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The mechanism of solid-state decompositions in a retrospective

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Abstract This is an overview of the early investigations into the mechanism of solid decompositions since the fundamental studies by Ostwald on catalysis during 1890–1902 and the first experimental study of the autocatalytic decomposition of Ag_2O by Lewis in 1905. In order to explain the formation mechanism of the solid product, Volmer suggested in 1929 that the decomposition of Ag_2O includes two sequential stages: first, a thermal decomposition of the oxide into gaseous silver atoms and oxygen molecules and second, the condensation of the supersaturated silver vapor. This revolutionary idea was immediately used by Schwab to explain the autocatalytic peculiarity of solid-state decomposition reactions. However, this mechanism did not receive the acceptance of the scientific community. On the contrary, as can be seen from the results presented at the conference "Chemical reactions involving solids" in Bristol in 1938, this model was dismissed as unrealistic and, as a result, was since forgotten. Instead, considerable attention at this conference was devoted to the disorder theory proposed earlier by Wagner and Schottky, and to the mechanism of ion transport in the solid crystals. During the subsequent 70 years, decomposition mechanisms have been interpreted, without visible progress, on the latter basis. The mechanism of congruent dissociative vaporization proposed independently in 1990 turned out to be in complete agreement with the Volmer–Schwab model. It has been treated with the same distrust. These historical events, in the author's opinion, are responsible for the prolonged stagnation in the development of solid-state decomposition theory.

Keywords Ag_2O decomposition · Autocatalysis · Congruent dissociative vaporization · Decomposition mechanism · Disorder theory

Introduction

Twenty years have gone by since the appearance of the model of solid-state decomposition via congruent dissociative vaporization (CDV) of the reactant [1, 2]. Despite the progress achieved in the elaboration of a self-consistent thermochemical approach [3–10], including its mechanistic, kinetic, and methodological aspects, and in the quantitative interpretation on its base of the decomposition mechanisms for different classes of compounds (oxides, sulfides, selenides, tellurides, nitrides, azides, hydroxides, clays, hydrates, nitrates, sulfates, carbonates, oxalates, and permanganates) as well as in the explanation of many unusual phenomena and puzzling effects (such as the Topley–Smith effect and the compensation effect), this model has not received any support by other researchers. One can ascribe this to the fatigue and apathy that have built up in the recent decades as a result of futile attempts at coming closer to the final goal by the traditional methods. The state of stagnation in the theory of solid-state decompositions is recognized even by the leading specialists in the field [11, 12]. Of interest is the evaluation of the present situation given recently by Galwey in the series of his important review articles [13–17].

> Almost all activities and priorities in this field after the mid 1970s have been transformed by the development of thermal analytical methods. This has resulted (apparently) in the virtually complete redirection of interest towards expanding the applications

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> of automated and efficient experiments techniques capable of providing a maximum amount of kinetic data from a minimum number of experiments. During this time, weaknesses in the underlying science of solids were disregarded, possibly even forgotten, but certainly not addressed. The inevitable consequence has been that the chemistry of these rate processes now lacks a coherent theoretical foundation [16]… In this situation, it might have been expected that a new theory, founded on established physical principles, would be universally welcomed, particularly a model of such general applicability and potential value, as that formulated by L'vov… However, the response, "Let us ignore it, and perhaps it will go away", appears to express the attitude of the thermal analysis community… If the situation described here does not initiate argument capable of resolving the differences identified, then the hope of making future progress towards developing understanding of the chemistry of thermal reactions must continue to be remarkably bleak [15].

The main purpose of this study is to reveal the reasons of this stagnant situation. In order to do this, we decided to review the history of the studies of the mechanism of thermal decomposition of solids over the first decades of the last century, beginning with the fundamental works by Ostwald on catalysis in 1890–1902 [18–20] and the first experimental investigation of autocatalytic decomposition of Ag_2O by Lewis in 1905 [21]. Many researchers, including some world-renowned scientists (Table 1), had taken part in the development of the main concepts in this field of physical chemistry (regrettably, the names of these scientists are rarely mentioned in the present-day literature on thermal analysis. In case the readers need to be reminded of their contributions to *Science*, we have included into Table 1 some of their biographic and professional characteristics).

Catalysis and autocatalysis

The history of the earlier studies into the mechanism of solid decompositions is related to the history of catalysis and, in particular, autocatalysis. Therefore, we start by citing of some fragments from the excellent book "Catalysis from the standpoint of chemical kinetics" by Schwab [22–24] that is closely connected to this topic. The historical introduction to this book contains the most important landmarks on the way of conversion of this branch of physical chemistry into the self-dependent field of Science.

> Berzelius might be able, about 1836, to apply his gifted synthetic touch to classification of a large number of separated data under a new collective idea, namely that of "Catalysis"… However, since it has been shown more recently that the search after one comprehensive theory was found to remain unfruitful, real increases in knowledge in this way have been small. This situation was changed for the first time, when, at the end of the 19th century, the young science of physical chemistry become master of still enigmatical concept and brought the quantitative method to bear in its elucidation. Ostwald was successful in this respect, in that he introduced the velocity of the change as a measure of catalytic action… The theory which Berzelius had arrived at empirically was overwhelmed in one blow by this introduction of reaction velocity into the problem, which, through its stated relationship to a measurable quantity, became the object of new and more exact inquiry. Every investigation of catalytic phenomena, to which we owe our more exact knowledge of the present day, dates from this moment…

Ostwald initiated wide-scale investigations in the field of catalysis [18]. In 1891, he has introduced the term "autocatalysis" [19]. In 1895, there appeared an article of fundamental importance: "On the Nature of Catalytic Processes" [18]. In 1897, he derived a theoretical equation for the rate of autocatalytic self-inductive reaction. The results of numerous investigations were summed by Ostwald in his review [20]. In Ostwald's opinion, the most probable of the different theories of catalysis is the theory of intermediate reactions with the formation of some intermediate products. The actual reaction rate should be determined by the rate of the first slower reaction. In the opposite case, its product would be the final product of the whole reaction. As shown below, this concept of intermediate reactions is entirely valid in the case of solid-state decomposition.

Solid catalysts

After a comprehensive analysis of homogeneous catalysis in gases and solutions, Schwab turns to consideration of different cases of heterogeneous catalysis [22–24]:

> We come next to the most important and interesting case, in which one solid accelerates the reaction of another. In the sense that the reaction product itself exerts this accelerating effect, practically all reactions in the solid state are catalytic. We shall cite only a few of these cases which have been studied in more detail (Table 2). We follow in this respect the treatment of Volmer [25] and of Schwab and Pietsch [26].

Table 1 The leading scientists in early studies of mechanisms of solid-state reactions

Name	Main scientific achievements[a]	Personal recognition, awards	Affiliation
Wilhelm Ostwald (1853–1932)	**Fundamental studies in catalysis**, chemical equilibrium and rates of reactions. Establishment and editing “Zeitschrift für physikalische Chemie”	Honorary member of learned societies in Germany, Sweden, Norway, the Netherlands, Russia, the UK, and the USA. 1909 Nobel Prize in Chemistry	Riga Polytechnic Institute (1881–1886). University of Leipzig, from 1887
Gilbert Newton Lewis (1875–1946)	**Autocatalytic decomposition of Ag_2O**. Valence and the nature of the chemical (covalent) bond. Theory of acids and bases. Thermodynamic concepts of activity, fugacity, and ionic strength. Deuterium studies	The Society of Arts and Sciences Medal as “‘the outstanding chemist in America.” Lewis became the mentor to 290 PhD recipients and 20 Nobel Prize winners. He was nominated for the Nobel Prize in Chemistry 35 times (in vain)	Massachusetts Institute of Technology (1905–1911). University of California, Berkeley, from 1912
Irving Langmuir (1881–1957)	Incandescent electric lamp. Hydrogen plasma welding. **Kinetic evaporation equations**. **Reaction boundary for solid decompositions**. Surface chemistry	Honorary Degrees from 15 Universities and 20 Medals awarded. “Langmuir” is a scientific journal published since 1985 by the American Chemical Society. 1932 Nobel Prize in Chemistry	Stevens Institute of Technology, Hoboken, New Jersey (1906–1909). General Electric Company (Schenectady, New York) from 1909
Max Volmer (1885–1965)	Stern–Volmer equation in photochemistry. Butler–Volmer equation in electrochemistry. Mercury vapor jet pump. **Phase formation theory**	President of the German Academy of Sciences in Berlin (1955–1958). The Institut für physikalische Chemie was renamed the Max-Volmer-Institut, Berlin	Technische Hochschule (Berlin) from 1922
Georg-Maria Schwab (1899–1984)	**Kinetic aspects in catalysis research**. The activity of different metal oxides in N_2O decomposition. The electron theory of catalysis	Honorary doctorates from the Universities of Berlin, Paris, Liege, and Hamburg. The Liebig Medal of the German Chemical Society	Wurzburg University (1925–1927). University of Munich, from 1928
Carl Wilhelm Wagner (1901–1977)	**Disorder theory and the mechanism of ion transfer in solids. Kinetics of oxidation of metals and alloys**	Director of the Max Planck Institute of Chemistry in Gottingen (1958–1968). Carl Wagner Memorial Award by the US Electrochemical Society	University of Jena (1928–1933). University of Darmstadt (1934–1945). Massachusetts Institute of Technology (1949–1958)

[a] The contribution to the theory of solid-state reactions is marked with bold

Table 2 The autocatalytic decomposition reactions [25, 26]

Reactant	Products
$2NaHCO_3$	$Na_2CO_3 + H_2O + CO_2$
Ag_2O	$2Ag + 1/2O_2$
$AgMnO_4$	$Ag + MnO_2 + O_2$
MCO_3[a]	$MO + CO_2$
$CuSO_4 \cdot 5H_2O$	$CuSO_4 \cdot 3H_2O + 2H_2O$
$BaCl_2 \cdot 2H_2O$	$BaCl_2 + 2H_2O$
$Ag_2C_2O_4$	$2Ag + 2CO_2$
$2KMnO_4$	$K_2O + 2MnO_2 + 3/2O_2$

[a] M = Cd, Mg, Pb, Fe, Co, and Zn

These reactions, with the exception of the decomposition of Ag_2O, were studied in the 1920s.

> It is the solid reaction product which, in each case, acts as catalyst. The reactions are all characterized by the fact that the new phase itself acts as the catalyst. The reactions, therefore, occur solely where the substrate is in contact with the product. As a consequence, the process consists in an increase of the reaction product at the cost of the reactant in a progressive displacement of the phase boundary between them. In many cases, as, for example, in the efflorescence of salt hydrates, this growth of reaction product can be observed visually…
>
> The characteristic of this, as of all autocatalytic reactions, is that reaction velocity initially rises, in this cases because the size of the interfaces increases, then reaches a maximum and finally falls, because the interfaces again become smaller by reason of the consumption of the reactant phase. This kinetic procedure was first observed by Lewis [18] in the decomposition of silver oxide…
>
> The question at once arises why this autocatalysis is apparently so general a law in reactions of the solid → solid type. There is a very general thermodynamic basis for this, which was first clearly pointed

> out by Ostwald [27] in the case of gypsum: "That such forms results at all, can only be understood if one assumes that the efflorescence can only occur at those places where hydrate and anhydrite touch each other, since the conditions for a definite dissociation pressure, the coexistence of both phases, holds only at such positions. The homogeneous part of the crystal has as little influence on the value of the dissociation pressure as the completely dehydrated material"… This point of view, first applied to the dehydration of gypsum, can obviously be generalized. Langmuir [28] expressed it in another form: "The phase rule… indicates that in the dissociation of calcium carbonate two solid phases, CaO and $CaCO_3$, are present together. In order that $CaCO_3$ may dissociate and form a phase of CaO (instead of a solid solution) it is necessary that the reaction shall occur only at the boundary between two phases.

Mechanism of autocatalysis

Schwab continues:

> The thermodynamic treatment does not include, however, any interpretation of the catalytic mechanism which brings about the localization of the reaction at the phase boundaries. The question, therefore, to be answered is what molecular mechanism is responsible for the reaction proceeding so very much faster at the phase boundaries than that occurring with negligible velocity in the interior of a phase… We may choose as an example, with Volmer [25], the reaction

$$2Ag_2O = 4Ag + O_2 \quad (1)$$

which was studied by Lewis [21]. We can separate it into two stages, firstly, a purely chemical decomposition of the oxide into silver atoms and oxygen molecules,

$$2Ag_2O = 4Ag(g) + O_2 \quad (2)$$

and, secondly, the deposition of the silver on the nuclei of crystalline silver already present

$$4Ag(g) = Ag_4(s) \quad (3)$$

> If reaction (2) is the rate-determining process, the catalysis involves a purely chemical process, namely, a diminution of the activation energy by adsorption and deformation at the active boundary lines…The establishment of equilibrium in reaction (2) leads to a supersaturation of silver vapour of about 10^4 fold.

When we compare the above model of solid decomposition mechanism, described by Schwab [22], with the CDV mechanism proposed 60 years later [1, 2], we observe their complete agreement. Indeed, in both cases the solid products are formed as a result of the condensation of low-volatility vapor species, and the energy released in the condensation (or adsorption) in the interface zone decreases the enthalpy (or activation energy) of the decomposition reaction. In the first case, interest in this mechanism was connected with the interpretation of vapor supersaturation, which is necessary (in line with the Volmer's theory [25]) for the formation of solid product, in the second, with the QMS observations of primary low-volatility products of decompositions in the gaseous state [1, 2]. Sixty years were needed to completely forget and then arrive at the same idea from another direction, and yet another 20 years to become aware of this historical paradox! Regrettably, the present author has discovered this only recently. How rarely do we find the time for a thorough consideration of previous studies published several decades earlier, in the fields related to current study. Such paradoxical and sometimes dramatic situations are not uncommon in Science (as the saying goes, "All novelties are well-forgotten relics").

Bristol conference

The fundamental book by Schwab [22], published in German in 1931, was translated into Russian [23] and English [24] in 1934 and 1937, respectively. However, the new model for the mechanism of solid decomposition proposed by Volmer and so skillfully and clearly presented by Schwab has found neither acceptance nor development by other specialists in this field. All the more, as can be seen from the results of the discussion of this problem in the framework of the conference "Chemical reactions involving solids" in Bristol in April 1938 (in the absence of Volmer and Schwab as participants), this model was dismissed as unrealistic without any quantitative analysis of the reasons. Professors Bernal, Garner, Jost, Mott, Polanyi, Wagner, Zawadzki, and other well-known scientists participated in this meeting. The Report of this meeting, including all the articles contributed, together with the discussion thereon, appeared in the *Transactions of the Faraday Society* [29]. Two papers (by Zawadzki and Bretsznajder [30] and Roginsky [31]) were devoted to the problem of vapor supersaturation.

As was emphasized by Zawadzki in the course of that general discussion [29]:

> Supersaturation is a necessary condition for the formation of nuclei… Supersaturation is also essential

> when already existing crystallites grow via the stages of plane nuclei'…

For the appearance of supersaturation, Zawadzki and Bretsznajder [30] proposed the following explanation:

> Our attempts at elucidating this phenomenon were based on the facts that the vapour pressure of liquids and solids varies with the particle size, and the crystallization of solutions yields large, well-developed crystals, or aggregates of small, agglomerated crystals, according to the degree of supersaturation of the solutions… We made use, for interpreting these spurious equilibriums, of models of systems consisting of crystals of different sizes, and assumed that the dissociation pressure of very finely divided $CaCO_3$ must exceed that of large crystals…

The decisive role of supersaturation in solid-state decomposition reactions was also supported by Roginsky. In his article "On the role of supersaturation and on the limiting stage in topochemical reactions," Roginsky [31] wrote:

> As an illustration of the influence of supersaturation on the character of the kinetic equation, consider the simple topochemical kinetics of the dehydration of crystal hydrates and of the decomposition of carbonates… In particular, there must be mentioned the interesting series of articles of Zawadzki and Bretsznajder. These authors having expressed opinions very near those mentioned above upon reactions involving two solid phases and have corroborated them with interesting experiments on the kinetics of decomposition and formation of carbonates.

In their analysis of the origin of vapor supersaturation, Zawadzki and Bretsznajder also considered other hypotheses, which in their opinion, were far from reality:

> 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 vapour phase to CO_2 and CaO, which then crystallizes; the actual reaction velocity is very many times greater than could correspond to this mechanism. It might be supposed that whilst $CaCO_3$ molecules do not actually enter the gaseous phase, they may escape from the space lattice… Here they may move freely, as described by Volmer, and may dissociate, after which the CaO produced would enter an appropriate place on the surface of a growing CaO crystal. A mechanism of this type allows for the direct application of Volmer and Stransky's theories of crystal growth. We do not, however, think that the above representation corresponds to the actual conditions; as 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, the grounds for this "conflict" remain unclear. On the contrary, as shown in Refs [3, 7], such a mechanism is in full agreement with these features. In the author's opinion, the above doubts as to the validity of the decomposition mechanism proposed by Volmer have played a crucial role in the entire history of the field.

Of greatest importance to this review would be uncovering the true reasons of the non-acceptance of the Volmer–Schwab model of decomposition mechanisms. Indeed, the present rejection of the CDV mechanism by the scientific community repeats the past situation, even though the theoretical and experimental basis for this model is nowadays much more solid and justified. Regrettably, we cannot propose any explanation for this repeated indifference except that of traditional conservatism (during two latter decades, the author could not receive any reasonable objections to the CDV mechanism despite all his general and private requests to the scientific community and to some eminent specialists in QMS and TA, respectively. It may be that these are simply absent).

Disorder theory

Considerable attention at the Bristol conference was devoted to the disorder theory proposed earlier by Wagner and Schottky [32], and to the mechanism of ion transport in the solid crystals. Wagner [33] presented a lecture on the mechanism of the movement of ions and electrons in solids and the interpretation of reactions between solids and Jost [34], on the energies of disorder in ionic crystals. The success that the disorder theory has had in other fields (semiconducting phenomena and solid-state electronics) allowed for its wider application to the mechanisms and kinetics of heterogeneous reactions. All generally accepted publications (the reviews and text books first of all [35–51]) on this problem over a period of 70 years (from 1937 to 2006) were based with minor variations on this concept. Only one publication (by Esin and Geld [39]) in this list contains a mentioning the two-stage model of Ag_2O decomposition described by Schwab [23]. The authors of text book [39] have ignored this model as unrealistic. The main argument (as in the case of work by Zawadzki and Bretsznajder [30]) was the much lower calculated rate of reaction (2) compared with the experimental magnitude [related to combination of both reactions (2) and (3)]. In doing so, Esin and Geld have ignored a presupposed *diminution of the activation* *energy by adsorption and deformation at the active boundary line* in the process of deposition of supersaturated Ag vapor in the interface zone, as was postulated by Schwab [23] for the substantiation of the observed autocatalytic peculiarity of solid-state decomposition reactions. Perhaps, this misinterpretation explains also the existing distrust to the CDV mechanism. Recall that the main supposition in this case, which is equivalent to the postulate by Schwab, is as follows: *The energy released in condensation of low-volatility product in the reaction interface partially decreases the total enthalpy of the decomposition reaction* [3].

A thorough analysis of the efficiency of the application of the disorder theory to the mechanisms and kinetics of heterogeneous reactions lies beyond the scope of this review. Nevertheless, it is worth noting that Volmer was rather conservative in his estimation of this theory. He notices [52, 53]:

> As is well known, the problem of structure defects and their role in various physical properties of crystals is the object of active discussion. However it is possible to accept as an indisputable fact the following statements: there are many factors causing infringement upon an ideal structure of a lattice and accordingly many kinds of structural defects: (1) the vacancies and occupied interstitial places fitting a condition of thermal balance of a crystal; (2) the defects which have arisen during the crystal growth; (3) cracks and splits inside and on the surfaces, which evolved from mechanical and thermal tensions or superficial damages. Each of these kinds of defects – probably there are others – can decisively impact on various physical properties. Only occasionally is it possible to distinguish between them. It is necessary to add that the idea of a regular structure or that of an ordered system of structural defects should be considered as erroneous. The corresponding theoretical proofs of this idea have been disproven. Experiment has also failed to confirm these assumptions.

Even greater doubts arise as to the applicability of the Wagner's disorder theory to the interpretation of the mechanism to any heterogeneous solid-state reactions. Indeed, as follows from work [33] by Wagner, this theory might be useful in the interpretation of the transport of ions and electrons through the layer of non-porous solid product formed in the process of the interaction of two solid reactants or the oxidation of metals. It is assumed that in this case, the rate of the whole process is controlled by the diffusion of ions within the solid product, and not by the decomposition reactions on the phase boundaries. However, the disorder theory turns out to be inefficient in cases of decomposition of individual reactants, as applied to the interpretation of such fundamental features of these reactions as autocatalysis, the appearance of low-volatility products in the gaseous phase, the impact of the gaseous environment on the kinetics of decomposition, the mechanism of formation and growth of nuclei, the nanostructure of product particles, and the topotaxy effect (practically all these features are quantitatively interpreted in the frame of the CDV mechanism and thermochemical approach in whole [3–10]).

Decomposition mechanism of silver oxalate in the frames of different approaches

The above statement can be illustrated on the example of the studies of the decomposition mechanism of silver oxalate (one of the model reactions in mechanistic investigations [11]). As is well known [54], Boldyrev investigated the peculiarities of this reaction in the framework of the theory of defects over a period of 40 years [55, 56]. As indicated in his review [56], the mechanism of $Ag_2C_2O_4$ decomposition corresponds to the scheme:

$$Ag_2C_2O_4 \rightarrow 2Ag(s) + 2CO_2 \qquad (4)$$

The primary stage of the decomposition is the breakage of the C–C bond in the oxalate ion. This breakage occurs simultaneously with the electron transfer from oxalate ion to acceptor, resulting in the formation of two CO_2 molecules. In his conclusion to the last very detailed review, Boldyrev has noted [56]:

> However, the scheme of the mechanism of the thermal decomposition of silver oxalate is still not completed… Further investigations are necessary into the mechanism of the growth of the silver nucleus, starting with the formation stage when the concentration of interstitial ions is important, and during the growth stage when this concentration has no effect. The question concerning the mechanism, by which the change of limiting stage occurs, remains open at the level of hypotheses and assumptions waiting to be verified… The same is true for the mechanism of the influence of heterophase additives, both organic and inorganic, on the thermal decomposition… The reasons for the catalytic action of the products of photolysis and radiolysis of silver oxalate on the rate of the following thermal decomposition still remain on the level of assumptions.

The strong inhibition effect of oxygen on the decomposition rate and the evolution of $CO_2 + CO$ mixture instead of CO_2 alone have been left in Ref. [56] without reasonable explanations.

The thermochemical approach (including the CDV mechanism as its basic constituent) to this problem turned out to be much more effective. The analysis of the literature data on the kinetics of this reaction by this author [57] allowed him to conclude that the actual scheme of decomposition should be different from reaction (4), namely:

$$Ag_2C_2O_4 \rightarrow 2Ag(g)_{\downarrow} + CO + CO_2 + {}^1\!/_2O_2 \quad (5)$$

This composition of the products was confirmed by the agreement between experimental and calculated enthalpy values of the corresponding reaction, and also by the retardation effect of gaseous products (CO_2 and O_2) on the decomposition rate. Silver vapor supersaturation for reaction (5) at 400 K reaches 10^{17}. The CDV mechanism accounts for some common features and differences in the reaction course for various metal oxalates. The condensation of the primary low-volatile products of decomposition, in particular, accounts for the induction and accelerating periods observed for Ag, Ni, Mn, and Pb oxalates. For HgC_2O_4, where no solid products are formed, these periods are absent. The difference in the chemical form of evolved oxygen (O_2 or O) is consistent with that observed in the dissociative vaporization of the corresponding oxides: Ag_2O, NiO, and HgO. The ratios of initial temperature of decomposition T_{in} to the E parameter averaged from the literature data for these oxalates are equal to 3.6 ± 0.2. This is in a good agreement with the theoretical prediction (3.4 ± 0.1). The difference in the parameters E for the nucleation and decelerating stages in the decomposition of $Ag_2C_2O_4$ and NiC_2O_4, 59 kJ mol^{-1} and 68 kJ mol^{-1}, respectively, is consistent with the calculated condensation energy returned to the reactant (in the interface zone), equal to 63 kJ mol^{-1} for both oxalates [3].

Our criticism of the theory of defects as applied to the mechanism of solid-state decompositions does not exclude the recognition of the strong impact of defects (especially, surface defects) on the development of the induction and accelerating periods of this process (in this regard, the response of a solid reactant to irradiation and mechanical treatment that may disturb mainly the surface layer of solid is absolutely understandable). However, this effect is important mainly in the range up to reaching the steady-state mode of decomposition, i.e. approximately, at the value of product yield, $\alpha < 0.3$. After the reaction covers the entire surface of solid reactant (this moment corresponds to the maximum slope of α–t curve), the impact of surface defects disappears. The further evolution of the reaction (decelerating stage) occurs with the constant rate determined by the thermochemical features of the decomposition reaction and contracted surface area of the reactant. This part of the whole decomposition process usually corresponds to the condition: $0.3 < \alpha < 0.95$. Contrary to common practice [11], only this steady-state region is used for the evaluation in the frame of the thermochemical approach [3–10].

Conclusions

- The two-stage scheme of solid-to-solid decomposition, proposed by Volmer in 1929 and clearly represented by Schwab in 1931 on the base of studies by Ostwald, Lewis, and Langmuir, and the mechanism of the congruent dissociative vaporization proposed 60 years later are in complete agreement, though the backgrounds of these discoveries differ substantially. Both proposals, in spite of their success in the interpretation of the basic decomposition peculiarities and the absence of reasonable scientific objections, have not received any support by other specialists in the field.
- Present stagnation of solid-state decomposition theory, in the author's opinion, has resulted from the dismissal of the Volmer–Schwab scheme (as unrealistic), on the one side, and the scientifically unsound application of the theory of defects to the simple decomposition reactions, on the other. These erroneous views have originated at the Bristol conference in 1938 and persist until now. The scientific community holds its silence on this problem though the further retention of this situation has no future for any progress ahead. In order to prevent undesirable situations such as this, it would be helpful, even if only rarely, to publish some sort of historical overviews on different problems of research and primarily stimulate the public discussions of the controversial problems at scientific meetings and in the press. The author hopes that this article will at last open such debates.

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