Kinetics of free-surface decomposition of dolomite single crystals and powders analyzed thermogravimetrically by the third-law method

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Abstract

The results of our thermogravimetric experiments on the decompositions of dolomite crystals and powders and some data reported in the literature were used for the determination of the E parameter of the Arrhenius equation by the third-law method and estimation of the self-cooling effect on the results of these determinations. The experimental values of the E parameters, obtained 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 $CaMg(CO_3)_2$ into gaseous CO_2, CaO and MgO with the simultaneous condensation of low-volatility CaO and MgO molecules. The second important result of this study is the first quantitative comparison of absolute rates of decomposition of powder samples and single crystals. Based on these results, a simple procedure was proposed for the determination of the E parameter by the third-law method from the data obtained for powder samples. It consists in the evaluation of the absolute decomposition rate of a powder sample (reduced to the unit of the outer surface area of a pellet formed by the powder sample in a cylindrical crucible). The value received is lowered by the empirical factor and then used for the calculation of the E parameter by the third-law method. The value of this factor (2.8 ± 0.4) does not depend on the temperature, residual pressure of air in the reactor, grain size and mass of a powder sample. This procedure permits to expand the application of the third-law method to the determination of decomposition kinetics for many solids available only in the powder form.
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1. Introduction

The decomposition of dolomite, $CaMg(CO_3)_2$, has been studied extensively because of its mineralogical interest and industrial importance [1–3] (the full list of works published in 1952–1976 has been given in

[3]). However, there are serious discrepancies in the values of the E parameter of the Arrhenius equation obtained by different workers and, even, by the same workers for different samples. For example, Britton et al. [2] found four different E values for different dolomite specimens (taken as pellets): 207, 219, 225, and 233 kJ mol^{-1}. Ten to 15 separate isothermal decompositions in vacuum were carried out with each specimen. The error of E determinations varied from 14 to 26 kJ mol^{-1}. Powell and Searcy [3]

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obtained from the torsion–Langmuir data (14 points in the range from 824 to 900 K) the E value $194.6 \pm 0.4 \, \text{kJ} \, \text{mol}^{-1}$. They used dolomite crystals as samples. The equivalent pressures of CO_2 were about four orders of magnitude lower than those for the equilibrium (torsion–effusion) measurements. The entropy change for the free-surface decomposition reaction was unusually low: only $93 \pm 6 \, \text{J} \, \text{mol}^{-1} \, \text{K}^{-1}$ per mole of CO_2. For the last 25 years, no progress in the interpretation of these discrepancies and anomalies has been achieved.

The purposes of this work were:

1. to apply the physical approach [4] and the new methodology of kinetic investigations based on the third-law method [5] to the determination of the E parameter and interpretation of the mechanism of dolomite decomposition,
2. to investigate a possibility of using powder samples for the determination of absolute rates of decomposition and the subsequent calculation of the E parameters, and
3. to explain some of the discrepancies and anomalies noted above.

2. Theoretical

2.1. Theoretical values of the E parameter

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

$$S(s) \rightarrow aA(g) \downarrow +bB(g) \downarrow +cC(g) \tag{1}$$
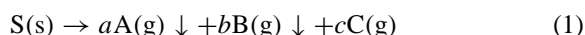
the E parameter for reaction (1) is:

$$E = \frac{\Delta_r H_T^\circ}{\nu} \tag{2}$$

where ν is the total number of moles of gaseous products $(a + b + c)$, and $\Delta_r H_T^\circ$ is the change of the enthalpy in reaction (1).

In order to take into account the partial transfer of the energy released in the condensation of low-volatility products A and B to the reactant, we introduce into the calculations of the enthalpy of decomposition reaction (1) two additional terms, $\tau a \, \Delta_c H_T^\circ(A)$ and

$\tau b \, \Delta_c H_T^\circ(B)$, where the coefficient τ corresponds to the fraction of the condensation energy transferred to the reactant. Thus, we can write

$$\begin{aligned} \Delta_r H_T^\circ = {} & a \, \Delta_f H_T^\circ(A) + b \, \Delta_f H_T^\circ(B) + c \, \Delta_f H_T^\circ(C) \\ & - \Delta_f H_T^\circ(S) + \tau a \, \Delta_c H_T^\circ(A) + \tau b \, \Delta_c H_T^\circ(B) \end{aligned} \tag{3}$$

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 dolomite decomposition, Eqs. (1) and (3) might be rewritten as

$$CaMg(CO_3)_2 \rightarrow CaO(g) \downarrow +MgO(g) \downarrow +2CO_2 \tag{4}$$
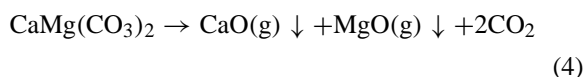
and

$$\begin{aligned} \Delta_r H_T^\circ = {} & \Delta_f H_T^\circ(CaO) + \Delta_f H_T^\circ(MgO) \\ & + 2\Delta_f H_T^\circ(CO_2) - \Delta_f H_T^\circ(CaMg(CO_3)_2) \\ & + 0.5\Delta_c H_T^\circ(CaO) + 0.5\Delta_c H_T^\circ(MgO) \end{aligned} \tag{5}$$

The magnitudes of thermodynamic functions (the entropy and enthalpy) for the components of decomposition reaction of dolomite and for the reaction as a whole (marked by bold) at 800 and 900 K are listed in Table 1. As follows from these data, the theoretical values of the E parameter for the decomposition of $CaMg(CO_3)_2$ at 800 and 900 K in accordance with reaction (1) are equal to 244.9 and 243.8 kJ mol^{-1}, respectively. A possible error (S.D.) in these calculations is within $2 \, \text{kJ} \, \text{mol}^{-1}$.

2.2. The third-law method for the determination of the E parameter

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

$$\Delta_r H_T^\circ = T(\Delta_r S_T^\circ - R \ln K_P) \tag{6}$$

where $\Delta_r S_T^\circ$ is the entropy change and K_P is the equilibrium constant for the reaction (1) in terms of the partial pressures, P, of the gaseous products:

$$K_P = P_A^a \times P_B^b \times P_C^c \tag{7}$$

Table 1
Thermodynamic functions used in the calculations [6,7]

Function[a]	Temperature (K)	
	800	900
S_T° (CaO_g)	254.0	258.4
S_T° (MgO_g)	251.0	257.0
S_T° (CO_2)	257.4	263.5
S_T° $(CaMg(CO_3)_2)$	355.8	384.6
$\Delta_r S_T^\circ$	**664.0 ± 0.4**	**657.8 ± 0.4**
$\Delta_r S_T^\circ / \nu$	**166.0 ± 0.1**	**164.5 ± 0.1**
$\Delta_f H_T^\circ$ (CaO_g)	70.7	74.4
$\Delta_f H_T^\circ$ (CaO_s)	−600.3	−595.0
$\Delta_f H_T^\circ$ (MgO_g)	61.5	66.7
$\Delta_f H_T^\circ$ (MgO_s)	−569.3	−564.4
$\Delta_f H_T^\circ$ (CO_2)	−361.0	−355.7
$\Delta_f H_T^\circ$ $(CaMg(CO_3)_2)$	−2220.3	−2195.8
$\Delta_c H_T^\circ$ (CaO)	−671.0	−669.4
$\Delta_c H_T^\circ$ (MgO)	−630.8	−631.1
$\Delta_r H_T^\circ$	**979.7 ± 8**	**975.1 ± 8**
$\Delta_r H_T^\circ / \nu$	**244.9 ± 2**	**243.8 ± 2**

[a] All S_T° values are in $J\,mol^{-1}\,K^{-1}$ and all ΔH_T° values are in $kJ\,mol^{-1}$. The uncertainties indicated here and in the text correspond to the S.D.

(The equilibrium character of decomposition reactions that is at the basis of the physical approach to the interpretation of the kinetics of thermal decomposition of solids [4] has received recently [5] strong experimental confirmation.) Taking into account Eqs. (2) and (7), Eq. (6) can be reduced to the equation

$$E = T \left(\frac{\Delta_r S_T^\circ}{\nu} - R \ln P_{eq} \right) \quad (8)$$

In this case, a measurement at only one temperature is sufficient for the determination of E but knowledge of absolute values of the entropy of all components in the reaction is necessary for the calculation. Table 1 contains these values for the $CaMg(CO_3)_2$ decomposition.

The equivalent pressure of the gaseous product C is related to the absolute rate of decomposition, J (in $kg\,m^{-2}\,s^{-1}$), by the Hertz–Langmuir equation [4]

$$P_{eq} = \frac{(2\pi MRT)^{1/2} J}{\gamma M} \quad (9)$$

where M is the molar mass of the gaseous product (CO_2) and $\gamma = 101325\,Pa\,atm^{-1}$ is the conversion factor from Pascals to atmospheres used to calculate partial pressures in chemical thermodynamics.

Our analysis of results reported in [7,8] 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-law and third-law methods to the determination of the E parameter for 20 different decomposition reactions [5].

As can be seen from a consideration of Eq. (8), 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.

2.3. Evaluation of the self-cooling effect

The magnitude of self-cooling can be easily estimated from Eq. (8) if we assume that the only reason of overestimation for the experimental E_{exp} value, calculated by the third-law method, is the effect of self-cooling. If we further assume that the E value at the lowermost temperature is free from this effect (i.e. the temperature of the sample, T_s, is equal to the temperature of the heater, T_h) and corresponds to the true value of the E parameter, E_{true}, then it is possible to find the actual temperature of the sample, T_s, for any higher temperature of decomposition. This temperature is:

$$T_s = T_h \frac{E_{true}}{E_{exp}} \quad (10)$$

if we neglect a small systematic decrease of both $\Delta_r S_T^\circ$ and $\Delta_r H_T^\circ$ values with temperature.

2.4. Comparison of absolute rates of decomposition for powders and a single crystal

For the application of the third-law method to the determination of the E parameter, it is necessary to know the absolute rate of sample decomposition J (in $kg\,m^{-2}\,s^{-1}$). On this reason, in our previous works [5,9,10], we used the data obtained for crystals or pressed pellets with a low porosity. In these cases, the effective surface area of decomposition could be evaluated from the known geometry of samples. This condition seriously restricts (or complicates) the investigations in case of powders. The evaluation of the

efficient surface area of powders with the undefined grain size and number of particles presents a serious problem. The application of the BET technique permits to determine this value. However, the decomposition of powders is not spatially homogeneous. Because of the self-cooling effect, the temperature of inner parts of the powder is lower than that of the surface. This fact was noted in many works (see for example, [2,11]) though no one tried to investigate this problem quantitatively.

L'vov et al. [12,13] 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 nth outermost layer. All the calculations are performed with the laboratory-developed computer program described in [13].

In addition to the temperature distribution, the program permits to calculate simultaneously the quantity

$$n_e \equiv \frac{\sum_{i=0}^{n} T_i^{-1/2} \exp(-E/RT_i)}{T_n^{-1/2} \exp(-E/RT_n)} \qquad (11)$$

corresponding to the effective number of powdered sample layers whose decomposition occurs at the same rate as that of the surface layer ($i = n$).

The ratio of decomposition rates for powders and a crystal at the same temperature of the heater can be easily calculated from the obvious equation

$$\frac{J_p}{J_c} = n_e \frac{\exp(E/RT_c)}{\exp(E/RT_p)} \left(\frac{T_c}{T_p} \right)^{1/2} \qquad (12)$$

taking into account the effective number of powdered sample layers, n_e, the temperature of the surface layer of powder (T_p) and the surface temperature of crystal (T_c).

The results of such calculations for the decomposition of dolomite at 811 K as a function of a total number of powder layers ($n = 10$ and 100) and values of the emittance parameter ($\varepsilon = 1, 0.3, 0.1, 0.03,$ and 0.01) are presented in Table 2 (high vacuum) and Table 3 (low vacuum). The following conclusions can be deduced from the analysis of these data:

1. In all cases, the self-cooling effect is increased with reducing of the emittance parameter.
2. The effect is more pronounced for powders. For example, at $\varepsilon = 0.01$, the surface temperature of the powder is 13–17 K lower than that for crystal. At $\varepsilon = 1$, this difference is only 6–7 K.
3. The self-cooling effect in low vacuum ($P_{air} = 2 \times 10^{-4}$ atm) is much smaller than that in high vacuum ($P_{air} < 3 \times 10^{-7}$ atm). For example, the self-cooling of crystal at $\varepsilon = 0.01$ is equal to −35 K in high vacuum and only −5 K in low vacuum.
4. The difference in the grain size and mass of a powder sample (n values) has practically no effect on the temperature distribution and the effective number of layers, n_e.

Table 2

Theoretically calculated ratio of decomposition rates for powders ($n = 10$ and 100) and a crystal of dolomite in high vacuum ($P_{air} < 3 \times 10^{-7}$ atm) at $T = 811$ K as a function of the emittance factor[a]

ε	Crystal		Powder ($n = 10$)		Powder ($n = 100$)		J_p/J_c	
	T (K)	n_e	T (K)	n_e	T (K)	n_e	$n = 10$	$n = 100$
1.0	810.3	1	804.8	3.28	803.9	2.66	2.57	2.00
0.3	808.7	1	799.4	2.07	798.8	1.86	1.36	1.19
0.1	805.2	1	792.2	1.54	791.8	1.47	0.85	0.80
0.03	797.2	1	781.4	1.27	781.2	1.25	0.61	0.59
0.01	786.0	1	769.1	1.15	769.0	1.14	0.51	0.50

[a] The values of thermodynamic functions listed in Table 1 were used.

Table 3
Theoretically calculated ratio of decomposition rates for powders ($n = 10$ and 100) and a crystal of dolomite in low vacuum ($P_{air} = 2 \times 10^{-4}$ atm) at $T = 811$ K as a function of the emittance factor[a]

ε	Crystal		Powder ($n = 10$)		Powder ($n = 100$)		J_p/J_c	
	T (K)	n_e	T (K)	n_e	T (K)	n_e	$n = 10$	$n = 100$
1.0	810.3	1	805.2	3.45	804.3	2.78	2.88	2.13
0.3	809.3	1	801.0	2.33	800.3	2.03	1.72	1.36
0.1	807.8	1	797.2	1.89	796.6	1.72	1.17	1.04
0.03	806.4	1	794.3	1.70	793.8	1.58	0.98	0.89
0.01	805.7	1	793.1	1.65	792.6	1.54	0.93	0.85

[a] The values of thermodynamic functions listed in Table 1 were used.

5. The difference in the decomposition rates for powders and a crystal is not very high. In the range of the ε parameter from 0.01 to 0.3, this difference is within a factor of 2 or smaller.

The last conclusion is extremely important for the application of the third-law method to the calculation of the E parameter in cases of powder samples. It means that, irrespective of the differences in temperature and surface area between powders and crystal, the absolute rate of powder decomposition can be approximately estimated taking into account only the outer surface area of powdered sample. The last value can be easily evaluated from the geometry (diameter) of the crucible and the thickness of powder layer in the crucible. As can be seen from Eq. (8), a two-fold difference in the absolute rate of decomposition can introduce not more than 4–5 kJ mol^{-1} error in the determination of the E parameter at 700–860 K.

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 per time unit, $\Delta m/\Delta t$, and the absolute crucible temperature. An open alumina crucible 5.7 mm inner diameter and 4.0 mm high was used as a sample container. Natural dolomite crystals about 2 mm × 2 mm × 1 mm in size and 10–11 mg in mass and dolomite powders of two different fractions (powder-1: 71–100 μm and powder-2: 0–71 μm) were used in experiments. The powdered sample introduced into a crucible was leveled and pressed manually

(about 1 kg mm^{-2}) into a flat pellet. The total surface area of pellet was calculated taking into account the crucible diameter and the width of pellet (estimated from the sample mass and the apparent density of dolomite powder measured separately). The surface area of the crystals was evaluated from the known mass and the density of dolomite (2860 kg m^{-3}) taking into account a parallelepiped shape of the crystals.

To reduce the self-cooling effect, the sample chamber was evacuated to a residual pressure of about 2×10^{-4} atm by a two-stage rotation pump. Pressure was measured with a thermal-conduction manometer. For comparison, some experiments were performed in high vacuum (at 8×10^{-8} atm) with the use of rotation and oil-diffusion pumps. All measurements have been conducted at continuous pumping under isothermal conditions. The heating rate of the sample from the room temperature to 800 K (or 825 K) was 10 K min^{-1} and from 800 K (or 825 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 10 min, to reach a constant rate of the decomposition. The changes of the mass and surface area of crystals and powders during this period were taken into account. A decrease of the surface area, as was checked experimentally, was proportional to $(1 - \alpha)^{2/3}$ where α is the decomposition degree. Temperature was measured with Pt–Pt10%Rh thermocouple placed with its junction immediately below the crucible. Temperature variations in the process of mass-change measurements (usually, during 10–20 min) did not exceed ±0.2 K. A single measurement of the decomposition rate takes entirely about 90 min.

4. Results and discussion

In addition to the results of our own experiments, some data on the dolomite decomposition reported in the literature will be used below for the determination of the E parameter by the third-law method 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

To measure the absolute rates of dolomite decomposition, one set of experiments with single crystals and three sets with two different powders at two temperatures (811–812 K and 834–835 K) were performed in low vacuum. Besides, two experiments were carried out at 807 K in high vacuum. The experimental conditions and the results of calculation of the E parameter by the third-law method are presented in Table 4. The following conclusions can be deduced from the data received:

1. The experimental values of the E parameter for crystals are very close to the theoretical ones: 244.8 kJ mol^{-1} at 812 K and 244.5 kJ mol^{-1} at 835 K. The maximum deviation from theory is about 2 kJ mol^{-1} (or <1%). The agreement between experiment and theory supports the mechanism of dissociative evaporation of dolomite and the validity of the physical approach to the interpretation of kinetics of solid-state reactions on the whole.

2. In comparison with the actual equivalent CO_2 pressure in the process of free-surface decomposition of dolomite, the equilibrium pressure of CO_2 at 812 and 835 K for the decomposition of dolomite up to the solid oxides

$$CaMg(CO_3)_2 \rightarrow CaO(s) + MgO(s) + 2CO_2$$

(13)
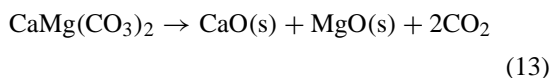
calculated from the thermodynamic functions listed in Table 1 is about 10^6 higher, i.e. even higher than that measured by the torsion–effusion method [3]. This discrepancy can be attributed to the underestimation of the decomposition rate in case of effusion experiments when the decomposition coefficient is very low ($<10^{-4}$).

3. The absolute rate of decomposition for powders, J_p, in all cases is higher than that for the crystals (J_c) and, as can be seen from the results received, the difference in the decomposition rates for powders and crystals is rather constant and does not depend on the temperature, residual pressure of air in the reactor, the mass of powder samples and the size of grains. The mean value of the ratio J_p/J_c at both temperatures (812 and 835 K) is equal to 2.8 ± 0.4. This value is higher than that expected from the model calculations (see Section 2.4). Most probably, this is related with the uneven surface of layers of powder. In particular, the surface formed by spherical particles is about twice in area compared with that for a flat surface. It might be higher than twice for grains with the irregular shape. In any case, the constancy of J_p/J_c value under different conditions and for different reactants deserves further investigation and substantiation.

4. After correction of the decomposition rates for powders for this empirical factor (2.8), the values of E parameter for powders closely approach those for crystals. The average E value is equal to 245.9 ± 1.4 kJ mol^{-1} for powders and 246.1 ± 0.9 kJ mol^{-1} for crystals.

5. The reproducibility of determination of the E parameter by the third-law method is very high. The averaged E values for experiments with different powders and sample masses are equal to 244.9 ± 0.6 kJ mol^{-1} at 807–812 K (5 points) and 247.4 ± 0.6 kJ mol^{-1} at 835 K (3 points).

6. The values of E parameter at higher temperatures in all cases are 1–3 kJ mol^{-1} higher than those at lower temperatures. This difference results from a higher value of the self-cooling effect. As follows from Eq. (10), the self-cooling for crystals ($T_s - T_h$) was equal to -6.9 K at 835.4 K and -2.3 K at 812 K. These data are in agreement with our model calculations at $\varepsilon = 0.01$ (Table 3).

4.2. The literature data

The only study related to the determination of the absolute rates of dolomite decomposition in vacuum was carried our 25 years ago by Powell and Searcy [3]. The decomposition was studied by the torsion–Langmuir method. Samples were prepared by cleaving the crystals into slices $\approx$1 mm thick. Sections with

Table 4
Experimental conditions and results of calculation of the E parameter by the third-law method

Sample[a]	Vacuum (atm)	T (K)	Mass (mg)	S_0 (mm²)	α_m[b]	S_m[c] (mm²)	$\Delta m/\Delta t$[d] (μg s⁻¹)	J (kg m⁻² s⁻¹)	J_{corr}[e] (kg m⁻² s⁻¹)	P (atm)	$(\Delta_r S^\circ_T/\nu)$[f] (J mol⁻¹ K⁻¹)	E (kJ mol⁻¹)
Crystal	2×10^{-4}	835.4	10.7	15.7	0.146	14.2	0.235	1.66×10^{-5}	1.66×10^{-5}	1.63×10^{-7}	165.5	246.8
Crystal	2×10^{-4}	812.0	10.4	15.3	0.117	14.1	0.108	7.63×10^{-6}	7.63×10^{-6}	7.35×10^{-8}	165.8	245.5
Powder-1	2×10^{-4}	835.5	10.7	55.7	0.510	34.6	1.45	4.19×10^{-5}	1.50×10^{-5}	1.47×10^{-7}	165.5	247.5
Powder-1	2×10^{-4}	811.0	10.7	55.7	0.365	41.2	0.943	2.29×10^{-5}	8.18×10^{-6}	7.93×10^{-8}	165.8	244.7
Powder-2	2×10^{-4}	834.5	10.7	54.6	0.511	33.9	1.55	4.57×10^{-5}	1.63×10^{-5}	1.57×10^{-7}	165.5	246.8
Powder-2	2×10^{-4}	811.8	10.7	54.6	0.353	40.8	1.06	2.60×10^{-5}	9.29×10^{-6}	9.00×10^{-8}	165.8	244.1
Powder-2	2×10^{-4}	835.5	40.0	64.6	0.147	58.1	2.32	3.99×10^{-5}	1.43×10^{-5}	1.40×10^{-7}	165.5	247.9
Powder-2	2×10^{-4}	811.3	40.0	64.6	0.100	60.3	1.23	2.04×10^{-5}	7.29×10^{-6}	7.07×10^{-8}	165.8	245.6
Powder-2	8×10^{-8}	807.3	40.0	64.6	0.088	60.8	1.17	1.93×10^{-5}	6.89×10^{-6}	6.66×10^{-8}	165.9	244.8
Powder-2	8×10^{-8}	806.9	40.0	64.6	0.087	60.8	1.04	1.71×10^{-5}	6.11×10^{-6}	5.90×10^{-8}	165.9	245.5

[a] Powder-1: 71–100 μm grains; powder-2: 0–71 μm grains. The apparent density of pellets, prepared from these powders, is equal to 1633 and 2062 kg m⁻³, respectively.

[b] The decomposition degree by the time of measurement.

[c] The surface area by the time of measurement. In case of powders, $S_m = S_0 (1 - \alpha_m)^{2/3}$.

[d] Measured in the interval from 70 to 80 s min.

[e] $J_{corr} = J$ for crystals and $J_{corr} = J/2.8$ for powders.

[f] Interpolated for 807, 812 and 835 K taking into account the values listed in Table 1.

Table 5
The E parameters and sample self-cooling calculated by the third-law method from the data reported in [3]

T_h [3] (K)	P [3] (atm)	$(\Delta_r S_T^\circ / \nu)^a$ $(J\,mol^{-1}\,K^{-1})$	E $(kJ\,mol^{-1})$	$T_h - T_s{}^b$ (K)
824	3.90×10^{-8}	165.6	253.3	28
838	5.69×10^{-8}	165.4	254.8	34
850	8.08×10^{-8}	165.2	255.8	38
851	8.34×10^{-8}	165.2	255.9	38
856	1.30×10^{-7}	165.1	254.2	33
861	1.17×10^{-7}	165.1	256.4	41
868	1.34×10^{-7}	164.9	257.3	44
871	1.57×10^{-7}	164.9	257.1	44
874	1.73×10^{-7}	164.9	257.3	45
876	1.76×10^{-7}	164.8	257.6	46
881	2.28×10^{-7}	164.7	257.1	46
884	2.44×10^{-7}	164.7	257.5	46
890	3.01×10^{-7}	164.6	257.6	47
900	4.24×10^{-7}	164.5	257.9	49

[a] The values listed in Table 1 were taken into account for interpolation.
[b] The interpolated values of E_{true} were used in the calculations by Eq. (10).

parallel faces were selected. A section was placed on the cell-support disk, and the cell lid was pressed tightly over it. The orifice diameter was about 3.0 mm. The vacuum was maintained at 3×10^{-8} atm by an oil-diffusion pump and a liquid-nitrogen cold trap. At the lower end of the temperature range at least 1 h was required to attain a steady pressure reading. The data reported in [3] together with the results of our calculation of the E parameter by the third-law method are presented in Table 5.

As can be seen from these data, the E parameter at lower temperatures ($254.1 \pm 1.1\,kJ\,mol^{-1}$ at 824–838 K) is $8\,kJ\,mol^{-1}$ higher than that in our experiments for the crystal decomposition ($246.1 \pm 0.9\,kJ\,mol^{-1}$ at 812–835 K). This difference is related with the effect of self-cooling which as predicted is more pronounced in high-vacuum conditions used in [3]. The temperature difference between the heater (furnace) and the sample calculated by Eq. (10) increases with temperature from 28 to 49 K. These values are in good agreement with the results of our model calculations at $\varepsilon = 0.01$ (Table 2) and with the values of self-cooling for crystals of calcite [9]: 40–66 K at 863–948 K. The P value (equivalent pressure) monotonously increases with temperature though the E parameter in the interval 868–900 K is practically constant: $257.4 \pm 0.3\,kJ\,mol^{-1}$.

The E parameter calculated by the second-law method taking into account the corrected for self-

cooling values of temperature is equal to 244.4 kJ mol^{-1} what naturally coincides with the theoretical value and is $50\,kJ\,mol^{-1}$ higher than the value reported by Powell and Searcy [3]. The erroneous low slope of the original $\log P$ versus T^{-1} plot explains a wrong (low) value of the entropy of decomposition per mole of CO_2 ($93\,J\,mol^{-1}\,K^{-1}$) calculated in [3]. Indeed, as can be seen from Eq. (8), a systematic error in E parameter introduces a systematic error (in the same direction) in $\Delta_r S_T^\circ / \nu$ value (this regularity is one of manifestations of the so-called kinetic compensation effect [4]). Therefore, the self-cooling effect is responsible for the underestimation of the both parameters (E and $\Delta_r S_T^\circ / \nu$) reported in [3].

5. Conclusions

The first conclusion from this study consists in a support of the mechanism of decomposition of dolomite in vacuum through the congruent dissociative evaporation of solid reactant with the simultaneous condensation of low-volatility products (metal oxides). This mechanism as applied to dolomite was discussed earlier [5,14]. However, only some fragmentary data from the literature were used for a comparison of theoretical and experimental kinetic parameters. Moreover, a small error has crept into the theoretical calculation of the E parameter: instead

of 244.6 kJ mol^{-1} at 824 K (this work) the value 234 kJ mol^{-1} was used [5,14]. The present study includes the analysis of the full data reported in [3] and, in addition, the results of our own experiments on the dolomite decomposition. These kinetic data are in excellent mutual agreement and correspond very well to the theoretical predictions.

The additional fact supporting the mechanism of dissociative evaporation of dolomite with the *simultaneous condensation* of low-volatility metal oxides is the formation of a poorly crystalline solid product [3] with the high surface area (21 m^2 g^{-1}). Indeed, it is difficult to imagine the formation of the ideal crystalline product in the process of simultaneous condensation of two oxides in the reaction interface.

The second important result of this study is the first quantitative comparison of absolute rates of decomposition of powder samples and single crystals. Based on these results, a simple procedure was proposed for the determination of the E parameter by the third-law method from the data obtained for powder samples. It consists in the evaluation of the absolute decomposition rate of a powder sample (reduced to the unit of the outer surface area of a pellet formed by the powder sample in a cylindrical crucible). The value received is lowered by the empirical factor and then used for the calculation of the E parameter by the third-law method. The value of this factor (2.8 ± 0.4) does not depend on the temperature, residual pressure of air in the reactor, grain size and mass of a powder sample though its constancy for other reactants deserves further investigation. This procedure permits to greatly expand the application of the third-law method to the determination of decomposition kinetics for many solids available only in the powder form. Appropriate investigations of MgCO$_3$, SrCO$_3$ and BaCO$_3$ decomposition kinetics are in progress.

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