J Therm Anal Calorim (2010) 100:967–974
DOI 10.1007/s10973-009-0628-9

Impact of the gaseous environment on the kinetics of solid-state decompositions

Boris V. L'vov

Received: 26 May 2009 / Accepted: 1 December 2009 / Published online: 5 January 2010
© Akadémiai Kiadó, Budapest, Hungary 2010

Abstract The main purpose of this study is to review the current state of the problem of the impact of gaseous environment on the kinetics of solid-state decompositions. Three different theoretical approaches to the interpretation of the decomposition kinetics have been considered. As it follows from the literature published over the past 80 years, the Arrhenius and Knudsen–Langmuir approaches based on the assumption of two different reaction mechanisms (congruent and incongruent) could not solve the problem. At the same time, successes in the application of the thermochemical approach that is based on the assumption of a unitary congruent dissociative vaporization mechanism with condensation of oversaturated vapor remain unnoticed by the TA community. Taking into account this situation, the author has outlined the key points of the thermochemical kinetics in a compact but rigorous and complete form once more. The revised kinetic equations for the different modes of decomposition, several important interrelations between the kinetic parameters, and, finally, the results in the interpretation or reappraisal of the main effects related to the impact of gaseous environment on the kinetics have been considered. In the framework of the thermochemical approach, the problem being discussed may be considered nowadays practically resolved.

Keywords Decomposition equations · Decomposition modes · Diffusion restriction · Impact of gaseous environment · Thermochemical kinetics · Topley–Smith effect · Zawadzki–Bretsznajder effect

Introduction

The impact of the gaseous environment on the kinetics of solid-state decomposition is one of the main problems in many technological applications and theoretical interpretation of this process. In spite of a rather long story of corresponding studies, the current views on this subject are very controversial. The comparison and analysis of results obtained in the framework of different thermoanalytical approaches is difficult because of the absence of critical and comprehensive reviews in this field. Regrettably, this situation is typical for many (if not all) aspects of thermal decomposition kinetics. As noted by Galwey and Brown in their book [1], "there is no doubt that the extensive but dispersed literature concerned with decompositions of solids is in need of review. The number of comprehensive surveys of this important, active and well-defined subject area that have been published in the last 50 years (the effective life-time of the topic) is remarkably small." The main purpose of this study is to review the current state of the particular problem that deals with the impact of gaseous environment on the kinetics of solid-state decompositions.

To start, it is necessary to recall that there are three different theoretical approaches for the interpretation of the decomposition kinetics: the traditional Arrhenius approach, the Knudsen–Langmuir approach, and the novel thermochemical approach. The first two in their final form were formulated in the 1950s and 1960s, respectively, the last

B. V. L'vov (✉)
Department of Analytical Chemistry, St. Petersburg State Polytechnic University, 195251 St. Petersburg, Russia
e-mail: borislvov@rambler.ru

Table 1 Bases 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 (CDV) with condensation of oversaturated vapor
Kinetics	Arrhenius kinetic equation	Hertz–Knudsen–Langmuir quasi-equilibrium equation for vaporization in vacuum	Langmuir quasi-equilibrium equations for vaporization in vacuum and in foreign gas complemented by the concepts of equimolar and isobaric modes of decomposition
Methodology	Arrhenius plot (differential) method	Second-law (differential) method	Third-law (absolute) method and/or second-law (differential) method

one, which has branched from the second approach, appeared in the 1980s. The bases of these approaches are presented in Table 1.

The literature

Of the several dozen publications related to the topic investigated, we have chosen only those [2–27] which are devoted to quantitative or semiquantitative evaluation of the impact of the gaseous environment on the kinetics of solid-state decomposition (Table 2). Two kinetic parameters were used for the characterization of the decomposition kinetics: the decomposition rate v and the Arrhenius parameter E. The equations for the rate of incongruent decomposition presented in some original works have a more complicated form in comparison to that given in Table 2. However, they can be deduced (by considering the contribution of different decomposition stages in the whole process) to two typical cases: a linear variation of v with P^{ext}

$$v = k(P^{\mathrm{eq}} - P^{\mathrm{ext}}) \tag{1}$$

and an inverse-law variation of v with P^{ext}

$$v = k(P^{\mathrm{eq}} - P^{\mathrm{ext}})/P^{\mathrm{ext}} \tag{2}$$

Here P^{eq} is the equilibrium partial pressure of the product for the incongruent (and reversal) decomposition reaction at the temperature of experiment and P^{ext} is the extensive partial pressure of the excess of gaseous product in the furnace. Both equations were derived under the assumption that $v \to 0$ as $P^{\mathrm{ext}} \to P^{\mathrm{eq}}$. It is easy to show that in this case the reduction of the rate v with rising P^{ext} should manifest itself in an increase of the E parameter [28].

The data in Table 2 allow the following conclusions.

- The list of the most important publications covers the period about 80 years (from 1931 to 2009). These works are distributed nearly evenly inside of this period with only two exceptions: the absence of publications in the 1940s (most likely, due to the Second World War) and active studies in the 1960s.
- The article by Topley and Smith [2] devoted to anomalous increase of the decomposition rate of $MnC_2O_4{\cdot}2H_2O$ with P^{ext} of H_2O vapor in the vicinity of 1 Torr opens this list. Over nearly 80 years since the discovery of this effect, several tens of publications appeared (see [29]) devoted to its study for different hydrates. Nevertheless, until now, there has been no generally accepted opinion on it [1].
- The retardation effect of the gaseous product on the decomposition rate has been investigated in the frames of all thermoanalytical approaches. Nevertheless, the conclusions of different researchers are contradictory (even for the same reactant). In the cases of Arrhenius and Knudsen–Langmuir approaches, a linear variation of v with P^{ext} was observed in [9, 11, 14, 18, 19], an inverse-law variation in [6, 9, 10, 12, 16, 20], and no significant variation in [3, 15]. Only an inverse-law variation of v with P^{ext} was observed in the cases of thermochemical approach [5, 17, 24]. It is worth noting that the thermochemical approach was used by Gilbert and Kitchener [5] for the interpretation of the congruent decomposition of CdO already in 1956.
- The monotonous rise of the E parameter with P^{ext} was experimentally observed by Zawadzki and Bretsznajder [4] in the example of $CaCO_3$ decomposition in the presence of CO_2. An increase of CO_2 pressure from 0.0013 to 0.06 bar was accompanied by the rise of the E parameter from 186 to 1536 kJ mol^{-1}. Later on, this effect was observed by Mauras (708–1580 kJ mol^{-1} at 0.03–0.26 bar CO_2 [7]), and Maciejewski and Baldyga (310–460 kJ mol^{-1} at 0.02–0.06 bar CO_2 [18]). Furthermore, it was observed for $CdCO_3$ decomposition (270–670 kJ mol^{-1} at 0.002–1 bar CO_2) by Pavlyuchenko and Prodan [8], and for $SrCO_3$ decomposition (850–36,600 kJ mol^{-1} at 4×10^{-5}–1 bar CO_2) by Zemtsova et al. [13]. However, this effect was not observed for many other reversible decomposition reactions (e.g., in the cases of $MgCO_3$ and $FeCO_3$ [28]). What is more, Criado et al. [23] could not reproduce this effect even for $CaCO_3$ (191 ± 5 kJ mol^{-1} at 0.013–0.2 bar CO_2).

Table 2 The impact of gaseous product on the kinetics of solid-state decompositions in the evolution of the Arrhenius, Knudsen–Langmuir, and thermochemical approaches (the list of publications)

Authors	Year	Ref.	Approach	Reactant	Product	Decomposition mechanism	Medium	Impact of product pressure on v or E
Topley and Smith	1931	[2]	Arrhenius	$MnC_2O_4{\cdot}2H_2O$	H_2O	Incongruent	Vacuum	Rise of v with P_{H_2O} in the vicinity of 1 Torr
Furnas	1931	[3]	Arrhenius	$CaCO_3$	CO_2	Incongruent	Air	No impact of P_{CO_2} on v
Zawadzki and Bretsznajder	1935	[4]	Arrhenius	$CaCO_3$	CO_2	Incongruent	Vacuum	$E \to \infty$ at $P^{ext}/P^{eq} \to 1$
Gilbert and Kitchener	1956	[5]	Thermochemical	CdO	O_2	Congruent	N_2	$v = k/(P_{O_2})^{1/2}$
Hyatt et al.	1958	[6]	Arrhenius	$CaCO_3$	CO_2	Incongruent	N_2	$v = k(P^{eq} - P^{ext})/P^{ext}$
Mauras	1960	[7]	Arrhenius	$CaCO_3$	CO_2	Incongruent	Vacuum	$E \to \infty$ at $P^{ext}/P^{eq} \to 1$
Pavlyuchenko and Prodan	1961	[8]	Arrhenius	$CdCO_3$	CO_2	Incongruent	Vacuum	$E \to \infty$ at $P^{ext}/P^{eq} \to 1$
Hashimoto	1961	[9]	Arrhenius	$CaCO_3$	CO_2	Incongruent	Vacuum	Linear variation at low T and nonlinear at high T
Cremer and Nitsch	1962	[10]	Arrhenius	$CaCO_3$	CO_2	Incongruent	Vacuum	$v = k(P^{eq} - P^{ext})/P^{ext}$
Ingraham and Marier	1963	[11]	Arrhenius	$CaCO_3$	CO_2	Incongruent	Air	$v = k(P^{eq} - P^{ext})$
Somorjai and Jepsen	1964	[12]	Knudsen–Langmuir	CdS	S_2	Congruent	Vacuum	$v = k/(P_{S_2})^{1/2}$
Zemtsova et al.	1971	[13]	Arrhenius	$SrCO_3$	CO_2	Incongruent	N_2	$E \to \infty$ at $P^{ext}/P^{eq} \to 1$
Koloberdin et al.	1975	[14]	Arrhenius	$CaCO_3$	CO_2	Incongruent	Air	$v = k(P^{eq} - P^{ext})$
Searcy and Beruto	1978	[15]	Knudsen–Langmuir	$CaCO_3$	CO_2	Incongruent	Vacuum	No variation of v when $P^{ext} < 0.01P^{eq}$
Darroudi and Searcy	1981	[16]	Knudsen–Langmuir	$CaCO_3$	CO_2	Incongruent	Vacuum	$v = k/P_{CO_2}$ when $P^{ext} < 0.01P^{eq}$
L'vov and Fernandes	1984	[17]	Thermochemical	Oxides M_aO_b	O_2	Congruent	Ar	$v = k/(P_{O_2})^{b/2a}$
Maciejewski and Baldyga	1985	[18]	Arrhenius	$CaCO_3$	CO_2	Incongruent	Vacuum	$v = k(P^{eq} - P^{ext})$ $E \to \infty$ at $P^{ext}/P^{eq} \to 1$
Dennis and Hayhurst	1987	[19]	Arrhenius	$CaCO_3$	CO_2	Incongruent	N_2	$v = k(P^{eq} - P^{ext})$
Rao et al.	1989	[20]	Arrhenius	$CaCO_3$	CO_2	Incongruent	N_2	$v = k(P^{eq} - P^{ext})/P^{ext}$
Malecki and Prochowska	1994	[21]	Arrhenius	Co_3O_4	O_2	Incongruent	Vacuum	$E \to \infty$ at $P^{ext}/P^{eq} \to 1$
Wang and Thompson	1995	[22]	Arrhenius	$CaCO_3$	CO_2	Incongruent	Vacuum	$v = k(P^{eq} - P^{ext})$
Criado et al.	1995	[23]	Arrhenius	$CaCO_3$	CO_2	Incongruent	Vacuum	E parameter does not depend on excess P_{CO_2}
L'vov	1997	[24]	Thermochemical	$CaCO_3$	CO_2	CDV and CaO-condensation	Vacuum	$v = k/P_{CO_2}$
L'vov	2001	[25]	Thermochemical	Hydrates Salt$\cdot b$H$_2$O	H_2O	CDV and salt-condensation	Vacuum	$E^i/E^e = 1 + b$
L'vov and Ugolkov	2004	[26]	Thermochemical	MCO_3 M: Ca, Sr	CO_2	CDV and MO-condensation	Vacuum/Ar/He/N_2	E^i parameter does not depend on P_{CO_2}
L'vov and Ugolkov	2009	[27]	Thermochemical	$KMnO_4$	O	CDV and (K_2O + MnO)-condensation	Air/Ar/He/CO_2	E and v do not depend on the environment (at atmospheric pressure)

- Twenty five years have gone since the publication of work [17], in which the existence of two different modes of decompositions (equimolar and isobaric) has been suggested. However, except for this author [24–26], no one has used this concept for interpretation of the kinetics of decomposition reactions. The possible reasons of this neglect might be the publication of article [17] in a journal, which is quite outside of the TA problems and some math uncertainties in the presentation of this conception in our previous works.

As it follows from the above consideration, the Arrhenius and Knudsen–Langmuir approaches to the interpretation of decomposition kinetics, based on the assumption of two different reaction mechanisms (congruent and incongruent) could not solve the problems related to the impact of the gaseous environment on the kinetics of solid-state decomposition. There are serious disagreements between the results obtained by different authors. In addition, interest in this topic in the frame of the Arrhenius approach over the latter 10–15 years, as can be seen from the content of the recent books [1] and [30], has diminished practically to zero. At the same time, the achievements in the application of the thermochemical approach to this problem remain unnoticed. Taking this situation into account, the author will discuss below the key points of thermochemical kinetics in a compact and improved form once more.

Thermochemical kinetics of solid-state decomposition reactions

Basic equations

Contrary to the traditional Arrhenius kinetics that is based on the Arrhenius equation

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

the kinetics of the thermochemical approach rely on the next quasi-equilibrium equations describing the vaporization process R(s) $\leftrightarrow$ R(g) in vacuum and in foreign gas.

$$J = MP/(2\pi MRT)^{1/2} \tag{4}$$

$$J = MDP/(zRT) \tag{5}$$

$$J = MDP/(rRT) \tag{6}$$

Equation 4 was derived by Hertz [31], Knudsen [32], and Langmuir [33]. Two other (diffusion) equations were derived by Langmuir [34]. In all the cases, the absolute rate of vaporization J (in units of kg m^{-2} s^{-1}) is proportional to the equilibrium vapor pressure P of reactant R. The other parameters are as follows: M is the molar mass, D is the diffusion coefficient of the vapor in foreign gas, z is the distance from the vaporization surface to the sink where the concentration of vapor molecules becomes zero, and r is the radius of a single spherical particle.

Decomposition modes

Consider the case of the decomposition of reactant R into gaseous products A and B in reaction R(s) $\leftrightarrow a$A(g) + bB(g). Under equilibrium conditions, the partial pressures of gaseous components are related with the equilibrium constants [35] through the equation:

$$K^\circ = \frac{K_\mathrm{P}}{(P^\circ)^v} = \frac{\left(P_\mathrm{A}^\mathrm{int}\right)^a\left(P_\mathrm{B}^\mathrm{int} + P_\mathrm{B}^\mathrm{ext}\right)^b}{(P^\circ)^v} \tag{7}$$

Here K° is the thermodynamic (or 'standard') equilibrium constant, K_P is the equilibrium constant (pressure basis), P° is the standard pressure ($P^\circ = 10^5$ Pa = 1 bar), $v = a + b$, P^int is the internal partial pressures of A and B components originated from the decomposition of reactant, and P^ext is the external partial pressure of gaseous component in a reactor. It follows from Eq. 7 that

$$P_\mathrm{A}^\mathrm{int} = (P^\circ)^{v/a}(K^\circ)^{1/a}/\left(P_\mathrm{B}^\mathrm{int} + P_\mathrm{B}^\mathrm{int}\right)^{b/a} \tag{8}$$

Under the conditions of congruent decomposition for which $J_\mathrm{A}/a = J_\mathrm{B}/b$, the ratio β of internal partial pressures

$$P_\mathrm{B}^\mathrm{int}/P_\mathrm{A}^\mathrm{int} \equiv \beta \tag{9}$$

is equal (in vacuum and in atmosphere of foreign gas, respectively) to:

$$\beta_1 = (b/a)\,(M_\mathrm{B}/M_\mathrm{A})^{1/2} \tag{10}$$

$$\beta_2 = bD_\mathrm{A}/\,(aD_\mathrm{B}) \tag{11}$$

From the congruency condition and at $P_\mathrm{B}^\mathrm{ext} < P_\mathrm{B}^\mathrm{int}$ (equimolar mode):

$$\left(P_\mathrm{B}^\mathrm{int}\right)^\mathrm{e} \approx P^\circ\left(\beta^a K^\circ\right)^{1/v} \tag{12}$$

From the congruency condition and at $P_\mathrm{B}^\mathrm{ext} > P_\mathrm{B}^\mathrm{int}$ (isobaric mode):

$$\begin{aligned}\left(P_\mathrm{B}^\mathrm{int}\right)^\mathrm{i} = \beta P_\mathrm{A}^\mathrm{int} &= \frac{\beta\,(P^\circ)^{v/a}(K^\circ)^{1/a}}{\left(P_\mathrm{B}^\mathrm{int} + P_\mathrm{B}^\mathrm{ext}\right)^{b/a}}\\ &\approx \beta(P^\circ)^{v/a}(K^\circ)^{1/a}/\left(P_\mathrm{B}^\mathrm{ext}\right)^{b/a}\end{aligned} \tag{13}$$

The quantity K° in Eqs. 12 and 13 is equal to:

$$K^\circ = \exp\frac{\Delta_\mathrm{r}S_T^\circ}{R}\exp\left(\frac{\Delta_\mathrm{r}H_T^\circ}{RT}\right) \tag{14}$$

where $\Delta_\mathrm{r}S_T^\circ$ and $\Delta_\mathrm{r}H_T^\circ$ are the entropy and enthalpy changes for the decomposition reaction, respectively.

Absolute rates of decomposition

For reaction R(s) ↔ aA(g) + bB(g), the final equations for the flow of gaseous products A and B were obtained after the insertion of $\left(P_{\mathrm{B}}^{\mathrm{int}}\right)^{\mathrm{e}}$, $\left(P_{\mathrm{B}}^{\mathrm{int}}\right)^{\mathrm{i}}$, and K° quantities into Eqs. 4 and 5:

$$J_{\mathrm{R}}^{\mathrm{e}} = \frac{M_{\mathrm{R}}P^{\circ}}{b(2\pi M_{\mathrm{B}}RT)^{1/2}}\beta_1^{a/v}\ \mathrm{EXP}^{\mathrm{e}} \tag{15}$$

$$J_{\mathrm{R}}^{\mathrm{i}} = \frac{M_{\mathrm{R}}(P^{\circ})^{v/a}}{b(2\pi M_{\mathrm{B}}RT)^{1/2}}\frac{\beta_1}{\left(P_{\mathrm{B}}^{\mathrm{ext}}\right)^{b/a}}\ \mathrm{EXP}^{\mathrm{i}} \tag{16}$$

$$J_{\mathrm{R}}^{\mathrm{e}} = \frac{M_{\mathrm{R}}D_{\mathrm{B}}P^{\circ}}{bzRT}\ \beta_2^{a/v}\ \mathrm{EXP}^{\mathrm{e}} \tag{17}$$

$$J_{\mathrm{R}}^{\mathrm{i}} = \frac{M_{\mathrm{R}}D_{\mathrm{B}}(P^{\circ})^{v/a}}{bzRT}\frac{\beta_2}{\left(P_{\mathrm{B}}^{\mathrm{ext}}\right)^{b/a}}\ \mathrm{EXP}^{\mathrm{i}} \tag{18}$$

where

$$M_{\mathrm{R}} = aM_{\mathrm{A}} + bM_{\mathrm{B}} \tag{19}$$

$$\mathrm{EXP}^{\mathrm{e}} \equiv \exp\frac{\Delta_{\mathrm{r}}S_T^{\circ}}{vR}\exp\left(-\frac{\Delta_{\mathrm{r}}H_T^{\circ}}{vRT}\right) \tag{20}$$

$$\mathrm{EXP}^{\mathrm{i}} \equiv \exp\frac{\Delta_{\mathrm{r}}S_T^{\circ}}{aR}\exp\left(-\frac{\Delta_{\mathrm{r}}H_T^{\circ}}{aRT}\right) \tag{21}$$

For reaction R(s) ↔ aA(g) + bB(g) → aA(s) + bB(g), which corresponds to the mechanism of CDV accompanied by condensation of the oversaturated vapor of product A [36], the final equations for the flow of gaseous product B differ from Eqs. 15 to 18 only in the use of factor M_{B} instead of M_{R}/b:

$$J_{\mathrm{B}}^{\mathrm{e}} = \frac{M_{\mathrm{B}}P^{\circ}}{(2\pi M_{\mathrm{B}}RT)^{1/2}}\ \beta_1^{a/v}\ \mathrm{EXP}^{\mathrm{e}} \tag{22}$$

$$J_{\mathrm{B}}^{\mathrm{i}} = \frac{M_{\mathrm{B}}(P^{\circ})^{v/a}}{(2\pi M_{\mathrm{B}}RT)^{1/2}}\frac{\beta_1}{\left(P_{\mathrm{B}}^{\mathrm{ext}}\right)^{b/a}}\ \mathrm{EXP}^{\mathrm{i}} \tag{23}$$

$$J_{\mathrm{B}}^{\mathrm{e}} = \frac{M_{\mathrm{B}}D_{\mathrm{B}}P^{\circ}}{zRT}\ \beta_2^{a/v}\ \mathrm{EXP}^{\mathrm{e}} \tag{24}$$

$$J_{\mathrm{B}}^{\mathrm{i}} = \frac{M_{\mathrm{B}}D_{\mathrm{B}}(P^{\circ})^{v/a}}{zRT}\frac{\beta_2}{\left(P_{\mathrm{B}}^{\mathrm{ext}}\right)^{b/a}}\ \mathrm{EXP}^{\mathrm{i}} \tag{25}$$

In the case of the decomposition of a single spherical particle, Eqs. 17 and 18, and Eqs. 24 and 25 can be used with only one difference: the quantity z should be substituted by the quantity r.

An analysis of thermochemical kinetics presented above in the form of Eqs. 4–25 leads to the following general conclusions.

- All the quantities and parameters entering the kinetic equations have a simple physical meaning and can be quantitatively characterized (in contrast to the Arrhenius equation).
- The kinetic equations satisfy the exponential dependence of the decomposition rate on temperature.
- The kinetic equations allow the determination of absolute values of the equilibrium partial pressures of decomposition products, which are directly related to the thermodynamic characteristics (enthalpy and entropy) of the reactions.
- The kinetic equations are applicable to measurements both in vacuum and in the presence of foreign gases (provided that these gases are inert to both the reactant and the products).

Interrelations between the kinetic parameters

An analysis of the above kinetic equations permitted to formulate the following important relationships between kinetic parameters in relation to the features of gaseous environment. These relationships can be used as criteria of the validity of the theory outlined.

- The value of the molar enthalpy, $\Delta_{\mathrm{r}}H_T^{\circ}/a$, for the isobaric decomposition mode does not depend on the partial pressure of the excess of gaseous product in the system, i.e., for any $P_{\mathrm{B}}^{\mathrm{ext}}$ magnitude if $P_{\mathrm{B}}^{\mathrm{ext}} > P_{\mathrm{B}}^{\mathrm{int}}$:

$$E^{\mathrm{i}} = \Delta_{\mathrm{r}}H_T^{\circ}/a = \mathrm{const} \tag{26}$$

- The decomposition rate in the isobaric mode, $J_{\mathrm{B}}^{\mathrm{i}}$, other factors being equal, is inversely related to the magnitude $\left(P_{\mathrm{B}}^{\mathrm{ext}}\right)^{b/a}$ i.e.,

$$J_{\mathrm{B}}^{\mathrm{i}} \propto \left(P_{\mathrm{B}}^{\mathrm{ext}}\right)^{-b/a} \tag{27}$$

- The ratio of the E parameters or molar enthalpies for the isobaric and equimolar decomposition modes, irrespective of the actual decomposition conditions (vacuum or foreign gas environment), satisfies the condition:

$$E^{\mathrm{i}}/E^{\mathrm{e}} = v/a = (a+b)/a \tag{28}$$

- The ratio of the Arrhenius parameters for the isobaric (A^{i}) and equimolar (A^{e}) decomposition modes equals in vacuum:

$$\frac{A^{\mathrm{i}}}{A^{\mathrm{e}}} = \beta_1^{b/v}\sqrt{T^{\mathrm{e}}/T^{\mathrm{i}}}\left(P^{\circ}/P_{\mathrm{B}}^{\mathrm{ext}}\right)^{b/a}\exp\frac{b\Delta_{\mathrm{r}}S_T^{\circ}}{avR} \tag{29}$$

and in foreign gas environment:

$$\frac{A^{\mathrm{i}}}{A^{\mathrm{e}}} = \beta_2^{b/v}\left(T^{\mathrm{e}}/T^{\mathrm{i}}\right)\left(P^{\circ}/P_{\mathrm{B}}^{\mathrm{ext}}\right)^{b/a}\exp\frac{b\Delta_{\mathrm{r}}S_T^{\circ}}{avR} \tag{30}$$

- The ratio of the A parameters for decompositions in vacuum (A_{vac}) and in atmosphere of foreign gas (A_{at}) is equal for the equimolar mode:

$$A_{\mathrm{vac}}/A_{\mathrm{at}} = zT_{\mathrm{at}}(\beta_1/\beta_2)^{a/v}\sqrt{R/(2\pi M_{\mathrm{B}}T_{\mathrm{vac}})}/D_{\mathrm{B}} \qquad (31)$$

and for the isobaric mode:

$$A_{\mathrm{vac}}/A_{\mathrm{at}} = zT_{\mathrm{at}}(\beta_1/\beta_2)\sqrt{R/(2\pi M_{\mathrm{B}}T_{\mathrm{vac}})}/D_{\mathrm{B}} \qquad (32)$$

Interpretation or reappraisal of the effects related to the impact of gaseous environment

The correctness of new ideas and theories in scientific research is commonly evaluated by their fruitfulness in the interpretation of problems that have accumulated in the fields under investigation and by their ability to predict unknown trends and effects. The thermochemical approach to the kinetics of solid-state reactions meets these criteria. This conclusion can be made after the consideration of the results presented in Table 3. The first three items in this table that are the direct consequences of theory (see Eqs. 26–28) have been convincingly supported experimentally [24, 25].

The Zawadzki–Bretsznajder effect is in contradiction to the theory (see Eq. 26) and in conflict with recent experimental data [23, 26]. As shown in [37, 38], the most probable reason of the erroneous results reported in [4, 7, 8, 13] is the low precision of E measurements related to the high values of $T_{\mathrm{max}}/(T_{\mathrm{max}} - T_{\mathrm{min}})$, which were in the range 30–100 [4, 8, 13]. (Here T_{max} and T_{min} are, respectively, the maximum and minimum temperature of experiment.) It is not surprising that with improvement of TA equipment over the latter 25 years no publications, which corroborated this effect, have appeared.

The discontinuities in the Arrhenius plots in electrothermal atomic absorption spectrometry (ET AAS) and TA, and the peculiarities of kinetic compensation effect were quantitatively interpreted by the existence of two different modes (equimolar and isobaric) of decomposition [17, 24]. An increase of the decomposition rate in the vicinity of 1 Torr pressure of gaseous product (the Topley–Smith effect) is related to an increase of thermal conductivity of gaseous medium under conditions of severe self-cooling of the reactant. The mechanism of this effect has been supported by theoretical modeling the process for two reactants: $Li_2SO_4 \cdot H_2O$ in H_2O [29], and $CaCO_3$ in CO_2 [39]. The retardation (diffusion) effect of foreign gas on the decomposition rate was investigated in [37, 38] in the example of $CaCO_3$. Self-cooling and self-heating effects in inert gas and in vacuum were investigated for some typical decomposition reactions in [40–42]. In all the cases, experimental results are in good agreement with theoretical calculations.

The independence of the $KMnO_4$ decomposition rate from the gaseous environment at atmospheric pressure [27, 43] is one of the examples that illustrates the predictive capability of the thermochemical approach. This remarkable feature of $KMnO_4$ has been predicted in [37, 38] on purely theoretical grounds.

Conclusions

The main purpose of this study was to review the current state of the problem of the impact of gaseous environment on the kinetics of solid-state decompositions. Three different theoretical approaches to the interpretation of the decomposition kinetics have been taken into account. As it follows from the literature published over the past 80 years, the Arrhenius and Knudsen–Langmuir approaches that are based on the assumption of two different reaction mechanisms (congruent and incongruent) could not solve the problem. There are serious disagreements between the results obtained by different authors. Interest in this topic in the frame of the Arrhenius approach over

Table 3 Use of the thermochemical approach for the interpretation or reappraisal of the effects and regularities related to the impact of gaseous environment on the kinetics of solid-state decompositions

Effect or regularity	First publication	Section in the book [38]
Invariance of the E^{i} parameter under excess pressure of gaseous product	[24]	5.3; 5.4
The retardation effect of gaseous product on the decomposition rate: $A^{\mathrm{i}} \propto (P_{\mathrm{B}})^{-b/a}$	[24]	5.3; 5.4
Dependence of the $E^{\mathrm{i}}/E^{\mathrm{e}}$ ratio on the stoichiometry of the decomposition reaction: $E^{\mathrm{i}}/E^{\mathrm{e}} = v/b$	[25]	5.3–5.5
The Zawadzki–Bretsznajder effect (rule)	[37]	5.3; 5.4
Discontinuities in the Arrhenius plots in ET AAS and TA	[17]	5.3; 5.4
The kinetic compensation effect	[37]	5.3–5.5
The Topley–Smith effect ($Li_2SO_4 \cdot H_2O$ in H_2O)	[29]	7.1; 7.2
The Topley–Smith effect ($CaCO_3$ in CO_2) and Searcy's experiments [15, 16]	[39]	7.3
The retardation (diffusion) effect of foreign gas on the decomposition rate	[37]	3.7
Self-cooling and self-heating effects in foreign gas and in vacuum	[40–42]	6.3; 7.3
Independence of $KMnO_4$ decomposition rate from gaseous environment at atmospheric pressure	[27, 43]	12

the latter 10–15 years has diminished practically to zero. At the same time, achievements in the application of the thermochemical approach that is based on the assumption of a unitary CDV mechanism remain unnoticed [36, 44, 45]. Taking this situation into account, the author has outlined the key points of the thermochemical kinetics in a compact but complete and rigorous form once more. The revised kinetic equations for the different modes of decomposition, several important interrelations between the kinetic parameters, and, finally, the results in the interpretation or reappraisal of the main effects related to the impact of gaseous environment on the kinetics have been considered. In the framework of the thermochemical approach, the problem being discussed may be considered nowadays practically resolved.

Acknowledgements The author thanks his colleague Dr. Leonid Polzik for the useful comments, and the author's grandson Nikita L'vov for the linguistic correction of this article.

References

1. Galwey AK, Brown ME. Thermal decomposition of ionic solids. Amsterdam: Elsevier; 1999.
2. Topley B, Smith ML. Function of water vapor in the dissociation of a salt hydrate. Nature. 1931;128:302.
3. Furnas CC. The rate of calcination of limestone. Ind Eng Chem. 1931;23:534–8.
4. Zawadzki J, Bretsznajder S. Über das Temperaturincrement der Reaktionsgeschwindigkeit bei Reaktionen vom Typus $A_{fest} = B_{fest} + C_{gas}$. Z Elektrochem. 1935;41:215–23.
5. Gilbert IGF, Kitchener JA. The dissociation pressure of cadmium oxide. J Chem Soc. 1956;3919–21.
6. Hyatt EP, Cutler IB, Wadsworth ME. Calcium carbonate decomposition in carbon dioxide atmosphere. J Am Ceram Soc. 1958; 41:70–4.
7. Mauras H. Étude cinétique isobare de la dissociation des systèmes solides (III). Dissociation du carbonate de calcium. Bull Soc Chim Fr. 1960;260–7.
8. Pavlyuchenko MM, Prodan EA. Heterogeneous chemical reactions. Minsk: Nauka Tekhnika; 1961 (in Russian).
9. Hashimoto H. The thermal decomposition of calcium carbonates (II). The effect of carbon dioxide. J Chem Soc Jpn. 1961;64: 1162–6.
10. Cremer E, Nitsch WZ. Über die Geschwindigkeit der $CaCO_3$-Zersetzung in Abhängigkeit vom CO_2-Druck. Z Elektrochem. 1962;66: 697–702.
11. Ingraham TR, Marier P. Kinetics studies on the thermal decomposition of calcium carbonates. Can J Chem Eng. 1963;8:170–3.
12. Somorjai GA, Jepsen DW. Evaporation mechanism of CdS single crystals. J Chem Phys. 1964;41:1389–93.
13. Zemtsova ZN, Pavlyuchenko MM, Prodan EA. Kinetics of thermal decomposition of $SrCO_3$ in atmosphere of CO_2. Vesti AN BSSR Ser Khim. 1971;5:21–6 (in Russian).
14. Koloberdin VI, Blinichev VN, Strel'tsov VV. The kinetics of limestone calcination. Int Chem Eng. 1975;15:101–4.
15. Searcy AW, Beruto D. Kinetics of endothermic decomposition reactions. 2. Effects of the solid and gaseous products. J Phys Chem. 1978;82:163–7.
16. Darroudi T, Searcy AW. Effect of CO_2 pressure on the rate of decomposition of calcite. J Phys Chem. 1981;85:3971–4.
17. L'vov BV, Fernandes GHA. Regularities in thermal dissociation of oxides in graphite furnace for atomic absorption analysis. Zh Analit Khim. 1984;39:221–31 (in Russian).
18. Maciejewski M, Baldyga J. The influence of the pressure of the gaseous product on the reversible thermal decomposition of solids. Thermochim Acta. 1985;92:105–8.
19. Dennis JS, Hayhurst AN. The effect of CO_2 on the kinetics and extent of calcination of limestone and dolomite particles in fluidized beds. Chem Eng Sci. 1987;42:2361–72.
20. Rao TR, Gunn DJ, Bowen JH. Kinetics of calcium carbonate decomposition. Chem Eng Res Des. 1989;67:38–47.
21. Malecki A, Prochowska-Klisch B. The influence of oxygen pressure on the kinetics of the thermal decomposition of Co_3O_4. J Therm Anal Calorim. 1994;41:1109–17.
22. Wang Y, Thompson WJ. The effect of steam and carbon dioxide on calcite decomposition using dynamic X-ray diffraction. Chem Eng Sci. 1995;50:1373–82.
23. Criado JM, Gonzales M, Malek J, Ortega A. The effect of the CO_2 pressure on the thermal decomposition kinetics of calcium carbonate. Thermochim Acta. 1995;254:121–7.
24. L'vov BV. Mechanism of thermal decomposition of alkaline-earth carbonates. Thermochim Acta. 1997;303:161–70.
25. L'vov BV. The physical approach to the interpretation of the kinetics and mechanisms of thermal decomposition of solids: the state of the art. Thermochim Acta. 2001;373:97–104.
26. L'vov BV, Ugolkov VL. Peculiarities of $CaCO_3$, $SrCO_3$ and $BaCO_3$ decomposition in CO_2 as a proof of their primary dissociative evaporation. Thermochim Acta. 2004;410:47–55.
27. L'vov BV, Ugolkov VL. Decomposition of $KMnO_4$ in different gases as a potential kinetics standard in thermal analysis. J Therm Anal Calorim. doi:10.1007/s10973-009-0143-z.
28. Prodan EA, Pavlyuchenko MM, Prodan SA. Regularities of topochemical reactions. Minsk: Nauka Tekhnika; 1976 (in Russian).
29. L'vov BV, Novichikhin AV, Dyakov AO. Computer simulation of the Topley–Smith effect. Thermochim Acta. 1998;315:169–79.
30. Stern KH. High temperature properties and thermal decomposition of inorganic salts with oxyanions. Boca Raton: CRC Press; 2000.
31. Hertz H. Über die Verdunstung der Flüssigkeiten, insbesondere des Quecksilbers, im luftleeren Raume. Ann Phys Chem. 1882;17: 177–200.
32. Knudsen M. Die Molekularströming der Gase durch Öffnungen und die Effusion. Ann Phys. 1909;28:999–1016.
33. Langmuir I. The vapor pressure of metallic tungsten. Phys Rev. 1913;2:329–42.
34. Langmuir I. The evaporation of small spheres. Phys Rev. 1918; 12:368–70.
35. Mills I. Quantities, units and symbols in physical chemistry. Oxford: Blackwell Science Publications; 1988.
36. L'vov BV. Role of vapor oversaturation in the thermal decomposition of solids. J Therm Anal Calorim. 2009;96:321–30.
37. L'vov BV. Thermal decomposition of solid and liquid substances. St. Petersburg: Polytech University Publisher; 2006.
38. L'vov BV. Thermal decomposition of solids and melts. New thermochemical approach to the mechanism, kinetics and methodology. Berlin: Springer; 2007.
39. L'vov BV. Mechanism and kinetics of thermal decomposition of carbonates. Thermochim Acta. 2002;386:1–16.
40. L'vov BV, Ugolkov VL. Kinetics and mechanism of dehydration of kaolinite, muscovite and talc analyzed thermogravimetrically by the third-law method. J Therm Anal Calorim. 2005;82:15–22.

41. L'vov BV. Fundamental restrictions of the second-law and Arrhenius plot methods used in the determination of reaction enthalpies in decomposition kinetics. J Therm Anal Calorim. 2008; 92:639–42.
42. L'vov BV, Ugolkov VL. The self-heating effect in the process of $KMnO_4$ decomposition in vacuum. J Therm Anal Calorim. 2008; 94:453–60.
43. L'vov BV, Ugolkov VL. Use of potassium permanganate as a possible kinetic standard in thermal analysis. Russ J Appl Chem. 2007;80:1289–94.
44. L'vov BV. Thermochemical approach to solid-state decomposition reactions against the background of traditional theories. J Therm Anal Calorim. 2009;96:487–93.
45. L'vov BV. The mechanism of solid-state decompositions in a retrospective. J Therm Anal Calorim. doi:10.1007/s10973-009-0579-1.