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Ups and downs in the theory of thermal decomposition of solids for 130 years

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Abstract This paper deals with the systematization and classification of the theory of thermal decomposition of solid materials. We analyze the main innovations during the 130 years since the publication of the classic works by van't Hoff in 1884 and Arrhenius in 1889. These innovations concern mainly the mechanism and kinetics of decomposition. In kinetics three different models are considered, the van't Hoff thermodynamic model, the activation model of Arrhenius, and the thermochemical model developed by the present author. The two latter models are respectively based upon the Boltzmann statistical theory of the energy distribution of activated particles and the statistical theory of evaporation due to Langmuir. The activation model is inconsistent with the thermodynamic model because of the different mode in which temperature impacts reaction rate: via the relative concentration of active particles, in the first case, and through the equilibrium constant, in the second. The thermochemical model describes the impact of temperature on the rate in the same manner as the thermodynamic model and is therefore suitable for a detailed interpretation of decomposition kinetics. For about 30 years, it has been experimentally tested and described in dozens of papers and in two monographs. However, because of the negative opinion of the ICTAC Kinetics Committee, it has until now laid in shadow of the old activation model. To overcome the lasting crisis in the kinetics of heterogeneous reactions, it is necessary to promote discussion of the current situation and search for appropriate ways to replace activation model by the thermochemical model.

Keywords Activation model · Kinetics of decomposition · Mechanism of decomposition · Statistical physics · Thermochemical model · Thermodynamic model

Introduction

About 130 years separate us from the appearance of the fundamental work of van't Hoff [1], in which the foundations of the theory of the mechanism and kinetics of thermal decomposition of solid materials were laid. In spite of the enormous efforts to further these studies, until now the scientific community has not been able to reach a consensus on this issue. The two existing theoretical models, the thermodynamic model (TDM) and the activation model (AM) associated, respectively, with the names of van't Hoff [1] and Arrhenius [2] are in a state of mutual confrontation. This is a roadblock for any attempt to solve the problems that have accumulated in this field. These are, firstly, the physical interpretation of the mechanisms and kinetics of decomposition reactions and, secondly, the development of a reliable scheme for the precise and accurate determination of the lifetime of materials depending on the phase of reactant (solid/melt), the environment and, most importantly, the temperature. Repeated appeals of this author to the scientific community over the last two decades to pay attention to great progress reached in regard to both problems within the thermochemical model (TCM), developed by the present author, were unnoticed or left without any comments and were even failed to be mentioned in current publications.

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The purpose of this paper is a critical analysis of events marking the path of these models in 130 years, and especially, of mistakes, which slowed the progress by many decades. Perhaps this will allow to better understand the dramatic consequences of indifference and silence for future progress in the field.

General view

The main steps in the development of the theory are represented in Table 1 and in accompanying comments. The number and choice of steps, with the exception, perhaps, of one or two cases, is unlikely to raise reader's objections. Table 1 shows not only the publications [1–61], corresponding to various innovations, but also the classification of these innovations depending on their belonging to different models, TDM, AM, and TCM, as well as to the main subjects of research: the kinetics (K) and mechanism (M) of thermal decomposition. From a cursory review of this classification, it is worth noting the significant difference in the numbers of AM and TDM studies in the first half, and of AM and TCM for the second half of Table 1 (steps 1–11 and 12–22, duration of 70 and 60 years, respectively). In the first case, these numbers are 7 and 4, and in the second, 1 and 9. This indicates the reduced interest of researchers to AM over the past 60 years. The numbers of steps that include the studies of kinetics and/or mechanism during all 130 years are in the ratio 16/11. This is understandable, as it is kinetics which is of main practical interest to thermal analysis.

Table 1 shows that the first two steps include the fundamental works of van't Hoff [1] and Arrhenius [2], related with the formulation of the thermodynamic and activation models, and eventually, with the present state of chemical kinetics. Difficult to explain, but the contribution of these scientists turned out to be undervalued, in the first case, and greatly exaggerated, in the second. It is worth to cite here the opinion of Laidler, one of the twentieth-century pioneers in chemical kinetics, on this point. (Keith Laidler completed his PhD in 1940 at Princeton University, with a thesis entitled "The Kinetics of Reactions in Condensed and Heterogeneous Systems", under Henry Eyring. Ladler published several books, over 250 scientific papers, and some reviews on the history of physical chemistry). In one of his late works [62], on the base of analysis of numerous documents, he wrote:

"There can be little question that the most outstanding contributions to chemical kinetics in the last century were those of the Dutch chemist Jacobus Henricus van't Hoff (1852–1911)…. Perhaps his most striking characteristic was his modesty. At no time did he ever enter into any controversy as to scientific priority; indeed in his writings he tended to stress the contributions of others and to deprecate his own. For this reason his work has never received the recognition it deserves. In chemical thermodynamics, especially in relation to chemical equilibrium, and in chemical kinetics, he was responsible for most of the concepts and relationships that are in current use by scientists today. In spite of this, modern textbooks of physical chemistry, while making full use of these concepts and equations, usually make little or no reference to the man in whose mind they originated….

Arrhenius, who always referred to van't Hoff in terms of the highest praise, worked in van't Hoff's laboratories, and their association was of great help in leading Arrhenius to his theory of electrolytic dissociation and to what is now usually called the 'Arrhenius equation'…. He gave it an interesting interpretation, in terms of equilibrium between reactant molecules and active molecules, which were assumed to undergo reaction very readily. As a result, this equation is now generally referred to as the 'Arrhenius equation', although it was certainly first given by van't Hoff, as Arrhenius acknowledges in his paper. The fact that Arrhenius is today given credit for the equation is another tribute to van't Hoff's modesty and lack of interest in claims of priority".

Below we will consider in more detail the contribution of both scientists to the mechanism and especially to the kinetics of solid-phase decomposition reactions.

Mechanism of solid-phase decomposition reactions

The similarity between chemical and physical processes (heterogeneous decomposition and evaporation/phase transition), which is usually rejected or disregarded from consideration by most authorities in thermal analysis and physical chemistry, was considered by van't Hoff in his monograph [1]. 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 $NH_5S = NH_3 + H_2S$, 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. (Alas, we have noticed this remark too late [61]: 130 years after its publication by van't Hoff [1] and 25 years after our

Table 1 Milestones in the history of thermodynamic, activation and thermochemical models (TDM, AM and TCM) for 130 years

Step	Year	Innovation	Model	Section[a]	References
1	1884	(1) Thermodynamic derivation of the exponential dependence of reaction rate *k* on temperature, which repeats the identical dependence of the equilibrium constant *K* (2) Intuitive remark on the physical similarity of evaporation and decomposition phenomena	TDM	K, M	[1]
2	1889	(1) The suggestion that reaction requires the activation of the reacting species up to the activation energies, which are greater than the molar enthalpies (2) The exponential rise of concentration of active species with temperature is derived from the Boltzmann's law	AM	K	[2]
3	1905	Discovery of the effect of autocatalysis in the case of the solid decomposition reaction $Ag_2O(s) = 2Ag(s) + 0.5O_2$	TDM	K	[3]
4	1913	Derivation of basic equations for the absolute rates of evaporation of metals and thermostable compounds in vacuum and inert gas using molecular physics	TDM	K	[4–6]
5	1916	Development of the collision theory based on the activation effect	AM	K	[7]
6	1929	Proposal of the 'two-step' mechanism of thermal decomposition that includes the dissociative evaporation of reactant and simultaneous condensation of oversaturated vapor of the low-volatility product: $Ag_2O(s) \leftrightarrow 2Ag(g) + 0.5O_2 \rightarrow 2Ag(s) + 0.5O_2$	TDM	M	[8–10]
7	1935	Development of the activated complex theory and the transition state theory	AM	K	[11, 12]
8	1938	The idea of a two-step mechanism of solid decomposition is rejected as unrealistic	AM	M	[13]
9	1938	The theory of defects/disorder, which introduced by Wagner as a basis of ion transport in solid crystals and metal oxidation, was used by the scientific community as a basis for a solid-phase decomposition mechanism	AM	M	[14–31]
10	1939	Development of formal kinetics based on description of experimental α–*t* curves by equations that take into account the 'nucleation and growth', geometrical, diffusional or some other factors	AM	K	[32, 33][b]
11	1955	Publication of the first fundamental monograph on physical chemistry of solid-phase reactions prepared by a group of eminent experts	AM	K, M	[17]
12	1960	Discovery of atomic oxygen evolution in the decomposition of some metal oxides		M	[34, 35]
13	1966	Estimation of atomization rates of solids in Atomic Absorption Spectrometry (AAS) using simple equations of Langmuir for metal evaporation in vacuum and inert gas	TCM	K	[36, 37]
14	1981	(1) Determinations of atomization rates of metal oxides in AAS by method of absolute reaction rates using the Langmuir diffusion equation (2) The first interpretation of the thermodynamic meaning of the *A* and *E* parameters	TCM	K	[38]
15	1983	Mass Spectrometric observations of low-volatility products in the gaseous phase during metal nitrates decomposition in vacuum	TCM	M	[39, 40]
16	1984	Effect of external pressure of O_2 on the atomization rate of metal oxides in AAS was studied and the 'equimolar' and 'isobaric' decomposition modes identified	TCM	K	[41]
17	1990	Formulation of the 'congruent dissociative evaporation' (CDE) mechanism of solid decomposition considering (including) partial contribution of condensation energy to the enthalpy of reaction and possible evolution of atomic oxygen in the decay	TCM	M	[42–45]
18	2000	Development of isoconversional method based on measurement of the rate constant at different heating rates and finding the variation of *E* parameter as a function of α	AM	K	[46–48]
19	2002	(1) It was found that the mean *T*/*E* ratio for decomposition of 100 reactants (taken from the literature) is 3.6 ± 0.4 K kJ^{-1} mol. This contradicts AM and supports TCM (2) The 'third-law method' was first applied for precise and accurate determination of the *E* parameter with the relative error lower than 1–2%	TCM	K	[49–52]
20	2006	Systematic treatment of theoretical and experimental results on the mechanism and kinetics of solid decomposition on the basis of the TCM in book form	TCM	K, M	[53, 54]
21	2008	Choice of $KMnO_4$ as an ideal kinetic standard for thermal analysis	TCM	K, M	[55, 56]
22	2014	Theoretical and experimental studies suggesting the insolvency of the hypothesis of activation energy and the associated activation models of solid-phase reactions	TCM	K, M	[57–61]

[a] K and M mean Kinetics and Mechanism

[b] Two pioneer works are marked. The full list of references presents, e.g., in [30]

formulation of the congruent dissociative evaporation (CDE) mechanism [42]).

However, this has not been the only oversight in the history of our studies. Idly browsing through a monograph on catalysis by Schwab [9], this author [63] found that almost the same two-step mechanism of decomposition of solids as our CDE mechanism was proposed (in the form of a hypothesis) by Volmer [8]. Schwab immediately appreciated its significance for the interpretation of the autocatalytic effect and included it in his book [10]. However, its fate was unsuccessful. 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 (in the absence of Volmer and Schwab among the participants), this model was rejected as unrealistic and was forgotten.

Zawadzki and Bretsznajder, who did participate in this conference, were the authors of this critical analysis. They wrote [13]: "It is known with certainty that the reaction $CaCO_3 = CaO + CO_2$ does not involve the volatilization of $CaCO_3$, followed by dissociation in the vapor phase to CO_2 and CaO, which then crystallizes; the actual reaction velocity is very many times greater than could correspond to this mechanism. Besides, such a mechanism would be in conflict with the topochemical nature of the process, with the results of pseudomorph formation, and with a number of other facts [30]".

Unfortunately, grounds for this "conflict" remain unclear. On the contrary, such a mechanism is in full agreement with these features. In our opinion, the above doubts as to the validity of the decomposition mechanism proposed by Volmer and Schwab have played a crucial negative role in the entire history of this topic. 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 [14]. Nobody knows the reason why Volmer and Schwab failed to defend a two-step mechanism in this dispute. Most likely, this can be attributed 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, while Schwab immigrated to Greece for 11 years.

Only 50 years later interest in studying the mechanism of solid-phase decomposition emerges again. This time it was stimulated by the development of electrothermal AAS in the 1970s and application of quadrupole mass spectrometry to the investigation of gaseous products in the process of low-temperature pre-treatment of metal nitrates. The history of these experiments was described recently in [60]. It should be noted that the first observation of low-volatile molecules in the gas phase, the interpretation of their appearance and the formulation of the CDE mechanism of decomposition have occurred absolutely independently of the remark of van't Hoff [1] on the similarity of evaporation and decomposition phenomena and Volmer and Schwab's hypothesis of a two-step decomposition mechanism [8–10]. Fortunately, that it happened!

It would seem that now the story of these searches is close to its resolution. Alas, it is not so. For more than 25 years that have gone since the discovery of the CDE mechanism [42–45] the scientific community did nothing to check its validity and apply it in their own studies, or at least to mention the appropriate publications. Apparently, the majority of researchers have not seen any reason to do this.

If the disorder theory is admitted as reliable for the interpretation of decomposition mechanism during 70 years behind the Bristol Conference in 1938 [16–31], this undoubtedly is a strong signal for any ordinary researcher: no sense to discuss any alternative conceptions and lose time….

Kinetics of solid-phase decomposition reactions

Before considering the history of these studies, we should recall some elementary concepts from thermodynamics. Classical thermodynamics is the phenomenological theory of macroscopic processes accompanied by energy conversion. As any other phenomenological theory, it is based on concepts given by experience and is based on experimentally established laws, the laws of thermodynamics. The phenomenological character of thermodynamics that is not connected with the molecular kinetic essence of the systems studied, leads, on the one hand, to important results with regard to the common for different systems physical properties, and on the other hand, limits the depth study of these properties because it does not allow to reveal the details of the phenomena being investigated. The theory that is based on the molecular structure of matter is called statistical physics. Its use can really give a deeper study of the thermodynamics of some systems. But it must not contradict the properties that have already been drawn from the thermodynamics.

Turning to the approaches used by van't Hoff and Arrhenius in the derivation and interpretation of the main kinetic equation under discussion, we clearly see that these two approaches relate to different sections of physical chemistry: phenomenological thermodynamics, in the first case, and statistical physics, in the second. As it is follows from the set of equations related to the thermodynamic and thermochemical models (Tables 2, 3), van't Hoff used Eq. 1 (Gibbs version of the Second Law) to show that the equilibrium constant of the reaction K is related to the temperature T and the enthalpy of reaction ΔH by Eq. 2 (van't Hoff isobar equation). Then, taking into account that

Table 2 Equations related to the thermodynamic model of van't Hoff and the thermochemical model of Langmuir−L'vov

Formula	Equations
$\ln K = \Delta S/R - \Delta H/(RT)$	1
$d \ln K/dT = \Delta H/(RT^2)$	2
$K = k_+/k_-$	3
$d \ln k/dT = E/(RT^2)$	4
$k = A \exp[-E/(RT)]$	5
$J_{vac} = MP/(2\pi MRT)^{0.5}$	6
$J_{gas} = MDP/(rRT)$	7
$A_aB_b(s/l) \leftrightarrow aA(g) + bB(g) \rightarrow aA(s) + bB(g)$	8
$K = (P_A^{int})^a (P_B^{int} + P_B^{ext})^b$	9
$J_{vac}^{e} = \frac{\gamma\beta^{a/v}M}{(2\pi MRT)^{0.5}} \exp\frac{\Delta S}{vR} \exp\left(-\frac{\Delta H}{vRT}\right)$	10
$J_{gas}^{e} = \frac{\gamma\beta MD}{rRT} \exp\frac{\Delta S}{vR} \exp\left(-\frac{\Delta H}{vRT}\right)$	11
$J_{vac}^{i} = \frac{\gamma\beta^{a/v}M}{(2\pi MRT)^{0.5}} \frac{1}{(P_B^{ext})^{b/a}} \exp\frac{\Delta S}{aR} \exp\left(-\frac{\Delta H}{aRT}\right)$	12
$J_{gas}^{i} = \frac{\gamma\beta MD}{rRT} \frac{1}{(P_B^{ext})^{b/a}} \exp\frac{\Delta S}{aR} \exp\left(-\frac{\Delta H}{aRT}\right)$	13
$J = r\rho k$	14

Table 3 Abbreviations in Eqs. 1–14

Symbol	Quantity
A	Pre-exponential factor in Eq. 5
A and B	Products of decomposition reaction
D	Diffusion coefficient of gas product in inert gas
E	Decomposition energy related to ΔH value
J	Absolute rate of evaporation (or decomposition)
K	Equilibrium constant
M	Molar mass
P	Pressure of the gaseous species
R	Gas constant
T	Thermodynamic temperature
ΔS	Change of entropy of reaction
ΔH	Change of enthalpy of reaction
k	Rate constant
r and ρ	Radius of reactant particle and its density
a and b	Stoichiometric coefficients to products A and B
v	Stoichiometric number ($v = a + b$)
β	Factor considering congruence of decomposition
γ	Conversion factor from bar to Pa
vac and gas	Subscripts: 'in vacuum' and 'in inert gas'
e and i	Superscripts: 'equimolar' and 'isobaric' modes
ext	Superscript to 'external' pressure of product B
int	Superscript to 'internal' pressure of both products

the equilibrium constant K is the ratio of the rate constants k_+ and k_- in the forward and backward directions (Eq. 3), he concluded that they obey the same equation, as in the case of K, i.e., to Eq. 4, where E is a value related to ΔH. The final result is the well-known Eq. 5.

Being derived from phenomenological thermodynamics (the Second Law), this equation should be valid for all equilibrium thermally induced processes irrespective of their different (mechanical, physical, chemical or biological) nature. In chemistry, in particular, it should be valid for all kinds of homogeneous and heterogeneous reactions, and the validity of this conclusion is the main advantage of thermodynamic approach used by van't Hoff.

A few years later (in 1889), exploring the rate of hydrolysis of cane sugar under the influence of mineral acids, Arrhenius [2] 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 equilibrium between inactive (normal) and active molecules that are directly involved in the reaction, and that this balance (n_a/n_0) varies with temperature in accordance with Eq. 5 predicted by van't Hoff. Arrhenius [3] proposed to interpret the parameter E as the activation energy of active molecules involved in the reaction and whose proportion of the total number of molecules is derived from the Boltzmann distribution.

The correctness of the substantiation by Arrhenius of the activation kinetic model 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. 5, was additionally explained by Arrhenius through the Boltzmann distribution of reaction particles (n_a/n_0) by energies, which is also exponentially dependent on T, although this is not only unneeded, but in principle is contrary to the spirit of the thermodynamic essence of the original equation. 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. Also, personal acquaintance and communication with Boltzmann during the visit of Arrhenius to the University of Graz in Austria in April 1887 could not have failed to play a role.

The intervention of statistical physics into results that are already obtained from thermodynamics is unacceptable if it is accompanied by a modification of these results, even in the form of "a physical justification and interpretation for it" (under IUPAC Goldbook definition) as it was in the above attempt of Arrhenius to introduce the activation concept into the purely thermodynamic approach of van't Hoff. Nevertheless, this is quite possible, if this intervention occurs in accordance with the thermodynamic concept. This took place in the process of our development of the thermochemical model, as illustrated in Table 2. As the basic equations, this author used Eqs. 6 and 7, which were derived from statistical (molecular) physics by Langmuir [4–6] for vacuum and inert gas conditions. It is noteworthy that in assessing the potential role of Eq. 6 for future studies, Langmuir prophetically noted: "The importance of this equation in the kinetics of heterogeneous reactions can hardly be over-emphasized" [5, p. 2250]. The most important feature of both of these equations is a fundamental relationship between the kinetic parameter J, the absolute rate of evaporation (simple or dissociative), and the thermodynamic parameter, the equilibrium partial pressure P of gaseous product related, in turn, to the equilibrium constant K. It means that use of these equations for the development of a thermochemical model of decomposition kinetics is in full agreement with the purely thermodynamic approach of van't Hoff. (It is strange that the existence of such a connection between kinetic and thermodynamic parameters of heterogeneous chemical reactions was ignored by most experts in the field of physical chemistry for over 100 years. As a rare exception from the literature devoted to heterogeneous kinetics could be mentioned some review papers of Galway [65, 66] with a strong criticism of concept of variable activation energy).

In order to apply Eqs. 6 and 7 to decomposition reactions, we proposed [41] to express the equilibrium pressure P_B^{int} for the first part of the two-step reaction (see reaction scheme 8) through the equilibrium constant K, the equilibrium partial pressures P_A^{int} and P_B^{int} (internal), determined by the development reaction, and the pressure of the gaseous product P_B^{ext} (external) that enters the reactor from the outside, in accord with Eq. 9. Depending on the ratio between P_B^{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_B^{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 course of 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., $P_B^{ext} \gg P_B^{int}$, and is kept constant during the measurement process ($P_B^{ext} = \text{const}$). After substitution of P_B^{int} values (for equimolar and isobaric modes) into each of Eqs. 6 and 7 and replacing the values of K on exponents of $\Delta S/R$ and $-\Delta H/(RT)$ according to Eq. 1, we obtain Eqs. 10–13, which can be used for the calculation of absolute decomposition rates of reactants (in kg m^{-2} s^{-1}) in equimolar and isobaric modes, in vacuum and inert gas environment, taking into account the composition and stoichiometry of reaction, the excess pressure of gas product in reactor, temperature and the thermochemical features of reaction. To evaluate the rate constant k of the decomposition reaction (in s^{-1}), in addition to Eqs. 10–13, Eq. 14 [64] must be used.

As can be seen from a comparison of Eqs. 10–13 with Eq. 5, they are in full agreement in relation to the dependence of the k and J parameters on temperature. However, Eqs. 10–13 contain much more additional information on details of decomposition kinetics, in particularly, on the physical meaning of the A and E parameters in Eq. 5 and the impact of excess pressure of gas product and inert gas in a reactor on the rate of decomposition. At the same time, as expected, the physical interpretation of the kinetics limits the application of this approach to only solid-phase decomposition reactions.

It is remarkable that the theoretical foundation of both, thermodynamic and thermochemical, models includes only 14 simple formulae (see Table 2), and all calculations can be performed with the help of a pocket calculator. For comparison, the total number of equations within the framework of isoconversional method recommended [47] as the most advanced variant of the activation model is close to 100, and use of them in practical work requires a solid grasp of higher mathematics and computer programming. And again, as in case of the CDE mechanism, the ICTAC Kinetics Committee keeps silence [47] on the thermochemical model, which was thoroughly described during last 30 years in the monographs [53, 54] and many regular papers and reviews. It is necessary to wish that the heads of ICTAC Kinetics Committee to be more objective and effective in the evaluation of kinetic concepts, which lie outside of views and interests of the ICTAC Kinetics

Table 4 Delay in acceptance of main achievements in study of the mechanism and kinetics of solid-phase decomposition

Step	Mechanism of decomposition	Delay/years	Step	Kinetics of decomposition	Delay/years
1	Evaporation	130	1	Equations 1–5	130
6	'Two-step'	85	4	Equations 6, 7	100
17	'CDE'	25	16	Equations 8–13	30

Committee. Similar claims to this Organization were expressed by some other researchers [67–69].

Conclusions

As a result of the consideration of events having occurred over 130 years of theoretical and experimental investigations into the mechanism and kinetics of solid-state decomposition reactions and related problems, some conclusions can be drawn that are important for understanding the reasons for the unsatisfactory state of theory and possible ways of improving this situation.

1. Table 4 contains the results of our evaluation of delay in acceptance of the main innovations in studies of the mechanism and kinetics of solid-phase decomposition. To date, as can be seen from this table, the implementation of these innovations was delayed by 25–130 years for the problem of the mechanism and by 30–130 years for the problem of kinetics. Silence and inactivity of the thermoanalytical community will only aggravate the crisis state of the theory in this field.
2. The main reason for the deep crisis in studies of the kinetics and mechanisms of heterogeneous reactions is the use of the Arrhenius activation model, which fundamentally contradicts to the thermodynamic model of van't Hoff. To overcome this crisis, it is necessary to replace the activation model of Arrhenius by the thermochemical model of Langmuir–L'vov, which is in full agreement with the purely thermodynamic approach of van't Hoff.
3. Historical justice should be restored. The name of the "Arrhenius equation" should be changed in favor of the "van't Hoff equation". This amendment should be viewed not as a reproof to Arrhenius, but rather as recognition of our long inability to recognize the mistake made by Arrhenius. Just realizing it, we can move on.

Acknowledgements The content of this article expresses my personal opinion about the crisis in theory of solid decomposition reactions and possible ways for its elimination. In absence of support of these ideas by the ICTAC Kinetics Committee and thermoanalytical community, I thank my wife Anna who alone divides my belief in the eventual success of these proposals. Many thanks are also to my grandson Nikita for a stylistic improvement of this manuscript.

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