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On the way from the activation model of solid decomposition to the thermochemical model

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Abstract The development of the technology and the theory of electrothermal atomization, which began in atomic absorption spectrometry about 60 years ago, led to a confrontation between the two alternative models used in the kinetics of heterogeneous chemical reactions: the activation model proposed by Arrhenius (Z Phys Chem 4:226–248, 1889) and based on the effect of activation, and the thermochemical model (TM) proposed by Langmuir (Phys Rev 2:329–342, 1913), which excludes the existence of this effect. An analysis of the events surrounding the creation and evolution of both models and a comparison of their fundamental principles and their application to the solution of actual problems show the shortcomings of the activation model and fundamental limitations in its applicability. The TM for the first time in the history of these studies allowed a quantitative estimation and a prediction of the lifetime for substances depending on the environment and temperature of their storage. It allows the calculation of the rate of reaction and the Arrhenius parameters taking into account the composition, stoichiometry and thermochemical characteristics of the reaction, the excess pressure of the gaseous product in the reactor and the physical properties of the reactant (sample size and the density of the reactant). Within the TM, it was possible to solve many of the accumulated problems, including the physical nature of the parameters of the Arrhenius equation, the effect of autocatalysis, the kinetic compensation effect and the Topley–Smith effect. To overcome the lasting crisis in the kinetics of heterogeneous reactions, it is necessary to advance the public discussion of the current situation and search for appropriate ways to replace the activation model by the TM.

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Introduction

The activation kinetic model (AM) has gained wide popularity and almost canonical recognition in the world of science, primarily in physical chemistry, chemical physics and in thermal analysis. Meanwhile, it is becoming increasingly clear that there is stagnation, or rather a crisis in the study of the kinetics and mechanisms of chemical processes, mainly heterogeneous. This is recognized even by the leading experts in this field [1]. It has manifested itself, in particular, in several facts enumerated below: in the decline or reorientation of interests of the universally recognized scientific schools established in the middle of the last century by Garner (University of Bristol); Searcy (University of California, Berkeley); Pavlyuchenko (Institute of General and Inorganic Chemistry, Minsk) and Boldyrev in the 1980s (Institute of Solid State Chemistry, Novosibirsk); in the reduction of basic publications on solid-state reactions in the periodic press and at the meetings, in the closing in 1990 of the journal *Reactivity of Solids*, specialized in kinetics and mechanisms of heterogeneous reactions, and also in the fruitlessness of the ICTAC projects, *Kinetic Standard* (1995) and *Computational aspects of kinetic analysis* [64].

The development of the new, thermochemical, approach to the study of the kinetics of heterogeneous reactions in the 1980s and the mechanism of congruent dissociative vaporization (CDV) in the 1990s have not received any recognition amongst the thermoanalytical community despite very serious achievements in the interpretation of many fundamental problems that have accumulated in this field, e.g. the physical essence of the Arrhenius parameters (A and E), the effect of autocatalysis, the Topley–Smith effect and the kinetic compensation effect. Note that all traditional kinetic theories based on the activation effect (the classical Arrhenius theory, as well as the collision and transition state theories) appeared fruitless in this respect.

The aim of this paper is to discuss the progress made over the last 30 years (but, unfortunately, neglected by the scientific community) in the development of the thermochemical model (TM) of solid-phase decomposition reactions, as expressed, in particular, in the successful interpretation of the above-mentioned effects. To do this, we first briefly recall the history of both approaches (AM and TM), and then, by the example of heterogeneous reactions, discuss the reasons that led to this crisis, and the prospects of overcoming it.

Historical overview

The history of the activation model

From the history of the birth and subsequent justification of the Arrhenius equation underlying the modern theory of chemical kinetics, it follows that the most essential precursor to its emergence was the fundamental work of van’t Hoff [2], published in

1884. Here, van't Hoff showed that the equilibrium constant of the reaction K is related to the temperature T and the heat of the reaction ΔH_T by the equation:

$$\frac{\mathrm{d}lnK}{\mathrm{d}T} = \frac{\Delta H_T}{RT^2} \tag{1}$$

Hence, as pointed out by van't Hoff, it follows that since the equilibrium constant K is the ratio of the rate constants k_{+1} and k_{-1} in the forward and backward directions, these constants may be expected to obey the same equation, i.e.

$$\frac{\mathrm{d}lnk}{\mathrm{d}T} = \frac{E}{RT^2} \tag{2}$$

where E is a value which may depend on temperature. It follows that

$$k = A\exp(-E/RT) \tag{3}$$

A few years later (1889), exploring the rate of hydrolysis of cane sugar under the influence of mineral acids, Arrhenius [3] found that the effect of temperature on the rate is too great to be explained by the change in translational energy of the molecules or the viscosity of the medium. Hence he concluded that there is an equilibrium between inactive (normal) and active molecules directly involved in the reaction, and this balance varies with temperature in accordance with Eq. 3 predicted by van't Hoff. Arrhenius [3] proposed to consider the parameter E as the activation energy of *active* molecules involved in the reaction and associated with the total number of molecules by the Boltzmann distribution. In the opinion of Gardiner [4], "this model and the basic equation might have remained merely suggested approximations, if not the appearance a few years later of a remarkable achievement of Max Bodenstein, which raised the Arrhenius model (with A and E as constants) to canonical status". By studying the gas-phase reaction $\mathrm{HI} + \mathrm{HI} = \mathrm{H}_2 + \mathrm{I}_2$ at different temperatures, Bodenstein [5] showed that it proceeds in accordance with Eq. 3, which was misinterpreted as evidence for the correctness of the Arrhenius hypothesis (see "How has the activation hypothesis appeared?" section). A detailed description of the events associated with the emergence of the Arrhenius equation is contained in the book by Stiller [6] and a review by Laidler [7].

The development of AM essentially ended in 1935–1938, when Eyring [8] and Evans and Polanyi [9] developed, respectively, the kinetic theory of the activated complex and the transition state theory, and Wagner [10] proposed a mechanism of transfer of ions and electrons in solids due to defects (disorder) of crystal lattices. This effect became the basis of the mechanism of solid interactions and decomposition for a long time. This model is still widely used in the study of heterogeneous processes; in Russia, in particular, in the writings by Boldyrev [11] and Tretyakov [12].

The history of the thermochemical model

The birth of TM (Table 1) [13–32] is associated with the research of Hertz [13] and Langmuir [14, 15] of the rate of evaporation of metals (with molar mass M) in a vacuum. Based on the molecular theory of gases (statistical mechanics) and the pioneering work of Hertz [13], Langmuir introduced the ratio, justly dubbed the Hertz–Langmuir equation

$$J = \frac{MP_{\mathrm{eq}}}{(2\pi MRT)^{1/2}} \tag{4}$$

It is noteworthy that in assessing the potential role of this equation in future studies, Langmuir prophetically noted: “The importance of this equation in the kinetics of heterogeneous reactions can hardly be over-emphasized” [15, p. 2250]. The most important feature of this equation is a fundamental relationship between

Table 1 Milestones in the development of the thermochemical model (TM) of solid decompositions

Year	Innovation
1882	The proportional relationship between the rate of Hg evaporation in a vacuum and its equilibrium vapor pressure has been discovered by Hertz [13]
1913	The derivation of basic equation for the absolute rate of vaporization of metal, A(s/l)↔A(g), using the statistical mechanics approach [14]
1916	Langmuir prophetically noted: “The importance of this equation in the kinetics of heterogeneous reactions can hardly be overemphasized” [15, p 2250]
1966	The Langmuir diffusion equation was used for estimation of atomization rates of Al_2O_3 aerosol particles in flames [16, 17]
1968	The introduction of the term *thermochemical kinetics* and the development of this concept for homogeneous reactions in the gaseous state by Benson [18]
1981	The extension of the Langmuir equation to dissociative vaporization of compounds: A_aB_b(s/l)↔aA(g) + bB(g). Kinetics of metal oxide atomization were studied by ET AAS [19]
1984	The consideration of the impact of external pressure of gaseous product on the reaction rate and identification two modes (regimes) of vaporization: equimolar and isobaric [20]
1990–1995	Discovery and study of the mechanism of congruent dissociative vaporization (CDV): A_aB_b(s/l)↔aA(g)↓ + bB(g). Decomposition of metal nitrates was studied by ET QMS [21–23]
1997	The derivation of coefficients of congruency β for dissociative vaporization [24]
1997	The derivation of the relationship between the rate constant k and the absolute rate of decomposition J for a spherical particle [25]
2002	The application of the third-law method to accurate determination of the E parameters [26]
1997–2005	Thermogravimetric investigation of mechanism and kinetics of decomposition of about 60 diverse solid reactants: oxides, nitrides, azides, hydroxides, clays, hydrates, nitrates, sulfates, carbonates, and oxalates [27, 28]
2006–2007	Systematization and generalization of theoretical and experimental results in a monograph (in two editions: in Russian [27] and in English [28])
2012	Application of TM to the mechanism of heterogeneous reduction of NiO by hydrogen [29]
2013	Application of TM to the mechanism of catalytic oxidation of CO on PtO_2 [30]
2013	Application of TM to interpretation of the mechanism of catalytic oxidation of H_2 on PtO_2 [31]
2013	Development of the general theory of heterogeneous reactions on the basis of the CDV mechanism [32]

the kinetic parameter J, the absolute rate of evaporation (simple or dissociative), and the thermodynamic parameter, the equilibrium partial pressure P_{eq} of gaseous product connected, in turn, with the equilibrium constant of the reaction K_P. The existence of such a connection between kinetic and thermodynamic parameters of chemical reactions is denied or ignored by most experts in the field of physical chemistry, which, in turn, serves as justification for the development of the AM models (collision theory and transition state theory), based on the effect of activation as a necessary condition for chemical interaction.

It so happened that the majority of events in the development of TM following the pioneering works of Langmuir (Table 1), has occurred with the participation of the present author [16–32]. The exception is an important contribution of Benson [18], which introduced the concept and the term *thermochemical kinetics* for homogeneous reactions in the gaseous state. In the preface to his book, Benson said: "The close relation between thermochemical properties and kinetic parameters which is involved in the theory and methods discussed in the present volume has inspired the somewhat unusual title *Thermochemical Kinetics*." (We encountered this book only in 2005 and used as the title of our approach the term *physical approach* for a long time, referring to the underlying statistical or molecular physics).

Our interest in applying the thermochemical approach to heterogeneous reactions emerged in the early 1960s, during the development of the method of electrothermal atomic absorption spectrometry (ET AAS) by the author of the present work. The first attempt to estimate the rate of evaporation of solid Al_2O_3 particles (as aerosol) with the formation of free atoms of Al and O in the flame at different temperatures has been described in the monograph [16]. However, the use of the equation that is valid for the evaporation of simple substances, to calculate the rate of dissociative evaporation of substances with the formation of several gaseous products was not sufficiently substantiated. Essentially, the systematic development of TM began only in the 1980s, marked by the widespread use in analytical laboratories of the electrothermal option of AAS. Among the achievements listed in Table 1, the most important are: first, the application of the Langmuir equation to cases of the dissociative evaporation of compounds [19] and the identification of two types (modes) of evaporation (equimolar and isobaric) [20], second, the elucidation of the mechanism of CDV [21, 22], and third, the application of the third-law method to the determination of the E parameters with a precision an order of magnitude higher than that obtained by the traditional method [26]. The last step was the application of TM to the reduction of nickel oxide by hydrogen [29] and the reactions of heterogeneous catalysis [30, 31] and, as a result, the development of the general theory of heterogeneous reactions on the basis of the unifying mechanism of CDV [32]. These four stages were separated by approximately ten-year intervals. Despite the importance of all these steps, the most important, undoubtedly, are the first step (identification of the two modes of evaporation) and the second step related to the mechanism of the CDV. Without them, the dissemination of TM onto a core group of solids that decomposes with the formation of solid products would have been simply impossible. Let us discuss these points in more detail.

Identification of two modes of evaporation

In order to use Eq. 4 for the decomposition reactions, it was proposed [20] for the reaction of the general form

$$\mathrm{A}_a\mathrm{B}_b(\mathrm{s/l}) \leftrightarrow a\mathrm{A(g)} + b\mathrm{B(g)}$$

to express the equilibrium pressure P_{eq} through the equilibrium constant, K_P, as

$$K_P = (P_{\mathrm{A}}^{\mathrm{int}})^a (P_{\mathrm{B}}^{\mathrm{int}} + P_{\mathrm{B}}^{\mathrm{ext}})^b \tag{5}$$

Here P_A^{int} and P_B^{int} correspond to the equilibrium partial pressures (internal), determined by the development reaction, and $P_{\mathrm{B}}^{\mathrm{ext}}$, the pressure of the gaseous products, entering the reactor from the outside. Depending on the ratio between $P_{\mathrm{B}}^{\mathrm{ext}}$ and P_B^{int} there are two different modes (regimes) of reaction. The mode in which the pressure of the product from outside ($P_{\mathrm{B}}^{\mathrm{ext}}$) is much less than its equilibrium value (P_B^{int}) is called *equimolar*. This condition involves not only the initial lack of product in the reactor, but also prevents its accumulation in the decomposition process. *Isobaric* is the name of the mode, in which the actual pressure of the gas product is significantly higher than the equilibrium value, i.e. $P_{\mathrm{B}}^{\mathrm{ext}} \gg P_B^{\mathrm{int}}$, and is kept constant during the measurement process ($P_{\mathrm{B}}^{\mathrm{ext}} = \mathrm{const}$).

From the condition of congruent evaporation in vacuum [24] it follows that

$$P_{\mathrm{B}}/P_{\mathrm{A}} = (b/a)(M_{\mathrm{B}}/M_{\mathrm{A}})^{1/2} \equiv \beta \tag{6}$$

Replacing P_{A} on P_{B} in Eq. 5 with the use of Eq. 6 and the well-known thermodynamic expression for K_P, we obtain values for P_{B} in the equimolar mode:

$$P_{\mathrm{B}}^{\mathrm{e}} = (\beta^a K_P)^{1/v} = \beta^{a/v} \exp\frac{\Delta_r S_T^{\circ}}{vR} \exp\left(-\frac{\Delta_r H_T^{\circ}}{vRT}\right) \tag{7}$$

and in the isobaric mode:

$$P_{\mathrm{B}}^{\mathrm{i}} = \beta P_A^i = \beta \frac{K_P^{1/a}}{(P_{\mathrm{B}}^{\mathrm{ext}})^{b/a}} \exp\frac{\Delta_r S_T^{\circ}}{aR} \exp\left(-\frac{\Delta_r H_T^{\circ}}{aRT}\right) \tag{8}$$

Here $\Delta_{\mathrm{r}}H_T^{\circ}$ and $\Delta_{\mathrm{r}}S_T^{\circ}$ denote the enthalpy and entropy of the decomposition reaction, the upper indices e and i, the used mode (equimolar and isobaric) and $v = a + b$. Substituting the values $P_{\mathrm{B}}^{\mathrm{e}}$ and $P_{\mathrm{B}}^{\mathrm{i}}$ in Eq. 4, we obtain two final equations for the absolute rate of dissociative decomposition in equimolar and isobaric modes:

$$J^{\mathrm{e}} = k^{\mathrm{e}} r_{\mathrm{m}} \rho = \frac{\gamma \beta^{a/v} M_{\mathrm{B}}}{b(2\pi M_{\mathrm{B}} RT)^{1/2}} \exp\frac{\Delta_r S_T^{\circ}}{vR} \exp\left(-\frac{\Delta_r H_T^{\circ}}{vRT}\right) \tag{9}$$

$$J^{\mathrm{i}} = k^{\mathrm{i}} r_{\mathrm{m}} \rho = \frac{\gamma \beta M_{\mathrm{B}}}{b(2\pi M_{\mathrm{B}} RT)^{1/2}} \frac{1}{(P_{\mathrm{B}}^{\mathrm{ext}})^{b/a}} \exp\frac{\Delta_r S_T^{\circ}}{aR} \exp\left(-\frac{\Delta_r H_T^{\circ}}{aRT}\right) \tag{10}$$

For the sake of completeness, we have included in these equations the rate constant k, which is associated with the value J by the relation [25]

$$J = k\, r_{\mathrm{m}} \rho \tag{11}$$

where ρ and r_{m} denote the density of the reactant and the actual radius of the sample (at the time of measurement) in the form of a single spherical particle. The coefficient $\gamma = 10^5$ Pa bar^{-1} translates P values in bar units, taken in the thermodynamic calculations, into Pa.

It should be noted that, simultaneously and independently of our studies, Eq. 4 was applied by Searcy and Beruto [33, 34] for the derivation of relationships for the congruent decomposition rates of solid and melts. However, despite intensive theoretical and experimental studies, Searcy's team failed to solve this problem. In our opinion, there were two reasons for this. First, these authors considered Langmuir's theory "as equivalent to the special case in transition state theory, in which the activated complex is identical with the reaction product" [34]. Second, the maximum rate of decomposition was derived [34] as a multiplication of the flows of the gaseous products, $J_{\mathrm{A}} \times J_{\mathrm{B}}$, instead of an obvious summation, $J_{\mathrm{A}} + J_{\mathrm{B}}$, which is used in our studies [27, 28]. The physical meaning of this $J_{\mathrm{A}} \times J_{\mathrm{B}}$ value is unclear.

The mechanism of congruent dissociative vaporization

Its essence consists of CDV of the substance (solid or melt) with a simultaneous condensation of oversaturated vapor of low-volatile product A(g):

$$\mathrm{A}_a\mathrm{B}_b(\mathrm{s/l}) \leftrightarrow a\mathrm{A(g)} + b\mathrm{B(g)} \rightarrow a\mathrm{A(s)} + b\mathrm{B(g)}$$

The existence of such a mechanism was found as a result of direct observation of low-volatile decomposition products (molecules and atoms) in the gas phase by ET quadrupole mass spectrometry (QMS) by Sturgeon et al. [35] and Holcombe et al. [36, 37]. The story of this discovery was outlined in [38]. The research objects were nitrates of Ag, Pb, Cd, Cu, Ni and Cr. Free Ag atoms and metal oxides molecules were observed in high vacuum as major decomposition products in the temperature range from 350 to 600 K. The calculation of equilibrium vapor pressure values for metal nitrates in the molten state was carried out in the usual way, without taking into account the condensation of low-volatile products [23]. For solids, the partial return to reactant of the energy released in the reaction zone (the interface) upon condensation of low-volatile product was taken into account. As a first approximation, it was assumed that condensation energy is equally distributed between the two solid phases (reactant and product). Later it turned out that the relative part of the returned condensation energy depends on the oversaturation degree of vapor and can be estimated on a semi-empirical basis [28]. A partial return of energy to the reactant in the process of interface formation reduces the enthalpy of the first stage of above reaction and thus explains the dynamics and energetics of autocatalysis. However, the mechanism of energy transfer to the reactant and the impact of vapor oversaturation on this transfer require further study.

The history of this discovery recently received an unexpected continuation. Randomly browsing through a monograph on catalysis by Schwab [39], this author [40] found that almost the same two-step mechanism of decomposition of solids was proposed (in the form of a hypothesis) by Volmer [41]. Schwab immediately appreciated its significance for the interpretation of the autocatalytic effect and included it into his book. However, its fate was unhappy. The mechanism was not adopted by the scientific community. On the contrary, as seen from the results of the international conference *Chemical reactions involving solids* in Bristol in 1938 [42] (in the absence of Volmer and Schwab among the participants), this model was rejected as unrealistic and was forgotten. During the next 70 years, the mechanism of solid-phase decomposition was interpreted by the majority of researchers on the basis of the Wagner theory of defects [10]. Nobody knows the reason why Volmer and Schwab failed to defend a two-step mechanism in this dispute. Most likely, this was due to the political situation in Germany in the late 1930s. Both scientists were subjected to political and racial persecution. Volmer was forced to resign from the Institute, and Schwab immigrated to Greece for 11 years.

Very recently, the CDV mechanism has found another unexpected source of support. The similarity between chemical and physical processes (heterogeneous decomposition and evaporation), which is usually rejected or omitted from consideration by many proponents of the AM [1, 11, 12], was considered by van't Hoff in his classic monograph [2]. Alas, we have noticed it too late. Here are a few excerpts from this work: "The phenomenon of equilibrium of two systems, or, if desired, two different states of matter, does not apply exclusively to the field of chemistry. A phenomenon of this kind has long been discovered in physics in the form of the phenomenon of evaporation, much earlier than something similar was seen in chemistry. Needless to mention that chemical equilibrium, expressed symbolically $NH_5S \leftrightarrow NH_3 + H_2S$, is similar to the equilibrium set by evaporation of liquid water into water vapor. Let us add that the analogy between physical and chemical phenomena, which are here referred to, is sometimes such that it is exceedingly difficult to establish the true nature of the phenomenon. These considerations lead to the conclusion that physical equilibrium is a special case of the simplest forms of chemical equilibrium". Any comments are superfluous here.

Results

The final equations to calculate the rate of reactions in both models

Probably, the most convincing argument in favor of a particular kinetic model is the comparison of the possibilities arising from the use of basic mathematical ratios to quantify, control and predict the kinetics taking into account the influence of experimental conditions and the physico-chemical characteristics (primarily thermochemical) of the studied objects. To this end, let us give such relations for both models, AM and TM. For AM such a relation can be considered the equation proposed by Eyring [8] in the framework of the theory of the activated complex:

$$k = A\exp\left(-\frac{\Delta H^{\neq}}{RT}\right) \tag{12}$$

where

$$A = \frac{k_{\mathrm{B}}T}{h}\exp\frac{\Delta S^{\neq}}{R} \tag{13}$$

In these equations, k_{B} and h are the Boltzmann and Plank constants, $\Delta S^{\neq}$ and $\Delta H^{\neq}$, the change of entropy and enthalpy at the transition of the molecule from the ground state to an activated complex. In the case where $\Delta S^{\neq} = 0$ (the activated complex retains the size and structure of the original molecule), $A \approx 3 \times 10^{13}\ \mathrm{s}^{-1}$ (at $T = 600$ K). The possibility of estimating the value of the parameter A is the main advantage of this theory compared to the original Arrhenius equation, although the correctness of this assessment, as we will see below, is questionable.

In the case of TM, the mathematical description of kinetics [27, 28] includes two different equations for the equimolar and isobaric modes. As it follows from Eqs. 9 and 10, in the first case:

$$k^{\mathrm{e}} = A^{\mathrm{e}}\exp\left(-\frac{\Delta_{\mathrm{r}}H_T^{\circ}}{vRT}\right) \tag{14}$$

where

$$A^e = \frac{\gamma\beta^{a/v}M_B}{br_m\rho\sqrt{(2\pi M_B RT)}}\exp\frac{\Delta_r S_T^{\circ}}{vR} \tag{15}$$

In the second case:

$$k^i = A^i\exp\left(-\frac{\Delta_r H_T^{\circ}}{aRT}\right) \tag{16}$$

where

$$A^i = \frac{\gamma\beta M_{\mathrm{B}}}{br_m\rho\sqrt{(2\pi M_{\mathrm{B}}RT)}}\frac{1}{(P_{\mathrm{B}}^{\mathrm{ext}})^{b/a}}\exp\frac{\Delta_r S_T^{\circ}}{aR} \tag{17}$$

These equations allow the calculation of the rate of reaction and Arrhenius parameters (A and E) taking into account the composition, stoichiometry and chemical characteristics of the components of the reaction, the excess pressure of gaseous product in the reactor and the physical properties of the reagent (sample size and the density of the reagent). The kinetic model of solid-phase reactions for the first time in the history of these investigations allowed a quantitative evaluation and prediction of the lifetime of substances depending on the atmosphere and temperature of storage. A striking example of the influence of the environment on the rate of reaction is an accepted technology for the storage of food (mainly fruit and vegetables) in a controlled atmosphere with a high concentration of CO_2 and H_2O and a reduced concentration of O_2. That this technology lowers the oxidation rate of organic substances (particularly carbohydrates) has been known for over

200 years [43]. However, the physico-chemical nature of this effect and its quantification hitherto remained unknown.

The correctness and accuracy of such calculations has been confirmed [44] in the case of the decomposition of $CaCO_3$ in a deep vacuum, air and CO_2. It was shown in particular that the value of the A parameter calculated by Eq. 15 is consistent with experiment and is three orders of magnitude lower than the value calculated by Eq. 13. This casts doubt on the correctness of the Eyring model. This is confirmed also by the difference in the change of the A parameter with temperature in the direction of increase (proportional to T)—by Eq. 13 and in that of decrease (proportional to $T^{1/2}$)—by Eqs. 15 and 17. Noteworthy is the strong influence of the excess pressure of product gas on the rate of decomposition. In the case of $CaCO_3$ this allows raising the temperature while maintaining the same rate of decomposition ($k \approx 10^{-6}$ s) with 800 K in vacuum to 1200 K in the presence of 1 bar CO_2. All known theories based on the effect of activation ignore even the existence of this effect.

Interpretation of some features of the kinetics and mechanism of thermal decomposition

In addition to fundamental advances (Table 1), which determined the evolution of TM over the last 100 years, we discuss below some of the results that were obtained in the process of applying TM to explain some unusual effects and patterns described in the literature. Most of them (in at least 20 out of 24 cases listed in [45]) received for the first time not only a qualitative but also a quantitative interpretation. Among the most unexpected and important for the further development of the theory are an assessment of the molar entropy of decomposition reactions and the influence of the crystal structure of the reagent on the composition of primary gaseous products.

In the first case [28], we are dealing with the proximity of the values of the molar entropy for the processes of dissociative sublimation and evaporation of any (simple and complex) substances at temperatures corresponding to the same partial pressure of product vapor. In particular, when the vapor pressure is within 10^{-7} bar, this value $\Delta_r S^\circ_T/\nu$ is equal to 150 ± 20 J mol^{-1} K^{-1}. This pattern, in fact, repeats the regularity that was observed by Trouton [46], namely, the proximity of entropy values for the evaporation of different liquids at boiling point (under vapor pressure 1 bar). In this case, $\Delta_r S^\circ_T/\nu \approx 90 \pm 10$ J mol^{-1} K^{-1}. This regularity turned out to be useful for the determination of the parameter E with the help of the third-law method in the absence of tabular data for the molar entropy.

In the second case [28], the objects of study were the decomposition reactions, in which primary gaseous products (mostly oxygen) appeared either in atomic or molecular state. An analysis of these data identified a correlation between the crystal structure of the reagent and product form. It turned out that molecular oxygen appears only for compounds with cubic structure (I). The decomposition of compounds with structure different from cubic (III, IIIa, IV and V), proceeds to atomic oxygen. Unfortunately, attempts to find an explanation for this pattern so far have failed (differences in the interatomic distances of O–O in the crystals were here insignificant). This discovery is of great importance for the explanation and prediction of the thermal stability of substances, especially high-energy materials.

The reason for the anomalous thermal stability of these substances under experimental conditions, which is expressed in very low coefficients of evaporation α_v, was identified almost 20 years ago [47, 48]. It lies in the difference of primary gaseous decomposition products from the equilibrium composition (assuming their presence in the form of molecules of O_2, N_2, P_4, As_4, and Sb_4). The objects of our analysis were metal azides [47], metal nitrides, HgO and some metalloids: P (red), As, and Sb [48]. Later on, this was extended to metal oxalates [49]. Of these objects, the smallest values of the coefficient α_v are observed for azides (10^{-13}–10^{-29}) and oxalates (10^{-10}–10^{-24}) which are considered explosive materials. For HgO at 700 K $\alpha_v \approx 10^{-6}$ and for P at 600 K $\alpha_v \approx 10^{-5}$. The crystal systems of all listed substances, in accordance with the above results, differ from the cubic [28].

Extremely successful in practical terms was our attempt to find the perfect kinetic standard to thermal analysis. Based on the concepts of the TM, such a standard, a priori, was chosen to be potassium permanganate $KMnO_4$ [28]. Experimental testing has confirmed this choice. The average value E of the 12 experiments in the atmosphere of various gases (He, air, CO_2 and Ar) was 138.3 ± 0.6 kJ mol^{-1} [50]. In a high vacuum ($<10^{-7}$ bar), due to the self-heating of the reactant (the decomposition reaction of $KMnO_4$ is slightly exothermic) the value of E was reduced to 127 kJ mol^{-1} [51].

The oldest of unresolved issues include the problem of the physical meaning of the A and E parameters in the Arrhenius equation (defined in [3]), the effect of autocatalysis ([52]), the kinetic compensation effect ([53]) and the effect of Topley–Smith ([54]). On average, about a 100 years have elapsed since their appearance. However, despite enormous efforts spent on their research, they have been interpreted only in the context of TM [28, 55]. All known theories based on the effect of activation (classical Arrhenius theory, collision theory and activated complex theory), were powerless in this respect. This result seems quite logical if we take into account that the effect of activation in decomposition reactions is, as we will see next, a matter of dispute.

Discussion

How has the activation hypothesis appeared?

It is unlikely we will ever get a reliable answer to this question. Therefore, we list below some facts, which may help the reader to form his own opinion about this.

The correctness of the substantiation by Arrhenius of the AM based on the thermodynamic equation of van't Hoff raises serious doubts. The dependence of the rate constant k upon the temperature, which logically follows from the exponential dependence of the equilibrium constant K upon T in the thermodynamic Eq. 1, was additionally explained by Arrhenius through the Boltzmann distribution of reaction particles on energies (also exponentially dependent on T), although this is not only unneeded, but in principle is not permitted. As noted by the very same Arrhenius [3], “In his wonderful book *Study of chemical dynamics* van’t Hoff gives *a theoretically sound formulation* (emphasis added) of the effect of temperature on reaction rate”. (“In seiner berühmten Arbeit *Etudes de dynamique chimique* giebt van’t Hoff eine theoretisch begründete Formulierung des Temperatureinflusses Reaktion auf die Geschwindigkeit”). And nevertheless.

Perhaps, Arrhenius was directed to this additional interpretation by the work of Austrian physicist Pfaundler [56], published in 1867 (now almost forgotten). In this article, Pfaundler discussed the exponential impact of temperature on the velocity of gaseous particles according to the Maxwell distribution. In addition, personal acquaintance and communication with Boltzmann during the visit of Arrhenius to the University of Graz in Austria in April 1887 may have played the role. Finally, 130 years ago, at the stage of formation of chemical thermodynamics, the pointlessness of the interpretation of thermodynamic regularities with the help of whatever physical models or mechanisms might not seem as obvious as it is today. However, even today, many proponents of the AM, for example, the authors, in general, of very useful tutorials [57, 58] forget that phenomenological chemical thermodynamics [59], which applies the van’t Hoff isobar equation, does not require the involvement of physical mechanisms for the interpretation of the exponential dependence of the equilibrium constant on temperature. This is established from thermodynamics.

The doubtfulness of these attempts is all the more obvious if we recall that the exponential dependence of rate on temperature is observed for many biochemical, physiological and even psychological processes listed in [57]. Among them, in particular, the author of [57] enumerates the frequency of chirping and flashes of fireflies in the range from 14.2 to 27 °C and the speed of the counting time by people with body temperature from 36.9 to 39 °C. What relation could this have to the Boltzmann distribution of activated particles by energies?

For many years, the existence of AM, its history and theoretical foundations were almost never subjected to critical analysis. We are aware of only two episodes (except for the critical position of the author, remaining unchanged for half a century). Let us first refer to the evaluation of the Bodenstein experiments [5], “which raised (in the opinion of Gardiner [4]) the Arrhenius model to canonical status”. Actually it was not so. The experiments of Bodenstein confirmed only the equilibrium distribution of the reaction products (in accordance with the equilibrium constant of this reaction). Indeed, to study the reaction, the different amounts of HI placed in glass containers. After heating to the desired temperature for various periods of time, the containers were quickly cooled, and the contents were analyzed for all three components [5]. In this way, Bodenstein was able to determine the equilibrium constant for this reaction at different temperatures, but not the temperature dependence of the rate of gas-phase reactions, too high for its direct measurement in the conditions of these experiments.

Very reasonable doubts about the applicability of AM in the case of heterogeneous reactions are contained in some works by Garn, for example, in [60]. The essence of his criticism was the difference of the energy distribution of particles in the solid from the gas, where the free translational motion of the molecules must obey the Boltzmann distribution law. For the surface layer of the crystal, the distribution of molecules by energy must be substantially narrower due to the rapid transfer of vibrational energy by the volume of the reagent. This difference inclined Garn to conclude: “The lack of a statistical distribution rules out the use of the Arrhenius equation unless it is independently verified for the particular system” [60].

The critical attitude of the author to the idea of activation in decomposition reactions was born in the mid-1960s, when, while preparing a monograph on AAS, he was faced with the estimation of the rate of atomization of solids [17]. Remaining unexplained was the difference between the kinetics of evaporation of metals, governed by simple, physically grounded laws, and the kinetics of thermal decomposition of compounds described by the Arrhenius equation with thermodynamically uncertain parameters. This distrust has affected the content of the book [16], where the activation model was not even mentioned. Later, as the accumulation of the results of the kinetic measurements for dissociative evaporation of metal oxides [19, 20] and metals nitrates [23], and also, of the critical analysis of published data for some carbonates [25] and oxalates [48], this distrust only strengthened. In a review [61], it resulted in the statement: “The effect of activation in the case of crystolysis reactions is no more than an illusion. The application of the original Arrhenius approach (and later on, the Polanyi–Wigner and Eyring–Evans–Polanyi treatments) to the kinetics of solid decompositions was wrong, and it resulted in a stagnation of the theory of crystolysis reactions for many years”. No response to this statement followed in the past 14 years, although this paper was cited (according to Scopus) 72 times.

Direct validation of thermochemical model

To further evaluate the correctness of TM, we held [62] a direct comparison of experimental E^{e} and E^{i} (*activation energies*) with molar enthalpies for 54 decomposition reactions, $\Delta_{\mathrm{r}}H_T^\circ/v$ and $\Delta_{\mathrm{r}}H_T^\circ/a$, for equimolar and isobaric modes, respectively. The reactants used in these experiments were as follows: oxides, hydroxides, hydrates, nitrates, sulfates, carbonates and oxalates of metals. In the calculations, we took into account two circumstances that distinguish the calculation scheme for real quasi-equilibrium conditions (by Langmuir) from the calculation scheme for the ideal equilibrium conditions of decomposition (by Knudsen). These include the CDV mechanism that takes into account the energy consumption for dissociative vaporization of the reactant with the partial return of condensation energy of the low-volatile product to the solid reactant, and, in some cases, the release of oxygen in the form of free O atoms instead of O_2 molecules.

The average values of relations $(\Delta_{\mathrm{r}}H_T^\circ/v)/E^{\mathrm{e}}$ and $(\Delta_{\mathrm{r}}H_T^\circ/a)/E^{\mathrm{i}}$ for all (without exception) 54 different reactions were equal to 1.0 ± 0.1. This allows us to argue more confidently than before that the effect of activation in heterogeneous reactions is an illusion and the decomposition of solids and melts does not require additional energy in excess of the molar enthalpy of the reaction. The fairly widespread belief (see, for example, [57, 58]) that the thermal stability of many substances owes its existence to an activation barrier that protects them from decomposition, is inaccurate. Actually this is due to the difference of the actual conditions of the reactions (by Langmuir) from idealized conditions (by Knudsen), the result of which is an underestimation of the true values of the reaction enthalpies. This fact, as noted in above Section *Interpretation of some features of the kinetics and mechanism of thermal decomposition* was first discussed about 20 years ago in [46, 47], and subsequently in [27, 28, 55, 62].

Therefore, at least in the context of heterogeneous reactions, such familiar terms as activation barrier, activated complex, activation energy and frequency factor retain their relevance only in the form of historical monuments or symbols. However, taking into account the traditions, the ease and convenience of Eq. 3, derived by van't Hoff from thermodynamics, the latter definitely can and should be used for the quantitative interpretation of A and E kinetic parameters in accordance with TM.

The breakthrough in the kinetic theory, which consists of replacing the activation model by the TM, should lead to remedy the current crisis in thermal analysis and extend the application area of chemical kinetics. Let us pause on these expectations.

Crisis in thermal analysis

More difficult is the elimination of the crisis in thermal analysis. The point is that the prolonged erroneous application of the activation model has led to the gradual displacement of the theory of chemical thermodynamics and molecular physics and their replacement by computational mathematics. Paradoxically, this was possible thanks to the great progress over the past 2–3 decades in the computerization and technical improvement of methods and devices for non-isothermal measurements. The failure of in a reliable simulation of the decomposition processes stimulated the emergence of the so-called *model-free* methods for studying kinetics. The most popular among them has become the isoconversional option.

Now the Kinetics Committee of ICTAC tries to convince the scientific community that this method, based on AM and excluding from consideration the influence of the reaction products on the kinetics, even in the absence of the original model representations about the processes of decomposition, allows one to obtain reliable and reproducible kinetic data [63]. This statement is rather doubtful. Unlike the results of previous unsuccessful attempts to prove the advantages of this method [64], the recommendations [63] are not accompanied by interlaboratory control and therefore are not reliable.

Unfortunately, this trend is becoming more common in thermal analysis. (According to Scopus, the number of citations for [63] in the period of 3 years reached 600). An attractive aspect of this approach for the specialists involved in this business is the ability to hide their failure to interpret a particular result, citing supposedly still unknown features of the AM. As an example, we refer to the development by Vyazovkin [65] of the concept of *variable activation energy* (decrease in E with increasing degree of decomposition α and temperature T). Within the TM, this mystical effect, which appeared in non-isothermal measurement conditions, was repeatedly interpreted as the transition from the isobaric mode of reaction (at low values α and *T*) to equimolar mode (at high values α and *T*) [20, 24–28, 66]. It is associated with the presence in the reactor volume of admixtures of O_2, H_2O, and CO_2, providing at low temperature the isobaric mode of decomposition. All substances ($CaCO_3$, NH_4NO_3, silk, $CaC_2O_4 \cdot H_2O$ and $Li_2SO_4 \cdot H_2O$) mentioned in [65] in connection to the observed effect, decompose releasing CO_2 and H_2O.

Extension of application area of chemical kinetics

Let us pause further on the prospects of the possible use of TM in other areas of kinetic studies, where the concept of activation of the reaction components is applied as widely as in the solid-phase thermal decomposition. It may include the area of gas-phase reactions and heterogeneous catalysis. In view of the universal for all chemical reactions thermodynamic nature of the exponential dependence of reaction rate constant on temperature (in the approximation of van't Hoff), it can be assumed that the thermochemical approach to the kinetics of activation in return is equally applicable to gas-phase reactions. To check this assumption, it would seem enough to compare experimental and calculated values of the parameters *E* and take into account the mechanism of the reaction and the influence of experimental conditions on the kinetics. However, there, the relevant physical models, which in the solid-phase reactions of decomposition are provided by the Hertz–Langmuir equation and the CDV mechanism, are not yet available. The concepts of collision theory, activated complex theory and even the chain reaction theory are insufficient for that purpose. However, even here there are exceptions. One of them is a well-known reaction of dinitrogen tetroxide dissociation to nitrogen dioxide: $N_2O_4(g) \leftrightarrow 2NO_2(g)$. The activation energy of this reaction (55 ± 3 kJ mol^{-1}) within the error of measurement is in agreement with the enthalpy of this reaction (56.5 kJ mol^{-1}) [66].

More clear and encouraging prospects for the use of TM are open in heterogeneous catalysis. Using the concepts developed for solid-phase decomposition reactions and the reduction of NiO by hydrogen [29], as well as a huge array of published data on catalytic CO oxidation on platinum, which have found wide application in the automotive industry, L'vov and Galway [30] proposed a new mechanism for this reaction. Instead of the known schemes based on the adsorption and interaction of the components of reaction at the catalyst surface and the subsequent desorption of products, the proposed mechanism involves two co-flowing process involving the catalyst: $PtO_2(s) + 2CO \leftrightarrow Pt(g) + 2CO_2$ and $Pt(g) + O_2 \leftrightarrow PtO_2(g) \rightarrow PtO_2(s)$. The first reaction determines the kinetics of the oxidation of CO, and the second reaction, the kinetics of a simultaneous restoration of the PtO_2 layer (reducing the amount of catalyst consumed for the oxidation of CO). Thermochemical calculations allowed (for the first time in the history of catalysis) to determine the enthalpy and absolute rate of the oxidation reaction. The results obtained agree well with the experimental data. The proposed mechanism explains the nature of restructuring of the catalyst surface and limited loss of platinum in the reaction process, the strong (quadratic) depressive influence of CO_2 on the rate of oxidation and the three-fold change of the parameter *E* with temperature. The same scheme was later successfully used [31] to interpret the catalytic oxidation of hydrogen on platinum, which was discovered 200 years ago, but still remained a mystery. Both examples confirm extremely interesting prospects in the application of TM to heterogeneous catalytic reactions.

Conclusion

The analysis of the emergence, development and current state of the two alternative models, activation and thermochemical, in the kinetics of heterogeneous chemical reactions indicates the need for replacement of the activation model by the TM to overcome the current crisis in the kinetic theory, as a whole, and in thermal analysis, in particular. The change of paradigms in this way, as the treatment of severe disease, may be difficult and prolonged. It is desirable that this process be accompanied by an open and objective discussion of this issue in press and at scientific conferences, and also be considered in programs of school and university education for new generations of specialists in physical chemistry, not burdened by the load of their past achievements in this area and therefore more receptive to fresh, unconventional ideas. Unfortunately, repeated appeals from the author to the scientific community with such proposals remain without any response. Alas, today, with the apparent support by the leadership of ICTAC of the activation model and the suppression of the TM, this area of science is full of distrust and conservatism. It remains to wait and hope. Even the longest night comes to an end.

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