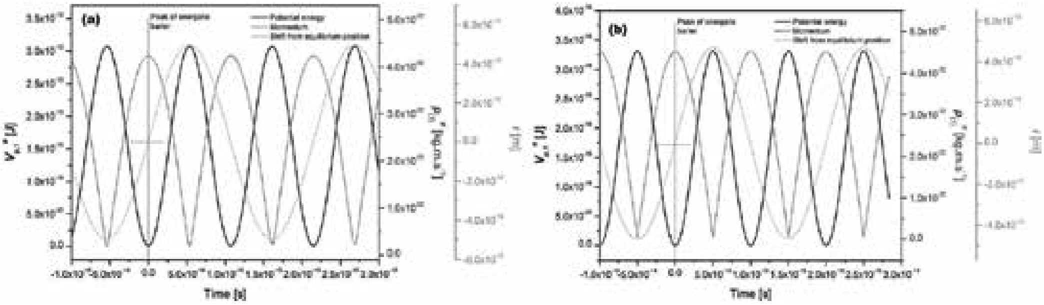

Figure 9. The change of potential energy and of momentum during the oscillation of activated complex during the process of thermal decomposition of calcite (a) and aragonite (b).

$$E_{(1)} = \frac{1}{2} m^{\#}_{(1)} \overline{v}^2 \left(\wp^2 - 1\right) \tag{128}$$

where $\wp = \sqrt{E_{(1)}/E_{(i,1)}} = 1$ (elastic collision) is the coefficient of restitution (COR). Its value is defined as the ratio of the final to initial relative velocity or the square root ratio of the final ($\boldsymbol{E}_{(1)}$) to initial energy ($\boldsymbol{E}_{(i,1)}$) of two collided objects[40].

The graphs of the wave function for the process of thermal decomposition of calcite (a) and aragonite (b) are shown in **Figure 8**. It can be seen that calcite with lower activation energy (**Table 1** and **Table 2**) has longer period ($2.15 \cdot 10^{-15}$ s^{-1}) than aragonite ($2.0 \cdot 10^{-15}$ s^{-1}). Furthermore, the wavelength is then only a tiny quantity of length of the energetic barrier (**Figure 7(a)**).

The changes of the potential energy and of momentum of activated complex during the oscillation around the equilibrium position, that is the peak of energetic barrier ($\boldsymbol{r} = 0$), is shown in **Figure 9**.

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[40] From this point of view, please see also the text (Van't Hoff statement) related to the discussion of Eq. 9 in Chapter 1.

The wave function (Eqs. 113 and 114) can also be approximated by the Taylor (Maclaurin, please refer to footnote 15 in Chapter 2) series expansion around the point $\boldsymbol{r}(0)$[41]:

$$r(0) = \frac{\lambda^{\#}}{\pi}\left(1 - \frac{x^2}{2} + \frac{x^4}{24} - \frac{x^6}{720}\cdots\right) \cong \frac{\lambda^{\#}}{\pi}; \text{ where } x = \sqrt{\frac{k_s^{\#}}{m_{(1)}^{\#}}t}. \tag{129}$$

For Eq. 126 (or Equation in Footnote 40) with the phase shift to the peak of energetic barrier, it is possible to write:

$$\begin{aligned} r(0) = \frac{\lambda^{\#}}{\pi}\left(x - \frac{x^3}{6} + \frac{x^5}{120} - \frac{x^7}{5440}\cdots\right) = \\ \sqrt{\frac{2E_{(1)}}{k_s^{\#}}}\left(x - \frac{x^3}{6} + \frac{x^5}{120} - \frac{x^7}{5440}\cdots\right) \end{aligned}. \tag{130}$$

Furthermore, it is also obvious (please refer to Eqs. 121–125) that:

$$E_{(1)} = \frac{1}{2}k_s^{\#}\left(\frac{\lambda^{\#}}{\pi}\right)^2 = \frac{1}{2}m_{(1)}^{\#}\overline{v}^2 \tag{131}$$

that is:

$$k_s^{\#}\left(\frac{\lambda^{\#}}{\pi}\right)^2 = m_{(1)}^{\#}\overline{v}^2 = \frac{\overline{p}_{(1)}^{\#}2}{m_{(1)}^{\#}} = 2E_{(1)} \tag{132}$$

where:

$$k_s^{\#} = m_{(1)}^{\#}\left(\frac{\overline{v}\pi}{\lambda^{\#}}\right)^2 \quad \left[\frac{kg}{s^2} = \frac{N}{m}\right]. \tag{133}$$

Since the activation energy per one activated complex is the sum of its kinetic ($\boldsymbol{E}_{(k,1)}$) and potential energy ($\boldsymbol{V}_{p,1}^{\#}$):

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[41] Since:

$$f(\boldsymbol{x}) = \cos(\boldsymbol{x}) \Longrightarrow f(0) = 1; \tag{a}$$

$$f'(\boldsymbol{x}) = -\sin(\boldsymbol{x}) \Longrightarrow f'(0) = 0; \tag{b}$$

$$f''(\boldsymbol{x}) = -\cos(\boldsymbol{x}) \Longrightarrow f''(0) = -1; \tag{c}$$

$$f'''(\boldsymbol{x}) = \sin(\boldsymbol{x}) \Longrightarrow f'''(0) = 0, \textit{etc.}; \tag{d}$$

the substitution to Eq. (a) in footnote 60 provides the series expansion according to Eq. 129.

$$E_{(1)} = E_{(k,1)} + V^{\#}_{p,1} \tag{134}$$

it can be written[42]:

$$E_{(1)} = \frac{1}{2} m^{\#}_{(1)} \omega^{\#2} A_p{}^2 \cos^2\left(\omega^{\#} t\right) + \frac{1}{2} k^{\#}_s A_p{}^2 \sin^2\left(\omega^{\#} t\right). \tag{135}$$

Because the frequency of $\boldsymbol{E}_{(k,1)}$ and $\boldsymbol{V}^{\#}_{(p,1)}$ is twice as high as the frequency of oscillation[43], the middle (average) potential ($\boldsymbol{V}^{\#}_{(p,1,av)}$) and the kinetic energy ($\boldsymbol{E}_{(k,1,av)}$) are of the same size during all periods. So, the relation of the middle activation energy ($\boldsymbol{E}_{(1,av)}$) of the reaction can be written as follows:

$$E_{(1,av)} = E_{(k,1,av)} = V^{\#}_{(p,1,av)} = \frac{1}{4} k^{\#}_s A_p{}^2 = \frac{E_{(1)}}{2}. \tag{136}$$

The value of "effective" shift ($\boldsymbol{r}_{ef}$) where the energy that corresponds to the value of $\boldsymbol{E}_{(1,av)}$ is reached, can be then calculated as follows (please refer to Eqs. (70) and (121)):

$$r_{ef} = \frac{1}{\sqrt{2}} A_p = 0.707\ldots r_{\ell} = \frac{r_{\ell}}{\sqrt{2}} = \frac{\overline{v}_x r_{\ell}}{\overline{v}}. \tag{137}$$

With respect to Eqs. (59) and (62), the relation can also be written:

$$\frac{E_{(1)}}{E_{(1,av)}} = \frac{\Delta H^{\#}}{\Delta U^{\#}} = \frac{K_B}{p} = 2. \tag{138}$$

Eq. 115 enables to use the principle of equivalency between undamped (the damping factor or ratio ζ = 0) harmonics oscillators (universal oscillator equation) in order to imagine or simulate the behavior of activated state as a serial RCL (Resistor, Inductor and Capacitor) or parallel RCL circuit:

$$\nu^{\#} = \frac{1}{2\pi} \sqrt{\frac{k^{\#}_s}{m^{\#}_{(1)}}} = \frac{1}{2\pi} \sqrt{\frac{1}{LC}}. \tag{139}$$

In the series RCL circuit the inductance $\boldsymbol{L}$ is equal to the mass of activated molecule $\boldsymbol{m}^{\#}_{(1)}$ and the elastnace $1/\boldsymbol{C}$ corresponds to the spring constant $\boldsymbol{k}^{\#}_s$. In the case of parallel RCL circuit the value of $\boldsymbol{k}^{\#}_s$ is equal to the magnetic reluctance $1/\boldsymbol{L}$ and $\boldsymbol{m}^{\#}_{(1)}$ to the capacitance $\boldsymbol{C}$.

If we conceive the idea that these oscillating systems are actually not undamped, but very slightly underdamped (factor ζ < < 1), there is an option to explain the decomposition of activated state, by the exponential decay of angular frequency and then by the energy (Eq. 115) of oscillator. That means that the energy of activated complex is not sufficient to

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[42] In the case that there is not any phase shift.

[43] Please refer also to Eq. 115 and to **Figure 9**.

overcome the peak of energetic barrier at certain time after its formation. Depending on actual position on reaction coordinate ($\boldsymbol{r(t)}$, refer to Eq. 124), the activated complex is decomposed into products or into reactants.

Since the rate of reaction is proportional to the decomposition of activated state, it should be proportional to the damping ratio as well. Therefore, the following approximation between the rate constant of reaction ($\boldsymbol{k}$) and dimensionless damping factor can be suggested:

$$k(T) = \zeta(T)\,\omega^{\#} = \zeta(T)\sqrt{\frac{k_s^{\#}}{m_{(1)}^{\#}}}. \tag{140}$$

In other words, the exponential decay of underdamped oscillator is equal to $\boldsymbol{k}$, that is the mean lifetime ($\boldsymbol{\tau} = 1/\boldsymbol{k}$) of activated complex decreases with temperature, while the value of damping factor increases with temperature. The rate of reaction then becomes faster. The substitution of Arrhenius formula (Eq. 7 in Chapter 1) to Eq. 140 then leads to the relation:

$$k_s^{\#} = m_{(1)}^{\#}\left(A\ \exp\left(-\frac{E_a}{RT}\right)/\zeta(T)\right)^2 = m_{(1)}^{\#}\left(\frac{k(T)}{\zeta(T)}\right)^2. \tag{141}$$

The value of so called $\boldsymbol{Q}$ factor of activated complex can then be calculated from the following relation:

$$Q = 2\pi\frac{Energy\ \ stored}{Energy\ \ lost} = \frac{2\pi\ E_{(1)}}{Energy\ \ lost} = \frac{1}{2\zeta(T)}. \tag{142}$$

Using the example of the process of thermal decomposition of aragonite applied in this book, the lost energy can be calculated (Eq. 142) to 8.622×10^{-37} J per one cycle of activated molecule, which is only very tiny fraction of its value.

Since the loss of energy per each cycle increases with the energy of the activation impulse, the same idea can be used to explain the decomposition of activated system which collects the energy $\boldsymbol{E} \geq \boldsymbol{E_a}$. In other words, if tunneling (please refer to Section 5 in Chapter 2) is not taken into the account, the energetic barrier behaves as an energy filter which allows only to the activated molecule with the energy of $\boldsymbol{E}_{\mathrm{a}}$ to pass through (to form the product). The systems with higher or lower energy are not allowed to go through the energetic barrier. The system with higher energy oscillates and loses its energy until it reaches the activation energy $\boldsymbol{E}_{\mathrm{a}}$ and in this stage it passes through. The condition must always be fulfilled that the net energy is the sum of activation energy and of the energy of reaction, that is $\Delta \boldsymbol{E_r} + \boldsymbol{E_a}$ (please see **Figure 7**).

5. Other parameters that affect the effective mass of activated state

As results from previous discussion, the effective mass as well as other derived parameters of activated complex are independent of the temperature at which the reaction proceeds at

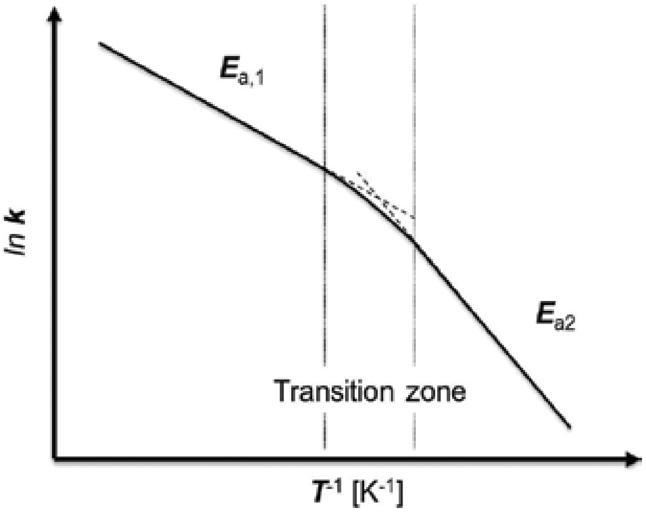

Figure 10. Hypothetical example of Arrhenius plot for the change of reaction mechanism with increasing temperature.

measurable rate[44]. Of course, that is possible only on the assumption that the change in temperature does not bring the change of reaction mechanism with different activation energy[45] (**Figure 10**). In that case, the activation energy, the mass of activated state as well as other above mentioned parameters of activated complex must be changed too. The example of that behavior can be found in previous works, e.g. [36, 37].

Since the effective mass of activated state could also be affected by the isotopic composition of the specimen (please refer to Section 5 in Chapter 2), the activation energy for the most cases of the process is actually Relative Activation Energy. The value of which depends on the isotopic composition of the sample. Please do not be confused with the apparent activation energy. This term is usually applied to the kinetics of processes of unknown or uncertain mechanism.

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[44] On assumption that the activation energy is independent of the temperature. As was firstly assumed by van't Hoff (please refer to discussion of Eq. 18 in Chapter 1), the activation energy could be a function of temperature. From this point of view, please refer also to the work of S. Vyazovkin and B.V. L'vov. Also according to our investigation, the activation energy is most probably the function of temperature, but within the temperature interval, where the reaction takes place in measurable rate, this change is usually smaller than the uncertainty of experimental results. We plan to publish our solutions on this topic in the future work.

[45] In this case, we can observe two or more linear parts in Arrhenius plot which are pertinent to the change of reaction mechanism. The mechanism crossing is usually gradual without an abrupt change of the slope. The effect of temperature on the reaction mechanism can be, for example, illustrated by the effect of temperature on the process of nucleation and diffusion. The increasing temperature makes the transport phenomenon's, for example, the diffusion toward growing nucleus of new phase, easier, but it also reduces overcooling, for example, driving force of nucleation, as well.

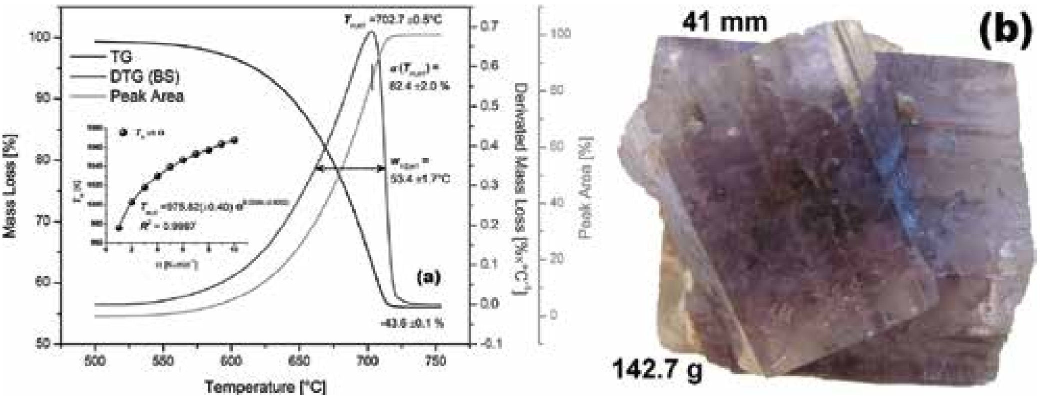

Figure 11. Thermal decomposition of aragonite (20 mg) heated with the rate of 1 K·min^{-1} under inert (N_2) atmosphere (a). DTG peak was subtracted to baseline (BS). The plot of $\boldsymbol{T}_{\mathrm{m}}$ vs. $\boldsymbol{\Theta}$ is shown in detail. Photograph of analyzed pseudo-hexagonal (violet crystals show a hexagonal outline) aragonite specimen (b).

The change in mass when reactants pass into the activated state is also affected by polymorphism[46], that is by the crystal structure. For example, the aragonite has higher $\boldsymbol{M}^{\#}$ than calcite, despite the fact that both minerals have the same chemical composition ($CaCO_3$), so their thermal decomposition can be described by the same chemical equation (Eq. 33 in Chapter 2).

The course of thermal decomposition of aragonite specimen (La Pesquera, Spain) is shown in **Figure 11**. In comparison with the process of thermal decomposition of calcite (**Figure 1**), the peak temperature of the process is higher. On the contrary, the full width at half maximum of peak ($w_{1/2}$) is lower for aragonite than for calcite.

The Arrhenius plot for the process of thermal decomposition of aragonite[47] is shown in **Figure 12**. The process of thermal decomposition of aragonite requires slightly higher activation energy (**Table 2**) than that of Iceland spar (**Table 1**). The mechanism of the process of thermal decomposition, which includes zero or decreasing nucleation rate of new phase and the diffusion controlled growth of new phase, is also very similar for calcite and aragonite. Please compare the data in **Table 1** (calcite) with those in **Table 2** (aragonite) for the demonstration of effect of polymorphism on the kinetics of thermal decomposition and properties of activated complex. Further research has shown that there is actually not any significant effect of the polymorphism of calcium carbonate[48] or its origin on the value of activation energy for the specimens of comparable purity [38].

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[46] Polymorphism is the ability of solids to crystallize in various structures in different intervals of temperature and pressure. In the case of chemical elements, the same ability is termed as allotropism (allotropy). For example, the calcite and aragonite are two polymorphs of $CaCO_3$ and graphite and diamond are two of allotropes of carbon.

[47] The chemical equation is the same as for calcite (Eq. 33 in Chapter 2). The Arrhenius and Eyring plot for the process of thermal decomposition of calcite can be found in Figure 2 in Chapter 2.

[48] This behavior can be explained by very small value of enthalpy of calcite (trigonal) ↔ aragonite (orthorhombic) phase transition (please refer also to the footnotes 18 and 19 in Chapter 2). The same cannot be said for vaterite, but this phase is the synthetic hexagonal calcium carbonate polymorph, that is, vaterite cannot be classified as a mineral.

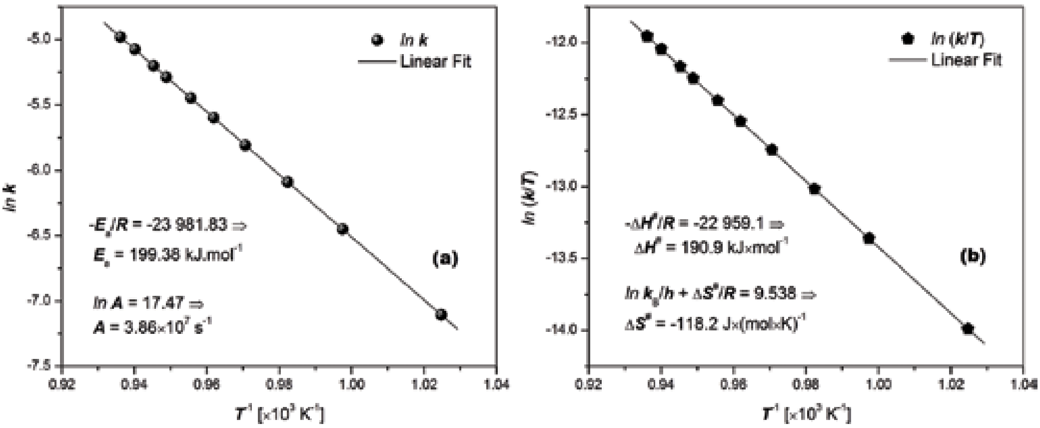

Figure 12. Arrhenius plot (a) and Eyring plot (b) for the process of thermal decomposition of aragonite.

The same cannot be recognized for polymorphs of $SrCO_3$, which was investigated in previous work [39]. The mass of activated state is higher for orthorhombic polymorph (0.165 kg·mol^{-1}) than for hexagonal (0.148 kg·mol^{-1}) strontium carbonate, but the effect of temperature change on the mechanism, that is the value of kinetic exponent $\boldsymbol{n}$, of thermal decomposition was included in this particular case. Furthermore, the kinetics of the thermal decomposition process and then the effective mass of activated state as well could be influenced by the formation of solid solution.

6. Conclusion

As was demonstrated in this chapter, the effective (reduced) mass of activated state is an important parameter of activated complex, which can be easily derived from the results of kinetic experiments. As was demonstrated on the example of calcite and aragonite, this change in mass when reactants pass into an activated state depends on real reaction mechanism, resp. on kinetic factor, which is often different from common transcript of the reaction. Therefore, the mass of activated state could be different from the value resulting from this equation, that is the sum of reactants multiplied by their stoichiometric coefficients.

The most important significance of this parameter lays also in the possibility of further definition of rate, density, energetic density, current mass density, momentum and many other properties of activated complex. Since the activation energy and the momentum of activated complex enable complete characterization of the motion of activated complex alongside the reaction coordinate, these parameters are its quantum numbers.

Furthermore, it is possible to introduce the idea to approximate the behavior of activated complex by the spring oscillation and to determine the nature of mass of activated complex as the reduced or effective mass of activated complex. This mass is also affected by the isotopic composition of the sample and by polymorphism.

Symbols and abbreviations

The following abbreviations and symbols are used in this book:

$\vec{j}^{\#}$	mass flux (mass current density) of activated complex
$\overline{v}_p$	the speed of the phase wave (phase velocity)
$\overline{v}_x$	the effective speed of activated complex, which corresponds to the scale parameter of Maxwell–Boltzmann distribution
$\Delta_r \boldsymbol{G}^{\circ}$	standard Gibbs free energy of the reaction
$\Delta_r \boldsymbol{G}$	Gibbs free energy of the reaction
$\Delta \boldsymbol{G}^{\#}$	Gibbs energy of activation
$\Delta \boldsymbol{H}^{\#}$	enthalpy of activation
$\Delta \boldsymbol{S}^{\#}$	entropy of activation
$\Delta \boldsymbol{U}^{\#}$	internal energy of activation
$\Delta \boldsymbol{V}^{\#}$	volume of activation, the change of volume when reactants pass into the activated state
$\boldsymbol{B}_{av}(\boldsymbol{x})$	the average value of approximation parameter $\boldsymbol{B}(\boldsymbol{x})$
$\boldsymbol{C}_{PA}$	Plouffe's constants
$\boldsymbol{C}_{PT}$	Pythagorean triple constant for hypotenuses
$\boldsymbol{E}_{(i,1)}$	initial energy of two collided object
$\boldsymbol{E}_0$	energetic difference between energy of activated state and reactants
$\boldsymbol{E}_a$	activation energy (Arrhenius activation energy)
$\boldsymbol{E}_p$	Planck energy ($1.956 \cdot 10^9$ J)
$\boldsymbol{E}_{th}$	activation energy (theoretically calculated)
$\widehat{\boldsymbol{H}}$	Hamiltonian (Evolutional) operator
$\boldsymbol{K}^{\#}$	equilibrium constant (formation of activated complex)
$\boldsymbol{K}^{+}$	equilibrium constant of activation ($\boldsymbol{K}^{\#} = \boldsymbol{K}^{+}$)
$\boldsymbol{K}_{\mathrm{b}}$	the bulk modulus
$\boldsymbol{L}_p$	Planck length ($1.616 \cdot 10^{-35}$ m)
$\boldsymbol{M}^{\#}$	the mass of activated state
$\boldsymbol{M}_{\mathrm{a}}$	Mach number

N_A	Avogadro constant ($6.022140857 \cdot 10^{-23}$ mol^{-1})
$Q_0^{\#}$	partition function of activated complex
Q_i	partition function of reactant molecules
$T^{\#}$	period of activated complex wave function
$\widehat{T}$	kinetic energy operator
T'	activated complex temperature term (E_a/R)
$V^{\#}$	molar volume of activated state ($V^{\#} = RT'/p$)
$\widehat{V}$	potential energy operator
$V_{p,1}^{\#}$	potential energy of activated complex
Z_p	the size of particle
$a^{\#}$	acceleration of activated molecule
g_j	degeneracy factor, that is the number of allowed equimolar quantum microstates
$k^{\#}$	activated state rate constant (coefficient)
$\overline{k}$	wave vector
k_B	Boltzmann constant ($1.38064852 \cdot 10^{-23}$ J·K^{-1})
k_{exp}	rate constant (experimentally determined)
k_{th}	rate constant (theoretically calculated)
$m_{(1)}^{\#,0}$	the invariant mass of activated complex
$\overline{p}$	momentum
$r^{\#}$	specific gas constant
$\overline{r}$	position vector
$r_{AC}^{\#}$	the effective diameter of activated complex
$t_{1/2}$	the half-life of activated complex
t_p	Planck time ($5.391 \cdot 10^{-44}$ s)
$t_\delta = 1/A$	the mean lifetime of activated complex, that is the time required to overcome energetic barrier
$\overline{v}$	the most probable speed of activated complex (the mode of Maxwell-Boltzmann distribution), which corresponds to the group velocity of the activation wave

$w_{1/2}$	full width at half maximum of peak (FWHM)
$\alpha_{Q^{\#}}$	coefficient of response of partition function to a change in temperature
β_{v}	dimensionless rate ratio of activated complex to the speed of light
ε_{j}	energy level of j-microstate
$\lambda^{\#}$	de Broglie wavelength of activated complex
$\nu^{\#}$	universal frequency ($\nu^{\#} = (k_B T)/h$), that is the frequency of decomposition of activated complex
$\nu^{\#}_{AC}$	universal frequency of activated complex ($\nu^{\#}_{AC} = \left(k_B T'\right)/h$)
ν_i	stoichiometric coefficients
$\rho^{\#}$	density of activated state
ρ_{sf}	steric factor
$\omega^{\#}$	angular frequency of activated complex
$\Delta = \nabla^2$	Laplace operator (Laplacian)
$\wp$	coefficient of restitution (COR)
ΔV	molar change in volume during reaction
A	frequency or pre-exponential Factor, sometimes prefactor
A'	temperature independent constant
AC	activated complex
ART	Absolute reaction rates theory
$B(x)$	approximation parameter in the Doyle equation for $\mathbf{p}(\mathbf{x})$
E	energy, usually reaction energy
F	force
G	gravitational constant (Universal constant or Newton's constant, 6.67408×10^{-11} m^3·kg^{-1}·s^{-2})
K	equilibrium constant of reaction
P	Ad hoc quantity, that is "fudge factor"
Q	partition function of the molecule and Q factor
R	Gas constant, also Molar, Universal or Ideal gas constant (8.3144598 J·K^{-1}·mol^{-1})

S	entropy
STR	Special theory of relativity
T	thermodynamic or absolute temperature
TST	Transition state theory
W	energetic difference between reactants and activated complex in basic state
Y	the constant term ($Y \approx 7.0383 \times 10^{-45} m^5/s^3$)
c	speed of light in vacuum (299,792,458 m·s^{-1})
$const.^{\prime\prime}$	square of temperature-rate kinetic coefficient
$const.^{\prime\prime\prime}$	temperature-rate kinetic coefficient
e	the base of natural logarithms (Euler's number, Napier's constant)
h	Planck constant (6.626070040 × 10^{-34} J·s)
k	reaction rate constant (coefficient)
m	mass
p	pressure
$p(x)$	temperature integral, where the quantity of $x = E_a/RT$
q	the heat of reaction
r	reaction rate (rate or speed of reaction) or shift from equilibrium position (according to the context)
Θ	heating rate
∇	Nabla (del) operator
β	thermodynamic beta (occasionally perk)
γ	Lorentz factor (term)
δ	the length of energetic barrier
κ	proportionality constant (transmission coefficient)
ν	frequency of harmonic oscillator
o	energy ratio
ς	damping factor
τ	fundamental temperature
ψ	wave function (psi)
ϕ	potential force-field

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Heterogeneous kinetics plays an important role in many scientific disciplines and industrial branches such as physical chemistry, materials science, chemical industry, ceramic industry, etc. Although many excellent books on theories and methods can be found, the aim of this book is to provide an unconventional insight into the heterogeneous kinetics and properties of the activated complex. The introduction of the effective mass of this instanton enables to calculate many other properties, such as the most probable speed of activated complex, the momentum, the energetic density, the mass flux, etc., and to define two quantum numbers of activated state, i.e., the activation energy and the momentum. The monograph is organized into three chapters. The first of them deals with a short historical background, which introduces the beginning of chemical kinetics in the historical context. The second chapter is dedicated to the transition state theory, and the third one explains the concept of effective mass and effective rate of activated state as well as other properties of activated complex.

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