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# THERMOCHEMICAL APPROACH TO SOLID-STATE DECOMPOSITION REACTIONS AGAINST THE BACKGROUND OF TRADITIONAL THEORIES

*B. V. L'vov*[*]

Department of Analytical Chemistry, St. Petersburg State Polytechnical University, St. Petersburg 195251, Russia

The novel thermochemical and traditional Arrhenius approaches to solid-state decomposition reactions have been evaluated from the standpoints of the number and the validity of the assumptions introduced in the theories, and achievements obtained over the last decade in the frameworks of both approaches. As it follows from the analysis, in both respects, the thermochemical approach is preferable. The so-called 'controversial' problem of the use of thermodynamic concepts and thermochemical data for the quantitative evaluation of decomposition kinetics in the thermochemical approach has also been discussed.

**Keywords:** *Arrhenius approach, congruent dissociative vaporization, kinetics, mechanism, methodology, oversaturation and condensation, thermochemical approach*

## Introduction

All things are difficult before they are easy. This proverb is especially valid with regard to novel ideas in some traditional fields of science that have remained unchanged during many decades. Such is indeed the case for the thermochemical approach to the mechanism, kinetics and methodology of solid-state decompositions.

Three possible approaches to the investigation of the kinetics and mechanisms of solid decompositions are known (Table 1). The first two (after Arrhenius and after Knudsen–Langmuir) in their final form were formulated in the 1960s, the last one (thermochemical), which has branched from the second approach, appeared in the 1980s. To avoid possible confusion, it is necessary here to make a remark. The terminology used has recently undergone some changes and refinements. The terms 'physical approach', 'specific enthalpy' and 'specific entropy' introduced and used in the previous communications of the author, e.g., in the reviews [1–3], have been replaced in recent publications by 'thermochemical approach', 'molar enthalpy' and 'molar entropy'.

Some additional comments should be made as to the selection of the term 'thermochemical approach' to replace 'physical approach'. The main motive for this change was identical to that given in the classical book by Benson [4] published 40 years ago. In the introduction to this book, Benson has noted: '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'.

Of the few responses to this novel approach (among which some papers by Galwey alone [5–7], and by Galwey and Brown [8] including their book [9] should be noted) the critical comments by Brown [10] deserve special consideration. These comments are as follows: 'L'vov has published a lot of controversial papers on what he has named his 'physical approach'. This approach is based upon the assumption of an initial step involving evaporation of the reactant, e.g.:

$$CaCO_3(s)\rightarrow CaCO_3(g)\rightarrow$$
$$CaO(g)+CO_2(g)\rightarrow CaO(s)+CO_2(g)$$

This is an interesting idea, which could be well applicable to a limited number of reactants, but its extension as a general mechanism covering all solid-state decompositions appears to conflict with two principles of Philosophy, namely, Occam's Razor, which requires that no more assumptions than are necessary should be made; and attempts to explain everything in terms of one principle, e.g. early Greeks 'all is water' and today's TOEs (theories of everything).

There is a need for a critical assessment of these suggestions that takes into account the adjustable parameters introduced and the complex mixture of kinetic and thermodynamic concepts.'

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[*] borislvov@rambler.ru

*1388–6150/$20.00*

*Akadémiai Kiadó, Budapest, Hungary*
*Springer, Dordrecht, The Netherlands*

**Table 1** Basics of the Arrhenius, Knudsen–Langmuir and thermochemical approaches

| Constituent | Arrhenius approach | Knudsen–Langmuir approach | Thermochemical approach |
|---|---|---|---|
| Mechanism | Congruent/incongruent dissociative vaporization | Congruent/incongruent dissociative vaporization | Congruent dissociative vaporization + condensation of oversaturated vapour |
| Kinetics | Arrhenius (kinetic) equation | Hertz–Knudsen–Langmuir (thermodynamic) equation | Langmuir (thermodynamic) equations for vaporization in vacuum and in foreign gas |
| Methodology | Arrhenius plot (differential) method | Second-law (differential) method | Third-law (absolute) method |

Two years later, Professor Brown kindly proposed to assist with the English edition of the author's book [11], first published in Russian. In the Foreword to the English edition of this book [12], he has noted: 'One of my motives in offering to assist with the English edition was to 'force' myself to pay close attention to his complex ideas and suggestions. I think I have come out of the process with a greater appreciation of some aspects, but still have to undergo a full 'conversion experience'! Time just did not allow lengthy exchanges between us and these will, perhaps, have to be postponed for future debates in the literature. My hope is that this translation will bring Professor L'vov's work to the attention of a wider audience and that this will promote constructive discussion of the assumptions made.'

It seems that the time has come for this discussion. The purpose of this paper is, firstly, to consider the number and the validity of the assumptions based on the formulation of the Arrhenius and thermochemical approaches and, secondly, to compare the effectiveness of both approaches in the creation and development of a fruitful, rigorous and self-consistent theory and a more efficient methodology of investigations.

## Assumptions in the different approaches

### *Mechanism of decomposition*

Let us begin with the Arrhenius approach (Table 1). Of the two (congruent and incongruent) mechanisms of decomposition used in this approach, the first (congruent) mechanism is so simple and obvious that it does not need additional substantiation. Its existence was proved theoretically and experimentally and does not cause any doubts or objections. In the general case, it can be presented as the two-stage process

$$R(s)\leftrightarrow R(g)\leftrightarrow aA(g)+bB(g) \qquad (1)$$

which includes the vaporization of the neutral molecule and its thermal dissociation into species (radicals or molecules).

The mechanism of incongruent decomposition, from the standpoint of the common Arrhenius approach, is fundamentally different from the above [9]. It includes as a necessary step the redistribution of crystal bonds and/or electron/proton/ion transfer within the ionic reactant along with the formation of free volatile molecules (e.g., $H_2O$, $NO_2$, $CO_2$), which are immediately released, and the neutral low-volatile molecules (salts, oxides or metals) of the main constituent, which remain immobile or slightly displaced in the course of the decomposition and form the solid product. The processes preceding the formation of free molecules of products have defied experimental analysis and therefore cannot be described quantitatively.

In contrast to the first (congruent) scheme, the second scheme appears, upon closer examination, rather questionable [12]. One of the points against it is that the forming solid product differs significantly from the solid reactant in its morphology. This manifests itself in the formation of conglomerates of separated nano-particles of product that are practically 'transparent' for an exhaust flow of gaseous products. Of even greater importance is the formation, in some cases, of two or three solid products in the form of different phases. This occurs, for example, in the decomposition of potassium permanganate ($KMnO_4$) up to potassium manganate ($K_2MnO_4$), manganese oxide ($MnO_2$) and potassium oxide ($K_2O$) or in the decomposition of talc ($MgO\cdot 4SiO_2\cdot H_2O$) up to crystalline enstatite ($MgSiO_3$) and the amorphous $SiO_2$. It is difficult to imagine such a transformation of a solid reactant into solid product(s), with different spatial distribution, without any intermediate stage related to a change of aggregate state. The other argument against the incongruent scheme is the direct observation of some low-volatility decomposition products (Ag, Cd, CoO, CrO, NiO, PbO and others) in the gaseous phase at 300–600 K by QMS [12]. In short, the additional assumption (or assumptions) is/are necessary to justify this very doubtful mechanism (Table 2).

In the framework of the thermochemical approach, the problem of the two different mechanisms (congruent and incongruent) is absent. A large body of data [11–13] shows that the decomposition of all the reactants occurs in accordance with the Scheme 1. The only difference between the reactions that end

**Table 2** Assumptions in the Arrhenius approach

| No. | Assumption | Validity |
|---|---|---|
| 1 | Mechanism of incongruent dissociative vaporization for decomposition of solid to solid: R($s$)→$a$A($s$)+$b$B($g$) (including the bond redistribution and electron/proton/ion transfer) | In conflict with the QMS observations of primary gaseous products and the differences in spatial distribution of reactant and solid product [12] |
| 2 | Rate equations in formal kinetics: acceleratory, sigmoid, diffusion and 'order of reaction' models | Pure speculative reasoning [9] |
| 3 | Arrhenius dependence of the decomposition rate on temperature: $k=A\exp(-E/RT)$ | Physical meaning of the parameters $A$ and $E$ is rather doubtful [9] |

with the formation of only gaseous products and the reactions that end with the formation of gaseous and solid products consists in the absence or presence of vapour oversaturation in the low-volatility product. Indeed, elementary thermochemical calculations show [13] that in all cases of formation of solid product in the process of the congruent dissociative vaporization of reactants, the equilibrium partial pressure of the main product, $P_{\text{eqp}}$, greatly exceeds its saturation vapour pressure, $P_{\text{sat}}$, and therefore causes the appearance of vapour oversaturation, $S\equiv P_{\text{eqp}}/P_{\text{sat}}$, and vapour condensation. Our studies have shown [11–13] that oversaturation is responsible for the formation and growth of nuclei, their shape and position, the transfer of condensation energy to the reactant, the existence of induction and acceleration decomposition periods, the reaction localization, the topotaxy effect and the nanocrystal struczure of the solid product. Variations in the energy transfer explain the increase of molar enthalpy with temperature and the decelerating influence of melting on the rate of decomposition.

Therefore, the reactions that end with the formation of gaseous and solid products can be presented by the scheme:

$$\mathrm{R}(s)\leftrightarrow \mathrm{R}(g)\leftrightarrow a\mathrm{A}(g)+b\mathrm{B}(g)\rightarrow a\mathrm{A}(s)+b\mathrm{B}(g) \quad (2)$$

In contrast to the first two reversible stages of Scheme 2, the last stage (condensation) is irreversible. In the absence of two primary stages, it is impossible to obtain the product vapour pressure above the solid product, which is higher than the saturation pressure for this product.

The realization of this scheme (the maintenance of the appropriate decomposition rate) assumes that the part ($\tau$) of the condensation energy evolved in the reaction interface transfers to the reactant and increases the rate of the first stage of this reaction. An analysis of the variations of the coefficient $\tau$ for 15 different compounds [11–13] allowed these magnitudes to be connected with the oversaturation of the vapour of the low-volatility component at the instant of decomposition (in statu nascendi). This dependence, with a correlation coefficient equal to 0.96 can be described by the equation:

$$\tau=0.351\log\log S+0.017 \quad (3)$$

This unusual (doubly logarithmic) correlation between $\tau$ and $S$ may become a key point in the understanding of the mechanism of condensation energy transfer. However, until then the existence of this correlation should be considered an assumption.

Therefore, in both cases (for the Arrhenius and thermochemical approaches) the mechanism of solid-to-solid decompositions requires additional assumptions. However, in the first case, the assumption is very doubtful. In the second, the assumption is more than reasonable.

### *Kinetics*

At least two more assumptions are introduced in the formulation of the kinetics of the Arrhenius approach (Table 2). They are related to the system of rate equations (acceleratory, sigmoid, diffusion and 'order of reaction' models [9]) and the Arrhenius dependence of the decomposition rate on temperature:

$$k=A\exp(-E/RT) \quad (4)$$

The application of all these equations to solid-state decomposition kinetics is not physically justified. The rate equations are based upon the processes of nucleation and growth of product nuclei by interface advance. In turn, these processes are the results of mental speculations on possible models of nucleus generation: single-step, instantaneous, linear, multi-step and branching nucleation [9]. At the same time, more simple and fundamental things remain unknown. As Jacobs, one of the founders of formal kinetics commented [14], 'we have no knowledge of how the first few hundred atoms are added to a nucleus…'

The use of the Arrhenius equation proposed for the homogeneous reactions is also open to question. The $A$ and $E$ parameters have rather doubtful physical meaning in heterogeneous reactions [9]. Therefore, the application of the rate equations and the Arrhenius equation to solid-state kinetics requires at least these two very doubtful assumptions (Table 2).

In contrast to this, the advantages of the thermochemical approach are obvious. The theory of vaporization developed by Hertz, Knudsen and

Langmuir about a century ago allows to interpreting and calculating the rate of solid-state decompositions basing on the thermochemical characteristics of vaporization schemes. The Langmuir vaporization equations [12] have been derived taking into account the simultaneous existence in the course of decomposition of two reverse processes (vaporization and condensation), which are in chemical equilibrium. This means, in particular, that the partial pressures of the primary products in reaction (2) under the steady-state decomposition conditions are associated with the equilibrium constant:

$$K_P=(P_A)^a(P_B)^b \tag{5}$$

This opens an opportunity for the use of thermodynamic concepts and thermochemical data in the quantitative evaluation of decomposition kinetics. It is interesting that the analysis of chemical equilibrium for vaporization/condensation processes helped Tolman [15] to formulate the general principle of microscopic reversibility used in other kinetic studies (e.g., in Eyring's theory of the transition state).

The determination of the maximum rates of decomposition $J$ (in kg $s^{-1}$ $m^{-2}$) and the related equilibrium partial pressures of the primary products does not require a knowledge of the reaction model. It is only necessary to know the surface area $s$ of the sample. For single crystals, it can be evaluated from the geometry of the sample. For powders and melts, the methods of $s$ determination have been described in [12]. The $J$ value should be measured when the rate reaches its steady-state mode and begins to decrease because of surface-area reduction. Certainly, the decomposition degree $\alpha$ should be taken into account, although the correction on the reduction of $s$ at $\alpha<0.3$ is rather small (<1 kJ $mol^{-1}$ at $T$=500 K).

The advantages of using the Langmuir equations rather than the Arrhenius equation consist not only in the introduction of the chemical-equilibrium concept into decomposition kinetics but also in the thermodynamic substantiation of the exponential dependence of the rate on temperature. Instead of the active-molecule hypothesis introduced by Arrhenius, this feature is interpreted as the influence of temperature on the equilibrium pressure of decomposition products. For the equimolar and isobaric decomposition modes, notions introduced by L'vov and Fernandes 25 years ago [16], this exponential dependence has the general form [12]:

$$J^{\mathrm{e}} \propto \exp[-\Delta_{\mathrm{r}} H_{\mathrm{T}}^{0}/(a+b)RT] \tag{6}$$

and

$$J^{\mathrm{i}} \propto (P_{\mathrm{B}})^{-b/a} \exp[-\Delta_{\mathrm{r}} H_{\mathrm{T}}^{0}/(aRT)] \tag{7}$$

where $\Delta_{\mathrm{r}} H_{\mathrm{T}}^{0}$ is the enthalpy of decomposition reaction.

These kinetic features of the thermochemical approach result from the fundamentals of molecular physics and chemical thermodynamics and do not need any additional assumptions. Therefore, the final number of assumptions is equal to three (as a minimum) in the Arrhenius approach (Table 2) and to only one in the thermochemical approach.

## Main achievements in theory and methodology in the different approaches

The advances in the development of the Arrhenius approach over the last decade, in the opinion of Brown [10], include only three innovations, two of which can be considered as methodological (the ICTAC Kinetics Project and the emphasis on isoconversional methods) and one innovation, as theoretical (Burnham's distribution activation energy model).

The main achievements in theory and methodology in the development of the thermochemical approach are listed in Tables 3 and 4. Twenty innovations enumerated in Table 3 have been discussed in detail in the book [12] and there is no point in repeating them again. Perhaps, it would be more important to bring attention to two methodological results (Table 4) related to the discovery of serious systematic errors of the Arrhenius plot and second-law methods and to the advantages of the third-law method in accuracy (in elimination of the systematic errors) and precision.

Indeed, the use of 'differential' (the second-law and Arrhenius plot) methods for the determination of the reaction enthalpies is valid only if these quantities are kept constant for different temperatures. It is easy to show that the values of $\Delta H$ measured by the second-law method ($\Delta H^{\mathrm{II}}$) are related to those obtained by the third-law method at the minimum and maximum temperatures of the experiments ($\Delta H_{\mathrm{min}}^{\mathrm{III}}$ and $\Delta H_{\mathrm{max}}^{\mathrm{III}}$) by the following equation [12, 17], which is strictly valid if a small decrease in the entropy change with a temperature increase is neglected:

$$\Delta H^{\mathrm{II}} = \frac{\Delta H_{\mathrm{min}}^{\mathrm{III}}/T_{\mathrm{min}} - \Delta H_{\mathrm{max}}^{\mathrm{III}}/T_{\mathrm{max}}}{1/T_{\mathrm{min}} - 1/T_{\mathrm{max}}} \tag{8}$$

As can be seen, equality of the molar enthalpies determined by the second- and third-law methods ($\Delta H^{\mathrm{II}}$=$\Delta H^{\mathrm{III}}$) can be reached if $\Delta H_{\mathrm{min}}^{\mathrm{III}} = \Delta H_{\mathrm{max}}^{\mathrm{III}}$. If $\Delta H_{\mathrm{max}}^{\mathrm{III}} > \Delta H_{\mathrm{min}}^{\mathrm{III}}$, then $\Delta H^{\mathrm{II}} < \Delta H_{\mathrm{min}}^{\mathrm{III}}$.

Analysis of the experimental data reported in the literature indicates that because of strong self-cooling (for the endothermic reactions in a high vacuum) and the condensation effect the systematic underestimation of the $\Delta H$ values, as determined by the second-law method equals 10–25% for reactants decomposed to gaseous products and 15–50% for reactants decom-

**Table 3** Main achievements in theory of solid-state decompositions on the basis of thermochemical approach

| Mechanism, effect or regularity | Ref.[a] |
|---|---|
| Thermochemistry of the induction, acceleratory and deceleratory periods | 2.4 |
| Effect of reaction localization | 2.4 |
| Mechanism of formation and growth of nuclei, their morphology | 2.4; 2.5 |
| Vapour oversaturation and structure of the product (X-ray amorphous or crystalline) | 2.6 |
| The equimolar and isobaric modes of decomposition | 3.5 |
| Relationship between the rate constant $k$ and the absolute rate of decomposition $J$ | 3.7 |
| Physical essence of the Arrhenius parameters ($A$ and $E$) | 3.7 |
| Criteria for vaporization/desorption identification | 5.1; 5.2 |
| Invariance of the E' parameter under pressure of gaseous product in the isobaric mode | 5.3; 5.4 |
| The retardation effect of gaseous products: $A^{\mathrm{i}}\propto(P_{\mathrm{B}})^{-\mathrm{b/a}}$ | 5.3; 5.4 |
| Dependence of the $E^{\mathrm{i}}/E^{\mathrm{e}}$ ratio on the stoichiometry of the decomposition reaction | 5.3; 5.5 |
| The Topley-Smith effect | 7 |
| Vapour oversaturation and the contribution of the condensation energy to the enthalpy | 8.1 |
| Increase of the reaction enthalpy with temperature for reactants decomposed to solids | 8.2 |
| Reduction of decomposition rate for melted reactants | 8.3 |
| Thermochemical analysis of the composition of primary products of decomposition | 9 |
| Effect of crystal structure of reactant on the composition of the primary gaseous products | 10 |
| The vaporization coefficient $\alpha_{\mathrm{v}}$ | 11 |
| The kinetic compensation effect | 12 |
| Study of $KMnO_4$ decomposition as a potential kinetics standard in TA | 12 |

[a] Section in the book [12]

**Table 4** Development of methodology in thermochemical studies

| Analysis, method or procedure | Ref.[a] |
|---|---|
| Analysis of fundamental restrictions of the Arrhenius plot and second-law methods as applied to thermochemical determination in solid-state kinetics | 4.2; 6.3; 8.2 |
| Substantiation of the metrological advantages (in precision and accuracy) of the third-law method | 4.4–4.8 |
| Estimation of the molar entropies for decomposition reactions | 4.5 |
| A consideration of the vaporization congruence in a calculation of the equilibrium constants | 3.5; 15.6 |
| Estimation of the molar enthalpies on the basis of the initial temperatures of decompositions | 5.1 |
| Evaluation of self-cooling and temperature distribution in powder reactant | 6.1–6.3 |
| Measurement of the absolute rates of decomposition for powders and melts | 15.1 |
| Determination of the molar enthalpies in an excess of gaseous product (e.g., in air atmosphere in the presence of $H_2O$ vapour and $CO_2$ impurity) | 15.4; 15.5 |

[a] Section in the book [12]

posed to solids [17]. On the contrary, the systematic overestimation of the $\Delta H$ value (by 30%) measured by the Arrhenius method has been revealed in the case of exothermic decomposition of $KMnO_4$ in a high vacuum [18]. Therefore, the use of these methods in decomposition kinetics is hardly acceptable. The replacement of the 'differential' (second-law and Arrhenius plot) methods by the 'absolute' third-law method in decomposition studies is desirable, if not obligatory.

As is evident from an analysis of the thermodynamic data (primarily of the enthalpies of formation and sublimation) listed for several hundreds of substances in a reference book [19], the determination of these constants by the third-law method yields values more precise, on the average, by an order of magnitude than those obtained using the second-law method. This can be traced to $\Delta_{\mathrm{r}} H_{\mathrm{T}}^{0}$ depending differently on random and systematic errors in the determination of the true reactant temperature and the measurement of the variables $P$, $J$ or $k$, a point that becomes obvious when comparing equation used in the case of the third-law method

$$\Delta_r H_T^0 = T(\Delta_r S_T^0 - R\ln K_P) \quad (9)$$

with Eq. (10) below for the second-law method:

$$\Delta_r H_T^0 = \frac{1}{1/T_{\min} - 1/T_{\max}} R\ln\frac{P_{\max}}{P_{\min}} = \frac{T_{\max}T_{\min}}{T_{\max} - T_{\min}} R\ln\frac{P_{\max}}{P_{\min}} \quad (10)$$

Here the quantities $P_{\max}$ and $P_{\min}$ are the pressures corresponding to the maximum and minimum temperatures of the experiment. (When drawing Arrhenius plots, the quantities $J$ or $k$ are used instead of the pressures $P$.) It can be seen that these expressions differ primarily by the presence of an additional factor in Eq. (10), namely, of the ratio $T_{\max}/(T_{\max}-T_{\min})$ or $T_{\max}/\Delta T$. The magnitude of this factor in different studies is usually in the range of 5–20 [12]. Thus, the error inherent in the use of the third-law method is about an order of magnitude lower than that provided by the two other methods.

The third-law method has never been used in kinetic studies by the Arrhenius approach because its use suggests measuring the equilibrium pressures of the primary products of decomposition. The thermochemical approach that is based on the Langmuir vaporization equations is ideally suits for this purpose.

## Conclusions

As can be seen from the data collected in Table 2, the number of assumptions used in the formulation of the Arrhenius approach is three times that for the thermochemical approach. Therefore, the reproach to this author with 'more assumptions than are necessary' [10] is hardly right especially in contrast to the traditional Arrhenius approach. It may be expected that the residual thermochemical assumption related to the mechanism of heat transfer to the reactant will be solved on the basis of solid-state physical chemistry and the experimentally estimated double-logarithmic dependence of the $\tau$ coefficients on the oversaturation $S$ of the product vapour in the reaction interface.

The critical note on 'the complex mixture of kinetic and thermodynamic concepts' [10] appears more significant. However, there are two points that are not taken here into account.. The first point is related to the actual mechanism of decomposition, which includes, as the first stage, the congruent dissociative vaporization of all reactants (regardless of the volatility of the main product) and, in the case of the formation of vapour oversaturation of the main product, its condensation to the solid product. Therefore, instead of two fundamentally different mechanisms of decomposition (congruent and incongruent) there is actually only one mechanism. The second point is related to the simultaneous existence in the course of decomposition of two reverse processes (vaporization and condensation), which are (virtually) in chemical equilibrium. It means, in particular, that the partial pressures of the primary products measured under the steady-state decomposition conditions are associated with the equilibrium constant $K_P$. This opens an opportunity to use thermodynamic concepts and thermochemical data for the quantitative evaluation of the decomposition kinetics.

The last reproach to the author is related to 'attempts to explain everything in terms of one principle, e.g. early Greeks 'all is water' and today's TOEs (theories of everything)' [10]. While agreeing with the wittiness of this principle (its formulation), the present author and, probably, the majority of other workers cannot agree with its application to scientific studies. In our opinion, the correctness of new ideas and theories in scientific researches should be evaluated primarily by their fruitfulness in the interpretation of as many problems as possible and by their capability to predict unknown trends and effects. The other general criteria that are applied to new theories are simplicity, internal consistency, experimental reliability (verifiability) and compliance with previous theories. The thermochemical approach to the kinetics of solid-state reactions used in our studies meets these criteria. It appears to be applicable not only to one or several particular examples of decomposition, but to virtually all of the most popular classes of reactions considered as models. The thermochemical approach is based on fundamental concepts in molecular physics (statistical mechanics) and chemical thermodynamics.

As a quantitative characteristic of the comparative efficiency of different approaches, the ratio I/A can be used (by analogy to the well-known notion of the impact factor). Here A and I are, respectively, the numbers of assumptions and innovations listed in Tables 2–4 or noted in the text. (Recall that the advances in the development of the Arrhenius approach over the last decade, in the opinion of Brown [10], include only three innovations.) The result of the comparison could be foreseen. The difference in the efficiency factor I/A for these approaches exceeds an order of magnitude.

In conclusion, it is interesting to present the prophetic opinion stated by Benson 40 years ago in the course of the preparation of his book 'Thermochemical Kinetics' [4]: 'I have omitted the very important areas of condensed phase reactions because the methods for their treatment have not reached the same stage of advancement as they have for the gas phase reactions. This is by no means a necessary condition and I hope that this book will provide the incentive for some hardy souls to extend the gas phase methods to condensed phases. All current indications are favorable in the outcome'.

As may be seen from the foregoing discussion, today this problem (the development of the thermochemical approach to solid-state decomposition reactions) is practically solved. There can be no doubts that by joint efforts this work could have been done much earlier and more successfully. However, the attitude of the TA community toward this approach, with the rare exception, has been (and remains) very skeptical. The author's attempts actively supported by Galwey [5–7, 20] to stimulate a sort of constructive and open discussion of the controversial points remain fruitless [21]. The TA community keeps silence.

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