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Thermochimica Acta 390 (2002) 5–19

thermochimica acta

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Decomposition kinetics of calcite: a new approach to the old problem

Boris V. L'vov[a,*], Leonid K. Polzik[a], Valery L. Ugolkov[b]

[a]Department of Analytical Chemistry, St. Petersburg State Technical University, St. Petersburg 195251, Russia
[b]Laboratory of Thermodynamics and Kinetics, Institute of Silicate Chemistry, St. Petersburg 199155, Russia

Received 14 January 2002; received in revised form 13 February 2002; accepted 20 February 2002

Abstract

In addition to the results of our own experiments on the decompositions of calcite crystals under high-vacuum (10^{-8} bar) and low-vacuum (10^{-2} bar) conditions, some data reported in the literature were used for the determination of the E parameters by the second- and third-law methods and discussion of the self-cooling effect on the results of these determinations. Analysis of these data supports the advantages of the third-law method compared with the second-law (and Arrhenius-plots) methods in relation to reliability of results obtained. The experimental values of the E parameters, obtained by different technique and under different conditions by the third-law method, are in excellent agreement with the theoretically predicted values based on the mechanism of congruent decomposition of $CaCO_3$ into gaseous species CO_2 and CaO with the simultaneous condensation of low-volatility CaO molecules. Indeed, the experimental values of the E parameters in the equimolar and isobaric modes of decomposition, obtained in this work under optimal conditions, are equal to 261 and 493 kJ mol^{-1}, respectively whereas the theoretical values at these temperatures equals to 253 and 505 kJ mol^{-1}. The application of the third-law method allowed to support the enormous influence of self-cooling on the results obtained by the usual second-law and Arrhenius-plots methods accepted in thermal analysis. The role of this effect is increased dramatically in the experiments performed under high-vacuum conditions. Contrary to the second-law method, the third-law method appears to be rather insensitive to reactant self-cooling in the process of decomposition and to the presence of gaseous product (CO_2) in the reactor.

Keywords: Kinetics; Calcite decomposition; Physical approach; Second-law method; Third-law method; Self-cooling

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1. Introduction

The decomposition kinetics of calcite is the most popular example of investigations in thermal analysis (TA). It is explained by great technological importance (manufacturing of lime) and an apparent simplicity of the corresponding reaction:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \qquad (1)$$

Despite the long story of these studies, there are no other example of more contradictory experimental kinetic parameters reported in the literature by different workers. The general situation discussed more then 25 years ago by Zsako and Arz [1] and 15 years ago by Maciejewski and Reller [2]. The reported apparent magnitudes of the Arrhenius parameters range from 110 to 1600 kJ mol^{-1} for the E parameter and from 10^2 to 10^{69} s^{-1} for the A parameter [1] (at the estimation by Maciejewski and Reller [2], the reported values of the E parameter differ even more: from 47 to 3800 kJ mol^{-1}).

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[*] Corresponding author. Tel.: +7-812-552-7741; fax: +7-812-247-4384.
E-mail address: blvov@robotek.ru (B.V. L'vov).

PII: S0040-6031(02)00080-1

The situation has not changed to the better in the recent years. In the recent comparative study of "computational aspects of kinetic analysis: the ICTAC kinetics project" reported in [3,4], all participants used the identical sets of numerical data for the decompositions of calcite in vacuum and nitrogen. In spite of this, different workers obtained from a computational procedure different kinetic parameters: from 58 to 262 kJ mol^{-1} for the E parameter and from 3 to 36 for the ln(A) (in s^{-1}) parameter. This situation, which is typical not only in the case of calcite, has led nowadays to the appearance of some pessimistic statements on the problem of a physical meaning of kinetic parameters on the whole. Considering the problem of a physical meaning of kinetic parameters, Maciejewski [4] claims: "it seems to be acceptable for everybody that kinetic calculations may be the not most efficient means of determining a reaction mechanism ..." Vyazovkin went still further [5]. He denies completely the concept of constant activation energy and suggests as alternative the concept of "variable activation energy" which is an unpredictable function of temperature and/or extent of reaction. It must agree with a conclusion that "there is evidence of stagnation in the field" [6].

In contrast to the situation described, there is another *physical* approach to the quantitative evaluation of kinetics and mechanisms of solid decompositions developed and efficiently used in atomic absorption spectrometry (AAS) over the last 35 years. This approach has been generated on the basis of classical works by Hertz [7] and Langmuir [8,9] on evaporation of metals and the attempts (unfortunately, not very efficient) of Searcy [10], Searcy and Beruto [11] in the 1970–1980s to apply the same ideas to the kinetics of dissociative evaporation of simple (binary) compounds.

The development of this approach in the framework of AAS involved several important steps. As early as in 1966, L'vov [12,13] applied the Langmuir diffusion equation to estimate the rate of dissociative evaporation of Al_2O_3 aerosol particles in flames used as atomizers in AAS and the magnitude of self-cooling effect attendant this process. In 1978, L'vov [14] gave a thermodynamic explanation of the proportional dependence of the initial temperature of analyte atomization in graphite furnaces on the E parameter. In the beginning of 1980s, the physical approach was used for the theoretical calculation of absolute rates of dissociative evaporation of metal oxides [15,16] and hydroxides [17]. In these works, two typical modes of dissociative evaporation (equimolar and isobaric) were revealed and identified and a physical meaning of the corresponding Arrhenius parameters (E and A) was interpreted for the first time. In particular, high values of the pre-exponential factors, A, sometimes reaching 10^{30} s^{-1} and more were interpreted. In 1989, L'vov et al. [18] demonstrated the appearance of metal oxides in the gaseous phase in the process of low-temperature pyrolysis (470–850 K) of nitrates and acetates of Bi, Pb, Cu, In, Mn, Ni and Co using the methods of electrothermal AAS. In the beginning of 1990s, the mechanism of congruent dissociative evaporation of metal nitrates was quantitatively substantiated on the basis of the direct quadruple mass spectrometric (QMS) observations of the low-volatility species of metals and metal oxides in the gaseous phase [19–21]. Thus, the main key points of the physical approach to the quantitative evaluation of kinetics and mechanisms of solid decompositions were revealed and formulated in the framework of electrothermal AAS and QMS more than 10 years ago.

Over the last 5 years, a series of 14 papers devoted to the application of this approach to the quantitative interpretation of some important features of solid-state (crystolysis) reactions and identification of decomposition mechanisms for several classes of solids in the framework of traditional TA has been published in this journal [22–35]. The features of considered crystolysis reactions are the following: the mechanism of nucleation and autocatalytic advance of decomposition reactions, the retardation of decomposition in the presence of gaseous products, the low decomposition coefficients α_v for many substances, the effect of self-cooling on the measurement of kinetic parameters, the Topley–Smith effect and the kinetic compensation effect. The physical approach has been successfully applied to the interpretation of kinetics of sublimation/dissociative evaporation of more than 110 substances from 20 different classes of solids: metals, non-metals, oxides, hydroxides, sulphides, selenides, tellurides, nitrides, azides, carbides, borides, fluorides, chlorides, bromides, iodides, carbonates, nitrates, sulphates, oxalates and hydrates.

In addition to this, several papers [36–40] devoted to the application of the physical approach to the interpretation of the mechanisms and kinetics of analyte release in electrothermal AAS have been published recently in *Spectrochimica Acta, Part B*. In particular, this approach was used for the identification of the true mechanism of analyte release between the bulk evaporation/desorption alternative and explanation of the mechanism of low-temperature migration of analyte in graphite furnaces at pyrolysis temperatures.

Strangely enough that, despite the indisputable advantages of the physical approach in comparison with the traditional *chemical* approach based on the Arrhenius concept of the activation effect, the physical approach is completely ignored in TA. None of the researchers tried to apply this approach in kinetic studies or, even, to comment the corresponding publications [15–40] (the book by Galwey and Brown [41] and two recent papers [6,42] of these workers are the only exceptions). As illustration, from eight papers on the physical approach published in *Thermochimica Acta* in 1997–1999 [22–29], only one paper was mentioned in the two-year 'fundamental review on TA' [43]. Is this a manifestation of the conservatism inherent in some stagnant fields of science or, simply, a result of the disappointment and apathy prevailing in TA? As can be deduced from the recent publications [3,4] in the special issue of *Thermochimica Acta*, devoted to "what has been achieved to date and what is expected to be available in 21st Century", the most important problem in the field of solid-state decompositions is the computational stage of kinetic analysis (some "encouraging" results of this project have been mentioned above).

The objectives of this work are, firstly, in the determination of the kinetics of thermal decomposition of calcite with the use of the new methodology based on the so-called third-law method [35], secondly, in the interpretation of the mechanism of its decomposition in the framework of a physical approach and, thirdly, in a more thorough investigation of the self-cooling effect responsible for a low reliability of the traditional second-law and Arrhenius-plots methods. The final goal of this work is to demonstrate the advantages of the physical approach over the chemical one using a popular example of the calcite decomposition as an illustration.

2. Theoretical models

2.1. Preliminary comments

As follows from the experience accumulated over the last century in the field of solid-state decomposition, most of these reactions, especially for polyatomic compounds, proceed under conditions far from equilibrium [41]. The main concept in the traditional chemical approach consists of the belief that the deviation from equilibrium is connected with the existence of the theoretically unpredicted energy barrier (activation energy) in the way of reaction. By contrast, the main concept in the physical approach consists of the belief that the decomposition of reactants into primary gaseous species proceeds under equilibrium conditions but the origin and composition of these primary products might differ from those at equilibrium. In the case of calcite, this difference consist in the decomposition of $CaCO_3$ into molecules of CO_2 and low-volatility gaseous molecules of CaO which subsequently condense with the formation of solid CaO.

The equilibrium character of decomposition reactions has received recently [35] a strong confirmation. The mean ratio of the initial temperature of decomposition, T_{in}, to the E parameter for 100 different substances (3.6 ± 0.4 kJ mol^{-1}) taken from the literature practically coincides with the value (3.6 ± 0.2 kJ mol^{-1}) predicted from equilibrium thermodynamics. The great advantage of the physical approach relative to the chemical one consists of the possibility for the quantitative description of the decomposition process using the laws of chemical thermodynamics. This possibility will be used in this work for the theoretical calculation and experimental determination of the E parameter.

The models employed in the theoretical calculation of the E parameters, have been described in a number of our recent publications [28–32] and, especially, in reviews [33,34]. The experimental determination of the E parameter can be performed by two ways based on the application of the second- and third-law methods. This topic was discussed in detail in [35]. Therefore, we are going to present below only some final relationships necessary for the calculations in this work.

2.2. Theoretical values of the E parameter

In the case of a solid compound S decomposed into gaseous products A and B with simultaneous condensation of low-volatility species A, that is

$$S(s) \rightarrow aA(g)\downarrow + bB(g) \tag{2}$$

the E parameter for reaction (2) should be different for the *equimolar* (in the absence of gaseous product B in the reactor atmosphere) and *isobaric* (in the presence of excess of the gaseous product B) modes of decomposition. We have

$$E^{e} = \frac{\Delta_r H_T^\circ}{v} = \frac{\Delta_r H_T^\circ}{a+b} \tag{3}$$

for the equimolar mode and

$$E^{i} = \frac{\Delta_r H_T^\circ}{v-b} = \frac{\Delta_r H_T^\circ}{a} \tag{4}$$

for the isobaric mode, respectively [28–34]. Here, v is the total number of moles of gaseous products, $(a+b)$, and $\Delta_r H_T^\circ$ is the change of the enthalpy in reaction (2). In both cases, the E parameter corresponds to the *specific enthalpy*, i.e. the enthalpy of the decomposition reaction reduced to one mole of primary products without including components of that present in excess.

In order to take into account the partial transfer of the energy released in the condensation of low-volatility product A to the reactant, we introduce into the calculations of the enthalpy of decomposition reaction (2) an additional term, $\tau a\,\Delta_c H_T^\circ(A)$, where the coefficient τ corresponds to the fraction of the condensation energy transferred to the reactant. Thus, we can write

$$\Delta_r H_T^\circ = a\,\Delta_f H_T^\circ(A) + b\,\Delta_f H_T^\circ(B) - \Delta_f H_T^\circ(S) + \tau a\,\Delta_c H_T^\circ(A) \tag{5}$$

For equal temperatures of the solid phases (product and reactant), one may expect equipartition of energy between the two phases, i.e. $\tau = 0.5$. For the majority of substances investigated up to now, the condition $\tau = 0.5$ is found to be valid. Therefore, in the case of calcite decomposition, the Eq. (5) might be rewritten as

$$\Delta_r H_T^\circ = \Delta_f H_T^\circ(CaO) + \Delta_f H_T^\circ(CO_2) - \Delta_f H_T^\circ(CaCO_3) + 0.5\,\Delta_c H_T^\circ(CaO) \tag{6}$$

The magnitudes of thermodynamic functions (the enthalpy and entropy) for the components of decomposition reaction of calcite and for the reaction as a whole (marked by bold) at 800, 900 and 1000 K are tabulated in Table 1. As follows from these data, the theoretical values of the E parameter for the decomposition of $CaCO_3$ at 900 K in accordance with reaction (2) are equal to 253 and 506 kJ mol^{-1} for the equimolar and isobaric modes, respectively. A maximum possible error (2S.D.) in these calculations is typically within a few kJ mol^{-1}.

Table 1
Thermodynamic functions used in the calculations [44]

Function	Temperature (K)		
	800	900	1000
$\Delta_f H_T^\circ$ (CaO(g)) (kJ mol^{-1})	70.7	74.4	78.1
$\Delta_f H_T^\circ$ (CaO(s)) (kJ mol^{-1})	−600.3	−595.0	−589.7
$\Delta_f H_T^\circ$ (CO_2) (kJ mol^{-1})	−361.0	−355.7	−350.4
$\Delta_f H_T^\circ$ ($CaCO_3$) (kJ mol^{-1})	−1133.9	−1121.9	−1109.6
$\Delta_c H_T^\circ$ (CaO) (kJ mol^{-1})	−671.0	−669.5	−667.9
$\Delta_r H_T^\circ$ (kJ mol^{-1})	**508.1**	**505.9**	**503.5**
S_T° (CaO(g)) (J mol^{-1} K^{-1})	254.0	258.4	262.3
S_T° (CO_2) (J mol^{-1} K^{-1})	257.4	263.5	269.2
S_T° ($CaCO_3$) (J mol^{-1} K^{-1})	193.2	207.3	220.2
$\Delta_r S_T^\circ$ (J mol^{-1} K^{-1})	**318.2**	**314.6**	**311.3**

2.3. Experimental values of the E parameter

Two different methods can be used for the experimental determination of the E parameter. The so-called 'second-law' method is based on the application of the van't Hoff equation:

$$\frac{d\ln K_P}{dT} = \frac{\Delta_r H_T^\circ}{RT^2} \tag{7}$$

where K_P is the equilibrium constant for the reaction (2) in terms of the partial pressures, P, of the gaseous products:

$$K_P = P_A^a P_B^b \tag{8}$$

After integration of Eq. (7), we receive

$$R\ln K_P = -\frac{\Delta_r H_T^\circ}{T} + \text{const.} \tag{9}$$

Taking into account Eqs. (2)–(4) and (8), we have in the case of $CaCO_3$ decomposition

$$R\ln P_{eq} = -\frac{E}{T} + \text{const.} \tag{10}$$

Here, P_{eq} is the equivalent pressure related to the rate of $CaCO_3$ decomposition, J, by the Hertz–Langmuir equation [34]:

$$P_{eq} = \frac{(2\pi MRT)^{1/2} J}{\gamma M_r} \tag{11}$$

Here, M_r is the molar mass of the reactant ($CaCO_3$), M the molar mass of the product (CaO or CO_2) and $\gamma = 10^5$ Pa bar^{-1} is the conversion factor from Pa to bars used to calculate partial pressures in chemical thermodynamics.

From measurements of J at several different temperatures, it is easy to obtain the E value (the slope of the plot in $R \ln P_{eq}$ versus T^{-1} scale). The advantage of this method consists in the possibility of using any parameter that is proportional to the P_{eq} value, instead of absolute values of P_{eq}. No values of thermodynamic functions are necessary for the calculations.

The so-called 'third-law' method is based on the direct application of the basic equation of chemical thermodynamics:

$$\Delta_r H_T^\circ = T(\Delta_r S_T^\circ - R \ln K_P) \tag{12}$$

where $\Delta_r S_T^\circ$ is the entropy change for the reaction (2). Taking into account Eqs. (2)–(4) and (8), Eq. (12) in the case of decomposition of $CaCO_3$ can be reduced to the equation

$$E^e = T\left(\frac{\Delta_r S_T^\circ}{2} - R \ln P_{eq}\right) \tag{13}$$

for the equimolar mode and to the equation

$$E^i = T(\Delta_r S_T^\circ - R \ln(P_{eq} P'_{CO_2})) \tag{14}$$

for the isobaric mode, where P'_{CO_2} is the external pressure of CO_2. In this case, a measurement at only one temperature is sufficient for the determination of E, but a knowledge of absolute values of the entropy of all components in the reaction is necessary for the calculation. These values are available now for the majority of substances [44–47]. Table 1 contains these values for the $CaCO_3$ decomposition.

The analysis of results reported in [44,48] for several tens of substances, has shown that the data calculated by the third-law method are, in general, the order of magnitude more precise than those calculated by the second-law method. This has been supported recently by the results of application of the second- and third-law methods to the determination of the E parameter for 20 different decomposition reactions [35].

As can be seen from a consideration of Eq. (13), the self-cooling effect results in the overestimation of the E values calculated by the third-law method. Therefore, it is preferable to use for the calculation the result(s) of low-temperature measurement when this effect is minimal. On the other hand, from a comparison of results at different temperatures, the magnitude of self-cooling effect can be easily estimated. In contrast to the third-law method, the self-cooling effect in case of the second-law method results in underestimation of the calculated results. Besides, the systematic error in this case is typically the order of magnitude higher [35].

2.4. *The self-cooling effect and measurements of the E parameters*

Most studies of the decompositions of powders and single crystals in TA tacitly assume that the temperature of the sample is equal to that of the furnace, and that the self-cooling due to some heat being expended in the endothermic decomposition can be neglected. However, as early as 1931, Smith and Topley [49] showed that the temperature of a single crystal in vacuum was lower than that in the heater by 4–8 K. It is rather obvious that, for powders, the self-cooling effect should be much greater.

L'vov et al. [25,27] proposed a fairly simple theoretical model and developed a program to compute the temperature of individual crystals and the layer-by-layer temperature distribution in powder samples during the course of their decomposition in vacuum and in the presence of foreign gases. It is suggested that the heat expended in decomposing a sample in a stationary regime is compensated by the radiation emitted by the heater (a crucible) and powder grains and through heat transfer by the gas molecules. Simulation of the temperature distribution, inside a powder sample, can be reduced to modeling the vertical distribution between horizontal layers of this material of thickness equal to the powder grain diameter. If the furnace temperature is the same on top and at the bottom of the sample, the analysis can be limited to considering only one half of such multilayered sample, from the central, 0th or 1st layer, to the $n_{1/2}$ outermost layer. All the calculations were performed with the laboratory-developed computer program described in [27].

The method of correction of the E parameter measured by the second-law method for the self-cooling effect consists in the following [25,27]. The deviation of the measured E parameter from the true value, which corresponds to the assumed spatially uniform sample heating up to the furnace temperature, is determined, first, by the difference between the temperatures of the heater, T_h, and of the sample surface, T_s, and second, by the effective number of powdered layers n_e involved in decomposition. The last factor corresponds to the effective number of powdered sample layers whose decomposition occurs at the same rate as that of the surface layer. Taking into account these two factors, the corrected value of the E parameter can be calculated using the relationship [25]:

$$E_{\text{cor}} = \frac{((1/T'_h) - (1/T''_h))E_{\text{exp}} + R\ln(n'_e/n''_e)}{(1/T'_s) - (1/T''_s)} \qquad (15)$$

Here, one and two primes refer, respectively, to the lower and higher points of the temperature interval used to determine E, and the subscript 'exp', to the experimental (original) value of the E parameter.

Eq. (15) can be applied not only to powders but also to single crystals. In this case, $n_e = 1$, and the calculation of corrections takes into account only the temperatures of the furnace and of the sample. In case of powders, for the calculation of n_e factors it is necessary to know the actual number of layers $n_{1/2}$ in one half of such multilayered sample. For spherical particles, this can be calculated using the relationship [25]:

$$n_{1/2} = \frac{6}{\pi^2}\frac{m}{\rho r_0 d^2} \qquad (16)$$

Here, m, ρ, r_0 and d are the mass and density of the reactant, the grain radius and the diameter of the balance crucible in which the sample is placed, respectively.

3. Experimental

The experiments were carried out with a Netzsch STA 429 instrument on the TG and DSC measuring head. The actual measured quantities were the mass change of the sample (with the resolution of about 1 μg) and the absolute crucible temperature. An open alumina crucible 6.5 mm diameter and 4.0 mm high was used as a sample container. Natural calcite crystals about 3 mm × 2 mm × 1 mm in size (maximum values) and about 9–14 mg in mass were used as samples. The surface area of the crystal was evaluated from the known mass and the density of calcite (2710 kg m^{-3}) taking into account a parallelepiped shape of the crystal.

The sample chamber could be evacuated to a residual pressure about 3×10^{-8} bar with the use of two-stage rotation and oil diffusion pumps. Pressure was measured with an ion gauge. Some of the experiments were carried out in a reduced atmosphere of helium under constant-volume conditions. In the latter case, the vacuum chamber was evacuated first. Then the pumps were cut off and helium was introduced up to 8 mbar. All measurements were performed under isothermal conditions. The heating rate of the sample from 273 to 853 K was 10 K min^{-1} and from 853 K to the desired temperature was 2 K min^{-1}. At the beginning of each measuring cycle, the system was heated at the temperature chosen, usually during 1 h, to reach a constant rate of the decomposition. The changes of the mass and surface area of a sample during this period were taken into account. Temperature was measured with Pt–Pt 10%Rh thermocouple placed with its junction immediately below the crucible. Temperature variations in the process of mass-change measurements (usually, during 30–60 min) did not exceed ±0.2 K.

4. Results and discussion

In addition to the results of our own experiments, some data on the calcite decomposition reported in the literature will be used in this paper for the determination of the E parameter by the second- and third-law methods and discussion of the self-cooling effect on the results of these determinations. The data of the present work will be considered first.

4.1. This work

Two different series of experiments on the decomposition of $CaCO_3$ have been carried out: in high-

Table 2

Values of the E parameter for the decomposition of $CaCO_3$ in high-vacuum (3×10^{-8} bar) calculated by the third-law method

T_h (K)	J (kg s^{-1} m^{-2})	P_{eq} (bar)	$\Delta_r S^\circ_T$ (J mol^{-1} K^{-1})	E (kJ mol^{-1})
863	3.0×10^{-6}	1.32×10^{-8}	315.9	266.5
890	5.73×10^{-6}	2.56×10^{-8}	315.0	269.5
892	6.08×10^{-6}	2.72×10^{-8}	314.9	269.6
921	1.49×10^{-5}	6.77×10^{-8}	313.9	271.0
948	2.91×10^{-5}	1.34×10^{-7}	313.0	273.1
Average				270 ± 2

vacuum (3×10^{-8} bar) with continuous pumping and in a reduced atmosphere of He (8 mbar) under constant volume conditions. The purpose of these two series was to investigate the effect of atmosphere on sample self-cooling and the results of determination of the E parameter in the equimolar and isobaric modes of decomposition.

The results of determination of the E parameter in these series of experiments are presented in Tables 2 and 3 and Fig. 1, respectively. From preliminary analysis of these data, it can be seen that, in agreement with our expectations:

(i) in all cases, the results of calculations of the E parameter by the third-law method (261–273 kJ mol^{-1}) are systematically higher than by the second-law method (182–191 kJ mol^{-1}) and
(ii) the experimental data obtained by the third-law method are very close to the theoretical value (253 kJ mol^{-1}) predicted by the physical approach.

The explanation of the differences in the slope and position of the ln P_{eq} versus 1000 K/T plots in Fig. 1 requires a more thorough consideration. As can be seen from this figure and Tables 2 and 3, the decomposition rate in low-vacuum (8 mbar) under constant volume conditions is twice as much as the decomposition rate in high-vacuum (3×10^{-8} bar) with continuous pumping. This is in contradiction with the reverse situation expected from the retardation effect of CO_2, evolved and accumulated in the chamber, on the process of sample decomposition in the constant volume experiments. As estimated from the mass of the sample decomposed by the moment of measurement, Δm, and the total volume of the vacuum chamber (28 l), the external CO_2 pressure, P'_{CO_2}, in the moment of measurements (see Table 3) is two orders of magnitude higher than the values of the equivalent pressure P_{eq} listed in the same table. Therefore, it should be expected that the decomposition rate under these conditions is lower than in high-vacuum. We explain this contradiction by the severe effect of self-cooling in case of high-vacuum experiments and its absence (or significant reduction), due to the additional heat conduction of the gas, in the presence of 8 mbar of He.

As noted above (see Section 2.3), the magnitude of self-cooling can be easily estimated from Eq. (13) if

Table 3

Values of the E parameters for the decomposition of $CaCO_3$ in an atmosphere of He (8 mbar) under constant volume conditions calculated by the third-law method

T_h (K)	m (mg)	$\Delta m/m$ (%)	Δm (mg)	J (kg m^{-2} s^{-1})	P_{eq} (bar)	$\Delta_r S^\circ_T$ (J mol^{-1} K^{-1})	E^e (kJ mol^{-1})	P'_{CO_2} (bar)	$(P_{eq}P'_{CO_2})^{1/2}$ (bar)	E^i (kJ mol^{-1})
857	13.6	1.53	0.208	5.10×10^{-6}	2.23×10^{-8}	316.1	261.0	3.63×10^{-6}	2.85×10^{-7}	485.7
897	12.2	6.69	0.816	1.25×10^{-5}	5.60×10^{-8}	314.6	265.6	1.46×10^{-5}	9.04×10^{-7}	489.8
935	13.3	16.4	2.18	3.25×10^{-5}	1.49×10^{-7}	313.4	268.7	4.00×10^{-5}	2.44×10^{-6}	494.0
954	13.9	22.7	3.15	5.33×10^{-5}	2.46×10^{-7}	312.8	269.9	5.81×10^{-5}	3.78×10^{-6}	496.5
974	12.5	34.4	4.30	1.04×10^{-4}	4.86×10^{-7}	312.2	269.8	7.81×10^{-5}	6.16×10^{-6}	498.4
Average							267 ± 4			493 ± 5

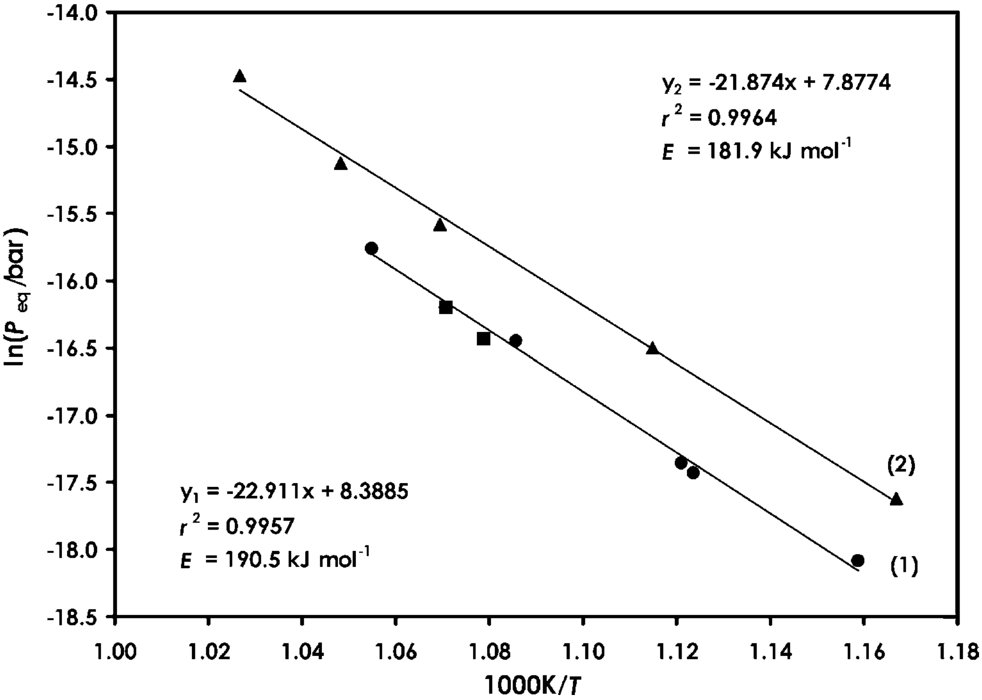

Fig. 1. The logarithms of the equivalent pressure, P_{eq}, for calcite crystals decomposed under different conditions against 1000 K/T: (1) in high-vacuum (3×10^{-8} bar) with continuous pumping ((■): data from Beruto and Searcy [51]) and (2) in an atmosphere of He (at the initial pressure of 8×10^{-3} bar) under constant volume conditions.

we suggest that the only reason of overestimation for the E_{exp} value, calculated by the third-law method, is the effect of self-cooling. Then, taking into account the true value of the E parameter, E_{true}, for the implied reaction, it is possible to find the real temperature of the sample, T_s, in the process of decomposition. This temperature is equal:

$$T_s = T_h \frac{E_{true}}{E_{exp}} \qquad (17)$$

if we neglect a small difference in $\Delta_r S_T^\circ$ values for T_s and T_h.

In case of calcite decomposition at about 900 K, $E_{true} = 253.0$ kJ mol^{-1}. Using this value and the magnitudes of E_{exp} listed in Table 2, the effect of self-cooling for calcite decomposition in high-vacuum was evaluated. These results are compared in Table 4 with the results of model calculations obtained as described in Section 2.4. The magnitude of the emittance factor $\varepsilon(T)$ in the model calculations was chosen in such a way that the discrepancy between the values compared would be minimum. As appeared, the magnitude $\varepsilon(T) = 0.005$–0.01 is optimal (in theory, the value of $\varepsilon(T)$ should increase with temperature). Some important conclusions can be deduced from these results.

We see, first of all, that the emittance factor $\varepsilon(T)$ under typical conditions of experiments used in TA is very small so that the main source of heating of the sample is the heat conduction of a foreign gas in the furnace. It means that the use of high-vacuum, as it

Table 4
Self-cooling effect for the decomposition of $CaCO_3$ in high-vacuum (3×10^{-8} bar)

T_h (K)	$T_h - T_s$ (K)	
	Third-law	Model[a]
863	40	33/24
890	51	49/38
892	52	50/39
921	58	69/57
948	66	89/75

[a] At $\varepsilon(T) = 0.005$ and 0.01, respectively.

prevails in many works, has no sense from the point of view of reliability of the results obtained. It is pertinent to discuss here a reason of a low value of the emittance factor used in the model calculations. The point is that the effective value of the $\varepsilon(T)$ factor corresponding to the heat radiation transfer from the alumina crucible to the calcite crystal covered by a layer of CaO product is actually a product of the emittance factors for all four surfaces: Al_2O_3, CaO (external), CaO (internal) and $CaCO_3$ (we neglect here the residual heat conduction via point contacts between a $CaCO_3$ reactant and microcrystals of CaO product). If we take into account that at 900 K the emittance factor for each of these surfaces is about 0.3 [50], than the product of these four factors is equal to 0.008. This value is very close to the magnitude of the emittance factor used in the model calculations. It is remarkable that the value of the emittance factor used by L'vov [34] for theoretical modeling of the Topley–Smith effect in case of the decomposition of calcite in the presence of CO_2 ($\varepsilon(T) = 0.015$) was also close to this value.

Now call attention to the data obtained in the second series of experiments performed under constant volume conditions in an atmosphere of He (8 mbar) (Table 3). As noted above, the conditions for these experiments to a greater extent correspond to the isobaric mode of decomposition when Eq. (14) should be applied for the calculation of the E^{i} parameter by the third-law method. Indeed, the average magnitude of the E^{i} parameter (493 ± 5 kJ mol^{-1}) calculated by this equation is in good agreement with the theoretical value (505 kJ mol^{-1} at 935 K).

Thus, all the experimental results obtained in this work support the deduced mechanism of calcite decomposition described by the general reaction (2) and explain in part the reasons of extreme diversity in experimental kinetic parameters reported in the literature by different workers. The major of these reasons is the severe self-cooling effect (especially, in high-vacuum) and the strong influence of this effect on the results obtained by the second-law (and Arrhenius-plots) methods.

4.2. The literature data

The experimental results reported by Beruto and Searcy [51], Wang and Thomson [52,53] and Maciejewski [3,4] will be considered below in the framework of the physical approach. In all the selected works, the measurements were performed under isothermal conditions and the samples used were single crystals or powdered samples with a known particle size. These conditions are obligatory for the correct application of the third-law method [35]. The massive collection of other studies performed under non-isothermal conditions or with sample particles of an undefined size is unsuitable for such consideration.

4.2.1. Beruto and Searcy

This work is cited in the literature on the calcite decomposition probably more often than any other. Its authors used the Langmuir (free-surface) method for determination of the decomposition rate, J, in the process of isothermal decomposition of calcite single crystals (40–65 mg) at temperatures from 927 to 1013 K [51]. The residual pressure during the decomposition was about 7×10^{-8} bar. The rate of decomposition measured continuously with a quartz microbalance was constant during practically the total period of decomposition. This was reached by fitting a crystal into the alumina cell, so that the decomposition occurred only under the open area of the crystal (25 mm^2). From the log J versus T^{-1} plot (15 points), the value of the E parameter (the "activation enthalpy", by terminology of Beruto and Searcy [51]) was calculated. This value was equal to 205 kJ mol^{-1}.

As can be seen from a comparison of the experimental conditions used by Beruto and Searcy [51] and those used in the present study, they appeared to be very similar. Therefore, no wonder that the absolute values of decomposition rate, J, and equivalent partial pressures, P_{eq}, measured in these works are in agreement. This is illustrated in Fig. 1: two lower temperature points (at 927 and 934 K) from [51] fall on our plot. The values of the E parameter calculated at this temperatures by the third-law method are equal to about 271 and 273 kJ mol^{-1} what naturally coincide with our values listed in Table 2.

Our previous conclusion about severe self-cooling of the reactant under high-vacuum conditions is also valid in this case. For example, the true temperature of calcite crystal at 1000 K, when $J = 1.0 \times 10^{-4}$ kg m^{-2} s^{-1} [51], $P_{\mathrm{eq}} = 4.7 \times 10^{-7}$ bar and $E_{\mathrm{exp}} = 276.7$ kJ mol^{-1}, is only 910 K. We can only repeat a conclusion made in [34]: the belief expressed by Beruto and Searcy in [51] (the design of the apparatus used in the present study reduces the heat transfer problem to a negligible source of error in the temperature and decomposition pressure range used) was too optimistic.

4.2.2. *Wang and Thomson*

These workers measured the rates of calcite decomposition using the dynamic X-ray diffraction (DXRD) technique [52,53]. The advantages of DXRD are twofold: the solid reactants, intermediates and products can be identified in situ and the powdered sample can be dispersed on the heating strip in a monolayer manner, which minimizes heat transfer resistance. Reaction conversion, α, versus time, t, data were obtained at seven different temperatures (440, 450, 460, 470, 480, 490 and 500°C) in a helium environment with a flow rate of $1\ \mathrm{l\,min^{-1}}$. The thickness of the calcite layer was one particle size or $1.87 \pm 0.50\ \mu\mathrm{m}$. The E parameter measured from the slope of the Arrhenius-plot was equal to $197 \pm 8\ \mathrm{kJ\,mol^{-1}}$ [53].

In the range of α higher than 0.3, the decomposition rate, J, was rather constant [52]. Therefore, it is possible to evaluate the absolute rate of decomposition on the basis of the initial values of the mass and surface area for a single particle. From the data reported in Fig. 7 of [52] at 743 K, we find: $J = 1.98 \times 10^{-7}\ \mathrm{kg\,m^{-2}\,s^{-1}}$ and using Eqs. (11) and (13) obtain $P_{\mathrm{eq}} = 8.08 \times 10^{-10}$ bar and $E = 248.4\ \mathrm{kJ\,mol^{-1}}$, respectively (at $\Delta_{\mathrm{r}}S^{\circ}_{743} = 320.4\ \mathrm{J\,mol^{-1}\,K^{-1}}$). This value is about 2% less than the theoretical one ($254.6\ \mathrm{kJ\,mol^{-1}}$). Most probably, this results from the estimation of the surface area for a single particle as that for the sphere. The true surface area is probably larger and, consequently, P_{eq} value is smaller. At twice as large surface area, the E parameter is increased to $252.6\ \mathrm{kJ\,mol^{-1}}$.

4.2.3. *Maciejewski*

The experimental data on the isothermal decomposition of $CaCO_3$ under high-vacuum conditions obtained by Maciejewski [4] have been used in the recent comparative study of "computational aspects of kinetic analysis: the ICTAC kinetics project" [3,4]. The results were obtained on a Mettler 2000C thermoanalyzer. Powdered samples 10 mg in mass were decomposed in the Pt–Rh crucible 6.3 mm in diameter at six different temperatures in the range from 788 to 823 K. The averaged radius of particles was $7.5\ \mu\mathrm{m}$ [54]. The residual pressure in the furnace was about 5×10^{-8} bar [3,4].

The α versus t curves are presented in Fig. 3 of [3]. We used in the calculations, the original tabulated data on α versus t [54]. The decomposition rate, J, can be expressed as

$$J = c\,\frac{\alpha_{k+1} - \alpha_k}{t_{k+1} - t_k}\,\frac{1}{(1 - \alpha_{k+1})^{2/3}} \qquad (18)$$

where the first factor takes into account the initial mass, m_0, and the total surface area of all N particles in the sample:

$$c \equiv \frac{m_0}{4\pi r_0^2 N} = \frac{r_0 \rho}{3} \qquad (19)$$

and the third factor takes into account reduction of the surface area with α. The dependence of the decomposition rate (in $\mu\mathrm{g\,m^{-2}\,s^{-1}}$) on the decomposition degree, α, at different temperatures is presented in Fig. 2. Contrary to the expectations, this dependence is rather complicated. Instead of constant J value at $\alpha > 0.2$–0.3, there are some periodical changes of J increased in amplitude with the temperature (the probable reason of this phenomenon will be discussed later. The surprising thing is that no one from the workers, who used these data in the calculations [3–5], mentioned this unusual fact). Taking into account the inconstant value of J, we used in the calculations (Table 5) the mean values of J, averaged in the interval of α from 0.3 to 0.9. It should be noted that the error in determination of the E parameters introduced by the uncertainty in these averaged data, even in the case of the most variable J value at 823 K, did not exceed $\pm 1.5\ \mathrm{kJ\,mol^{-1}}$. At all other temperatures, it was smaller than $\pm 1\ \mathrm{kJ\,mol^{-1}}$.

The other additional problem in these calculations was the temperature reduction into the depth of powdered sample and the necessity to know the effective number of powdered layers, n_{e}, involved in decomposition, i.e. the number of powdered sample layers whose decomposition occurs at the same rate as that of the surface layer. For the calculation of n_{e} factor it is necessary to know the actual number of layers $n_{1/2}$ in one half of such multilayered sample. Using Eq. (16) and above-mentioned magnitudes of parameters, we obtained $n_{1/2} = 8$. The magnitudes of n_{e} factor were

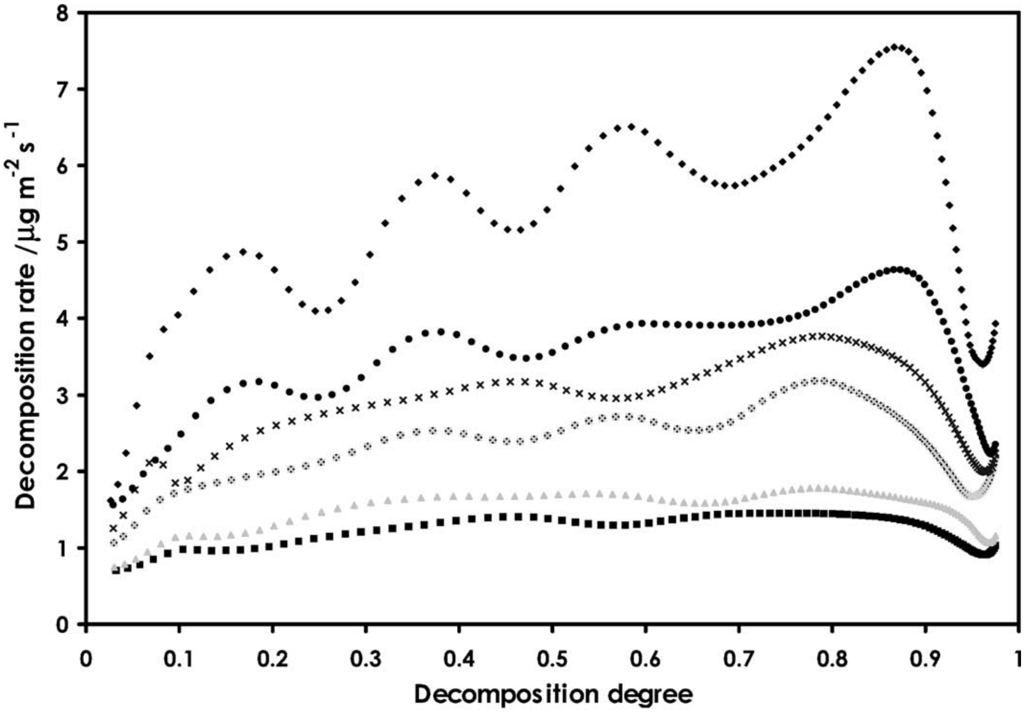

Fig. 2. The rate of $CaCO_3$ decomposition as a function of the decomposition degree at different temperatures (from bottom to top): 788, 793, 803, 808, 813 and 823 K.

calculated by the use of a computer program described in [27]. All necessary parameters and results of calculations are summarized in Table 5. The efficient value of $\varepsilon(T)$ was chosen to be equal to 0.09 as a product of the emittance factors (0.3) for two adjacent surfaces of CaO. For comparison, three different situation are considered when a powdered sample is heated homogeneously ($n_e/n_{1/2} = 1$), self-cooling is taken into account ($n_e/n_{1/2}$ as it is) and only surface layers of powder participate in the decomposition ($n_e/n_{1/2} = 1/8$).

As can be seen, the values of the E parameter in the first two cases are very similar (246 ± 4 kJ mol^{-1}) and only in the last case the E parameter is 4% lower (236.0 ± 0.2 kJ mol^{-1}). As a whole, the final results obtained by the third-law method remain invariant

Table 5

Values of the E parameter for the decomposition of $CaCO_3$ calculated by the third-law method on the basis of experimental results reported in [3,4,54][a]

T_h (K)	$n_e/n_{1/2}$	J[b] (kg s^{-1} m^{-2})	P_{eq} (bar)			$\Delta_r S^\circ_T$ (J mol^{-1} K^{-1})	E (kJ mol^{-1})		
			$n_e/n_{1/2} = 1$	$n_e/n_{1/2}$ as it is	$n_e/n_{1/2} = 1/8$		$n_e/n_{1/2} = 1$	$n_e/n_{1/2}$ as it is	$n_e/n_{1/2} = 1/8$
788	0.556	1.38×10^{-6}	5.80×10^{-9}	1.04×10^{-8}	4.64×10^{-8}	318.6	249.8	246.0	236.2
793	0.516	1.67×10^{-6}	7.04×10^{-9}	1.36×10^{-8}	5.63×10^{-8}	318.4	250.0	245.7	236.3
803	0.443	2.69×10^{-6}	1.14×10^{-8}	2.57×10^{-8}	9.12×10^{-8}	318.1	249.8	244.4	235.9
808	0.410	3.31×10^{-6}	1.41×10^{-8}	3.44×10^{-8}	1.13×10^{-7}	317.9	249.9	243.9	235.9
813	0.380	4.00×10^{-6}	1.71×10^{-8}	4.50×10^{-8}	1.37×10^{-7}	317.7	250.0	243.5	236.0
823	0.328	6.21×10^{-6}	2.66×10^{-8}	8.11×10^{-8}	2.13×10^{-7}	317.4	250.0	242.3	235.7
							249.9 ± 0.1	244.3 ± 1.4	236.0 ± 0.2

[a] At $r_0 = 7.5 \times 10^{-6}$ m, $\rho = 2710$ kg m^{-3}, $\varepsilon(T) = 0.09$, $n_{1/2} = 8$ and $P_{air} = 5 \times 10^{-8}$ bar.

[b] Averaged values for α from 0.3 to 0.9.

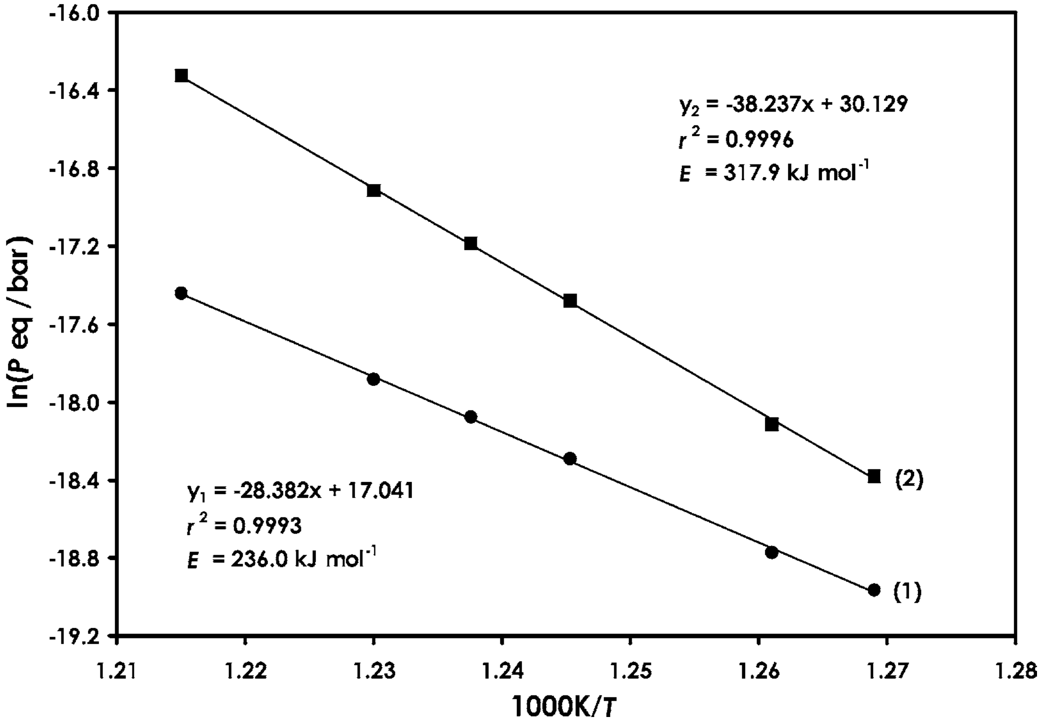

Fig. 3. The logarithms of the equivalent pressure, P_{eq} (averaged for α from 0.3 to 0.9) as a function of 1000 K/T for the decomposition of powdered $CaCO_3$ in high-vacuum [3,4,54]: (1) uncorrected and (2) corrected (for self-cooling) data listed in Table 5.

enough to the effect of self-cooling. A slight (2 and 4%) underestimation of the E parameter compared to theory in the first two cases (as in the case considered in Section 4.2.2) results, most probably, from the evaluation of the surface area for a single particle as that for the sphere. The values of the E parameter calculated from the results in Table 5 by the second-law method are equal to 236 and 318 kJ mol^{-1} for the uncorrected and corrected (for self-cooling) $n_e/n_{1/2}$ ratios (Fig. 3). The first value is about 20 kJ mol^{-1} lower and the second value (obviously overcorrected) is about 60 kJ mol^{-1} higher than the theoretical value (254 kJ mol^{-1}). We again convince ourselves that the results obtained by the second-law method, in contrast to the results obtained by the third-law method, are extremely sensitive to the effect of self-cooling and appropriate temperature corrections. Compared with 2% difference between the averaged values of E for the uncorrected and corrected $n_e/n_{1/2}$ ratios in case of the third-law method (see Table 5), the difference in the E values in case of the second-law method exceeds 30%.

Returning to the appearance of the periodical changes of the decomposition rate (Fig. 2) it is safe to assume that this phenomenon is connected with the temperature inhomogeneity of a powdered sample. As is clear from our model calculations, the temperature difference between the central and the surface layer of powdered samples used in [3,4] ranges up to 20–30 K (at 803–823 K). It means that the nucleation and acceleration periods of decomposition for the reactant in each of the central layers of a powder should be delayed in comparison with that for the outer layer up to the moment of the complete decomposition of the reactant in the outer layer. It is clear from this that the number of peaks in the process of the complete decomposition of a powdered sample should be commensurable to the number of layers, $n_{1/2}$. In cases under consideration, a number of peaks is half as many compared with a number of layers. It is conceivable that at a rather loose packing of the particles every two outer layers of the powder are heated equally by the radiation emitted by the heater and, as a result of that, only four peaks are observed instead of eight. Be it as

Table 6
Values of the *E* parameter (in the equimolar mode) for the decomposition of $CaCO_3$ calculated by the second and third-law methods

Temperature (K)	Sample	Atmosphere (bar)	Gas dynamics	E (kJ mol^{-1})		Reference
				Second-law	Third-law[a]	
863–948	Crystal	Air (3×10^{-8})	Pumping	191	266.5	This work
836–974	Crystal	He (8×10^{-3})	Constant volume	182	261.0	This work
927–1013	Crystal	Air (7×10^{-8})	Pumping	205	271	[51]
713–773	Powder	He (1)	Flow (1 l min^{-1})	197	248.4	[53]
788–823	Powder	Air (5×10^{-8})	Pumping	236	249.8	[3,4,54]

[a] At the lowermost temperatures, uncorrected for self-cooling.

it may, this interesting phenomenon deserves further investigation.

5. Conclusions

All the results for the *E* parameter obtained in this work and calculated from the experimental results reported in the literature are listed in Table 6. Analysis of these data supports the advantages of the third-law method compared with the second-law (and Arrhenius-plots) methods in relation to reliability of results obtained. The experimental values of the *E* parameters, obtained by different technique and under different conditions by the third-law method, are in the range from 248 to 271 kJ mol^{-1}. These values are in good agreement with the theoretically predicted values based on the mechanism of congruent decomposition of $CaCO_3$ into gaseous species CO_2 and CaO with simultaneous condensation of low-volatility CaO molecules. Indeed, the experimental values of the *E* parameters in the equimolar and isobaric modes of decomposition, measured in this work under optimal conditions, are equal to 261 and 493 kJ mol^{-1}, respectively whereas the theoretical values at these temperatures are equal to 253 and 505 kJ mol^{-1}. The small residual discrepancies might be in most cases appropriately interpreted. In cases of single-crystal experiments, the *E* values are somewhat overestimated because of the self-cooling effect (in high-vacuum) or the retardation effect of CO_2 (under constant-volume conditions). In cases of powders, the *E* values are slightly underestimated because of the difference of surface area for real sample particles from that for the spherical ones (as used in the calculations).

The application of the third-law method allowed to support the enormous influence of self-cooling on the results obtained by the usual second-law and Arrhenius-plots methods accepted in TA. The role of this effect is increased dramatically in the experiments performed under high-vacuum conditions when the emission of heater at, typically, a very low value of the emittance factor (of about 0.01) is the only source of reactant heating. The difference in temperatures of the heater and reactant at moderate temperatures (<1000 K) and decomposition rates which correspond to P_{eq} from 10^{-8} to 10^{-6} bar can reach several tens and even 100°. Contrary to the second-law method, the third-law method appears to be rather insensitive to reactant self-cooling and to the presence of gaseous product (CO_2) in the reactor.

This work can be considered as the first attempt to measure, calculate and interpret the kinetics of a solid-state decomposition reaction on the basis of the physical approach and the new methodology relying on the third-law method. It is hoped that these investigations will be continued by other workers. Perhaps, this is the only way to avoid being in stagnation, as it actually is.

Acknowledgements

We thank Dr. A.K. Galwey for the useful comments on the first draft of this paper and a continual moral support of our investigations. The authors are thankful also to Dr. M. Maciejewski for sending to us the details of experimental conditions and the stimulating alpha-time data for the $CaCO_3$ decomposition in vacuum used in [3–5].

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